Synthesis, Structure and Reactivity of Group 4 Metal Complexes Bearing Cyclopentadienyl-Carboranyl Ligands

SIT, Mei Mei

A Thesis Submitted in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy
in
Chemistry

The Chinese University of Hong Kong
September 2010

Thesis/Assessment Committee

Professor Kevin Wing Por Leung (Chair)

Professor Zuowei Xie (Research Supervisor)

Professor Chun-Yu Ho (Committee Member)

Professor Wa-Hung Leung (External Examiner)

Acknowledgement

I would like to express my sincere thanks to my supervisor, Professor Zuowei Xie, for his guidance, encouragement, and help during my study in the past five years. He is responsible for involving me in the fascinating research of carborane chemistry and helping me complete writing of this dissertation as well as the challenging research that lies behind it.

I would like to thank Ms. Hoi-Shan Chan for the determination of single-crystal X-ray structures.

I am also grateful to my group mates, Dr. Meihua Xie, Dr. Mak-Shuen Cheung, Dr. Yi Sun, Dr. Liang Deng, Dr. Hao Shen, Dr. Shikuo Ren, Dr. Zaozao Qiu, Ms. Dongmei Liu, Mr. Jian Zhang, Mr. Xiaodu Fu, Ms. Jingying Yang, Mr. Fengrui Zheng, Mr. Rixin Wang, Mr. Xiao He, Mr. Yang Wang for their helpful discussion and suggestions.

I also thank my friends and officers of the Department of Chemistry and Graduate School for their help and supports during the course of my study.

I am greatly indebted to The Chinese University of Hong Kong for the award of a Postgraduate Studentship and to the Hong Kong Research Grants Council for the financial support.

Abstract

The amine exchange reaction between [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M($NMe_2$)$_2$ (M = Zr, Hf, Ti) and N, N'-dimethylethylenediamine or N, N'-dimethylpropane-1,3-diamine gave [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^2$-$N(Me)(CH_2)_2N(Me)$] (M = Zr, Ti) or [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^2$-$N(Me)(CH_2)_3N(Me)$] (M= Zr, Hf, Ti) in good yields. The metal-nitrogen bonds in these group 4 metal diamide complexes were very reactive toward unsaturated polar organic substrates, such as RNC, RNCS, RNCO, R-N=C=N-R and RCN to give multiple insertion products. The carbodiimide and XylNC (Xyl = 2,6-$Me_2C_6H_3$) insertion products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^3$-$N(Me)(CH_2)_3N(Me)C(=NR)NR$] (M = Zr, R = ^{i}Pr, Cy; M = Hf, R = Cy) and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M- [$\eta^2$:$\eta^2$-$N(Xyl)=CN(Me)(CH_2)_3N(Me)C=N(Xyl)$] (M = Zr, Hf) also showed reactivities toward unsaturated molecules, resulting in the de-insertion of carbodiimide and XylNC. Different reactivity patterns were observed, depending on the nature of metal atoms and substrates.

[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$]($NHMe_2$)$_2$ was prepared by amine elimination reaction between [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$ and 1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$. It underwent ligand substitution reaction with XylNC to generate [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][2,6-$(CH_3)_2C_6H_3N=C]_2$ and

reacted with THF to give ring opening product $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}S_2C_2B_{10}H_{10}][\sigma\text{-}O(CH_2)_4NHMe_2]$. Zirconium-promoted nucleophilic reaction of dimethylamine with various kinds of unsaturated polar organic substrates, such as PhCN, PhNCO, ^{n}BuNCS and MA were studied.

Direct deboration of group 4 metal carboranyl complexes was achieved by reactions of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ (M = Zr, Hf), $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ or $[\eta^5{:}\sigma\text{-}H_2C(C_{13}H_8)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with excess diamines. The resultant metal dicarbollide complexes $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)]$ and $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3NH(Me)]$ were active toward unsaturated molecules, like ^{n}BuNCS, ^{i}Pr-N=C=N-^{i}Pr and ^{n}BuNC, to give mono-insertion products. $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3NH(Me)]$ was able to be deprotonated by ^{n}BuLi to give a lithium salt $\{[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3N(Me)Li]\}_2$. It reacted with $[HNEt_3][BPh_4]$ to afford cationic zirconium species $[\{\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr\{\eta^2\text{-}NH(Me)(CH_2)_3NH(Me)\}][BPh_4]$. The dichloro species $[\{\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Li(DME)_3]$ (M = Zr, Hf) were reduced by sodium metal to produce a new class of metallacarbornes bearing *arachno*-η^6-C_2B_9 tetraanion.

摘 要

$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ (M = Zr, Hf, Ti) 和 N,N'-二甲基乙二胺或 N,N'-二甲基丙二胺发生胺交换反应以较好产率得到胺交换产物 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2\text{-}N(Me)(CH_2)_2N(Me)]$ (M = Zr, Ti) 或 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2\text{-}N(Me)(CH_2)_3N(Me)]$ (M= Zr, Hf, Ti)。这些第四族金属二胺基化合物中的金属-氮键非常活泼，可以和含极性官能团的有机底物，如异腈，异硫氰酸酯，异氰酸酯，碳化二亚胺或腈类化合物发生反应，得到多插入产物。其中碳化二亚胺以及 2,6-二甲基苯异腈插入的产物 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NR)NR]$ (M = Zr, R = ^{i}Pr, Cy; M = Hf, R = Cy) 和 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M\text{-}[\eta^2{:}\eta^2\text{-}N(Xyl)=CN(Me)(CH_2)_3N(Me)C=N(Xyl)]$ (M = Zr, Hf) 可以和不饱和底物发生反应，从原配合物中脱除碳化二亚胺和 2,6-二甲基苯异腈。其反应特征取决于金属原子和底物的性质。

$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}](NHMe_2)_2$ 可以通过 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ 和 1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$ 之间的胺消除反应得到。它可以和 2,6-二甲基苯异腈发生配体交换反应得到 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][2,6\text{-}(CH_3)_2C_6H_3N=C]_2$，也可以和四氢呋喃反应得到开环产物 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr$

$[\eta^2\text{-}S_2C_2B_{10}H_{10}][\sigma\text{-}O(CH_2)_4NHMe_2]$。研究表明在锆的促进下，二甲胺可以和许多极性不饱和底物，比如苯腈，苯氰酸酯，正丁基异硫氰酸酯以及丙烯酸甲酯发生亲核加成反应。

第四族金属碳硼烷化合物$[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ (M = Zr, Hf)，$[\eta^5\text{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ 或 $[\eta^5\text{:}\sigma\text{-}H_2C(C_{13}H_8)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ 可以直接和过量的二胺发生脱硼反应，得到金属碳硼烷化合物。其中 $[\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)]$ 及 $[\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3NH(Me)]$ 可以和不饱和分子，例如正丁基异硫氰酸酯，二异丙基碳化二亚胺或正丁基异腈发生反应，得到单插入产物。化合物$[\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3NH(Me)]$可以在丁基锂的作用下去质子化得到相应的锂盐$\{[\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr\text{-}[\eta^2\text{-}N(Me)(CH_2)_3N(Me)Li]\}_2$，或者和四苯基硼三乙铵盐反应得到锆阳离子化合物$[\{\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr\{\eta^2\text{-}NH(Me)(CH_2)_3NH(Me)\}][BPh_4]$。碳硼烷金属二氯化物$[\{\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Li(DME)_3]$ (M = Zr, Hf) 可以被金属钠还原得到一类新的金属碳硼烷含有 η^6-配位的鸟巢型结构的十一顶点碳硼烷四价阴离子。

Abbreviation

br	broad
^{n}BuLi	*n*-butyl lithium
^{t}Bu	*tert*-butyl
Bn	Benzyl
CAd	carbon-atom-adjacent
CAp	carbon-atom-apart
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	doublet (NMR)
DCC	dicyclohexylcarbodiimide
DIC	diisopropylcarbodiimide
dd	doublet of doublets (NMR)
DME	dimethoxyethane
DMEDA	N,N'-dimethylethylenediamine
DMPDA	N,N'-dimethyl-1,3-propanediamine
Et	ethyl
Et_2O	diethyl ether
IR	infrared spectroscopy
m	multiplet (NMR)
M	metal
Me	methyl
NMR	nuclear magnetic resonance spectroscopy

Ph	phenyl
PPN	bis(triphenylphosphine)iminium cation
^{n}Pr	*n*-propyl
^{i}Pr	*iso*-propyl
Py	pyridine
s	singlet (NMR)
t	triplet (NMR)
THF	tetrahydrofuran
TMS	trimethylsilyl
xs	excess
Xyl	2,6-dimethylphenyl

List of Compounds

9b'	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NCy)NCy]$	55
10a	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=N^tBu)S]$	57
10a'	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NXyl)S]\cdot(C_7H_8)_{0.5}$	57
10b	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^3\text{-}N(Me)(CH_2)_3N(Mc)C(=N^tBu)S]$	57
11a	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}\{OC(=NC_{10}H_7)N(C_{10}H_7)C(=O)\}N(Me)(CH_2)_3N(Me)C(NC_{10}H_7)O]$	61
12a	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}(Xyl)N{=}CN(Me)(CH_2)_3N(Me)C{=}N(Xyl)]$	62
12b	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}(Xyl)N{=}CN(Me)(CH_2)_3N(Me)C{=}N(Xyl)]$	62
13a	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}\{N^nBu\}\{N^nBu\}[(=C)\text{-}C{=}CHN(^nBu)CH_2N[(CH_2)_3N(Me)N\text{-}C{=}N(^nBu)]]$	65
13b	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}\{N^nBu\}\{N^nBu\}[(=C)\text{-}C{=}CHN(^nBu)CH_2N[(CH_2)_3N(Me)N\text{-}C{=}N(^nBu)]]$	65
14a	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}\{NR\}\{NR\}[(=C)\text{-}C{=}CHNRCH_2N[(CH_2)_3N(Me)N\text{-}C{=}NR]]$ (R = 2-morpholinethyl)	68
14b	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}\{NR\}\{NR\}[(=C)\text{-}C{=}CHNRCH_2N[(CH_2)_3N(Me)N\text{-}C{=}NR]]$ (R = 2-morpholinethyl)	68
15a	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}\{NCH_2Ph\}\{NCH_2Ph\}[-C(=CH_2Ph)N(Me)(CH_2)_3N(Me)C{=}N(CH_2Ph)]$	70
15b	$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}\{NCH_2Ph\}\{NCH_2Ph\}[-C$	70

	(=CH_2Ph)N(Me)$(CH_2)_3$N(Me)C=N(CH_2Ph)]	
16a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{$NCH_2TMS$}=C{CNCH(Me)Si($Me_2$)N($CH_2TMS$)C=}N(Me)$(CH_2)_3$N(Me)C=N$CH_2TMS$]	73
16b	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-{$NCH_2TMS$}=C{CNCH(Me)Si($Me_2$)N($CH_2TMS$)C=}N(Me)$(CH_2)_3$N(Me)C=N$CH_2TMS$]	73
17a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{$NCH_2Ph$}{$NCH_2Ph$}[-C(-C≡N)CN(Me)$(CH_2)_3$N(Me)C=N$CH_2Ph$]	78
18a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^3$-N(Ph)=CN(Me)$(CH_2)_3$N(Me)C=N(Ph)C(NCy)NCy]	86
18b	{[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^3$-N(Ph)=CN(Me)$(CH_2)_3$N(Me)C=N(Ph)C(NCy)NCy]}$_2$•$(C_7H_8)_2$	89
19a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^3$-N(Ar)=CN(Me)$(CH_2)_3$N(Me)C=N(Ar)C(NCy)NCy]•$(C_7H_8)$ (Ar = *p*-$CH_3C_6H_4$)	86
20a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\sigma$:$\eta^2$-N(Me)$(CH_2)_3$N(Me)C=N($CH_2)_3$C=C(N^{i}Pr)N^{i}Pr]	90
21a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N(^{n}Bu))C=N(^{n}Bu)]	95
21b	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N(^{n}Bu))C=N(^{n}Bu)]	97
22a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=NR)C=NR] (R = 2-morpholinethyl)	97
22b	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=NR)C=NR] (R = 2-morpholinethyl)	97
23a	[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N($CH_2TMS$))C=N($CH_2TMS$)]	97

List of Figures

Contents

Chapter 1. Introduction

Carboranes are a class of boron hydride clusters in which one or more polyhedral boron vertices are replaced by carbon atoms.[1] Generally, these electron-deficient compounds can be classified into four classes, *closo*, *nido*, *arachno*, and *hypho*, according to the number of skeletal electrons and vertices.[2] Compared to the borane analogues, carboranes are usually highly stable toward moisture and air. They are also thermally stable and robust. For example, the neutral icosahedral carborane cage can be heated to 600 °C without decomposition, and the C_2B_9-cage ions remain unchanged after several hours of heating in acidic or basic solution.[3] These properties make carboranes potentially good ligands in organometallic chemistry, and progress in the chemistry of group 4 metal carborane complexes is presented in the following sections.

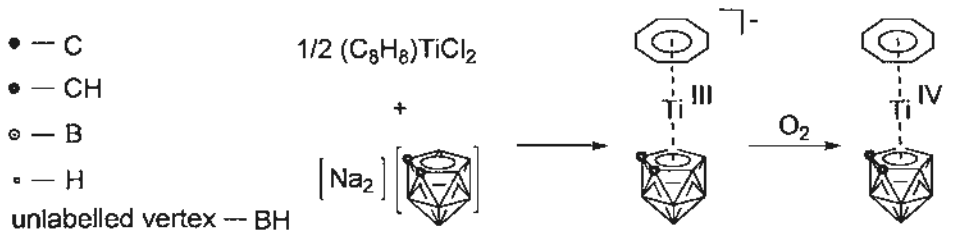
It is noted that in the following schemes a black dot in the polyhedrons represents a carbon atom, a hollow black dot stands for a C(H) vertex, a solid white circle stands for a boron atom, an open circle is for H atom and unlabelled vertex in the polyhedrons represents a B(H) vertex. If a vertex contains an atom other than B and C, the heteroatom is shown explicitly.

1.1. Group 4 Metal Complexes Bearing *nido*-C_2B_9 Ligands

The dicarbollide ligand $[C_2B_9H_{11}]^{2-}$, which was first prepared in 1960s by Hawthorne from the deboration reaction of *o*-carborane with KOH/MeOH,[4] is isolobal and isoelectronic to Cp^-.[5] It can coordinate to the metal centers in an η^5-fashion by contributing six delocalized π-electrons to the metal center and serve as good inorganic π ligand, initiating the metallacarborane chemistry.[6]

The first group 4 metallacarborane $[(C_2H_5)_4N][3\text{-}(\eta^8\text{-}C_8H_8)\text{-}3\text{-}Ti\text{-}1,2\text{-}C_2B_9H_{11}]$ was reported by Hawthorne in 1976, from the reaction of $[(C_8H_8)TiCl]_2$ with $Na_2C_2B_9H_{11}$, followed by cation exchange with $(C_2H_5)_4NBr$. This Ti(III) complex can be oxidized to the neutral air stable Ti(IV) species $3\text{-}(\eta^8\text{-}C_8H_8)\text{-}3\text{-}Ti\text{-}1,2\text{-}C_2B_9H_{11}$. These transformations were summarized in Scheme 1.1.[7]

Scheme 1.1. Synthesis of titanacarborane $3\text{-}(\eta^8\text{-}C_8H_8)\text{-}3\text{-}Ti\text{-}1,2\text{-}C_2B_9H_{11}$.

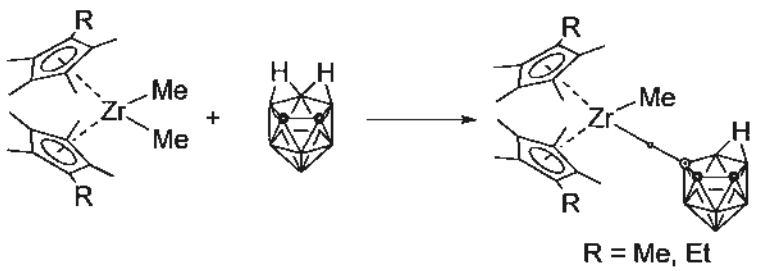


Besides salt metathesis reaction, alkane elimination is also useful in the synthesis of group 4 metallacarboranes. Reactions between neutral $C_2B_9H_{13}$, which contains two acidic protons, and $Cp^*_2ZrMe_2$ or $(etmcp)_2ZrMe_2$ (etmcp = C_5Me_4Et) in pentane, afforded the monomethyl complexes $Cp^*_2ZrMe(C_2B_9H_{12})$ or $(etmcp)_2ZrMe(C_2B_9H_{12})$ in high yield (Scheme 1.2). But single crystal structure of $(etmcp)_2ZrMe(C_2B_9H_{12})$ revealed that the $[(etmcp)_2ZrMe]^+$ cation bonds to the $[C_2B_9H_{12}]^-$ anion solely through a Zr-H-B bond to a terminal hydride on the *nido*-C_2B_3 face instead of the η^5-manner. It was regarded that the bulky peralkylcyclopentadienyl ligand prevents the approach of the carborane anion to the metal. These two neutral Zr complexes can catalyze ethylene polymerization under mild conditions.[8]

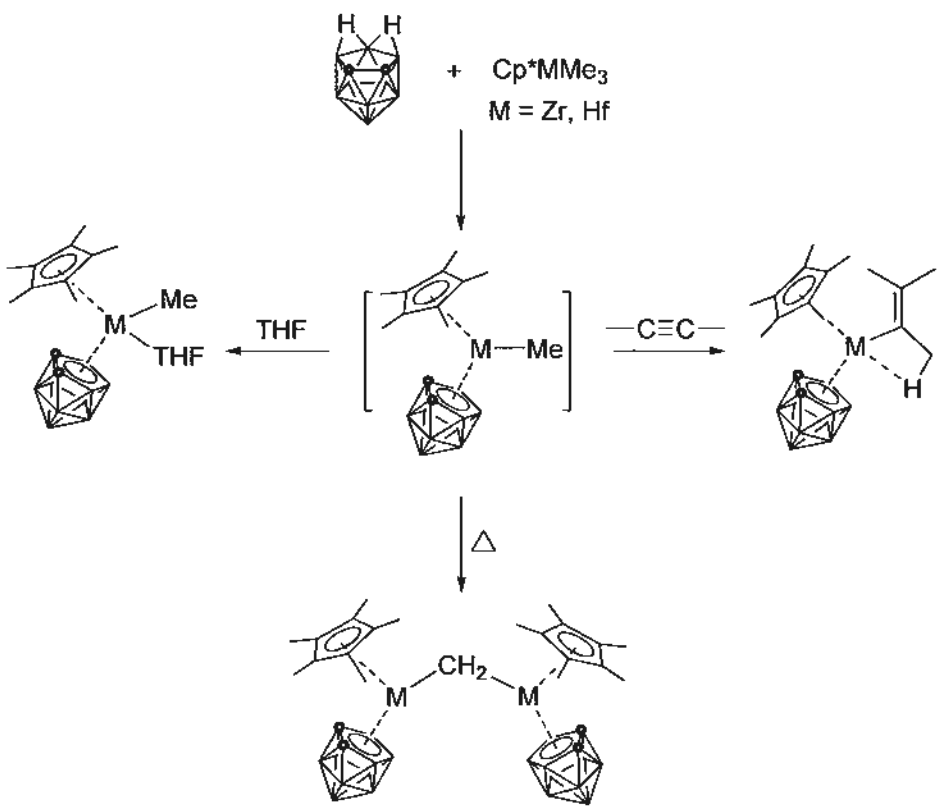
Other group 4 metal alkyl complexes with one Cp ligand, $[(Cp^*)(C_2B_9H_{11})M(Me)]_n$, were synthesized from the equimolar reaction of $C_2B_9H_{13}$ with Cp^*MMe_3 (M = Zr, Hf) in aromatic solvents. These metal alkyl complexes can catalyze the polymerization of ethylene and oligomerization of propylene. Also, it can form THF adducts $(Cp^*)(C_2B_9H_{11})M(Me)(THF)$ which do not undergo exchange

with free THF on the NMR time scale at 23 °C. Both the Zr and Hf complexes react with 2-butyne to give the monomeric alkenyl complexes $(Cp^*)(C_2B_9H_{11})M[C(Me)=CMe_2]$. Furthermore, they can undergo methane elimination to afford the methylidene-bridged complexes $[(Cp^*)(C_2B_9H_{11})M]_2(\mu\text{-}CH_2)$ (Scheme 1.3).[5a]

Scheme 1.2. Synthesis of zirconocene carborane complexes $Cp^*_2ZrMe(C_2B_9H_{12})$ and $(etmcp)_2ZrMe(C_2B_9H_{12})$.

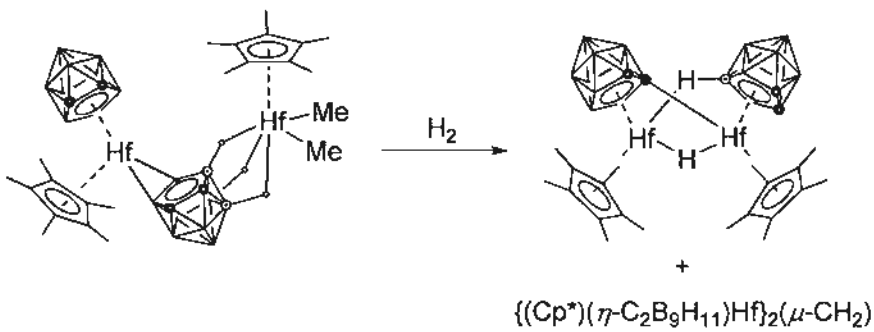


Scheme 1.3. Synthesis and reactivity of group 4 metal alkyl complexes $[(Cp^*)(C_2B_9H_{11})MMe]_n$.



The structure of $[(Cp^*)(C_2B_9H_{11})Hf(Me)]_n$ was reported later. It does not adopt a polymeric structure rather an unsymmetrical dinuclear structure $(\eta^5\text{-}Cp^*)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^2\text{:}\eta^3\text{-}C_2B_9H_{11})Hf(\eta^5\text{-}Cp^*)Me_2$. This Hf species can react with H_2 to yield the hafnium hydride complex $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_2B_9H_{10})Hf(Cp^*)H$, which can catalyze the hydrogenation of internal alkynes to *cis*-alkenes (Scheme 1.4).[9,10]

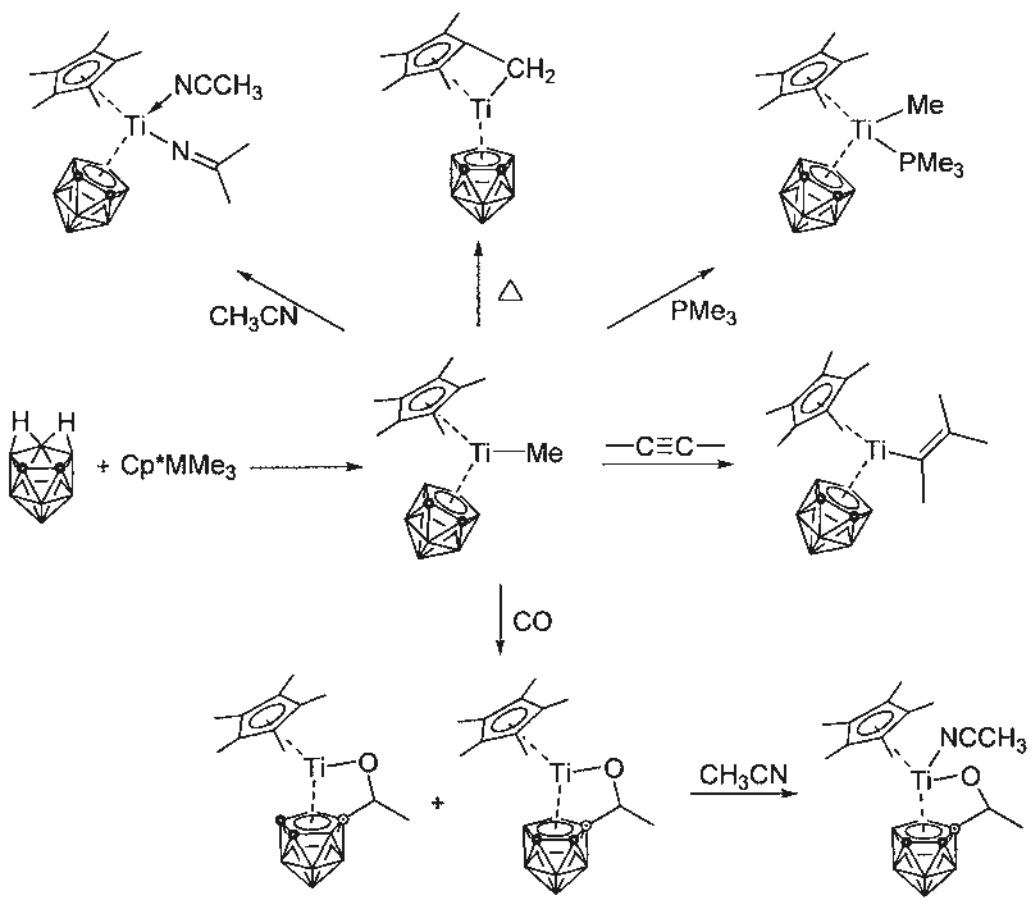
Scheme 1.4. Synthesis of hafnium hydride $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_2B_9H_{10})Hf(Cp^*)H$.



The titanium analogue was also studied. The reaction of an equimolar amount of Cp^*TiMe_3 with $C_2B_9H_{13}$ resulted in the formation of a 14-electron Ti(IV) species $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})TiMe$. X-ray studies revealed that the titanium dicarbollide complex adopts a bent metallocene structure, in contrast to the dinuclear structures found in Hf analogues. Each metallocene unit is linked by weak Ti-H-B interactions to form polymeric chain. Different from the Zr and Hf analogues, it is not thermally stable and decomposes at 23 °C to yield a monomeric fulvene complex $(\eta^6\text{-}C_5Me_4CH_2)Ti(\eta^5\text{-}C_2B_9H_{11})$, rather than a binuclear species $\{(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Ti\}(\mu\text{-}CH_2)$. This result shows the high degree of steric hindrance in the Ti complex. The Ti alkyl complex forms labile adducts with PMe_3 and THF. Insertion of CH_3CN afforded $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Ti(N{=}CMe_2)(CH_3CN)$, which loses

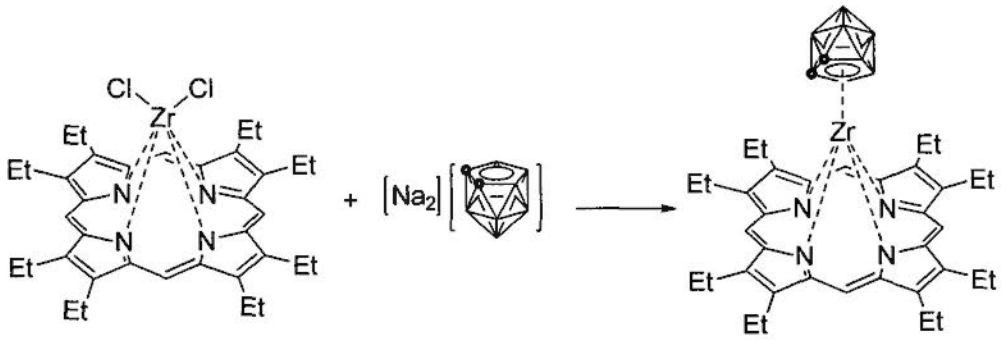
CH_3CN upon recrystallization, and reacts with ethylene to afford insertion product $(\eta^5\text{-Cp}^*)(\eta^5\text{-}C_2B_9H_{11})$TiEt and propene. It can also react with CO (0.5 – 1 atm) in toluene to yield a mixture of $Cp^*(\eta^5{:}\eta^1\text{-8-CHMeO-}C_2B_9H_{10})$Ti and $(Cp^*)(\eta^5{:}\eta^1\text{-4-CHMeO-}C_2B_9H_{10})$Ti in a molar ratio of 1:4. Both complexes contain a linked carborane-alkoxide ligand but differ in the site at the central boron of the C_2B_3 open face. ^{13}C labeling experiment shows that the formation of acyl complex $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})$TiC(=O)Me occurred first, then rearrangement took place to give the B-H bond activation products. Further treatment of $Cp^*(\eta^5{:}\eta^1\text{-4-CHMeO-}C_2B_9H_{10})$Ti with CH_3CN afforded the CH_3CN coordination complex $Cp^*(\eta^5{:}\eta^1\text{-4-CHMeO-}C_2B_9H_{10})$Ti(NCMe), which has been structurally characterized. These transformations are summarized in Scheme 1.5.[11-13]

Scheme 1.5. Synthesis and reactivity of titanacarborane $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})$TiMe.



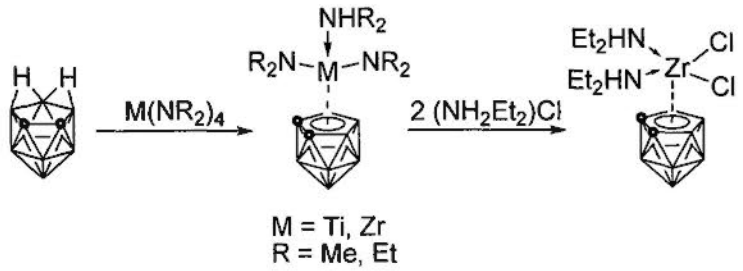
The first example of group 4 metal complex incorporating both porphyrin and *nido*-C_2B_9 ligand was synthesized by Hawthorne in 1992. This mixed sandwich complex (OEP)Zr(η^5-$C_2B_9H_{11}$) (OEP = dianion of octaethylporphyrin) was obtained from the simple metathesis reaction between (OEP)$ZrCl_2$ and [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ in refluxing THF (Scheme 1.6).[14]

Scheme 1.6. Synthesis of (OEP)Zr(η^5-$C_2B_9H_{11}$).



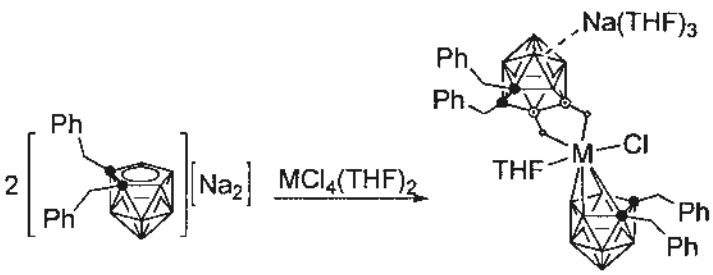
Amine elimination reactions of $C_2B_9H_{13}$ and $M(NR_2)_4$ (M = Ti, Zr; R = Me, Et) yielded the half sandwich complexes (η^5-$C_2B_9H_{11}$)$M(NR_2)_2(HNR_2)$. X-ray analyses revealed that (η^5-$C_2B_9H_{11}$)$Zr(NEt_2)_2(HNEt_2)$ adopts a three-legged piano stool geometry with one η^5-bound dicarbollyl ligand and three nitrogen atoms. (η^5-$C_2B_9H_{11}$)$Zr(NEt_2)_2(HNEt_2)$ underwent facile ligand substitution with THF, 4-picoline, and reacted selectively with 2 equiv of $[H_2NEt_2]Cl$ to give (η^5-$C_2B_9H_{11}$)$ZrCl_2(HNEt_2)_2$ (Scheme 1.7).[15]

Scheme 1.7. Synthesis of group 4 metallacarboranes.



Our group has studied the effects of cage carbon substitutions on bonding interactions between the dicarbollide and the metal ion and on the reactivity of the resulting metallacarboranes using $(C_6H_5CH_2)_2C_2B_9H_9^{2-}$ and $[o\text{-}C_6H_4(CH_2)_2]C_2B_9H_9^{2-}$ as ligands. Interaction of $MCl_4(THF)_2$ (M = Zr, Hf) with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ in THF afforded the bis(carboranyl) complexes $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2MCl(THF)\}\{Na(THF)_3\}$, rather than the half sandwich complexes (Scheme 1.8). Treatment of $(C_6H_5CH_2)_2C_2B_9H_{11}$ with $M(NEt_2)_4$ (M = Ti, Zr) in toluene gave monocarboranyl complexes $[\eta^2\text{-}(C_6H_5CH_2)C_2B_9H_9]M(NEt_2)_2(HNEt_2)$ (M = Ti, Zr) in good yields (Scheme 1.9). When a less bulky yet rigid moiety of *o*-xylylene was used, a bent-metallocene type complexes $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]_2M(THF)_2$ (M = Zr, Hf) was obtained from the reaction of $MCl_4(THF)_2$ with $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_x$ in toluene (Scheme 1.10).[16]

Scheme 1.8. Synthesis of bis(carboranyl) complexes $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2MCl(THF)\}\{Na(THF)_3\}$.

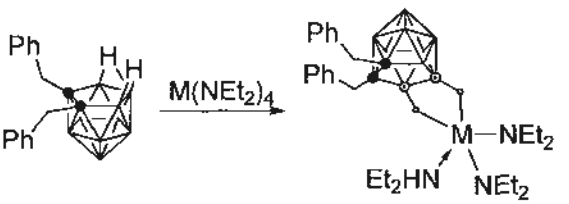


M = Zr, Hf

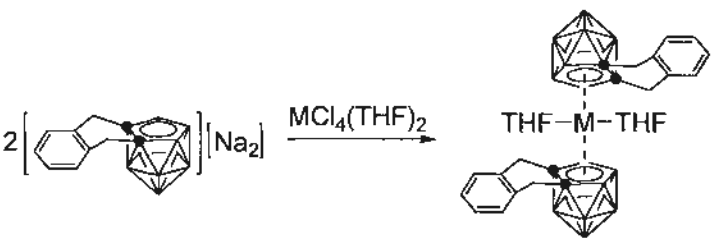
Group 4 metal complexes containing constrained-geometry ligands have attracted considerable attention because they are very active catalysts for copolymerization of α-olefins. Kang and co-workers reported the first constrained-geometry complex $[\eta^5:\eta^1\text{-}RC_2B_9H_9\text{-}CH_2NMe_2]TiCl_2$ (R = Me, H) and $[\eta^5:\eta^1\text{-}C_2B_9H_9\text{-}CH_2NMe_2]_2M$ (M

= Ti, Zr, Hf), in which the central metal atoms were in the formal oxidation state of +4. These metallacarboranes were obtained from the reaction of deprotonated ligand [*nido*-7-NMe_2CH_2-7,8-$RC_2B_9H_9$]$^{2-}$ with MCl_4 in THF. The structure of the full-sandwich zirconacarborane [η^5:η^1-$C_2B_9H_9$-CH_2NMe_2]$_2$Zr was confirmed by single-crystal X-ray analyses (Scheme 1.11).[17] The titanacarboranes [η^5:η^1-$RC_2B_9H_9$-CH_2NMe_2]$TiCl_2$ (R = Me, H) exhibit moderate catalytic activities for ethylene polymerization in the presence of MAO.[17] Hosmane and coworkers reported the synthesis of other constrained-geometry group 4 metal complexes [η^5:η^1-$C_2B_9H_{10}$-CH_2NH]$MCl(THF)_n$ (M = Zr, n = 1; Ti, n = 0). These metallacarboranes were obtained from a 1:1 molar reaction of triple salt of the [*nido*-7-($NHCH_2$)-7,8-$C_2B_9H_{10}$]$^{3-}$ trianion with MCl_4 in THF, whose structures have not been confirmed by X-ray analyses yet (Scheme 1.12).[18]

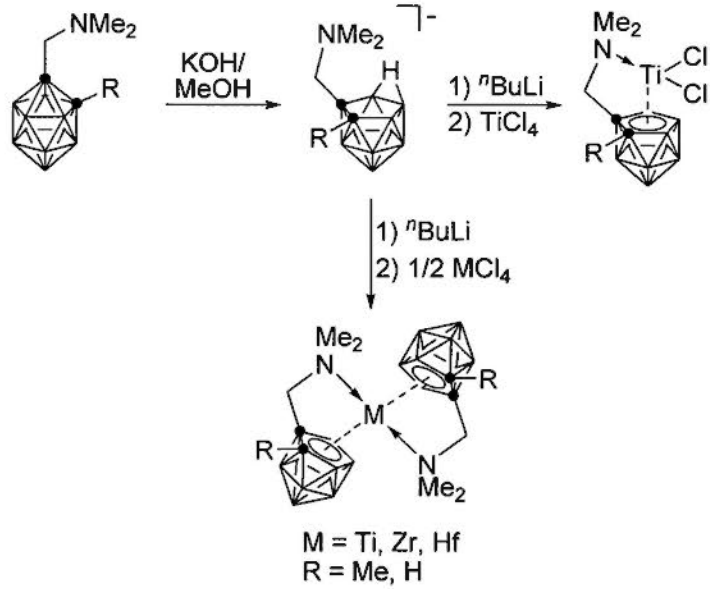
Scheme 1.9. Synthesis of monocarboranyl complexes [η^2-($C_6H_5CH_2$)$C_2B_9H_9$]$M(NEt_2)(HNEt_2)$.



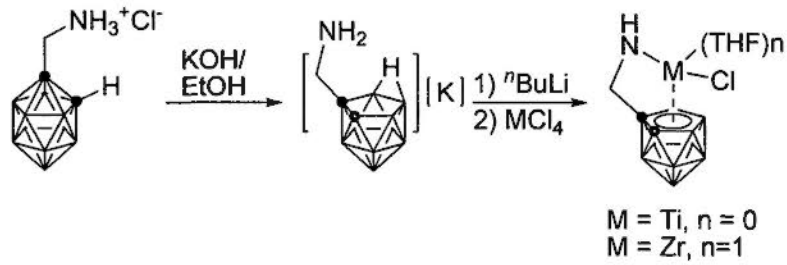
Scheme 1.10. Synthesis of bent-metallocene of complexes [{*o*-$C_6H_4(CH_2)_2$}$C_2B_9H_9$]$_2M(THF)_2$.



Scheme 1.11. Synthesis of constrained-geometry complexes containing [*nido*-7-NMe_2CH_2-7,8-$RC_2B_9H_9$]$^{2-}$ ligands.

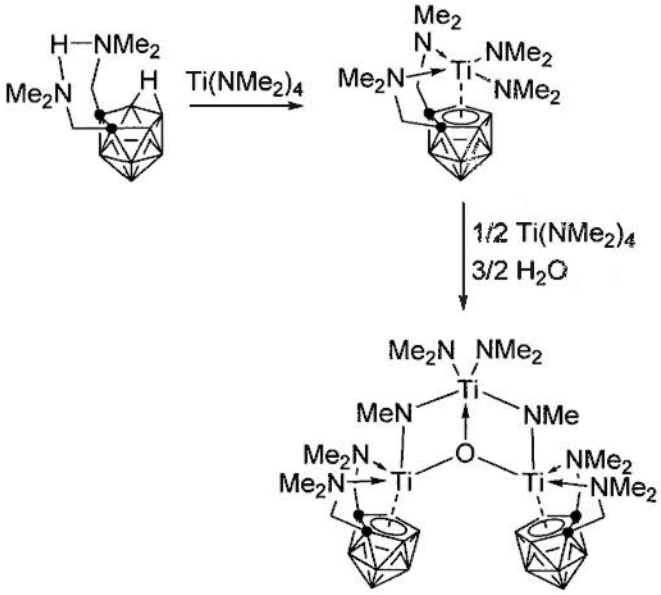


Scheme 1.12. Synthesis of constrained-geometry complexes [η^5:η^1-$C_2B_9H_{10}$-CH_2NH]$MCl(THF)_n$.



Kang and coworkers also reported the preparation of multidentate dicarbollide ligand *nido*-7,8-$(NMe_2CH_2)_2$-7,8-$C_2B_9H_{11}$, and the corresponding group 4 metallacarboranes. Interaction of *nido*-7,8-$H(NMe_2CH_2)_2$-7,8-$C_2B_9H_{11}$ with $Ti(NMe_2)_4$ in toluene afforded the half-sandwich complex [η^5:η^1-$(NMe_2CH_2)_2C_2B_9H_9CH_2NMe_2$]$Ti(NMe_2)_2$. This titanacarborane reacted with 0.5 equiv of $Ti(NMe_2)_4$ and 1.5 equiv of water to give oxo-bridged trimetallic complex [η^5:η^1-{$(NMe_2CH_2)C_2B_9H_9CH_2NMe_2$}$Ti(NMe)]_2$-$\mu^3$-O-$Ti(NMe_2)_2$ (Scheme 1.13).[19]

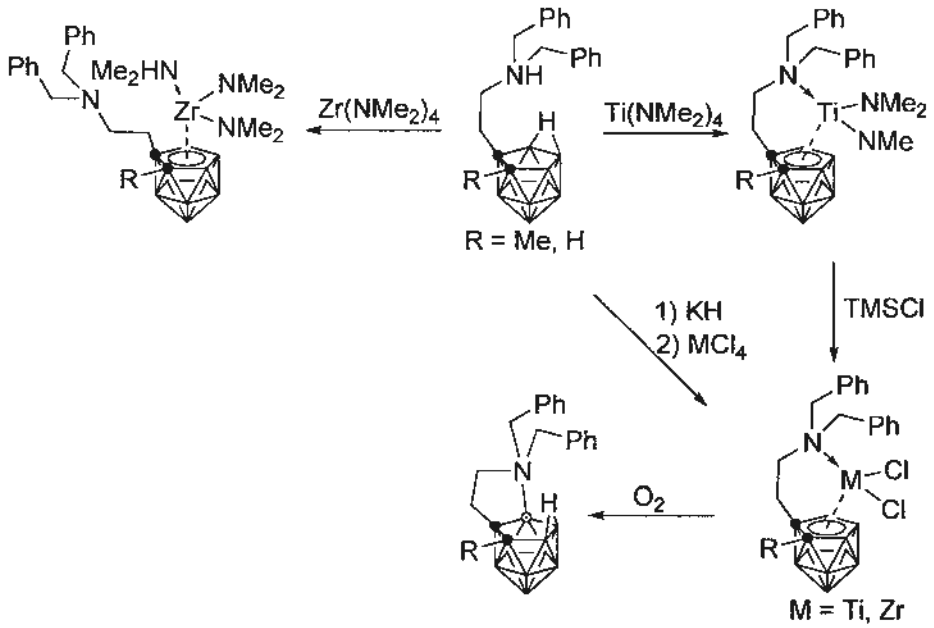
Scheme 1.13. Synthesis of titanacarboranes containing multidentate dicarbollide ligand [*nido*-7,8-(NMe_2CH_2)$_2$-7,8-$C_2B_9H_{10}$]$^{2-}$.



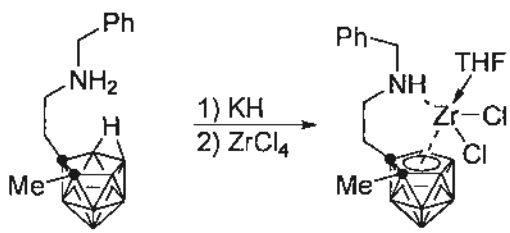
The Kang's group reported various types of constrained-geometry complexes in 2005. Reaction of the potassium salt of ligand [*nido*-7-$NBz_2(CH_2)_2$-8-$C_2B_9H_{10}$]$^{2-}$ with $ZrCl_4$ gave the constrained-geometry complex [(η^5-$RC_2B_9H_9$)$(CH_2)_2$(η^1-NBz_2)]$ZrCl_2$ (R = Me, H). Reaction of *nido*-7-$HNBz_2(CH_2)_2$-8-$C_2B_9H_{11}$ with $Ti(NMe_2)_4$ afforded the titanium amide complex [(η^5-$RC_2B_9H_9$)$(CH_2)_2$(η^1-NBz)]$Ti(NMe_2)_2$, which can be converted to the corresponding chloride species [(η^5-$RC_2B_9H_9$)$(CH_2)_2$(η^1-NBz_2)]$TiCl_2$ by treatment with TMSCl. These titanium dichloride species undergo unusual B,N-cyclization reaction to generate an exocyclic dicarbollide *exo*-B,N-*nido*-7,11-$NBz_2(CH_2)_2$-8-R-7,8-$C_2B_9H_9$ (R = Me, H) when reacted with O_2. In contrast, the reaction of the dicarbollide with $Zr(NMe_2)_4$ gave the untethered half-sandwich metallacarborane [(η^5-$RC_2B_9H_9$)$(CH_2)_2$(NBz_2)]$Zr(NMe_2)_2(NHMe_2)$, in which the dibenzylamine sidearm was not coordinated to the Zr metal, which was presumably owing to the steric interaction between the dibenzyl unit and the

dicarbollyl ligand (Scheme 1.14).[20] The sterically less hindered mono-benzylamino-dicarbollide ligand reacted with $ZrCl_4$ in toluene to give the constrained-geometry complex $[(\eta^5\text{-}CH_3C_2B_9H_9)(CH_2)_2(\eta^1\text{-}NBz_2)]ZrCl_2(THF)$ (Scheme 1.15).[20]

Scheme 1.14. Synthesis and reactivity of group 4 metallacarboranes containing $[nido\text{-}7\text{-}NBz_2(CH_2)_2\text{-}8\text{-}C_2B_9H_{10}]^{2-}$ ligand.



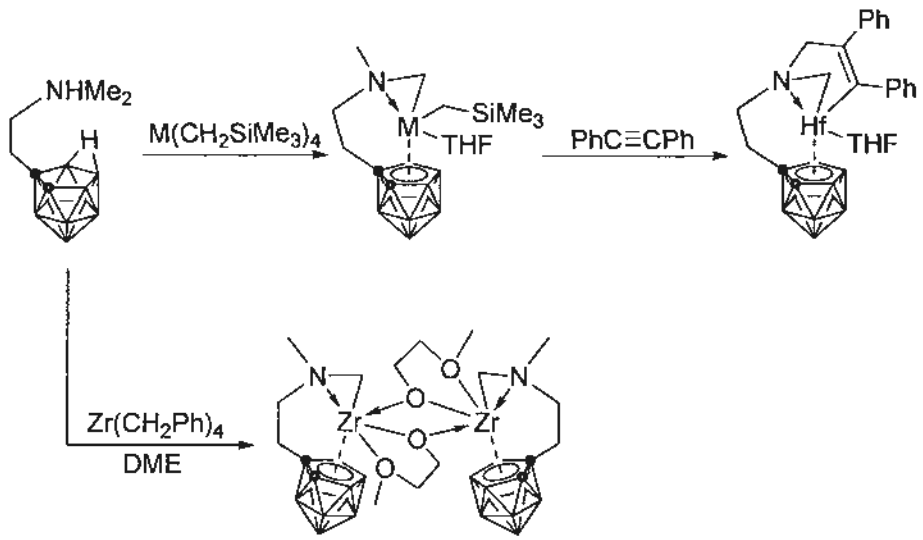
Scheme 1.15. Synthesis of constrained-geometry complex $[(\eta^5\text{-}CH_3C_2B_9H_9)(CH_2)_2(\eta^1\text{-}NBz_2)]ZrCl_2(THF)$.



Interaction of $7\text{-}Me_2N(H)CH_2CH_2\text{-}7,8\text{-}C_2B_9H_{11}$ with $M(CH_2TMS)_4$ in toluene gave the C-H bond activation products $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]M(CH_2TMS)(THF)$ (M = Zr, Hf). Insertion

of diphenylacetylene into the Hf-C bond and subsequent elimination of $SiMe_4$ generated a new metallacyclic complex $[\sigma:\sigma:\eta^1:\eta^5\text{-}\{(CH_2)[(CH_2)PhC{=}CPh]N(CH_2)_2C_2B_9H_{10}\}]Hf(THF)$. On the other hand, treatment of 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ with $Zr(CH_2Ph)_4$ in refluxing DME gave the C-H/C-O bond activation species $[\{\eta^1:\sigma:\eta^5\text{-}[MeN(CH_2)CH_2CH_2]C_2B_9H_{10}\}Zr(\mu:\eta^1\text{-}OCH_2CH_2OCH_3)]_2$, which was supposed to come from the reaction of intermediate $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2Ph)$ with DME (Scheme 1.16).[21]

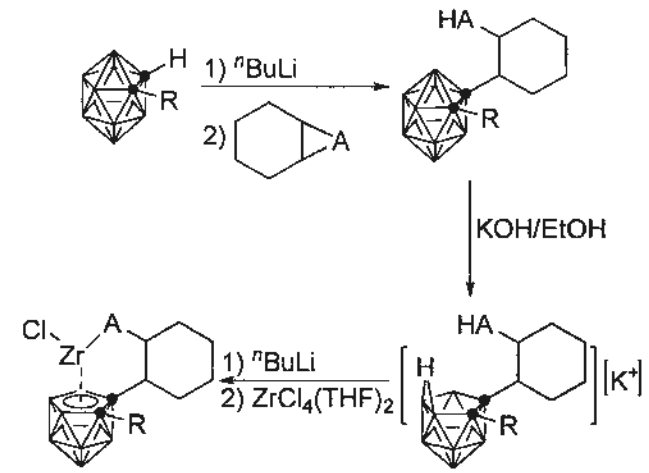
Scheme 1.16. Synthesis and reactivity of group 4 metallacarboranes incorporating $[7\text{-}Me_2NCH_2CH_2\text{-}7,8\text{-}C_2B_9H_{10}]^{2-}$ ligand.



Dicarbollide ligands with cyclohexyl oxide[22] or aminocyclohexyl sidearms[23] were synthesized from the reaction of carborane monolithium salt with cyclohexene oxide or 7-azabicyclo [4.1.0] heptanes, respectively. Interaction of $[nido\text{-}1\text{-}R\text{-}2\text{-}(2'\text{-}AC_6H_4)\text{-}1,2\text{-}C_2B_9H_9]^{3-}$ (A = O, R = Me or A = NH, R = Ph) with $MCl_4(THF)_2$ produced the corresponding half-sandwich metallacarboranes $[\eta^5:\sigma\text{-}7\text{-}R\text{-}8\text{-}AC_6H_4(C_2B_9H_9)]MCl$ (M = Zr, Ti) in moderate yields. The Merrifield's

peptide resin substituted dicarbollide ligand [*nido*-1-(2'-AC_6H_4)-2-polystyryl-1,2-$C_2B_9H_9$]$^{3-}$ and the corresponding half sandwich zirconacarborane [η^5:σ-7-(2'-AC_6H_4)-8-polystyryl-($C_2B_9H_9$)]ZrCl were also synthesized (Scheme 1.17). These zirconacarboranes can catalyze polymerization of ethylene and vinyl chloride in toluene to give high molecular weight polymers.[22,23]

Scheme 1.17. Synthesis of group 4 metallacarboranes incorporating dicarbollide ligands with cyclohexyl oxide or aminocyclohexyl sidearms.

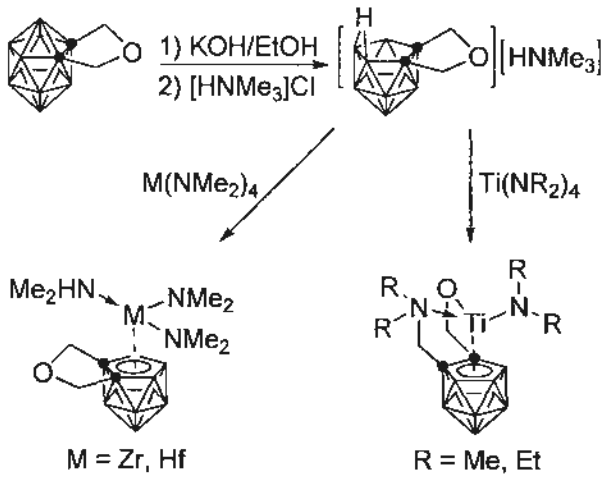


A = O, R = Me or peptide resin
A = NH, R = Ph or peptide resin

Amine elimination reaction between $M(NR_2)_4$ and $[Me_3NH][7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]$ gave [η^5-(CH_2OCH_2)$C_2B_9H_9$]M(NMe_2)$_2$($NHMe_2$) (M = Zr, Hf) or unexpected C-O bond cleavage product [σ:η^1:η^5-(OCH_2)(R_2NCH_2)$C_2B_9H_9$]Ti(NR_2) (R = Me, Et) (Scheme 1.18). The formation of the titanium species was found to be a convenient and practical method for the synthesis of constrained-geometry half-sandwich metallacarboranes with two different sidearms.[24] This titanacarborane reacted with a variety of unsaturated molecules such as R-N=C=N-R, CS_2, RNCS, R_2C=C=O, RCN, RNC and RNCO to give the Ti-N bond mono-insertion products (Scheme 1.19). The

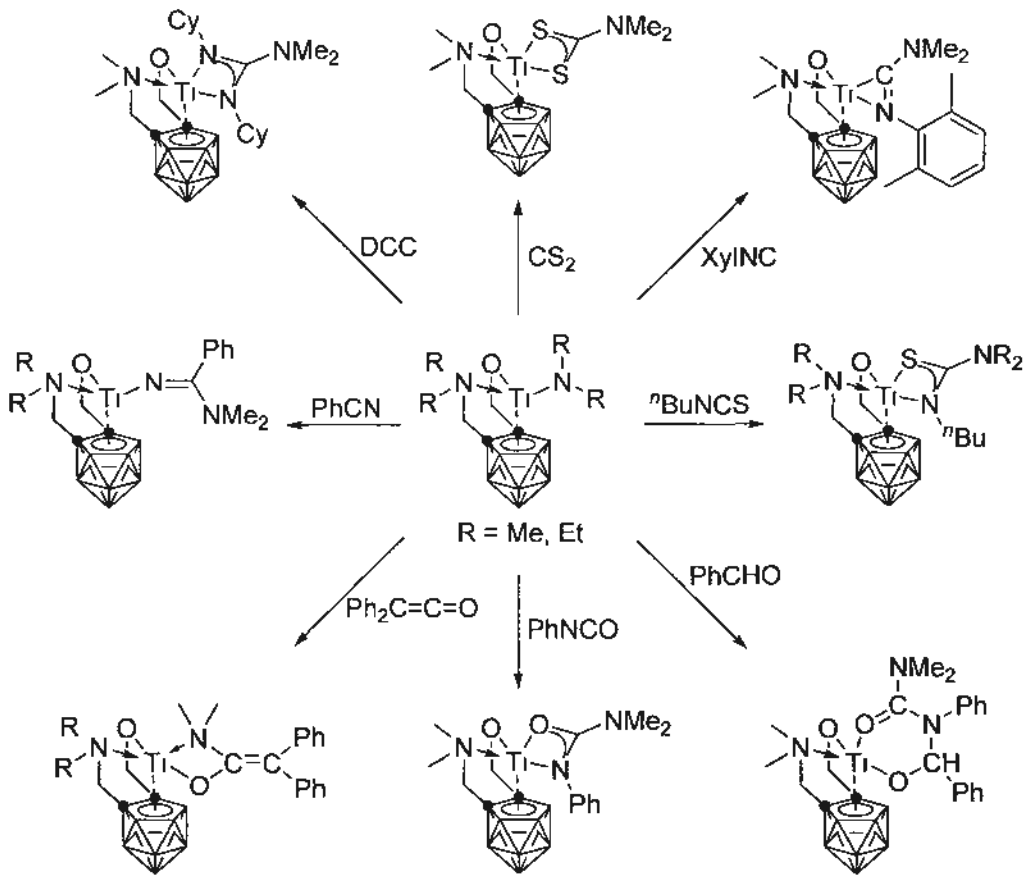
Ti-O bond remained inert in these reactions.[24] Moreover, the half-sandwich titanacarborane amide $[\sigma:\eta^1:\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti(NMe_2)$ can catalyze guanylation of amines in a broad substrate scope.[25]

Scheme 1.18. Synthesis of group 4 metal amides bearing dicarbollyl ligand.

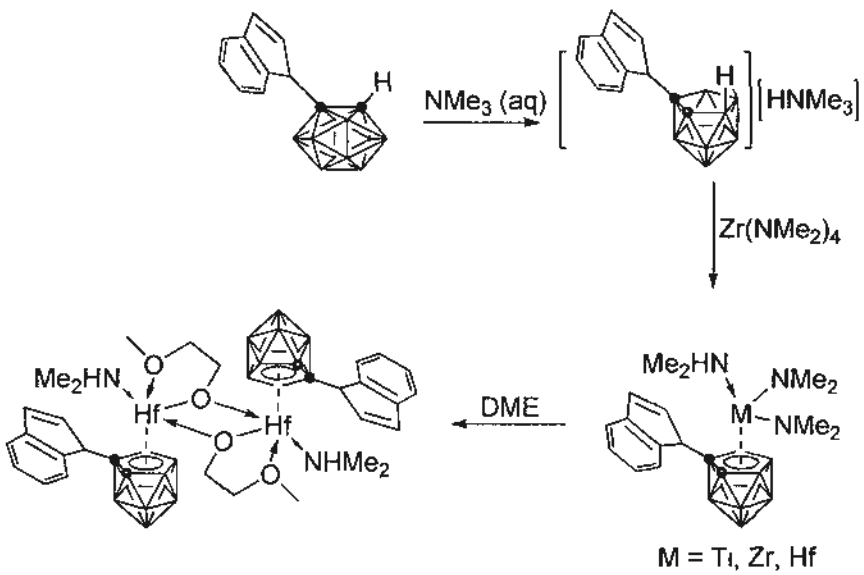


Constrained-geometry dicarbollide $[Me_3NH][7\text{-}C_9H_7\text{-}7,8\text{-}C_2B_9H_{11}]$ was obtained from the reaction of 1-indenyl-1,2-carborane with NMe_3 aqueous solution. Equimolar reaction of this complex with $M(NMe_2)_4$ (M = Zr, Hf) afforded structurally unique complexes $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]M(NMe_2)_2(NHMe_2)$ (M = Ti, Zr, Hf) in good yields (Scheme 1.20).[26] Reaction of $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$ with carbodiimides were studied. The results showed that the guanidinato ligand is not always inert, and can undergo C-N bond cleavage to generate amides and carbodiimides.[27] Dissolving $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Hf(NMe_2)_2(NHMe_2)$ in DME led to the isolation of a C-O bond cleavage product $[\{\eta^5\text{-}(C_9H_7)C_2B_9H_{10}\}Hf(NMe_2)(\mu:\eta^1\text{-}OCH_2CH_2OCH_3)]_2$ in 12 % yield. The formation of this Hf species was proposed to proceed through a σ-bond metathesis reaction as shown in Scheme 1.20.[26]

Scheme 1.19. Reactivity of titanacarboranes $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(R_2NCH_2)C_2B_9H_9]Ti(NR_2)$.



Scheme 1.20. Synthesis and reactivity of group 4 metallacarboranes incorporating $[7\text{-}C_9H_7\text{-}7,8\text{-}C_2B_9H_{10}]^{2-}$ ligand.

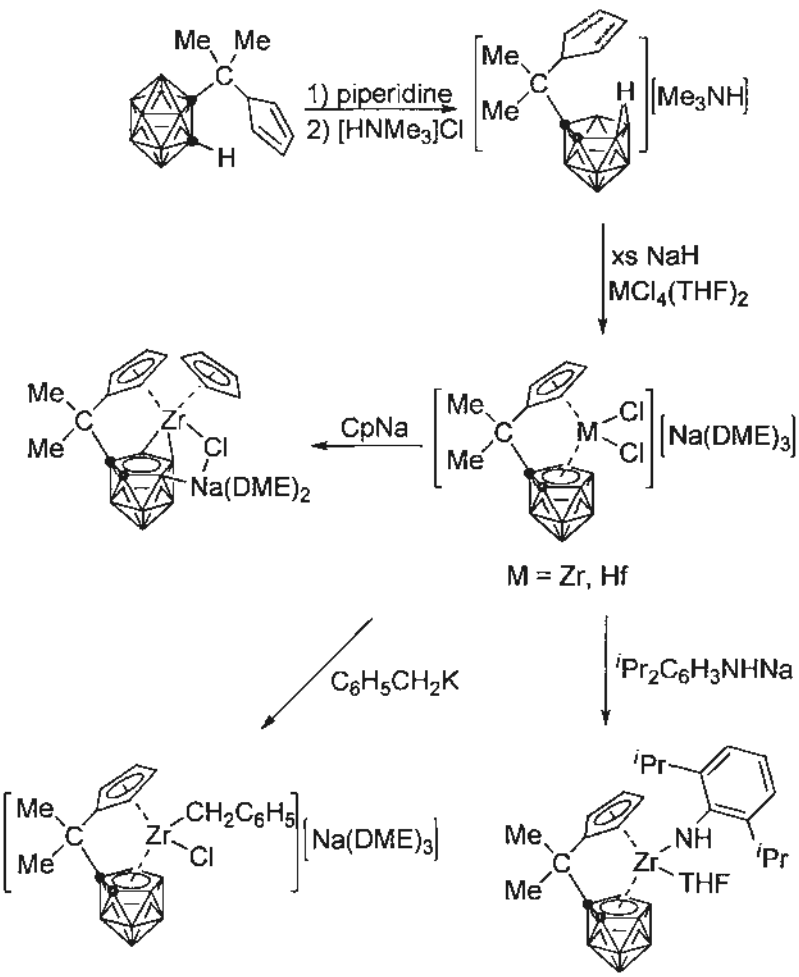


Recently, our group has reported the selective deboration of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ using piperidine/EtOH as deboration reagent. Its group 1 metal salts were useful synthons for the preparation of group 4 metallocenes. X-ray studies revealed that the presence of a Me_2C linkage in these group 4 complexes increases the open coordination sphere of the central metal significantly, in comparison with the corresponding unbridged complexes $(Cp^*)(C_2B_9H_{11})MCH_3$, which make the synthesis of neutral metal alkyls unsuccessful. The neutral group 4 metal amide species $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3{}^iPr_2)(THF)$ was obtained from the reaction of $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ with $NaNHC_6H_3{}^iPr_2$ in THF, and the relatively short Zr-N distance suggested the presence of $p_\pi(N)$-$d_\pi(Zr)$ interaction. Such an electronic plus steric effect imposed by the two ^{i}Pr groups lead to the formation of a neutral metallacarborane. Both $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr, Hf) and $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ exhibit very high activities in ethylene polymerization after activation with a large amount of MAO. The active species were suggested to be the neutral group 4 metal methyl complexes $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]MCH_3$. These transformations are summarized in Scheme 1.21.[28]

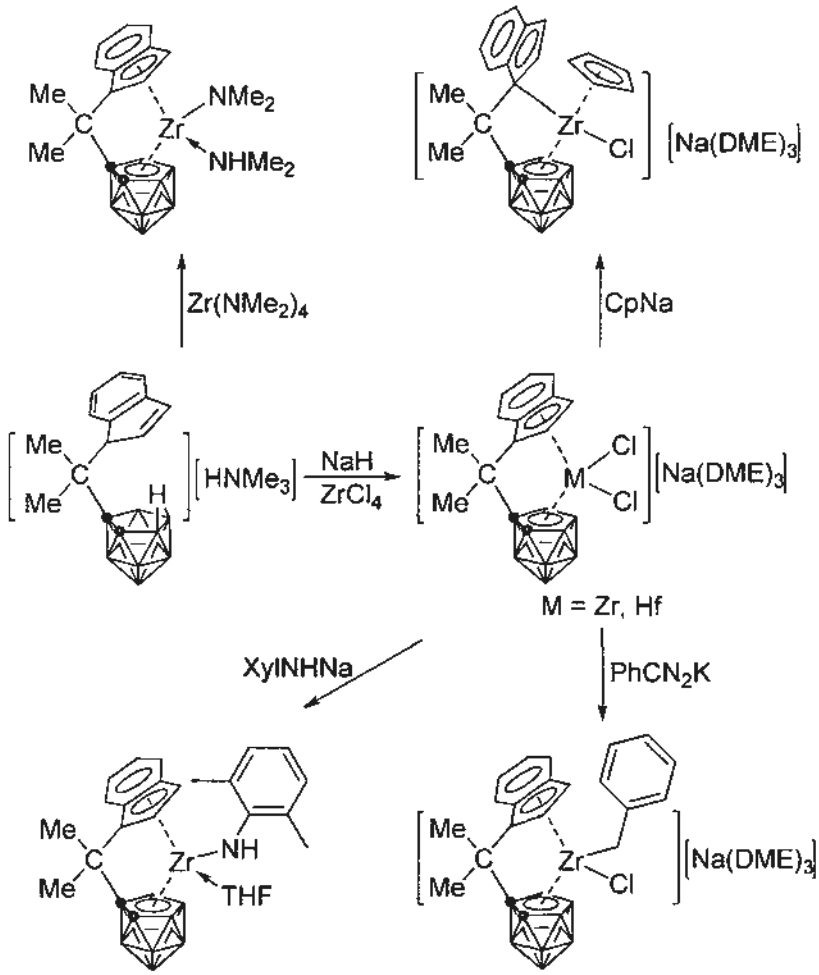
Later, an indenyl analogue $Me_2C(C_9H_7)(C_2B_9H_{11})^-$ was synthesized by the same method, and was expected that the diverse bonding mode (η^5-η^3-η^1) between the central metal and five-membered ring of the indenyl ligand could facilitate the formation of neutral metal alkyls. Treatment of the trianionic salt of the ligand with $MCl_4(THF)_2$ afforded the mixed sandwich complex *trans*-$[\{\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr, Hf). Complex ions were always obtained when the dichloro species reacted with KCH_2Ph or C_5H_5Na.

Also, no NaCl elimination was observed upon heating their DME solution. Neutral metallocenes can be achieved only in the presence of amido or alkoxyl coligands, which can be ascribed to the p_{π}-d_{π} interactions. Complexes *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$MCl_2$][$Na(DME)_3$] (M = Zr, Hf) and *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl(CH_2C_6H_5)$][$Na(DME)_3$] are active catalysts for ethylene polymerization after activation by a large amount of MAO, but their activities are lower than the corresponding cyclopentadienyl analogues. These transformations are summarized in Scheme 1.22.[29]

Scheme 1.21. Synthesis and reactivity of metallacarborane containing $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ ligand.



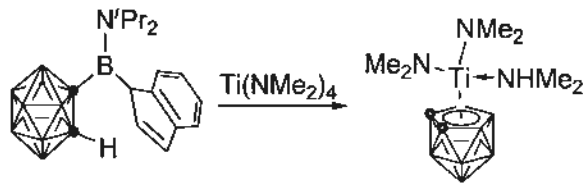
Scheme 1.22. Synthesis and reactivity of metallacarborane containing $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ ligand.



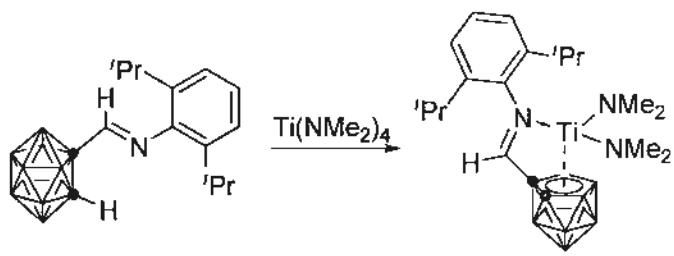
Interaction of *closo*-carborane ligand with group 4 metal amides sometimes afforded the metallacarborane amides, in which the carborane cages were deborated to a $[nido\text{-}C_2B_9]^{2-}$ anion. Treatment of $^{i}Pr_2NB(C_9H_7)(C_2B_{10}H_{11})$ with an equimolar amount of $Ti(NMe_2)_4$ in toluene led to the isolation of the deborated product $(\eta^5\text{-}C_2B_9H_{11})Ti(NMe_2)_2(NHMe_2)$ (Scheme 1.23). But the reaction was very complicated as monitored by ^1H NMR. It was assumed that NMe_2 group in $Ti(NMe_2)_4$ might attack the bridging B atom and the carborane cage, leading to the formation of $(\eta^5\text{-}C_2B_9H_{11})Ti(NMe_2)_2(NHMe_2)$.[30] Another carborane ligand, $1\text{-}(CH{=}NC_6H_3{}^{i}Pr_2\text{-}2,6)\text{-}1,2\text{-}C_2B_{10}H_{11}$, reacted with $Ti(NMe_2)_4$ in toluene at 70 °C to

give the deborated species $[\eta^1:\eta^5$-$(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Ti(NMe_2)_2$ (Scheme 1.24).[31] The xylene analogue 1-$(CH{=}NC_6H_3Me_2$-2,6)-1,2-$C_2B_{10}H_{11}$ also reacted with $Ti(NMe_2)_4$ to give a mixture of $[\eta^1:\eta^5$-$(Me_2C_6H_3N{=}CH)C_2B_9H_{10}]Ti(NMe_2)_2$ and $[\eta^1:\eta^5$-$(Me_2N)CH(NMe_2)C_2B_9H_{10}]Ti(NMe_2)_2$, as evidenced by NMR spectroscopy (Scheme 1.25). These reactions suggested that the in situ generated $HNMe_2$ might act as the deboration agent for the formation of the two metallacarboranes.[31] Moreover, interaction of $(C_{13}H_9)(^iPr_2N)P(=O)(C_2B_{10}H_{11})$ with $Zr(NMe_2)_4$ in toluene at room temperature or at 110 °C in a sealed vessel gave amine elimination product $[\sigma{:}\sigma$-$(C_{13}H_8)(^iPr_2N)P(-O)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ or deborated product $[\eta^1:\eta^5$-$(C_{13}H_9)$-$(^iPr_2N)P(=O)(C_2B_9H_{10})]M(NMe_2)_2$ (M = Ti, Zr) in moderate yield. Complex $[\sigma{:}\sigma$-$(C_{13}H_8)(^iPr_2N)P(-O)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ was stable in refluxing toluene, but converted to the deborated species $[\eta^1:\eta^5$-$(C_{13}H_9)$-$(^iPr_2N)P(=O)(C_2B_9H_{10})]Zr(NMe_2)_2$ in the presence of excess $HNMe_2$ (Scheme 1.26).[32]

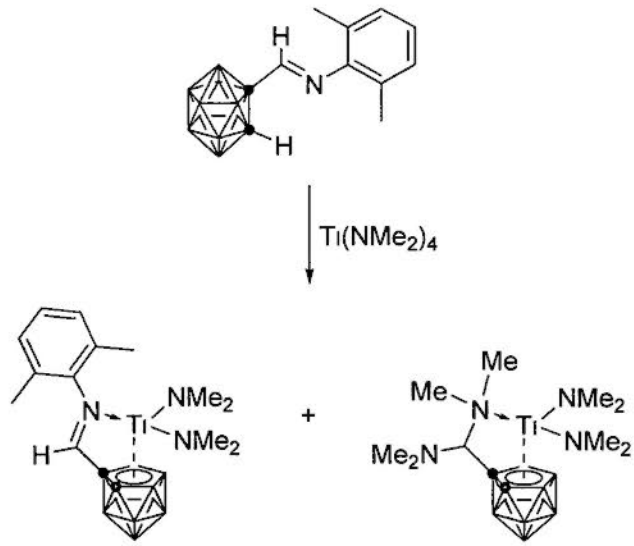
Scheme 1.23. Reaction of $Ti(NMe_2)_4$ with $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ ligand.



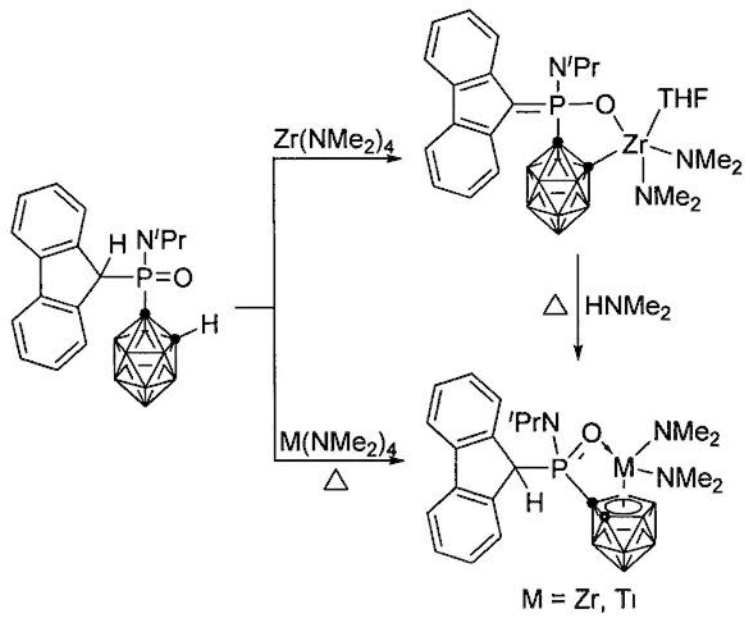
Scheme 1.24. Reaction of $Ti(NMe_2)_4$ with 1-$(CH{=}NC_6H_3{}^iPr_2$-2,6)-1,2-$C_2B_{10}H_{11}$ ligand.



Scheme 1.25. Reaction of $Ti(NMe_2)_4$ with 1-(CH=$NC_6H_3Me_2$-2,6)-1,2-$C_2B_{10}H_{11}$ ligand.

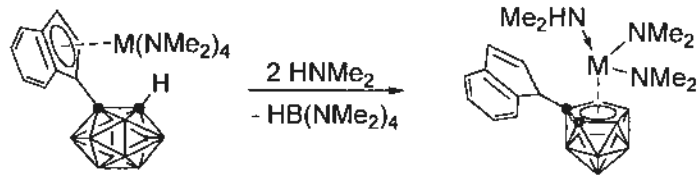


Scheme 1.26. Reaction of $M(NMe_2)_4$ with $(C_{13}H_9)(^iPr_2N)P(=O)(C_2B_{10}H_{11})$ ligand.



Besides the single atom bridged carborane ligands, the group 4 metal amide complexes $[\eta^5\text{-}(C_2B_{10}H_{11})C_9H_6]M(NMe_2)_3$ (M = Zr, Hf) derived from the 1-indenyl-1,2-carborane can be converted to the corresponding metallacarborane $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]M(NMe_2)_2(NHMe_2)$ in the presence of $HNMe_2$ (Scheme 1.27).[26]

Scheme 1.27. Reaction of $[\eta^5\text{-}(C_2B_{10}H_{11})C_9H_6]M(NMe_2)_3$ with $HNMe_2$.



1.2. Group 4 Metal Complexes Bearing *closo*-C_2B_{10} Ligands

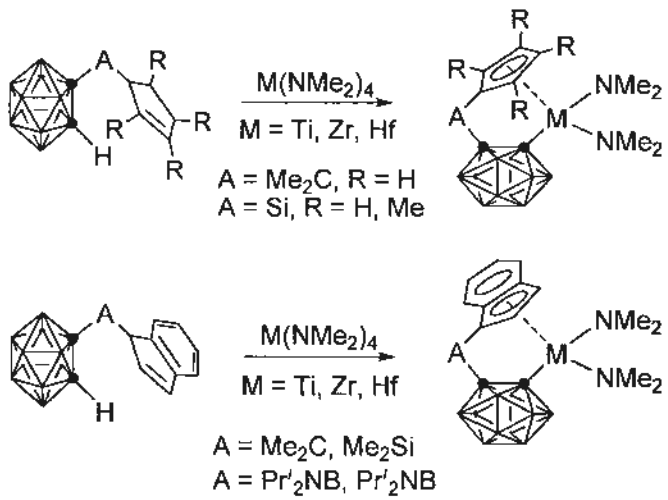
Group 4 metal "constrained-geometry" complexes bearing a *closo*-carboranyl ligand is of interest as they contain M-C_{cage} σ-bonds, which would be active toward unsaturated molecules. Thus several kinds of ligands R-$C_2B_{10}H_{11}$ were prepared and used to synthesize metal complexes bearing *closo*-carboranyl ligand, and their reactivities were also studied.[33]

A series of versatile ligands, $A(C_5HR_4)(C_2B_{10}H_{11})$ (A = Me_2C, R = H; A = Me_2Si, R = H, Me), $A(C_9H_7)(C_2B_{10}H_{11})$ (A = Me_2C, Me_2Si, Pr^i_2NB, Pr^i_2NP), $Me_2Si(C_9H_6CH_2CH_2G)(C_2B_{10}H_{11})$ (G = OMe, NMe_2) and $A(C_{13}H_9)(C_2B_{10}H_{11})$ (A = H_2C, Me_2Si), have been developed.[33] Their group 4 "constrained-geometry" complexes $[\eta^5\text{:}\sigma\text{-}A(C_5HR_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ (A = Me_2C, R = H; A = Me_2Si, R = H, Me), $[\eta^5\text{:}\sigma\text{-}A(C_9H_6)(C_2B_{10}H_{10})]M(NMe_2)_2$ (A = Me_2C, Me_2Si, $^tPr_2NB$, $^tPr_2NP$) were synthesized by treatment of $M(NMe_2)_4$ (M = Ti, Zr, Hf) with 1 equiv of $A(C_5HR_4)(C_2B_{10}H_{11})$ (A = Me_2C, R = H; A = Me_2Si, R = H, Me) or $A(C_9H_7)(C_2B_{10}H_{11})$ (A = Me_2C, Me_2Si, $^tPr_2NB$, $^tPr_2NP$), respectively, as shown in Scheme 1.28.[33] The planarity of the nitrogen atoms and noticeably short M-N bonds in these complexes indicate the sp^2 hybridization of the N atoms and partial $N(p_\pi)\rightarrow M(d_\pi)$ interactions.[33]

Reactions of $[\eta^5\text{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (A = C, Si) toward polar unsaturated molecules were investigated in detail. The results showed that

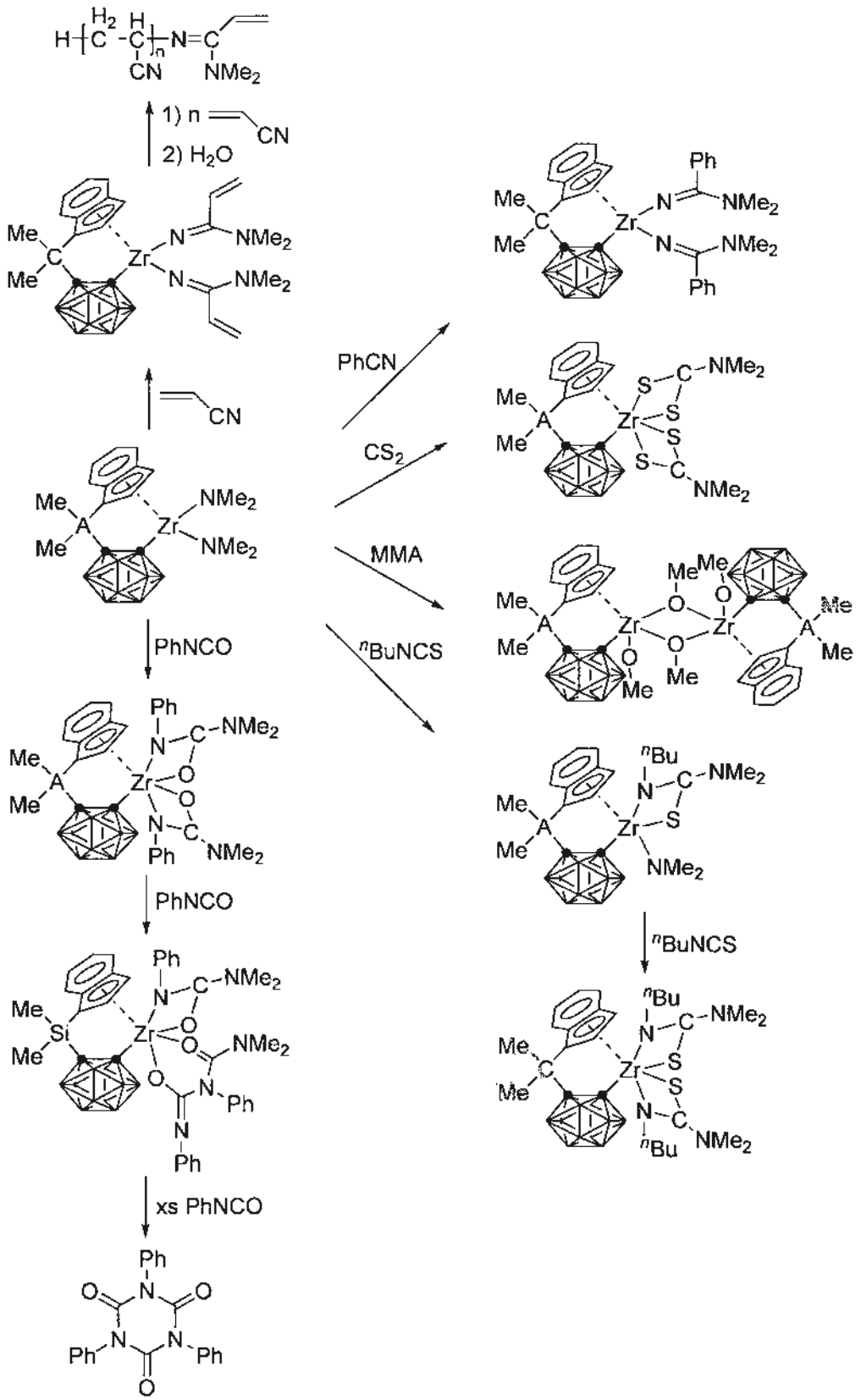
unsaturated molecules such as CS_2, PhCN, CH_2=CHCN, ^{n}BuNCS and PhNCO insert exclusively into the Zr-N bond affording the mono-, di-, or tri-insertion products depending on the substrates, whereas the Zr-C_{cage} bond remains intact (Scheme 1.29). The preference of Zr-N over Zr-C_{cage} insertion is mainly governed by steric factors.[34]

Scheme 1.28. Synthesis of constrained-geometry group 4 metal amide complexes.

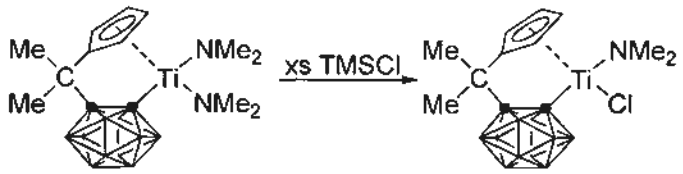


The above constrained-geometry carboranyl group 4 metal amides can be conveniently converted into the corresponding chloride complexes by interaction with $[HNMe_3]Cl$ or TMSCl, depending on the ligands and the group 4 metal ions. Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ with excess TMSCl in toluene generated the corresponding monochloro metal amide $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ (Scheme 1.30).[35] The zirconium chloride species $[HNMe_3][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2$ (A = C, Si) can also be synthesize by treatment of $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with 2.5 equiv of $[HNMe_3]Cl$ in a typical yield of 85% (Scheme 1.31). The Zr-C_{cage} bond remains intact in these reactions even in the presence of excess $[HNMe_3]Cl$, indicating that the Zr-C σ bond is well protected by the carborane moiety.[35]

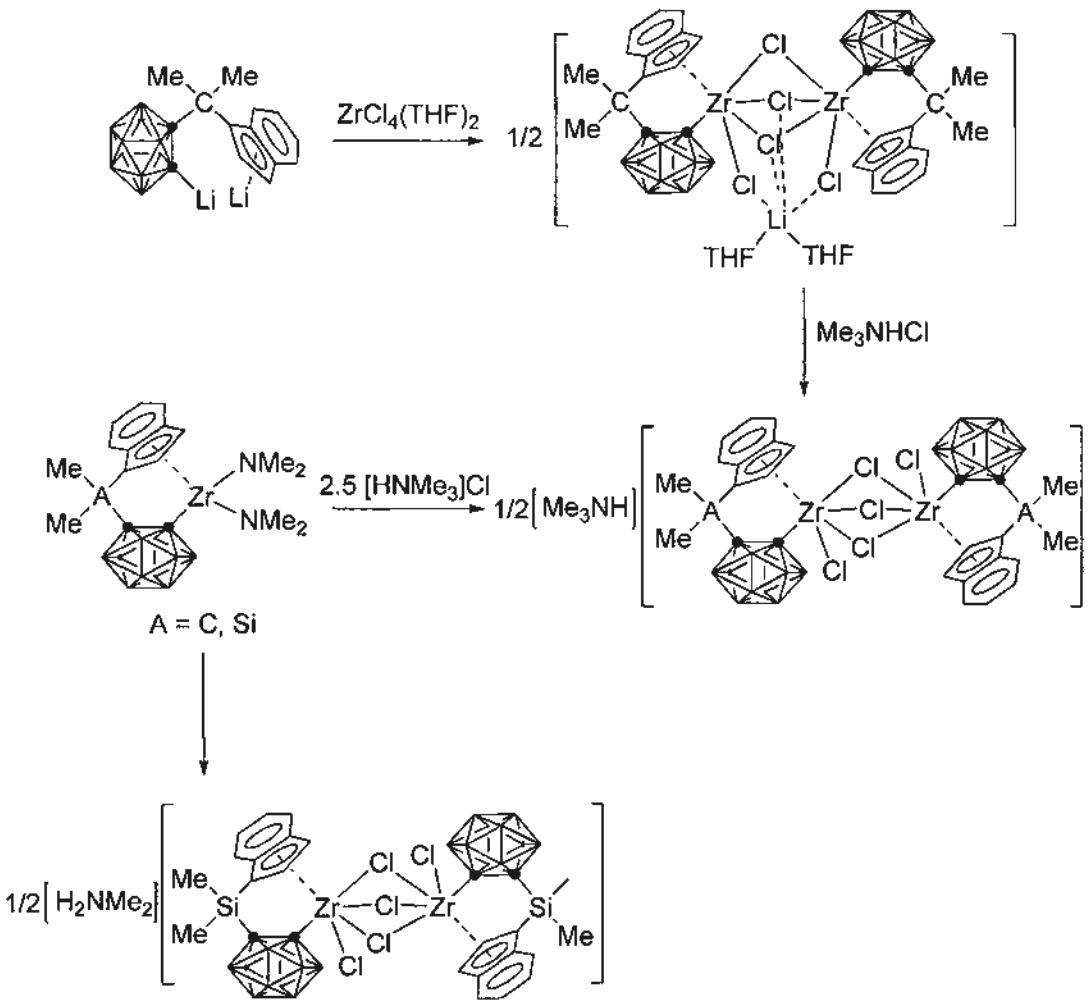
Scheme 1.29. Reactivity of $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$.



Scheme 1.30. Synthesis of titanium chloride species $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$.



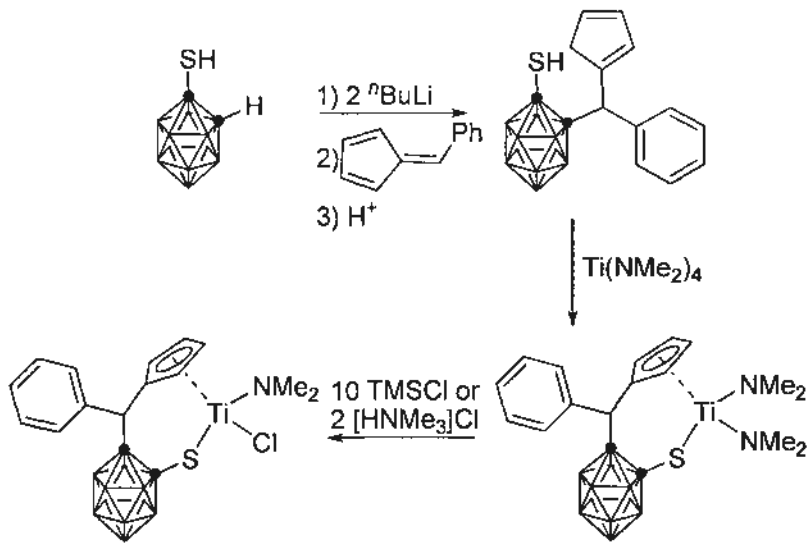
Scheme 1.31. Synthesis and reactivity of zirconium complexes containing carbon-bridged indenyl-carboranyl ligand.



A new carboranyl-thiol-appended cyclopentadiene ligand, 1-SH-2-$[C_5H_5CH(Ph)]$-*closo*-1,2-$C_2B_{10}H_{10}$ was prepared from the equimolar reaction of dilithium salt of 1-SH-*closo*-1,2-$C_2B_{10}H_{11}$ with 6-phenylfulvene. Reaction of this

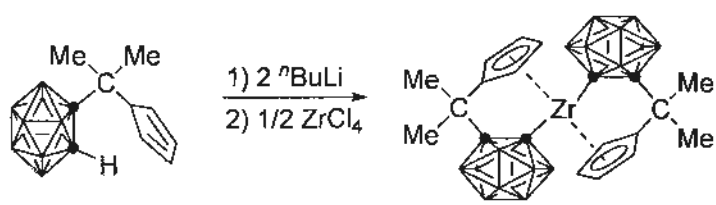
ligand with $Ti(NMe_2)_4$ gave the titanium amide complex [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$]$Ti(NMe_2)_2$, which can be converted to the corresponding monochloro species [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$]$TiCl(NMe_2)$ in the presence of TMSCl or $[HNMe_3]Cl$ (Scheme 1.32).[36]

Scheme 1.32. Synthesis of titanium complexes containing carboranyl-thiol-appended cyclopentadiene ligand.



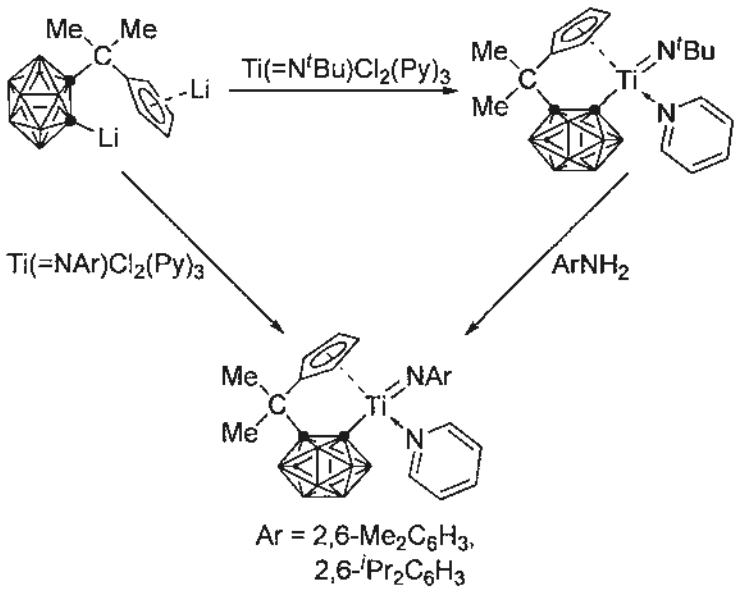
Salt metathesis reaction of the dilithium salt of the carbon-bridged cyclopentadienyl-carboranyl ligand $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ with $ZrCl_4$, in 2:1 molar ratio, afforded *rac*-Zr[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$_2$ as air stable white crystals (Scheme 1.33), which can catalyze the formation of syndiotactic PMMA in THF in the absence of any cocatalysts.[37]

Scheme 1.33. Synthesis of *rac*-Zr[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$_2$.

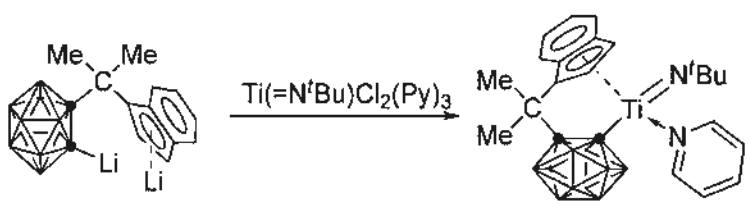


Several titanium imido complexes were synthesized through simple metathesis reactions. Treatment of $Ti(=NR)Cl_2(py)_3$ (R = ^{t}Bu, 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$) with 1 equiv of dilithium salt of the carbon-bridged carboranyl ligand $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$ or $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$ gave new constrained-geometry titanium imido complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=NR)(py)$ (Scheme 1.34) or $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Ti(=N^tBu)(py)$ in 42 – 70% isolated yield (Scheme 1.35).[38]

Scheme 1.34. Synthesis of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=NR)(py)$.

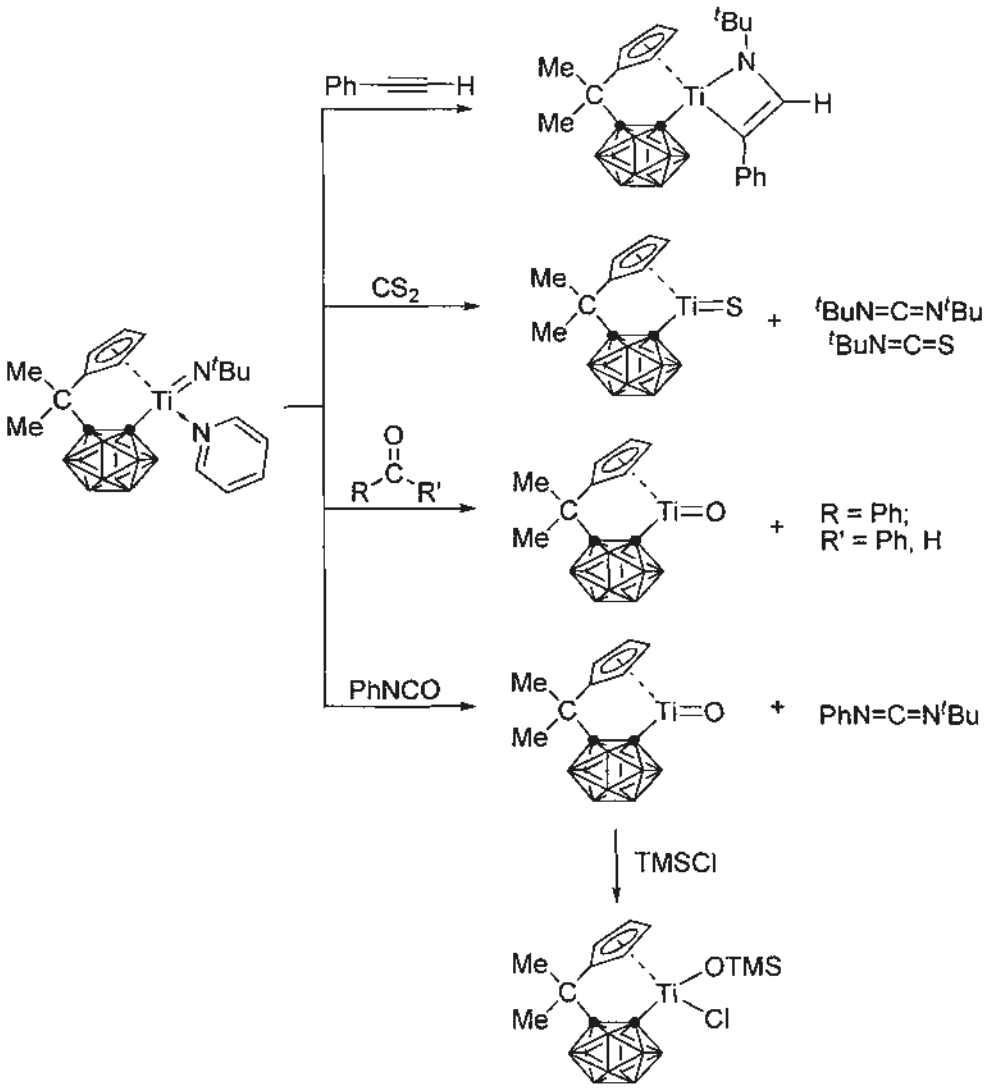


Scheme 1.35. Synthesis of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Ti(=N^tBu)(py)$.



Their reactivities toward unsaturated molecules were studied. The reaction with CS_2, PhNCO, Ph_2CO and PhCHO gave either N/S or N/O exchange products in addition to the formation of titanium oxo/sulfide oligomers (Scheme 1.36).[38]

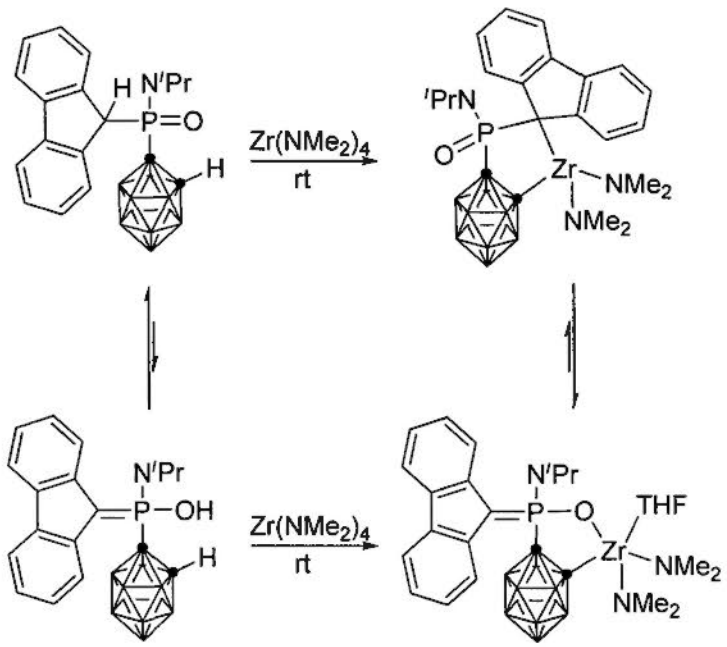
Scheme 1.36. Reactivity of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=N^tBu)(py)$.



Two new trivalent and pentavalent phosphorus-bridged ligands $(C_{13}H_9)(^iPr_2N)P(C_2B_{10}H_{11})$ and $(C_{13}H_9)(^iPr_2N)P(=O)(C_2B_{10}H_{11})$ were synthesized. They showed a significant difference in the reactions with group 4 metal amides. There was no reaction between $(C_{13}H_9)(^iPr_2N)P(C_2B_{10}H_{11})$ and $M(NR_2)_4$ in toluene even at high temperature, which may be due to the less acidic and sterically more

demanding fluorenyl group. However, the pentavalent P ligand reacted with $Zr(NMe_2)_4$ at room temperature to generated the amine elimination product [σ:σ-$(C_{13}H_8)(^iPr_2N)P(-O)(C_2B_{10}H_{10})]Zr(NMe_2)_2$. These differences may be ascribed to the stronger acidity of the two acidic protons in $(C_{13}H_9)(^iPr_2N)P(=O)(C_2B_{10}H_{11})$ over $(C_{13}H_9)(^iPr_2N)P(C_2B_{10}H_{11})$, or the formation of ylide $(C_{13}H_8)=P(^iPr_2N)(OH)(C_2B_{10}H_{11})$ which provide the driving force for the reaction (Scheme 1.37).[32]

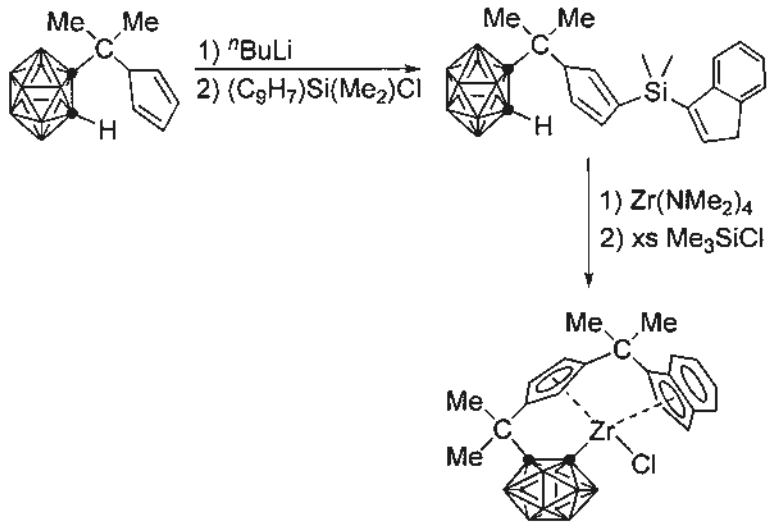
Scheme 1.37. Synthesis of phosphorus-bridged carboranyl zirconium complex [σ:σ-$(C_{13}H_8)(^iPr_2N)P(-O)(C_2B_{10}H_{10})]Zr(NMe_2)_2$.



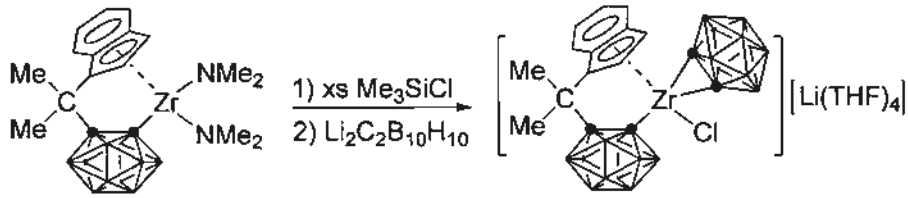
Recently, the synthesis and characterization of the new double *ansa*-type ligand $Me_2Si(C_9H_7)(C_5H_5\text{-}3\text{-}(Me_2C)\text{-}C_2B_{10}H_{11})$ was reported, which was prepared from the reaction of monolithium salt of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Li$ with $(C_9H_7)Me_2SiCl$ in Et_2O. Treatment of this ligand with $Zr(NMe_2)_4$ in refluxing hexane produced $[Me_2Si(\eta^5\text{-}C_9H_6)[\eta^5:\sigma\text{-}C_5H_4\text{-}3\text{-}(Me_2C)\text{-}C_2B_{10}H_{10}]]Zr(NMe_2)$, which can be converted to the monochloro species $[Me_2Si(\eta^5\text{-}C_9H_6)[\eta^5:\sigma\text{-}C_5H_4\text{-}3\text{-}(Me_2C)\text{-}C_2B_{10}H_{10}]]ZrCl$ in

the presence of excess TMSCl. These transformations are summarized in Scheme 1.38.[39]

Scheme 1.38. Synthesis of *ansa*-zirconocene complex $[Me_2Si(\eta^5\text{-}C_9H_6)[\eta^5{:}\sigma\text{-}C_5H_4\text{-}3\text{-}(Me_2C)\text{-}C_2B_{10}H_{10}]]ZrCl$.



Scheme 1.39. Synthesis of zirconocene-carboryne complex.

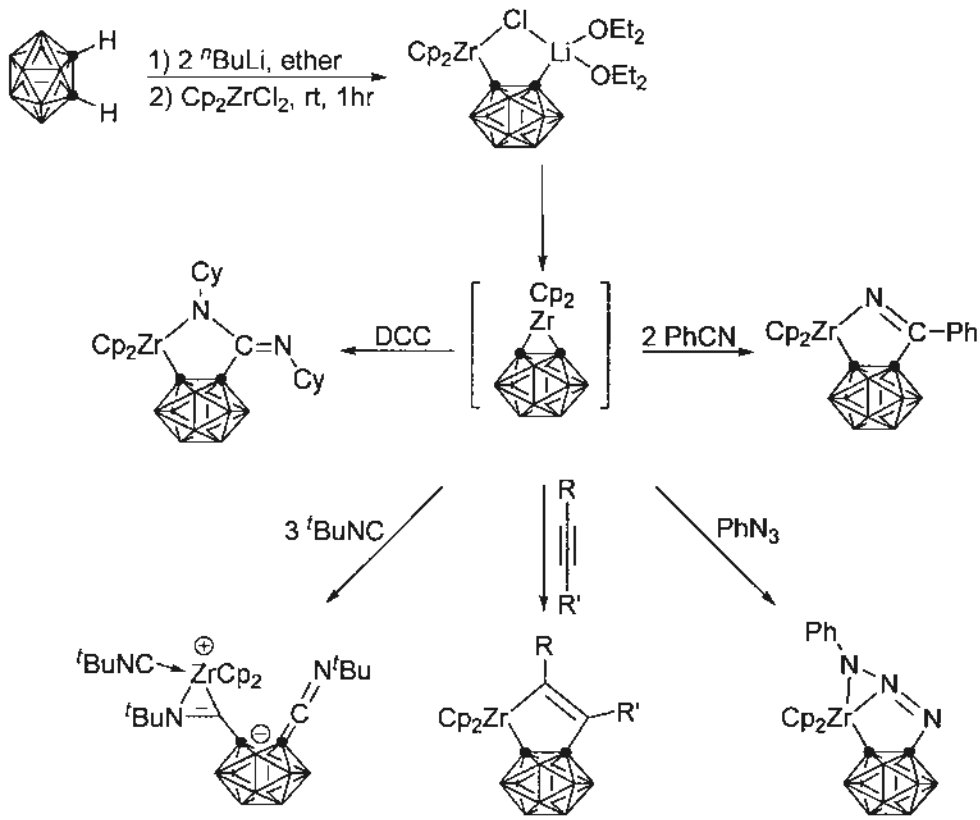


Metallacarboryne, in which the metal center is linked to two cage carbons, is a three-dimensional relative of benzyne. Treatment of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with excess TMSCl, followed by reaction with 1 equiv of $Li_2C_2B_{10}H_{10}$ afforded the first zirconocene-carboryne complex $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$ in 60% yield in 2003 (Scheme 1.39). This complex is found to be extremely air and moisture sensitive. The molecular orbital calculations suggested that the bonding interactions between Zr and the 1,2-dehydro-*o*-carborane are best described as a resonance hybrid of both

the Zr-C σ- and Zr-C π-bonding forms as shown in Scheme 1.40, which is similar to that observed in the Zr-benzyne complex. However, it showed no reactivity toward unsaturated molecules as the Zr center is negatively charged.[40]

Scheme 1.40. Possible bonding interaction in zirconocene-carboryne complex.

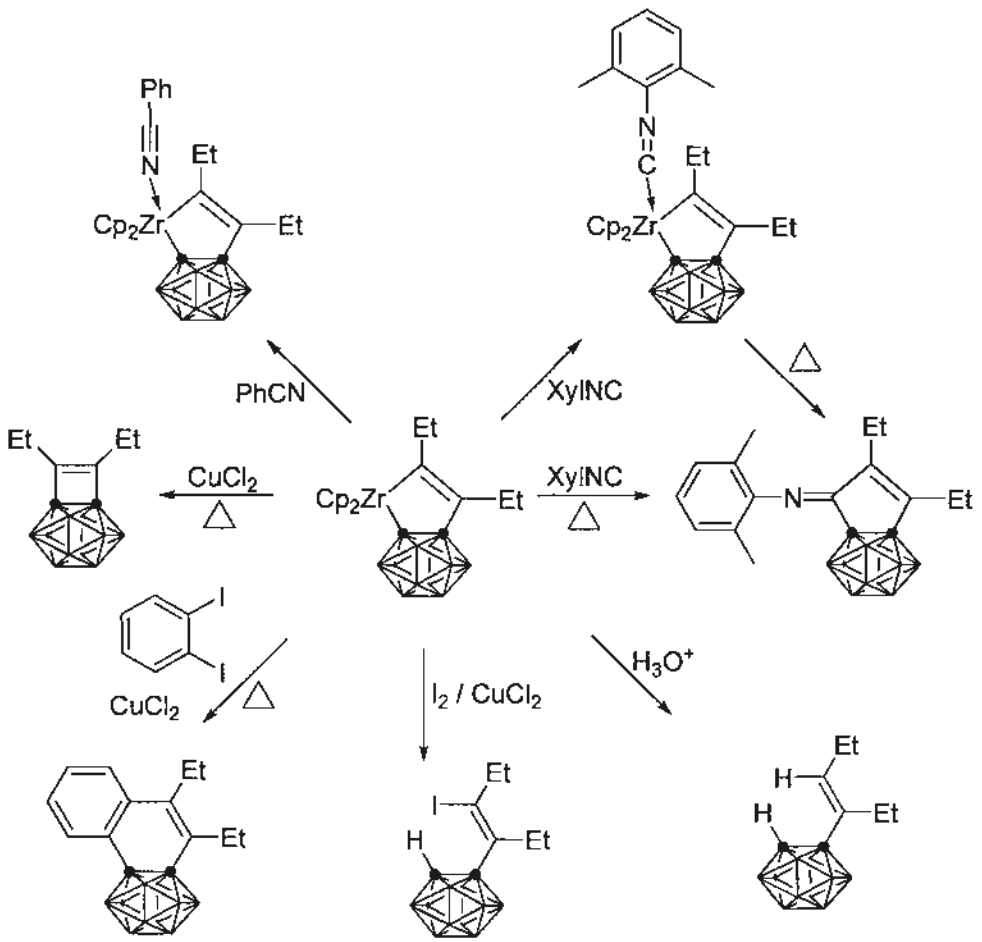
Scheme 1.41. Synthesis and reaction of zirconocene-carboranyl complex.



An unprecedented zirconocene-carboranyl complex $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ was synthesized in 2005 by interaction of Cp_2ZrCl_2 with an equimolar amount of $Li_2C_2B_{10}H_{10}$ in Et_2O at room temperature (Scheme 1.41). It was unstable, and decomposed slowly at room temperature, but can serve as an efficient precursor of the zirconocene-carboryne species,

$Cp_2Zr(\eta^3\text{-}C_2B_{10}H_{10})$, to react with a series of unsaturated molecules such as DCC, PhN_3, ^{t}BuNC and PhCN to give substituted carboranyl zirconium complexes in moderate to high yields as shown in Scheme 1.41. This result clearly showed that this zirconocene-carboryne complex shows very similar reactivity to that of zirconocene-benzyne complexes in the reaction with polar unsaturated substrates.[41] It can also react with internal alkynes in refluxing toluene to afford a series of zirconacyclopentenes incorporating a carboranyl unit in moderate to high yield.[42,43]

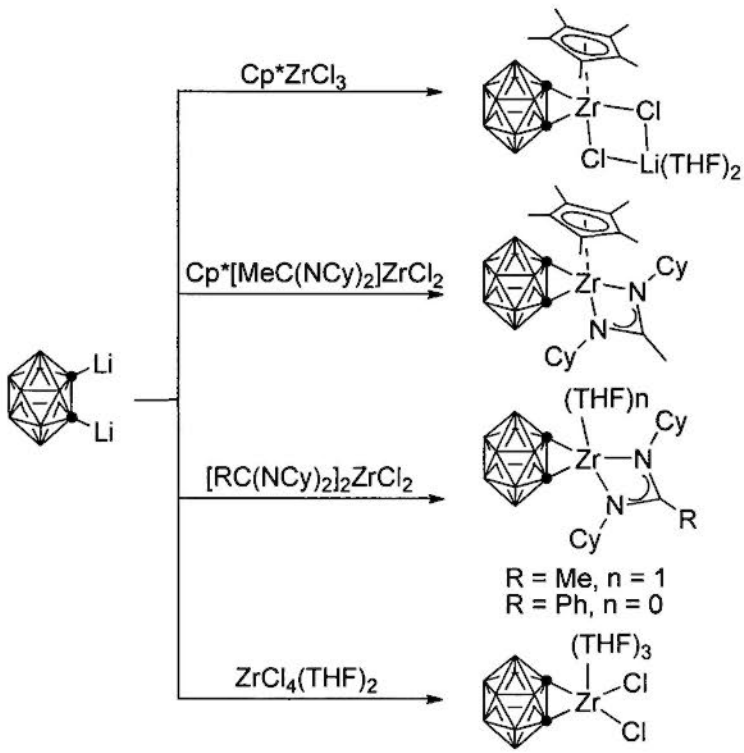
Scheme 1.42. Reactivity of zirconocyclopentene complex.



The zirconocyclopentene complex $[Cp_2ZrC(Et)=C(Et)]$-1,2-$C_2B_{10}H_{10}$ is a very useful intermediate for the synthesis of a variety of functional carboranes. In addition to share some reactivities with zirconacyclopentadienes

$Cp_2Zr[C(R)=C(R)-C(R)=C(R)]$, the zirconocyclopentene complex has unique properties of its own due to the presence of highly sterically demanding carboranyl unit. It can couple with *o*-diiodobenzene in the presence of $CuCl_2$ to generate the naphthalocarborane. Also, C-C coupling product 1,2-$[C(Et)=C(Et)]$-1,2-$C_2B_{10}H_{10}$ can be obtained in the presence of $CuCl_2$ in toluene at elevated temperature in 46% isolated yield. It also reacted with unsaturated molecules like PhCN and XylNC, afforded the PhCN or XylNC coordinated species. XylNC mono-insertion species can be obtained when the reaction mixture was heated in toluene. Moreover, $[Cp_2ZrC(Et)=C(Et)]$-1,2-$C_2B_{10}H_{10}$ can be hydrolyzed under acidic media, or reacted with I_2/CuCl to afford the mono-substituted carborane 1-$[CI(Et)=C(Et)]$-1,2-$C_2B_{10}H_{11}$. These reactions are summarized in Scheme 1.42.[42]

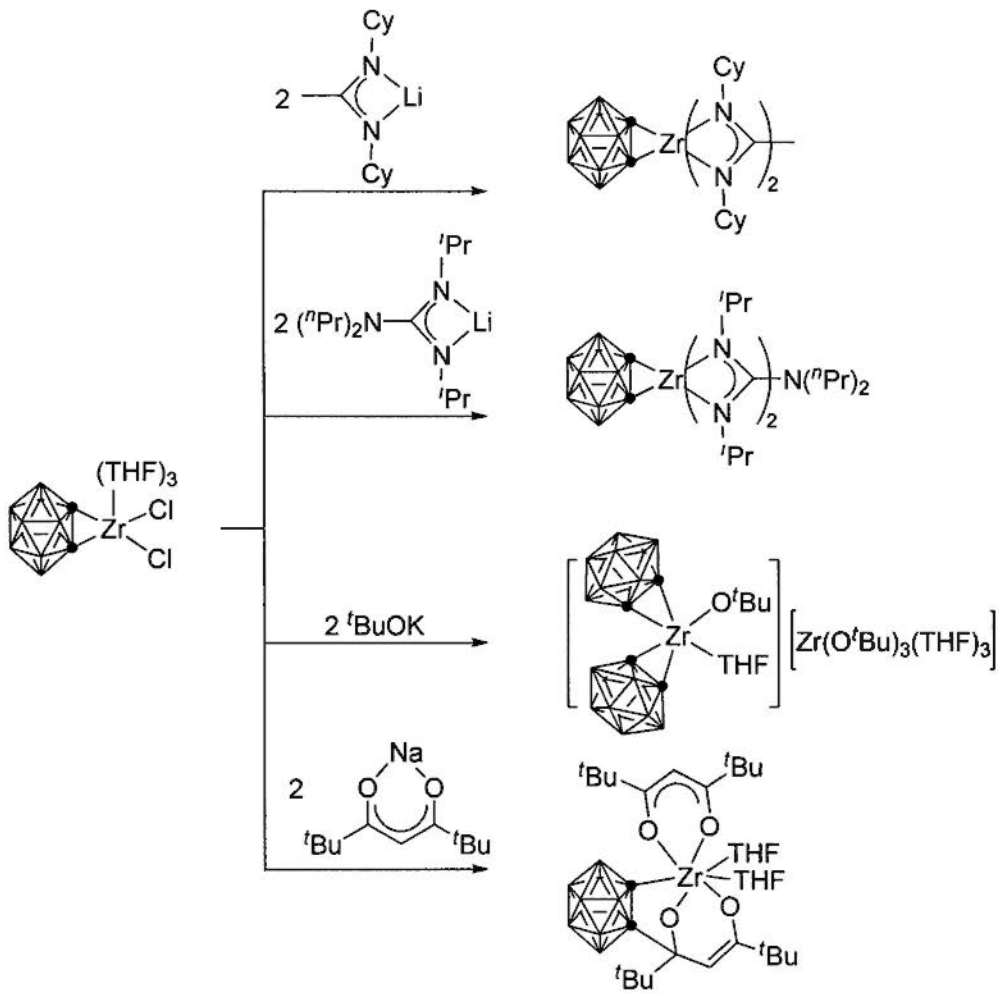
Scheme 1.43. Reaction of zirconium chlorides with $Li_2C_2B_{10}H_{10}$.



A series of Zr-carboryne complexes have been prepared and characterized from the reaction of carborane dilithium salt with zirconium dichloride species (Scheme

1.43) or salt metathesis reactions between $[\eta^5\text{-}C_2B_{10}H_{10}]ZrCl_2(THF)_3$ and anionic ligands (Scheme 1.44). These reactions show that both steric and electronic factors of the ligands have significant effects on the formation of resultant complexes.[44]

Scheme 1.44. Reaction of dichlorozirconium-carboryne with nucleophiles.



1.3. Group 4 Metal Complexes Bearing *nido*-C_2B_{10} Ligands

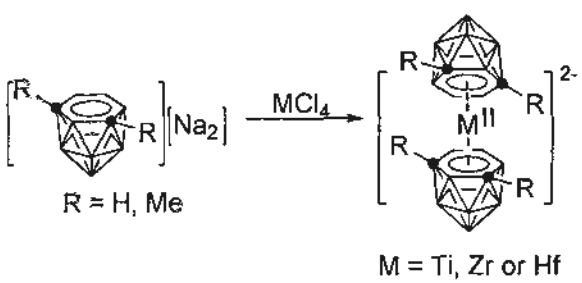
The 12-vertex *nido*-carborane anion $[C_2B_{10}H_{10}R_2]^{2-}$ is another kind of π-ligand that can be derived from *o*-carboranes. These ligands can be easily synthesized by the reduction of *o*-$C_2B_{10}H_{10}R_2$ with group 1 metals. Three types of anions are normally observed depending on the R groups. When no C,C'-linkage is present,

$[7,9\text{-}C_2B_{10}H_{10}R_2]^{2-}$ is formed in which the two cage carbons are separated by one boron atom. When the two cage carbons are linked in a small ring, $[7,8\text{-}C_2B_{10}H_{10}R_2]^{2-}$ isomer is afforded. A large ring size will lead to the formation of $[7,10\text{-}C_2B_{10}H_{10}R_2]^{2-}$ isomer (Chart 1.1). The 7,8- and 7,9- 12-vertex *nido*-carborane anions are very useful synthons for numerous metallacarboranes of *s*-, *p*-, *d*- and *f*-elements, and the former of which are well studied.[45]

Chart 1.1. Isomers of *nido*-carboranes.

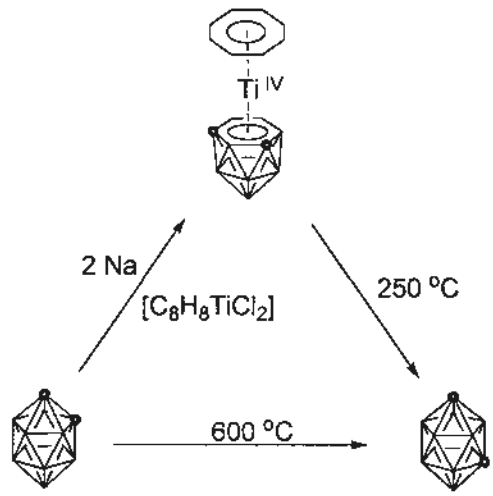
In 1975, Hawthorne and coworkers reported the synthesis and characterization of several new metallacarboranes incorporating *nido*-$C_2B_{10}H_{12}^{2-}$ ligands, including the group 4 metallacarboranes. Treatment of [*nido*-7,9-$C_2B_{10}H_{10}R_2$]Na_2 with MCl_4 (M = Ti, Zr or Hf) in THF gave, after cation exchange, group 4 metallacarboranes in general formula $[(C_2H_5)_4N]_2[4,4'\text{-}M(1,6\text{-}(CH_3)_2\text{-}1,6\text{-}C_2B_{10}H_{10})_2]$ (Scheme 1.45). Crystal structure of the Ti complex revealed that the metal center was η^6-bound to two *nido*-carborane cages. The metal ions were reduced to the oxidation state of +2 by the *nido*-$R_2C_2B_{10}H_{10}^{2-}$ anion.[7]

Scheme 1.45. Synthesis of group 4 metallacarboranes $[(C_2H_5)_4N]_2[4,4'\text{-}M(1,6\text{-}(CH_3)_2\text{-}1,6\text{-}C_2B_{10}H_{10})_2]$.



Titanacarboranes bearing cyclopentadienyl or η^8-cyclooctatetraenyl ligands were synthesized in a very similar manner. The cation exchange product $[Et_4N][4\text{-}(\eta^8\text{-}C_8H_8)\text{-}4\text{-}Ti\text{-}1,6\text{-}C_2B_{10}H_{12}]$ was isolated and structurally characterized.[7] This Ti(III) species can be oxidized to the Ti(IV) complex $4\text{-}(\eta^8\text{-}C_8H_8)\text{-}4\text{-}Ti\text{-}1,6\text{-}C_2B_{10}H_{12}$ which undergoes a new lower energy pathway for the conversion of *ortho*- to *meta*- carborane $1,7\text{-}C_2B_{10}H_{12}$ at 250 °C in high yield (>95%). This conversion is shown in Scheme 1.46.[7]

Scheme 1.46. Conversion of *ortho*- to *meta*- carborane via a titanacarborane.

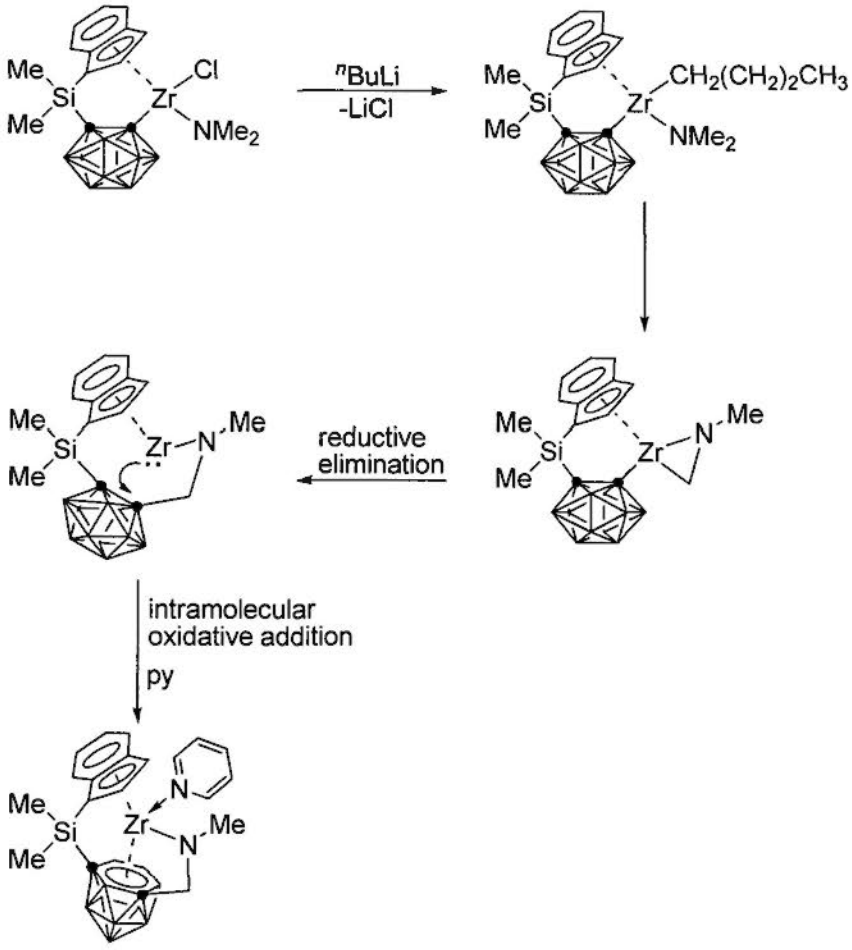


The first structurally characterized high-valent group 4 metallacarboranes bearing *nido*-C_2B_{10} ligand was reported by our group in 2002. Treatment of $[\eta^5\text{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]ZrCl(NMe_2)$ with 1 equiv of ^{n}BuLi in THF/pyridine gave the unprecedented complex $[\eta^5\text{:}\eta^6\text{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10}CH_2NMe)]Zr(py)$, through an unexpected intramolecular oxidative-addition/electron-transfer reaction as shown in Scheme 1.47.[46]

Another carborane ligand *closo*-$1\text{-}[Si(Me)_2N(H)R]\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = $2,6\text{-}(Me_2CH)_2C_6H_3$) was reported by Hosmane and coworkers from the reaction of $Li_2[1,2\text{-}C_2B_{10}H_{10}]$ with $N(R)HSi(Me)_2Cl$. This ligand can be reduce by sodium

naphthalide in THF to give the sodium salt $[Me_2Si(NR)(nido\text{-}C_2B_{10}H_{11})]Na_3$. Further treatment with an equimolar amount of MCl_4 in THF produced constrained-geometry group 4 metallacarboranes $[\sigma{:}\eta^6\text{-}Me_2Si(NR)(C_2B_{10}H_{11})]MCl(THF)_n$ (M = Ti, n = 0; M = Zr, n = 1). These reactions were shown in Scheme 1.48.[47]

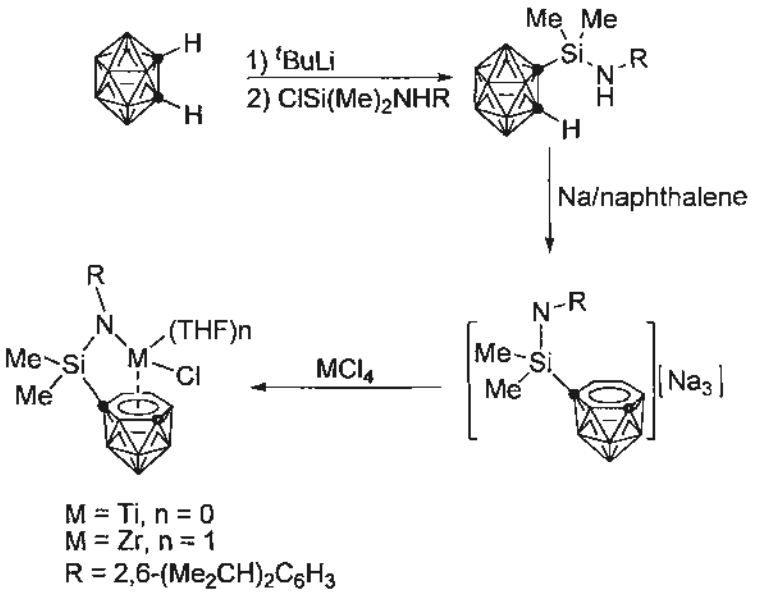
Scheme 1.47. Synthesis of high-valent zirconacarborane $[\eta^5{:}\eta^6{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10}CH_2NMe)]Zr(py)$.



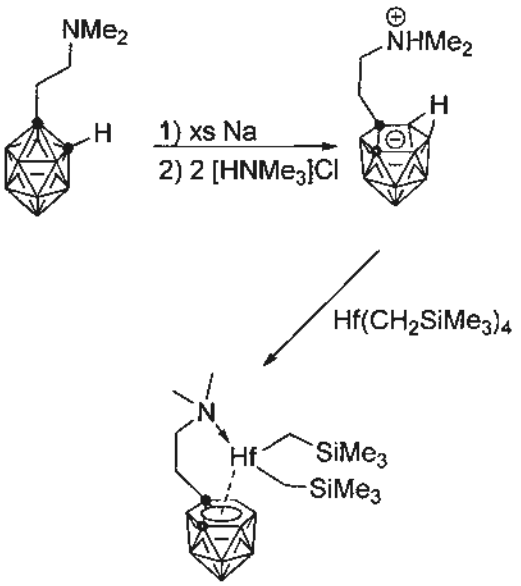
The first example of half-sandwich group 4 metallacarborane alkyls incorporating *nido*-C_2B_{10} ligand was synthesized by alkane elimination reaction of the zwitterionic salt $Me_2NHCH_2CH_2\text{-}7,9\text{-}C_2B_{10}H_{12}$ with $Hf(CH_2SiMe_3)_4$ (Scheme 1.49). The development of the carborane zwitterionic salt, which provides the second acidic proton, enables acid-base reaction, representing a new route to high-valent group 4

metallacarboranes. Also, it can stabilize the resultant metal alkyl complexes via the intramolecular coordination.[48]

Scheme 1.48. Synthesis of constrained-geometry group 4 metallacarboranes $[\sigma{:}\eta^6\text{-}Me_2Si(NR)(C_2B_{10}H_{11})]MCl(THF)_n$.



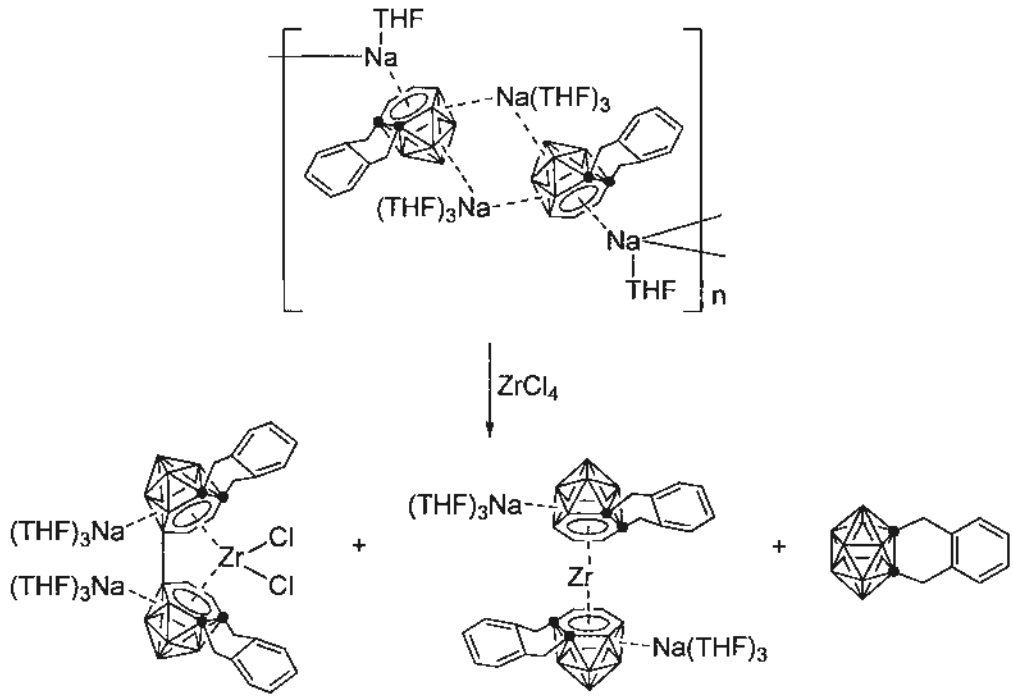
Scheme 1.49. Synthesis of half-sandwich group 4 metallacarborane alkyls.



The reaction between $ZrCl_4(THF)_2$ and equimolar amount of carbon-adjacent (CAd) carborane salt $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$ gave the

unprecedented full-sandwich high valent zirconacarborane containing the unusual B-B-linked bis(carboranyl) ligand $[o\text{-}C_6H_4(CH_2)_2C_2B_{10}H_9]_2^{4-}$ in 8% isolated yield, while the formation of this product is not clear. The major product in this reaction was found to be the Zr(II) species $\{[o\text{-}C_6H_4(CH_2)_2C_2B_{10}H_{10}]_2Zr\}\{Na(THF)_3\}_2$, which was isolated in 49% yield. This Zr(II) complex is the first structurally characterized divalent zirconacarboranes. This reaction is outlined in Scheme 1.50.[49]

Scheme 1.50. Reaction of $ZrCl_4(THF)_2$ with $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$.

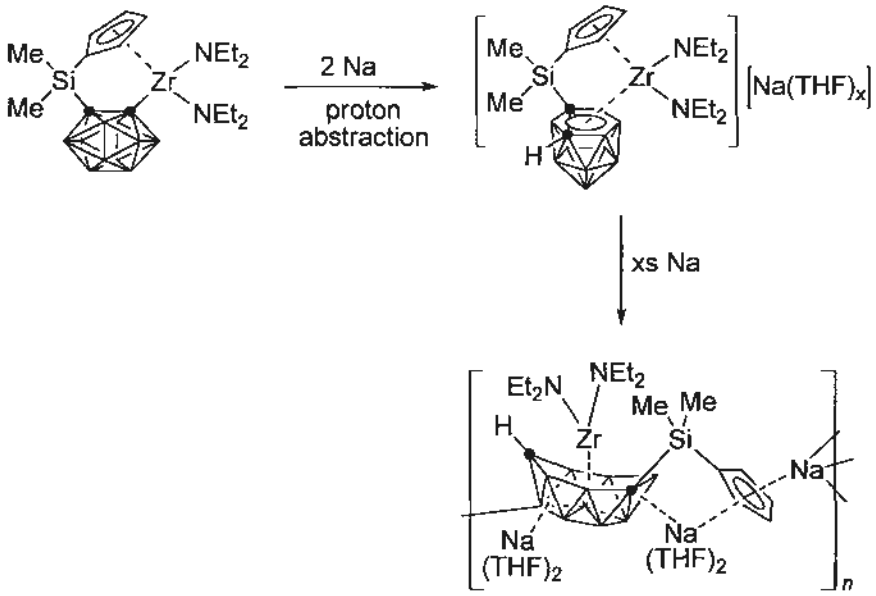


1.4. Group 4 Metal Complexes Bearing *arachno*-C_2B_{10} Ligands

The first high-valent zirconacarborane bearing η^7-carboranyl ligand $[\{(\mu\text{-}\eta^5)\text{:}\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$ was prepared and structurally characterized from direct reduction of $[\eta^5\text{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ with excess Na metal in THF (Scheme 1.51).

It is formed by reduction of *closo*-C_2B_{10} carboranyl ligand and proton abstraction from solvent to give the *nido*-C_2B_{10} intermediate. This intermediate was further reduced by Na metal to give the final product. This work shows that the *arachno*-$C_2B_{10}H_{12}^{4-}$ tetraanion can effectively stabilize the high oxidation state of the group 4 metals.[47]

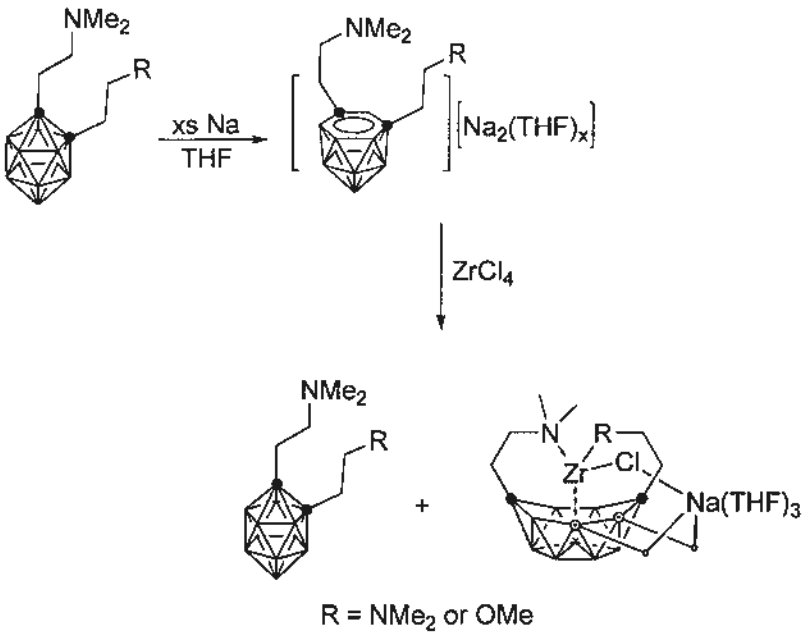
Scheme 1.51. Synthesis of zirconacarborane $[\{(\mu\text{-}\eta^5)\text{:}\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$.



Another zirconacarborane incorporating an η^7-*arachno*-carboranyl ligand was reported in 2005 by our group. Reaction of [*nido*-$(Me_2NCH_2CH_2)RC_2B_{10}H_{10}]Na_2$ (R = $MeOCH_2CH_2$, $Me_2NCH_2CH_2$) with $ZrCl_4(THF)_2$ afforded the unprecedented zirconacarborane $[\eta^1\text{:}\eta^1\text{:}\eta^7\text{-}(Me_2N(CH_2)_2)RC_2B_{10}H_{10}]Zr(\mu\text{-}Cl)Na(THF)_3$ (Scheme 1.52). The formation of these complexes was presumably regarded to pass through a Zr(II) intermediate, followed by intramolecular electron transfer from the metal center to the *nido*-carborane to afford the final products. These results suggested that heteroatom-containing pendent sidearms on the carborane cage are both electronically and entropically necessary for the formation of zirconacarborane

bearing the *arachno*-C_2B_{10} ligand. By changing the nature of substituents R, controlled syntheses of divalent metallacarborane of the type $[(nido\text{-}R_2C_2B_{10}H_{10})_2M]^{2-}$ (M = group 4 metals) or high-valent metallacarboranes of the type $(arachno\text{-}R_2C_2B_{10}H_{10})M$ can be achieved.[50]

Scheme 1.52. Synthesis of Zr(IV) complexes bearing η^7-*arachno* carborane ligand.



1.5. Research Objectives

The research objectives of this thesis include (1) reactivity of group 4 metal diamides toward various kinds of unsaturated organic molecules, (2) synthesis and reactivity of group 4 metal disulfides incorporating a carbon-bridged cyclopentadienyl-carboranyl ligand and (3) synthesis and reactivity of group 4 metal complexes bearing $[Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_2B_9H_{10})]^{3-}$ ligand. The details of our work on the above subjects are described in the following chapters.

Chapter 2. Synthesis, Structure and Reactivity of Group 4 Metal Diamides Incorporating Carbon-Bridged Cyclopentadienyl-Carboranyl Ligands

2.1. Introduction

Reactivity studies on $[\eta^5:\sigma\text{-A}(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (A = Me_2C,[34] Me_2Si,[34] $^iPr_2NP$[51]) and $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)X$ (X = Cl, alkyl) complexes[52] indicate that the unsaturated molecules insert into the M-N bonds in the absence of the $M\text{-}C_{alkyl}$ bonds and the $M\text{-}C_{cage}$ bonds remain intact, and thus the relative reactivity follows the trend: $M\text{-}C_{alkyl}$ > M-N >> $M\text{-}C_{cage}$.[52] Since the $M\text{-}C_{cage}$ and $M\text{-}C_{alkyl}$ bond distances are almost identical, the preference of M-N over $M\text{-}C_{cage}$ insertion is suggested to most likely be governed by steric factors.[34,51-53] On the other hand, $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]_2Zr$ was reported to catalyze the polymerization of MMA in the absence of any cocatalyst through the action of the nucleophilic cage atom.[37] Complexes $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(\eta^5\text{-}C_5Me_5)Cl$ (M = Ti, Zr) are active catalysts for ethylene polymerization in the presence of modified MAO. Possible involvement of the activation of the $M\text{-}C_{cage}$ σ bond is suggested.[54] With this in mind, a question subsequently arises as to whether the mobility of the carborane cage plays a role in the migratory insertions aforementioned as the cage is tethered to the cyclopentadienyl unit in comparison with the terminal amido groups. One possible way to address this issue is to link the two terminal amido groups via several methylene moieties, lowering their mobility and then to investigate the reactivity patterns of the resultant metallacycles toward unsaturated molecules. In this regard, we synthesized carbon-bridged cyclopentadienyl-carboranyl group 4 metal

complexes incorporating diamido ligands [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^2$-$N(Me)(CH_2)_nN(Me)$] (M = Ti, Zr, Hf, n = 2, 3) and studied their reactivities toward unsaturated molecules.

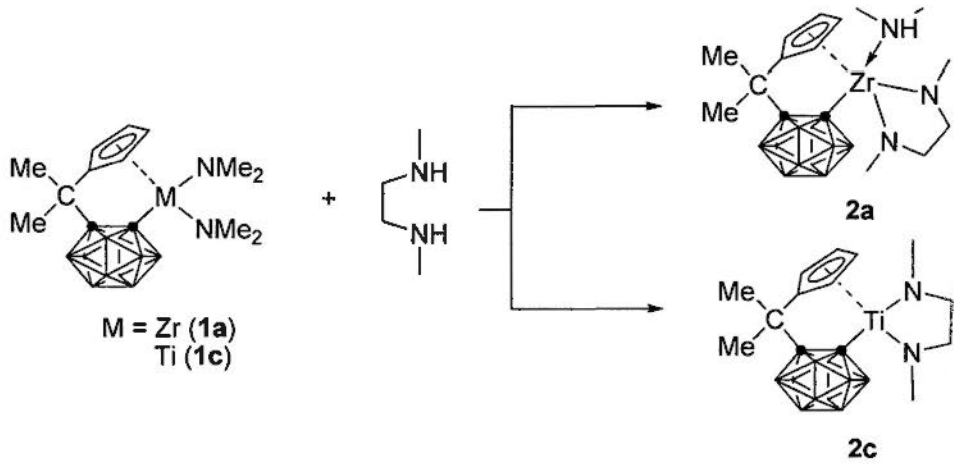
2.2. Synthesis and Characterization of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^2$-$N(Me)(CH_2)_nN(Me)$] (M = Ti, Zr, Hf, n = 2, 3)

Salt metathesis and amine elimination are two useful methods for the preparation of metal amides.[17-18,20-21,33,36,46-48,50,55] However, reactions of $LiN(Me)(CH_2)_2N(Me)Li$ with 0.5 equiv of {[η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Zr-($\mu$-Cl)$_{1.5}$Cl}$_2${Li(THF)$_2$}[35] or 1 equiv of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$ZrCl_2$[40] in THF did not afford isolable pure products. On the other hand, treatment of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M$(NMe_2)_2$[35] (M = Zr, **1a**; M = Hf, **1b**; M = Ti, **1c**) with 1.1 (M = Zr) or 5 (M = Ti) equiv of DMEDA in toluene gave the corresponding zirconium or titanium amide complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$-$N(Me)(CH_2)_2N(Me)$]($NHMe_2$) (**2a**) in 73% yield, or [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti[$\eta^2$-$N(Me)(CH_2)_2N(Me)$] (**2c**) in 68% yield, respectively (Scheme 2.1). The formation of volatile $HNMe_2$ and chelating effect of the bidentate diamido ligand provide the driving forces for the above reactions. It is noted that much excess of diamine is needed for **1c** to accelerate the reaction. Both complexes were fully characterized by ^1H, ^{13}C and ^{11}B NMR as well as elemental analyses. Complex **2a** contained a coordinated $HNMe_2$ molecule probably due to the relatively larger size of the Zr atom.

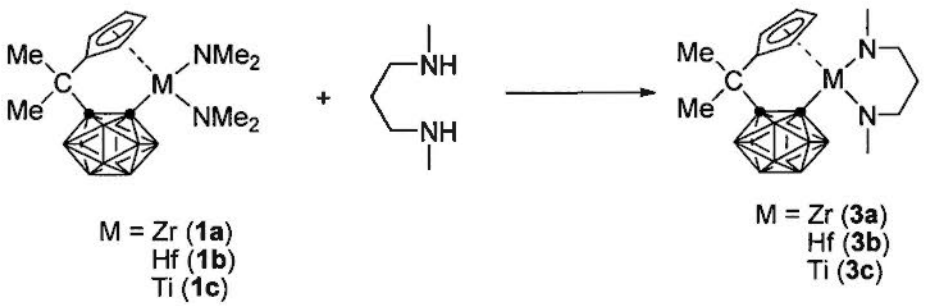
In a very similar manner, complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^2$-$N(Me)(CH_2)_3N(Me)$] (M = Zr (**3a**), Hf (**3b**) and Ti (**3c**)) were prepared in 64 ~ 82% isolated yields from the reactions of **1a**, **1b** or **1c** with DMPDA in toluene (Scheme

2.2). They showed similar spectroscopic features without coordination of $HNMe_2$, presumably owing to the formation of sterically more demanding six-membered metallacycles.

Scheme 2.1. Reaction of complexes **1a** and **1c** with DMEDA.



Scheme 2.2. Reaction of complexes **1a**, **1b** and **1c** with DMPDA.



The molecular structures of **2c** and **3c** were confirmed by single-crystal X-ray analyses, and shown in Figures 2.1 and 2.2, respectively. Key structural data are compiled in Table 2.1 for comparison. The Ti atom in each complex is η^5-bound to the five-membered ring of the cyclopentadienyl group, σ-bound to a carborane cage atom and two nitrogen atoms in a distorted-tetrahedral geometry. The average Ti-C_{ring} distances of 2.326(8) Å in **2c** and 2.367(3) Å in **3c**, the Ti-C_{cage} distances of 2.173(8) Å in **2c** and 2.199(3) Å in **3c**, the average Ti-N distances of 1.869(6) Å in

2c and 1.882(2) Å in **3c** are very comparable to each other. These measured values are close to those of 2.369(3) Å, 2.209(2) Å, and 1.894(2) Å observed in their parent complex **1c**[35] and other titanium amides.[55] The C_{ring}-C-C_{cage} angles of 109.6(7)° in **2c** and 108.4(3)° in **3c**, the C_{cent}-Ti-C_{cage} angles of 105.9° in **2c** and 105.3° in **3c** are very similar to the corresponding values of 108.5(2)° and 105.0° found in **1c**.[34] The N-Ti-N angle of 96.2(4)° in **2c** is, however, significantly smaller than that of 105.6(1)° in **3c** and 106.1(2)° in **1c**.[35] These data suggest that the coordination geometry around the Ti atom in **3c** and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ is almost identical, and no ring strain is built after linking two nitrogen atoms by three methylene units.

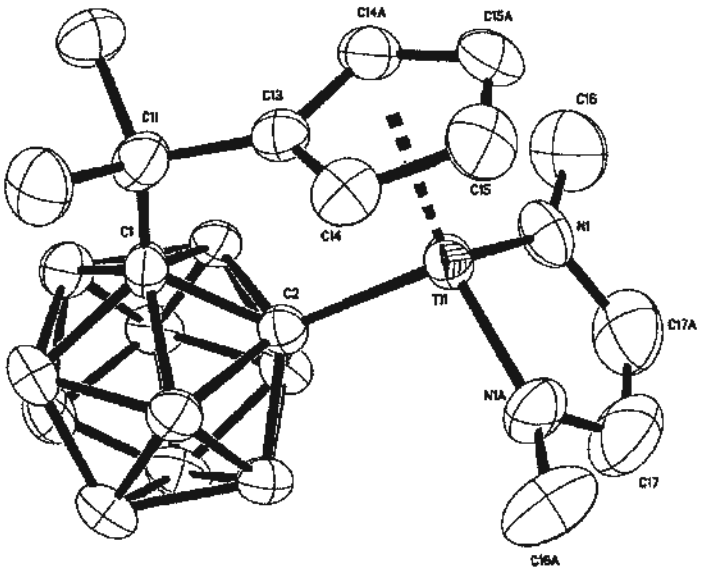


Figure 2.1. Molecular structure of

$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[\eta^2\text{-}N(Me)(CH_2)_2N(Me)]$ (**2c**).

Table 2.1. Selected bond distances (Å) and angles (°) [a]

Complex (M)	**2c** (Ti)	**3c** (Ti)	**4a** (Zr)	**4c** (Ti)	**5a** (Zr)	**6a** (Zr)	**7a** (Zr)
av M-C_{ring}	2.336(8)	2.367(3)	2.502(4)	2.367(6)	2.516(6)	2.530(6)	2.542(4)
av M-Cent	2.024	2.207	2.394	2.285	2.371	2.461	2.439
av M-C_{cage}	2.173(8)	2.199(3)	2.394(3)	2.285(5)	2.371(5)	2.461(5)	2.439(3)
av M-N_{amide}	1.869(6)	1.882(2)			2.217(5)	2.075(4) 2.279(4)	2.090(3)
av M-N_{amine}						2.443(5)	2.403(3)
av M-N_{imine}			2.236(3)	2.112(5)			2.408(3)
av M-N_{imide}							2.265(3)
av M-$N_{nitrile}$						2.320(5)	
C_{cent}-M-C_{cage}	105.9	105.3	100.6	103.2	98.1	96.8	96.3
C_{ring}-C-C_{cage}	109.6(7)	108.4(3)	110.9(2)	109.1(4)	109.2(5)	109.9(4)	110.4(3)
N-M-N	96.2(4)	105.6(1)	118.6(1)	118.0(2)	93.7(2)		

[a] Cent: the centroid of the cyclopentadienyl ring.

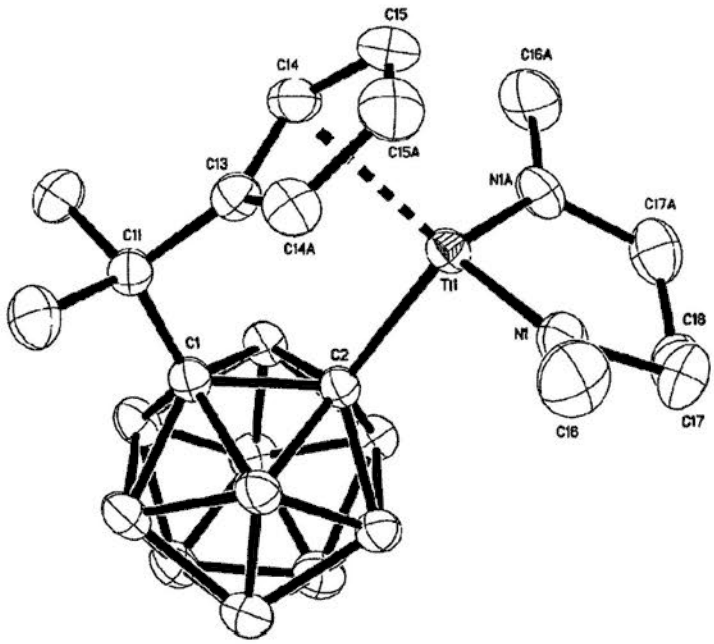


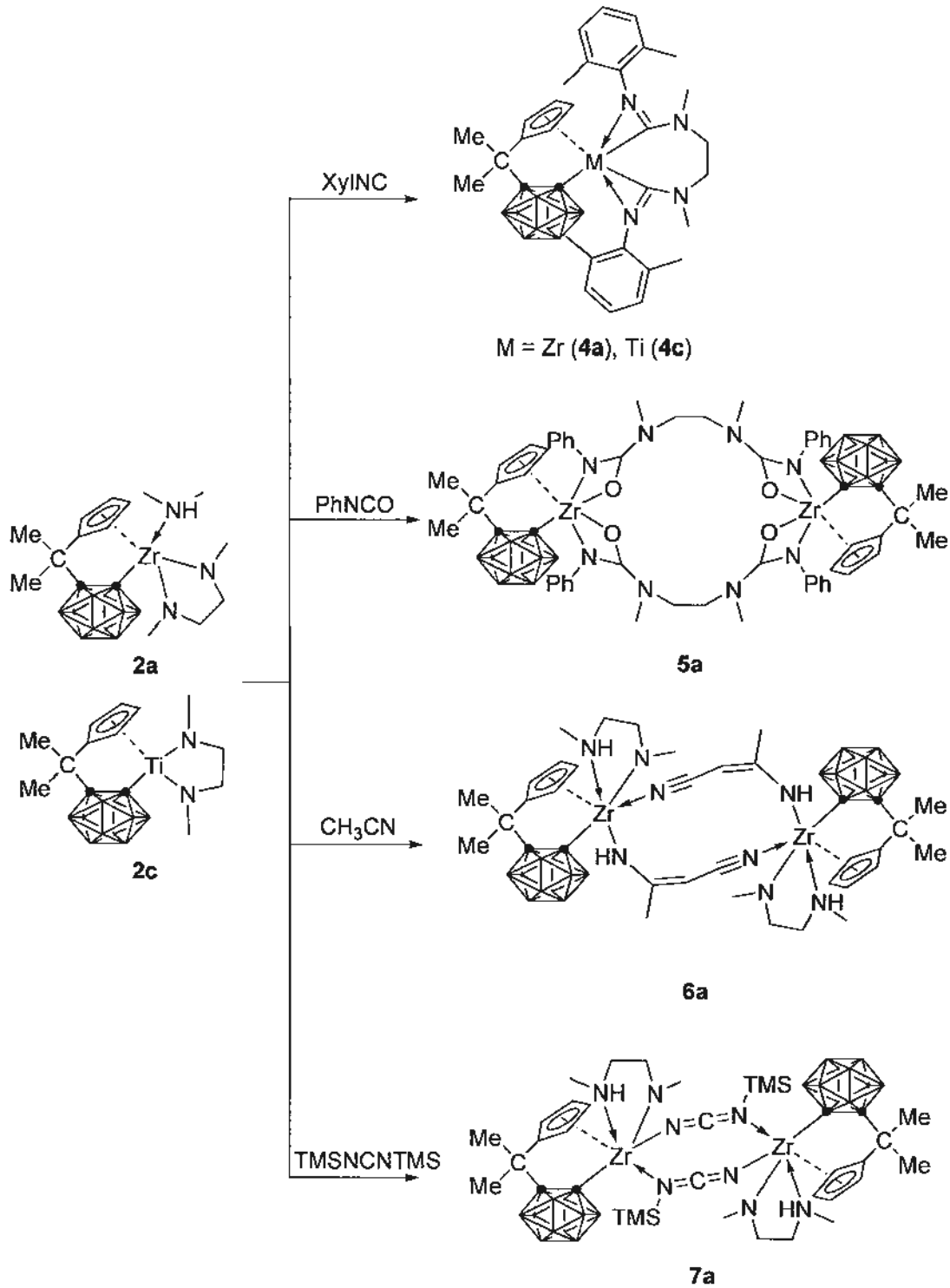
Figure 2.2. Molecular structure of

$[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[\eta^2\text{-}N(Me)(CH_2)_3N(Me)]$ (**3c**).

2.3. Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2\text{-}N(Me)(CH_2)_2N(Me)]$ (M = Ti, Zr) with Unsaturated Molecules

Reaction of **2a** or **2c** with 2 equiv of XylNC in toluene at room temperature gave the diinsertion products $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M\text{-}[\eta^2{:}\eta^2\text{-}XylN{=}CN(Me)(CH_2)_2N(Me)C{=}NXyl]$ (M = Zr, **4a**; M = Ti, **4c**) in 58 ~ 70% isolated yields. Only diinsertion products were isolated in the presence of 1 or more equiv of XylNC (Schemes 2.3). The results showed that XylNC molecules inserted exclusively into the M-N bond giving ring expansion products, and the M-C_{cage} bond remained intact regardless of the ring size of the metallacycles. They were characterized by various spectroscopic techniques and elemental analyses. The unique N-*C*=N resonance at ~205 ppm was observed in the ^{13}C NMR spectra of the insertion products.

Scheme 2.3. Reactions of complexes **2a** or **2c** with unsaturated molecules



Single-crystal X-ray analyses confirmed the molecular structures of **4a** and **4c**, and showed half benzene of solvation for both **4a** and **4c**. Complexes **4a** and **4c** are isostructural and isomorphous. Figures 2.3 and 2.4 show the structures of **4a** and **4c**,

respectively. In these structures, the central metal atom is coordinated by an η^5-cyclopentadienyl ligand, a cage carbon atom and two η^2-iminocarbamoyl ligands in a five-legged piano stool geometry. As indicated in Table 2.1, the average Zr-C(sp^2) distance of 2.162(3) Å in **4a** and Zr-N(sp^2) distance of 2.236(3) Å in **4a** are close to the corresponding values of 2.259(4) Å and 2.221(3) Å in $Zr(NMeCyc)_2[C(NXyl)NMeCyc]_2$,[56a] 2.209(8) Å and 2.143(6) Å in $(\eta^5\text{-}C_9H_6)Zr[C(NMe_2)=N(2,6\text{-}Me_2C_6H_3)]_2Cl$.[56b] The average Ti-C($sp^2$) distance of 2.033(6) Å in **4c** and Ti-N(sp^2) distance of 2.111(5) Å in **4c** are close to the corresponding values of 2.061(5) Å and 1.955(4) Å in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(Cl)[\eta^2\text{-}C(NMe_2)=N(C_6H_3Me_2\text{-}2,6)]$,[52] 2.032(5) Å and 1.982(4) Å in $(\eta^5\text{-}C_9H_6)Ti[C(NMe_2)=N(2,6\text{-}Me_2Ph)]Cl_2$.[56b]

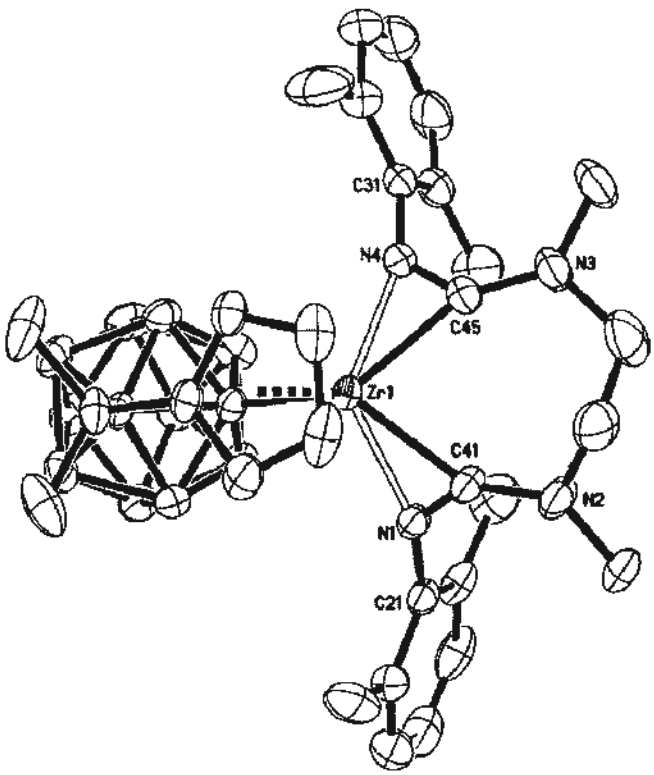


Figure 2.3. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2{:}\eta^2\text{-}(Xyl)N{=}CN(Me)(CH_2)_2N(Me)C{=}N(Xyl)]$ (**4a**).

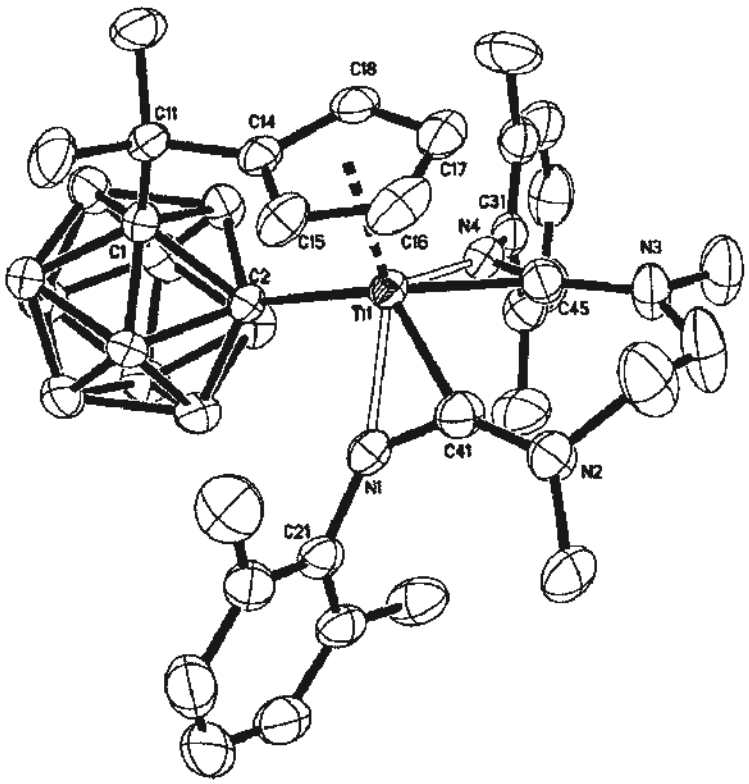


Figure 2.4. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti\text{-}[\eta^2{:}\eta^2\text{-}(Xyl)N{=}CN(Me)(CH_2)_2N(Me)C{=}N(Xyl)]$ (**4c**).

Treatment of **2a** with 1 or 2 equiv of PhNCO in DME at room temperature afforded a diinsertion product $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\mu\text{-}\eta^2{:}\eta^2\text{-}OCN(Ph)N(Me)(CH_2)_2(Me)N(Ph)NCO]\}_2$ (**5a**) in 69% isolated yield (Scheme 2.3). A characteristic N-*C*=O resonance at 156.1 ppm was observed in the ^{13}C NMR spectrum of **5a**. Unlike $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}N(Ph)C(NMe_2)O]_2$ (A = Me_2C,[34] Me_2Si,[34] $^iPr_2NP$[51]), **5a** did not show any activity towards excess PhNCO. The reasons are presumably owing to the steric effects imposed by very crowded coordination environments around the Zr atom in **5a**, which may also lead to the formation of the dinuclear complex bearing an 18-membered metallacyclic ring.

Such a dimeric structure was confirmed by a single-crystal diffraction study and

shown in Figure 2.5. Each Zr atom is η^5-bound to a cyclopentadienyl ring, η^2-bound to each of two OC(NMeR)NPh moieties and σ-bound to a cage carbon atom in a five-legged piano stool geometry. The average Zr-C_{ring} distance of 2.516(6) Å and Zr-C_{cage} distance of 2.371(5) Å are very close to the corresponding values found in **4a**. The average Zr-N/O distances of 2.217(5)/2.196(4) Å compare well with the 2.242(3)/2.165(3) Å observed in $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Ph)C(NMe_2)O]_2$[34] and 2.186(4)/2.161(3) Å in $[\eta^5:\sigma\text{-}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OCN(Ph)][\eta^2\text{-}OC(NMe_2)N(Ph)C{=}(NPh)O]$.[51]

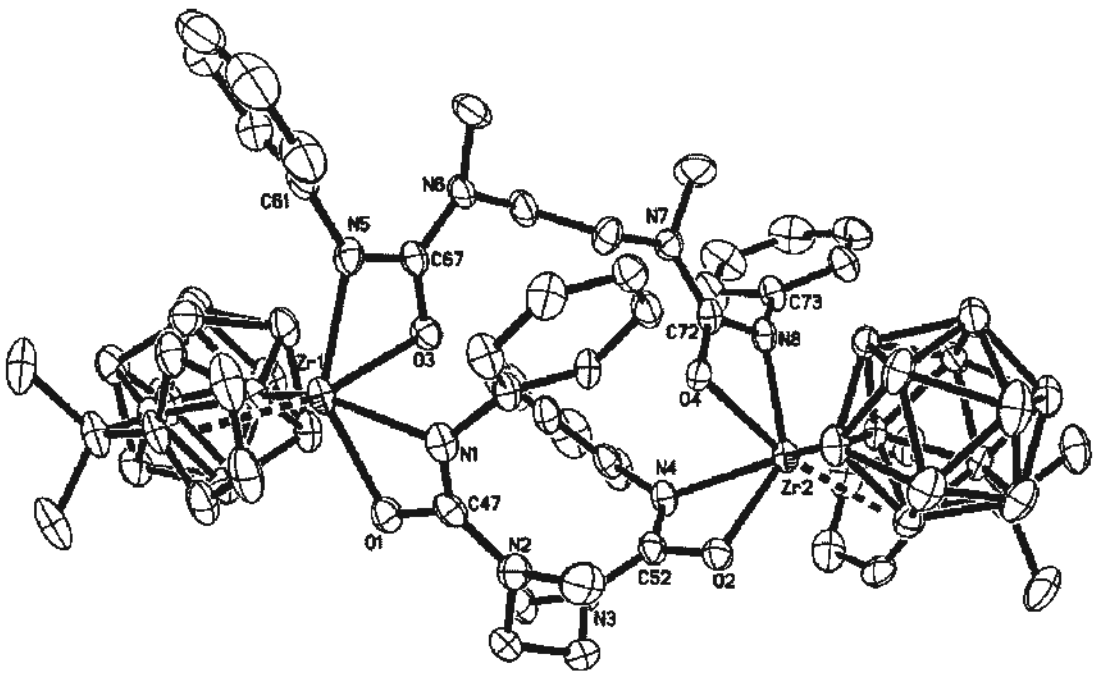


Figure 2.5. Molecular structure of$\{[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\mu\text{-}\eta^2\text{:}\eta^2\text{-}OCN(Ph)N(Me)(CH_2)_2(Me)N(Ph)NCO]\}_2$ (**5a**).

On the other hand, interaction of **2a** with 2 equiv of CH_3CN in DME at room temperature gave an unexpected product $\{[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)][\mu\text{-}NHC(CH_3){=}CHC{\equiv}N]\}_2$ (**6a**) in 42% isolated yield (Scheme 2.3). The NMR data were not obtainable due to the insolubility of **6a** in

organic solvents. Its composition and molecular structure were unambiguously confirmed by elemental analyses and single-crystal X-ray analyses.

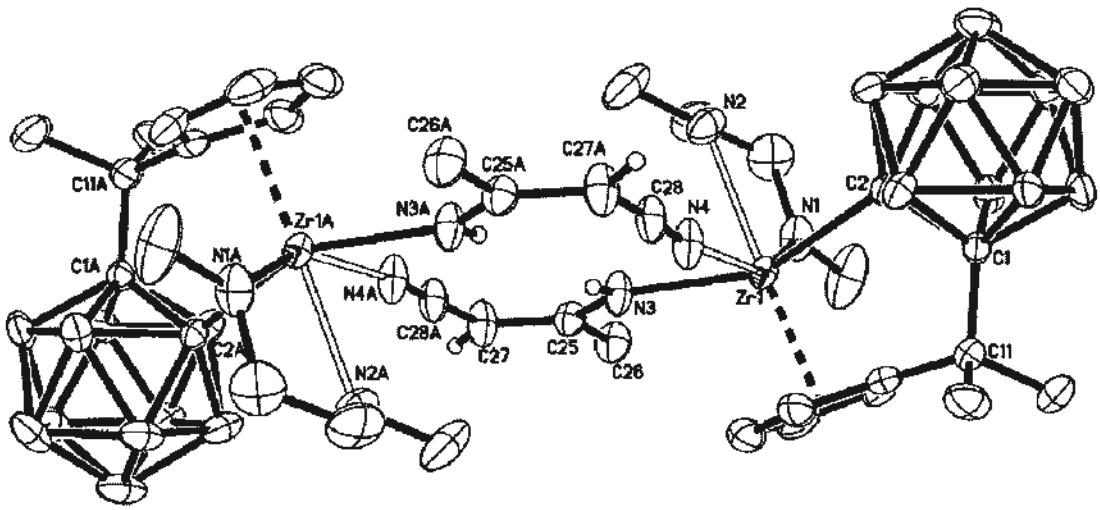
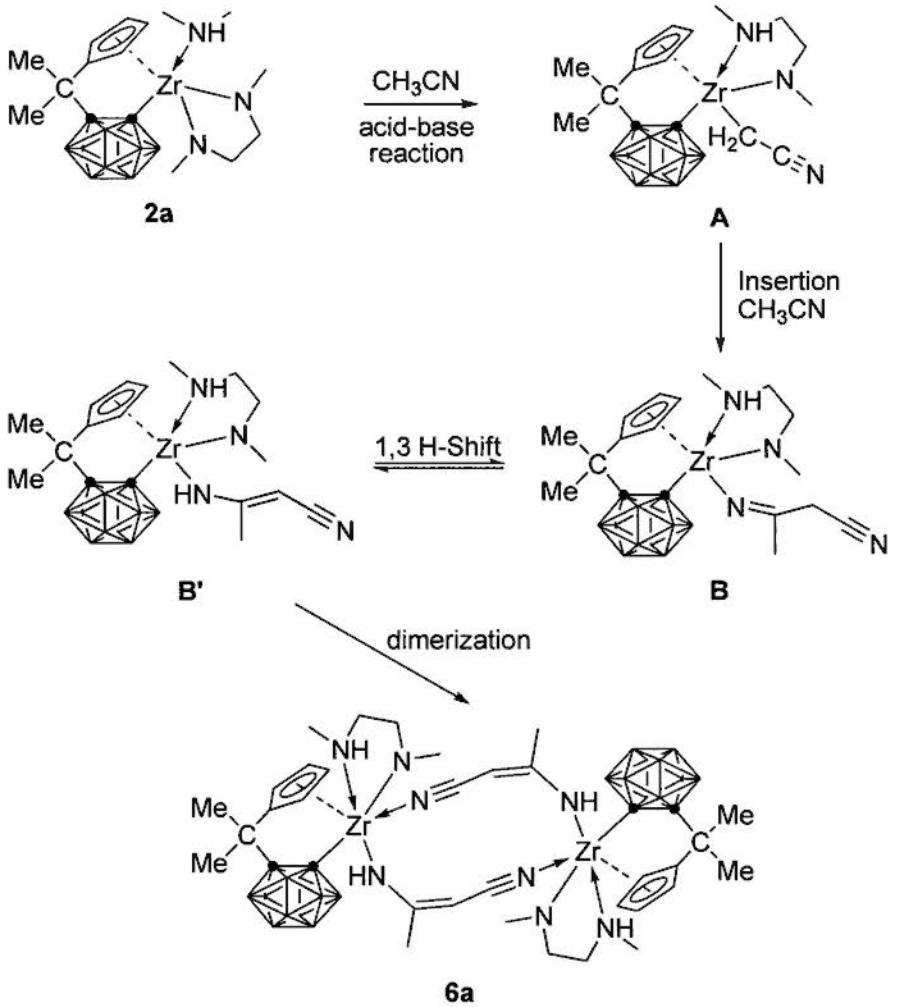


Figure 2.6. Molecular structure of{[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$-N(Me)$(CH_2)_2$NH(Me)][$\mu$-NHC$(CH_3)$=CHC≡N]}$_2$ (**6a**).

As shown in Figure 2.6, each Zr atom is coordinated to an η^5-cyclopentadienyl ring, a cage carbon atom and four nitrogen atoms in a five-legged piano stool geometry. A much shorter Zr-N(1) distance of 2.075(4) Å over the Zr-N(2) distance of 2.443(5) Å and the planar geometry of N(1) suggest that N(1) is the amido nitrogen and N(2) is the amino nitrogen. The Zr-N(3)/N(4) distances of 2.279(4)/2.320(5) Å, C(28)-N(4)/C(27) distances of 1.149(7)/1.387(8) Å and C(25)-N(3)/C(27) distances of 1.316(7)/1.392(7) Å as well as the planarity of the N(4)-C(28)-C(27A)-C(25A)-N(3A) fragment indicated some electron delocalization over such a unit. These structural data imply that the N(3) atom is best described as an amido nitrogen formed via intramolecular proton shift. Scheme 2.4 shows a possible reaction pathway for the formation of **6a**. Acid-base reaction between **2a** and CH_3CN gives the intermediate **A** which contains Zr-C_{alkyl}, Zr-C_{cage} and Zr-N bonds. The second equivalent of CH_3CN inserts into the Zr-C_{alkyl} bond to afford the

monoinsertion species **B/B'**, which dimerizes to form the final product **6a**. This result suggests that the reactivity follows the order: Zr-C_{alkyl}> Zr-N>> Zr-C_{cage}.

Scheme 2.4. Proposed mechanism for the formation of **6a**.

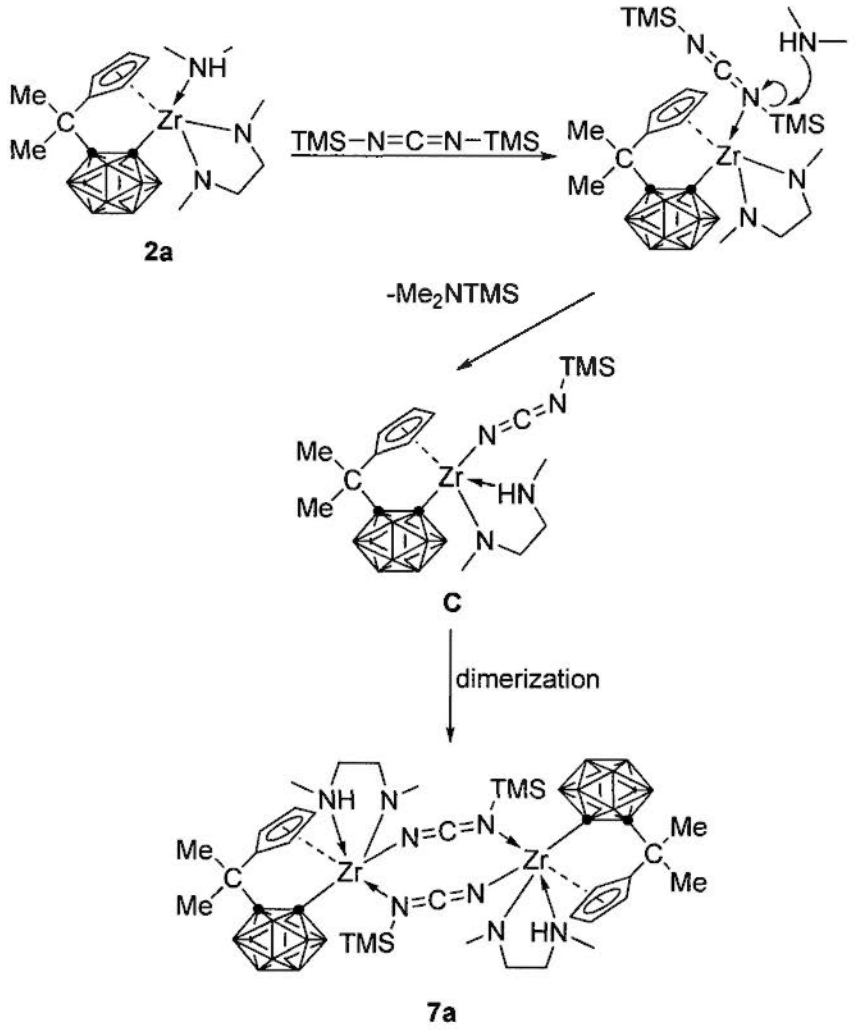


Complex **2a** reacted with TMS-N=C=N-TMS in toluene at room temperature to afford a desilylation product {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$-$NMe(CH_2)_2NHMe$][$\mu$-TMSN=C=N]}$_2$ (**7a**) in 53% isolated yield (Scheme 2.3). This complex was fully characterized by various spectroscopic techniques. A unique N=*C*=N resonance at 125.1 ppm was observed in its ^{13}C NMR spectrum.

As shown in Figure 2.7, the coordination environment of the Zr atom in **7a** is very similar to that observed in **6a**. The C(26)-N(4)/N(3) distances of 1.167(4)/1.286(4) Å

and the linearity of the N(3)-C(26)-N(4) unit suggest that the N=C=N moiety remains in the product, which is consistent with the NMR results. The Zr-N(1)/N(2) distances of 2.403(3)/2.090(3) Å and the planarity of the N(2) indicate that N(2) is the amido nitrogen and N(1) is the amino nitrogen. Scheme 2.5 shows a proposed mechanism for the formation of **7a**.

Scheme 2.5. Proposed mechanism for the formation of **7a**.



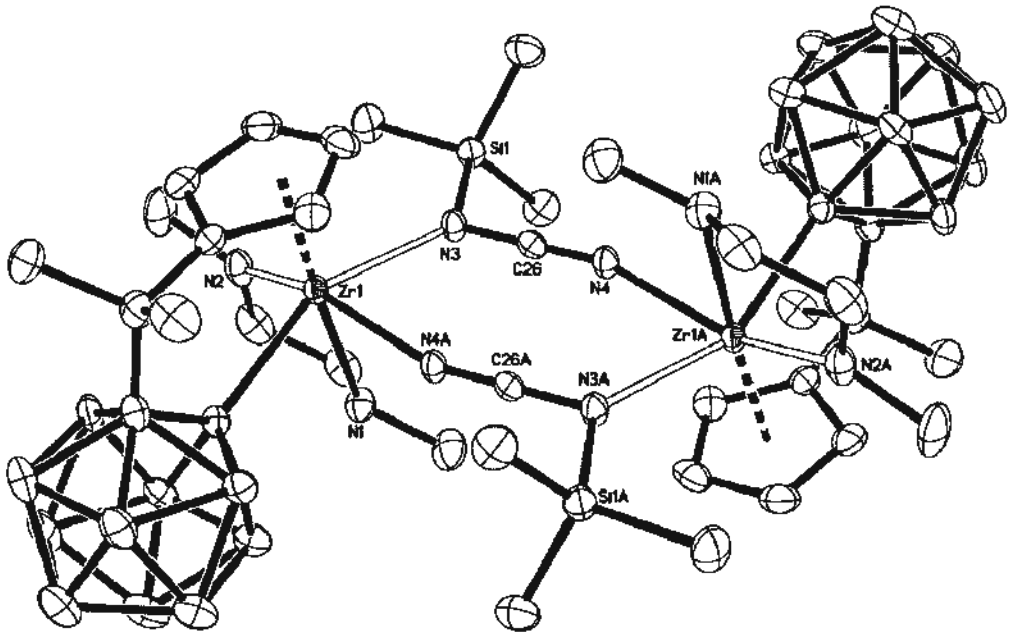
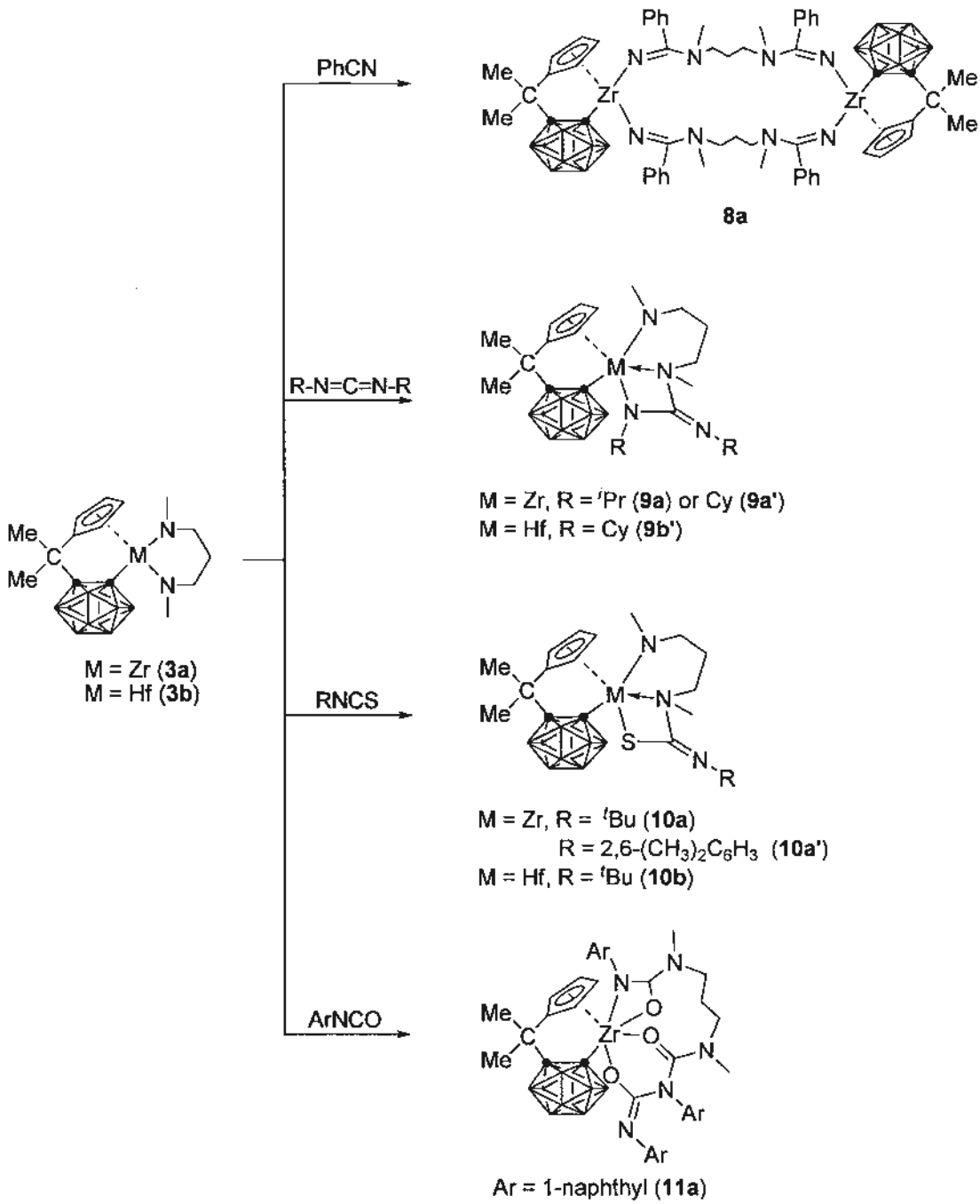


Figure 2.7. Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)][\mu\text{-}TMSN{=}C{=}N]\}_2$ (**7a**).

2.4. Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2\text{-}N(Me)(CH_2)_3N(Me)]$ (M = Zr, Hf) with Unsaturated Molecules

Reaction of **3a** with 2 equiv of PhCN in DME at room temperature generated a diinsertion dimeric complex $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\mu\text{-}N{=}C(Ph)N(Me)(CH_2)_3N(Me)C(Ph){=}N]\}_2$ (**8a**) in 61% isolated yield (Scheme 2.6). Such a ring expansion reaction led to the formation of a 20-membered metallacyclic ring. Its ^{13}C NMR spectrum exhibited a unique resonance of N=*C*-N at 163.4 ppm. The molecular structure of **8a** was further confirmed by single-crystal X-ray analyses with 0.75 THF of solvation. As shown in Figure 2.8, each Zr atom is coordinated by an η^5-cyclopentadienyl ring, a cage carbon atom and two nitrogen atoms in a four-legged piano stool geometry. The average Zr-N distance of 1.958(9) Å is close to the corresponding value of 1.972(2) Å observed in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr[N{=}C(Ph)NMe_2]_2$.[34]

Scheme 2.6. Reaction of **3a** or **3b** with unsaturated molecules.



Treatment of **3a** or **3b** with 1 equiv of DIC or DCC in toluene at room temperature gave the monoinsertion products $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NR)NR]$ (M = Zr, R = ^{i}Pr (**9a**) or Cy (**9a'**); M = Hf, R = Cy (**9b'**)) in 54 ~ 69% isolated yields. No multiple insertion products were isolated in the presence of excess carbodiimide (Scheme 2.6). The results showed that

carbodiimide molecules can only insert into one M-N bond giving an η^2-coordinated guanidinato group, and the other M-N bond remains intact. The guanidinate ligand adopts an asymmetric fashion of coordination, which has only been reported for limited examples.[57] It is noteworthy that **3a** did not react with TMS-N=C=N-TMS even in refluxing toluene, indicating that the coordinated $HNMe_2$ in **2a** played a role in the desilylation process.

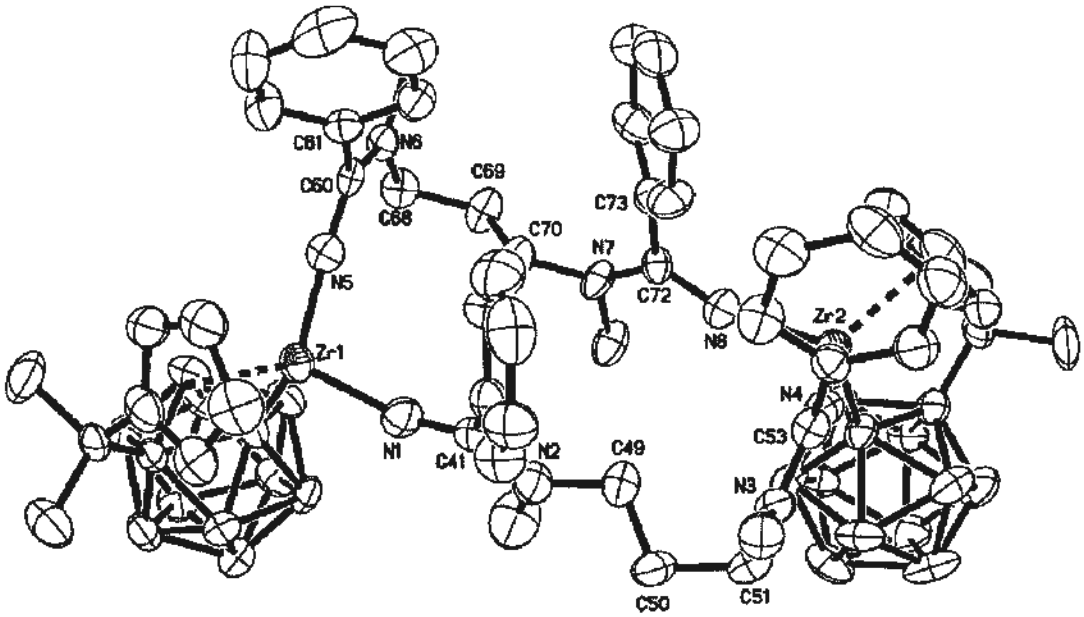


Figure 2.8. Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\mu\text{-}N{=}C(Ph)N(Me)(CH_2)_3N(Me)(Ph)C{=}N]\}_2$ (**8a**), showing one of the two crystallographically independent molecules in the unit cell.

Complexes **9a**, **9a'** and **9b'** were characterized by various spectroscopic techniques and elemental analyses. The unique N-C=N resonances at about 150 ppm were observed in their ^{13}C NMR spectra. Molecular structures of **9a'** and **9b'** were further confirmed by single-crystal X-ray analyses, showing that they are isostructural and isomorphous with a toluene of solvation. Figures 2.9 and 2.10 show the structures of **9a'** and **9b'**, respectively. The central metal atom is coordinated by

an η^5-cyclopentadienyl ligand, a cage carbon atom, an amido group and an η^2-guanidinato ligand in a four-legged piano stool geometry. As indicated in Table 2.2, the key structural features in **9b'** and **9c'** are well comparable with the literature data. The Zr-N_{amido} and Hf-N_{amido} distances of 2.037(2) Å and 2.031(4) Å show typical M-N single bonds.[58]

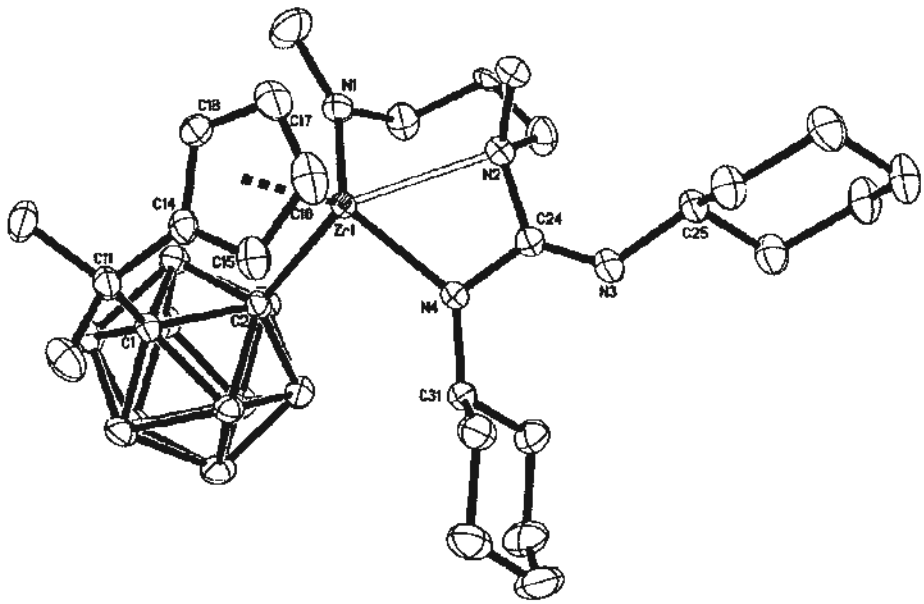


Figure 2.9. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NCy)NCy]$ (**9a'**).

Interaction of **3a** or **3b** with 2 equiv of ^{t}BuNCS or XylNCS in toluene at room temperature afforded isothiocyanate monoinsertion products $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NR)S]$ (M = Zr, R = ^{t}Bu (**10a**) or Xyl (**10a'**); M = Hf, R = ^{t}Bu (**10b**)) in 52 ~ 81% isolated yield. Their ^{13}C NMR spectra exhibited unique resonances of N=*C*-S at about 160 ppm. Still, only one isothiocyanate was inserted to the M-N bond, regardless excess amount of reagents used. The structures of **10a**, **10a'** (with 0.5 toluene of solvation) and **10b** were shown in Figures 2.11, 2.12 and 2.13, respectively. Each metal atom is

coordinated by an η^5-cyclopentadienyl ring, a cage carbon atom, two nitrogen and one sulphur atoms in a four-legged piano stool geometry. Like the DCC or DIC inserted species **9a**, **9a'** and **9b'**, one of the η^2-coordination N atoms is originated from the bridging amide group, but not from the unsaturated molecule, which is very different from that observed in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}SC\text{-}(NMe_2)N^nBu]_2$.[34] It might be due to the ring-strain of the bridging amido ligand.

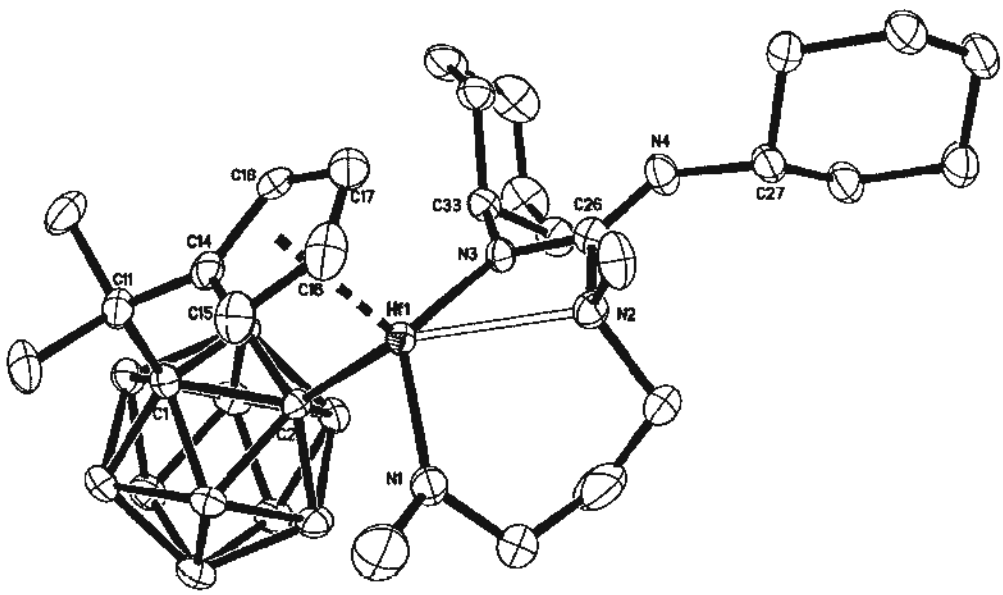


Figure 2.10. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NCy)NCy]$ (**9b'**).

Table 2.2. Selected bond distances (Å) and angles (°) [a]

Complex (M)	**8a** (Zr) [b]	**9a'** (Zr)	**9b'** (Hf)	**10a** (Zr)	**10a'** (Zr)[b]	**10b** (Hf)	**11a** (Zr)
av M-C_{ring}	2.497(11)	2.505(3)	2.490(5)	2.488(2)	2.485(5)	2.473(5)	2.516(5)
av M-Cent	2.203	2.201	2.184	2.181	2.180	2.166	2.217
av M-C_{cage}	2.341(9)	2.378(2)	2.387(4)	2.376(2)	2.367(4)	2.344(4)	2.350(4)
av M-N_{amide}		2.037(2)/ 2.161(2)	2.031(4)/ 2.144(3)	2.004 (2)	1.994(4)	1.984(4)	
av M-N_{amine}		2.453(2)	2.358(4)	2.410(2)	2.419(4)		
av M-N_{imide}	1.958(9)						
av M-S				2.592(1)	2.624(2)	2.572(2)	
C_{cent}-M-C_{cage}	99.7	98.4	98.3	99.8	99.9	100.3	97.6
C_{ring}-C-C_{cage}	110.5(8)	110.1(2)	110.4(3)	109.8 (2)	110.2(4)	109.5(4)	109.9(3)
N-M-N	105.8(3)						

[a] Cent: the centroid of the cyclopentadienyl ring. [b] Average values of the two crystallographically independent molecules in the unit cell.

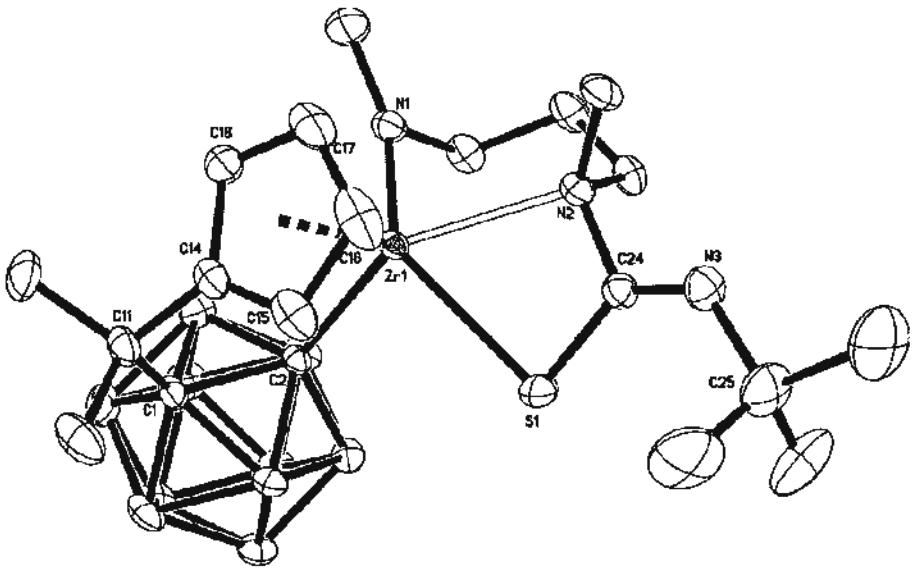


Figure 2.11. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^3$-$N(Me)(CH_2)_3N(Me)C(=N^tBu)S$] (**10a**).

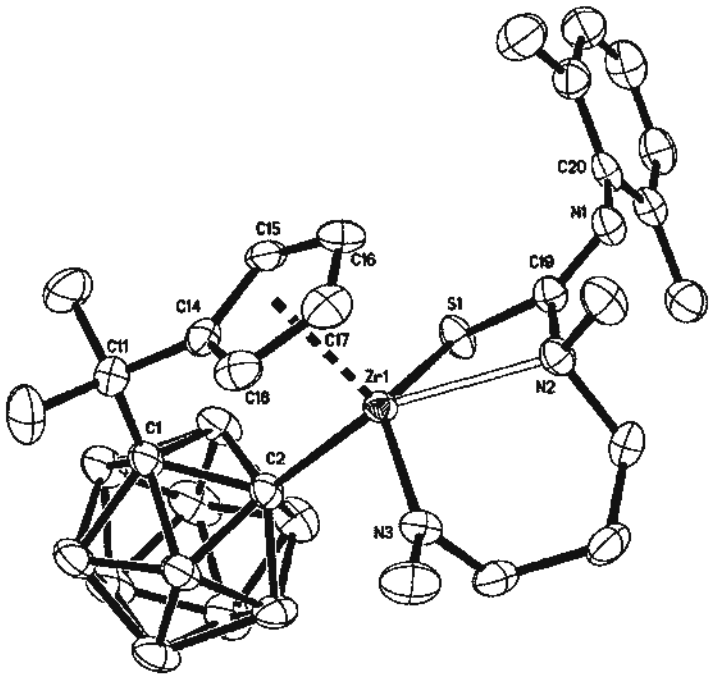


Figure 2.12. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^3$-$N(Me)(CH_2)_3N(Me)C(=NXyl)S$] (**10a'**), showing one of the two crystallographically independent molecules in the unit cell.

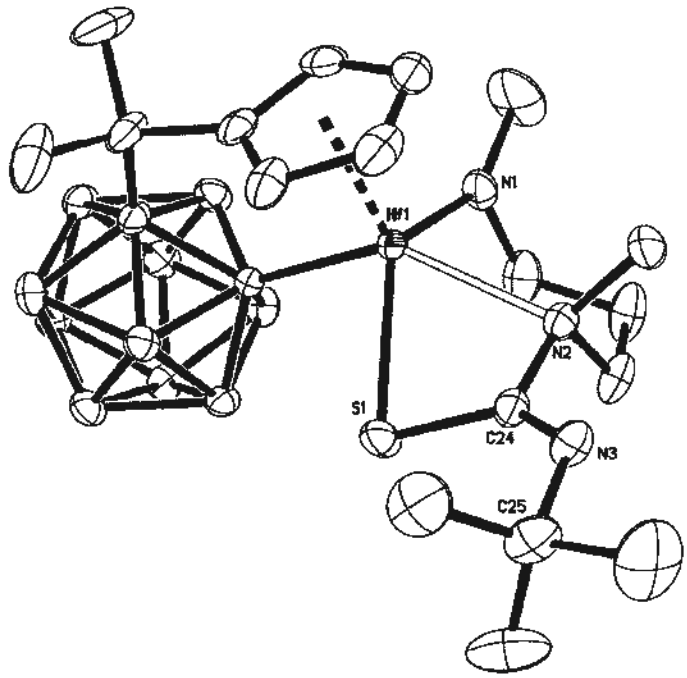


Figure 2.13. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf-[$\eta^3$-$N(Me)(CH_2)_3N(Me)C(=N^tBu)S$] (**10b**).

Reaction of **3a** with 3 equiv of ArNCO (Ar = 1-naphthyl) in toluene at 60 °C afforded a triinsertion product [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$:$\eta^2$-{$OC(=NC_{10}H_7)N(C_{10}H_7)C(=O)$}$N(Me)(CH_2)_3N(Me)C(NC_{10}H_7)O$] (**11a**) in 69% isolated yield. Similar to that of [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$,[34] one of ArNCO molecule inserts into one Zr-N bond, while two insert into the other Zr-N bond, giving a spiro[3.5]metallacycle, if the bridging $N(Me)(CH_2)_3N(Me)$ unit is ignored. The structural parameters indicate that there are some electronic delocalization among O(1)-C(19)-N(1), O(2)-C(35)-N(4) and O(3)-C(46)-N(5) units. The ^1H and ^{13}C NMR showed that four isomers existed in the solution with a molar ratio of 1.5:1:1:0.5, one of which was crystallized out and confirmed by single-crystal X-ray diffraction studies (Figure 2.14). The formation of four isomers is presumably owing to the steric effect imposed by constrained-geometry ligand and the bulky naphthalene rings, which restricts the rotation of the naphthalyl

substituents. The Zr-N(1)/O(1) distances of 2.211(4)/2.167(3) Å are compare well with the 2.186(4)/2.161(3) Å in $[\eta^5{:}\sigma\text{-}^t Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OCN(Ph)][\eta^2\text{-}OC(NMe_2)N(Ph)C{=}(NPh)O]$[51] and 2.217(5)/2.196(4) Å in **5a**.

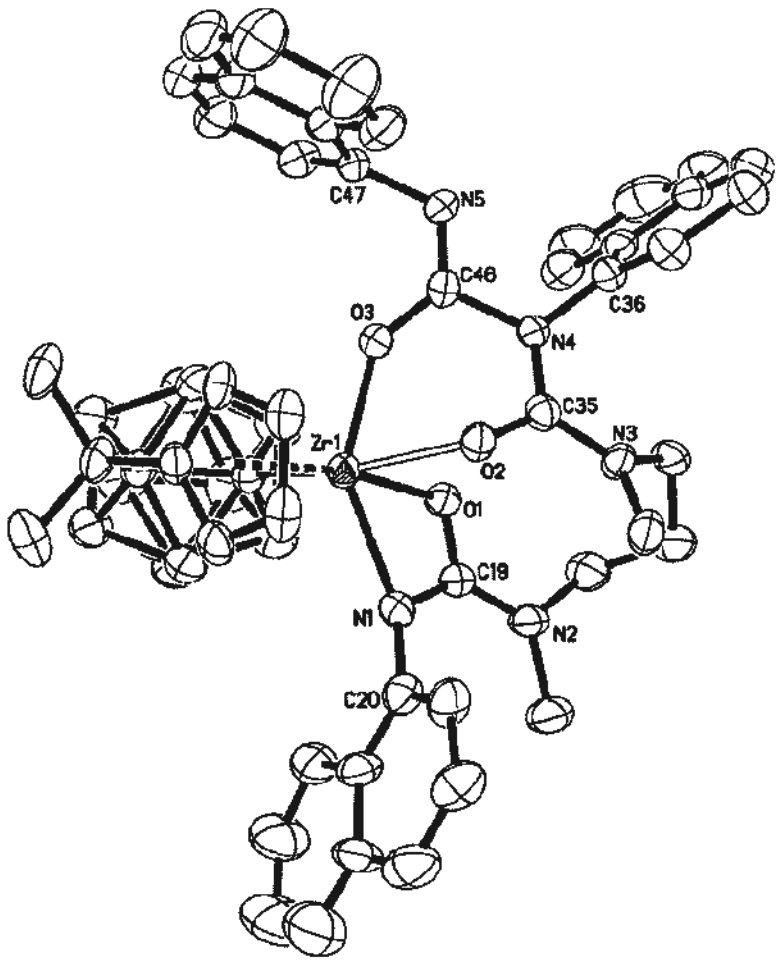
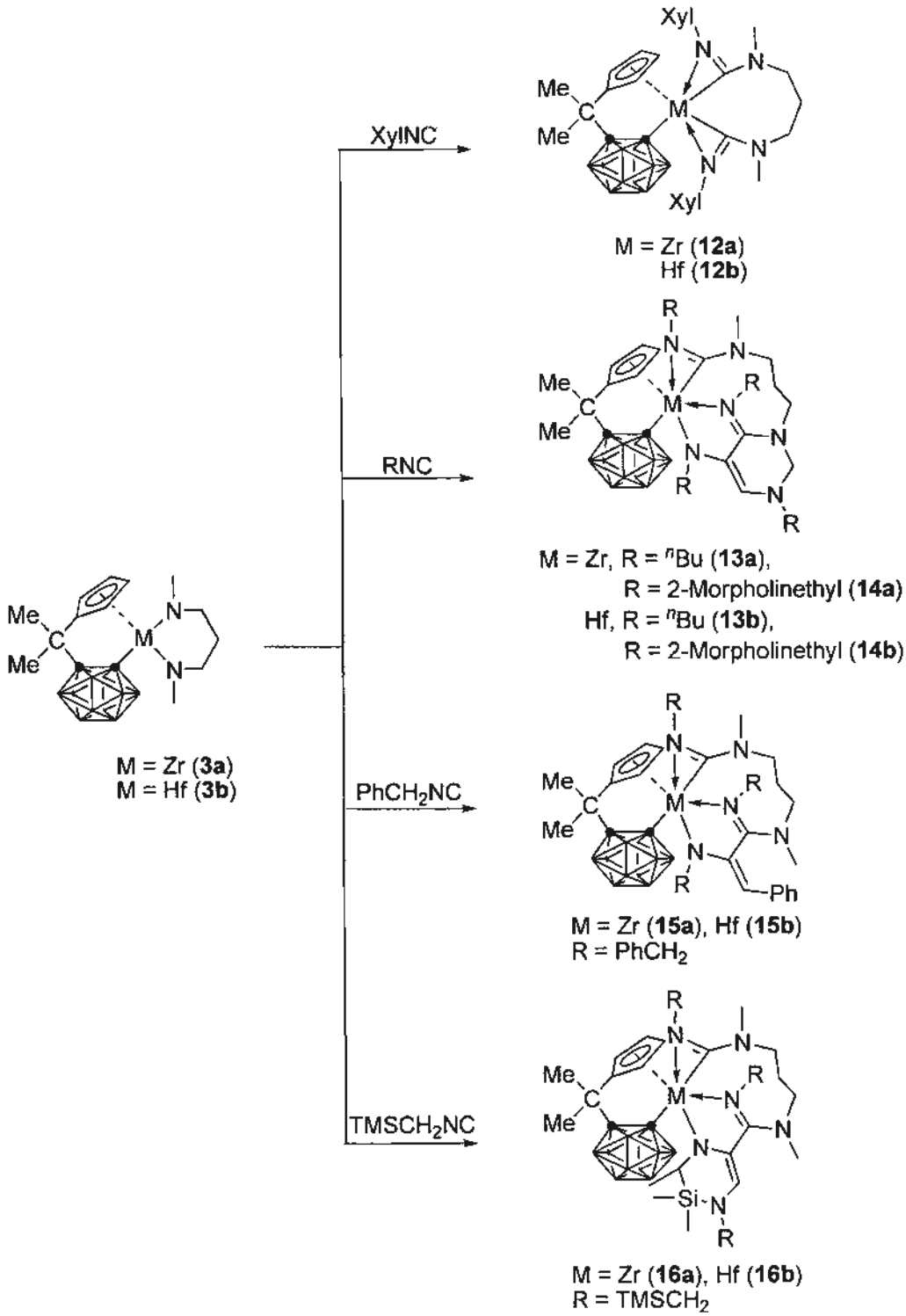


Figure 2.14. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}\{OC(=NC_{10}H_7)N(C_{10}H_7)C(=O)\}N(Me)(CH_2)_3N(Me)C(NC_{10}H_7)O]$ (**11a**).

Reaction of **3a** or **3b** with 2 equiv of XylNC in toluene at room temperature gave the diinsertion products $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2{:}\eta^2\text{-}(Xyl)N{=}CN(Me)(CH_2)_3N(Me)C{=}N(Xyl)]$ (M = Zr, **12a**; M = Hf, **12b**) in 58 ~ 63% isolated yields. Similar to complexes **2a** and **2c**, only diinsertion products were isolated in the presence of **1** or more equiv of XylNC (Schemes 2.7). No further reaction was observed. The titanium species **3c** did not react with XylNC in a C_6D_6

solution even at 90 °C for 3 days. It may be due to the larger ring size of the amide ligand that prevents the insertion of XylNC.

Scheme 2.7. Reaction of **3a** or **3b** with isocyanides.



They were characterized by various spectroscopic techniques and elemental analyses. The ^{13}C NMR was not obtainable due to very poor solubility in organic solvents. The molecular structures of **12a** and **12b** were further confirmed by X-ray analyses and shown in Figures 2.15 and 2.16, respectively. Similar to complex **4a** and **4c**, the central metal atom is coordinated by an η^5-cyclopentadienyl ligand, a cage carbon atom and two η^2-iminocarbamoyl ligands in a five-legged piano stool geometry. The average Zr-C(sp^2) distance of 2.190(3) Å and Zr-N(sp^2) distance of 2.212(2) Å are comparable well with 2.162(3) Å and 2.236(3) Å in **4a**.

Unlike XylNC in which only diinsertion products were formed, complexes **3a** or **3b** reacted with other isocyanides bearing α-CH_2 unit, such as *n*-butyl-, 2-morpholinethyl-, benzyl- and trimethylsilylmethyl-isocyanide to afford multiple insertion products (Schemes 2.7).

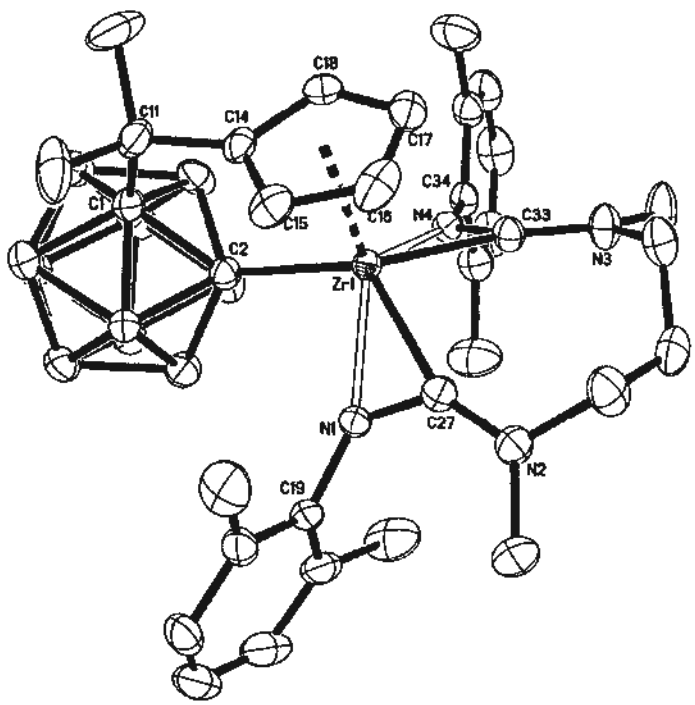


Figure 2.15. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2{:}\eta^2\text{-}(Xyl)N{=}CN(Me)(CH_2)_3N(Me)C{=}N(Xyl)]$ (**12a**).

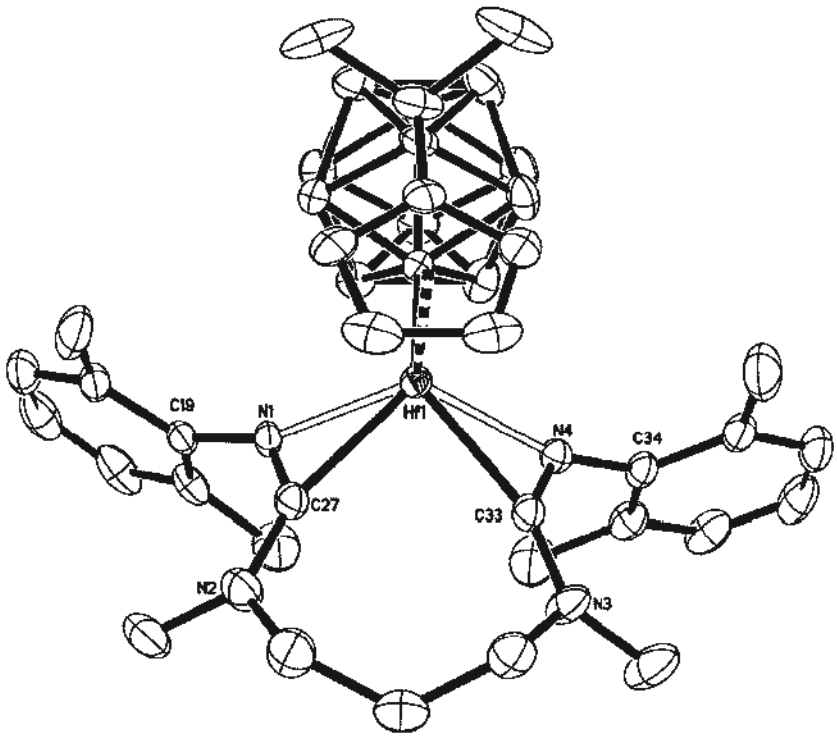


Figure 2.16. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf\text{-}[\eta^2{:}\eta^2\text{-}(Xyl)N{=}CN(Me)(CH_2)_3N(Me)C{=}N(Xyl)]$ (**12b**).

Treatment of **3a** or **3b** with 4.5 equiv of ^{n}BuNC at 60 °C in toluene gave tetrainsertion products $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2{:}\eta^2\text{-}\{N^nBu\}\{N^nBu\}\text{-}[(=C)\text{-}C{=}CHN(^nBu)CH_2N[(CH_2)_3N(Me)N\text{-}C{=}N(^nBu)]]$ (M = Zr, **13a**; M = Hf, **13b**) in about 55% isolated yield. The ^{1}H NMR spectra showed that the reactions were completed in 2 days. Only multiple insertion products were observed in the presence of 1 or more equiv of ^{n}BuNC. No intermediate was detected.

Four multiplets in the region 6.52 – 5.92 ppm assignable to the cyclopentadienyl protons and two singlets at about 1.7 ppm attributable to the two diastereotopic methyl groups of the bridging CMe_2 unit, a singlet at about 5.8 ppm of the characteristic olefinic hydrogen, two doublets in the region 3.75 to 3.35 ppm corresponding to the two diastereotopic NCH_2N protons and one singlet at ~2.5 ppm for one NMe group, were observed in the ^{1}H NMR spectra of **13a** and **13b**. The

unique M-N(^{n}Bu)=C-C, M-N(^{n}Bu)=C-*C* and N(^{n}Bu)C=*C*H resonances at ~165, ~129 and ~130 ppm were found in the ^{13}C NMR spectra of **13a** and **13b**.

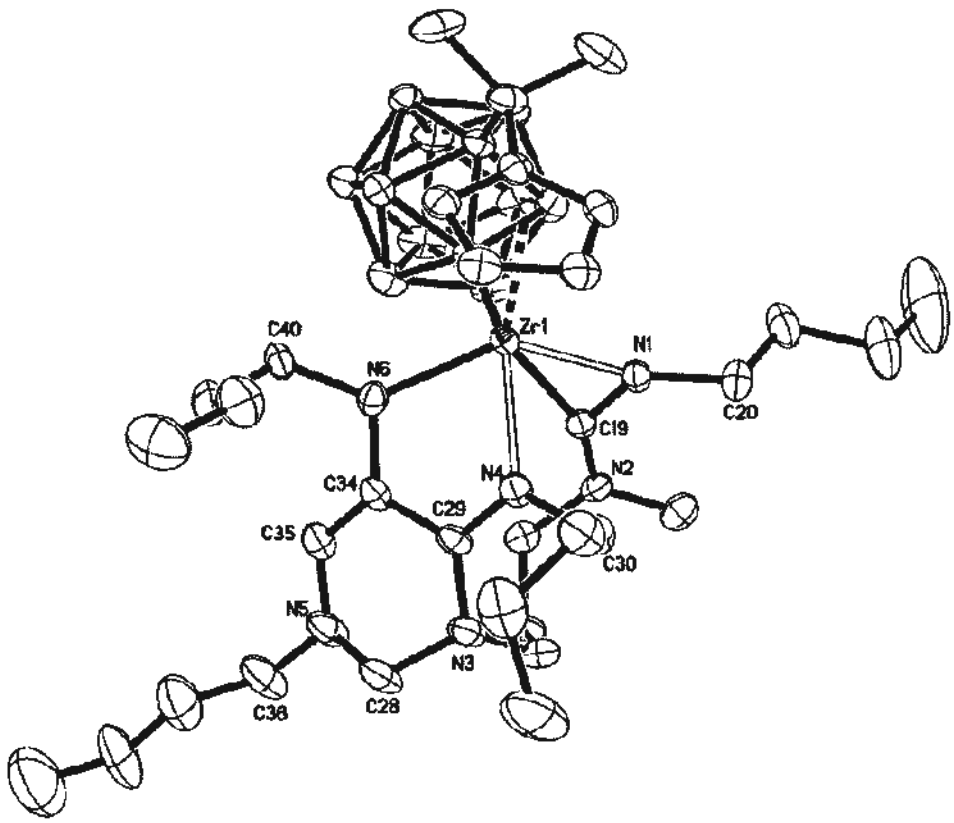


Figure 2.17. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{N^{n}Bu}-{N^{n}Bu}[(=C)-C=CHN(^{n}Bu)CH_2N[$(CH_2)_3$N(Me)N-C=N(^{n}Bu)]] (**13a**).

The molecular structure of **13a** and **13b** were confirmed by single-crystal X-ray analyses and shown in Figures 2.17 and 2.18, respectively. Complex **13a** and **13b** are isostructural and isomorphous, in which the central metal atom is η^5-bound to the cyclopentadienyl ring, σ-bound to a cage carbon atom, η^2-bound to an iminocarbamoyl ligand and η^2-bound to the amino-imino-tetrahydropyrimidine group in a five-legged piano stool geometry. There is clearly a six-membered ring formation in these structures. A C-H bond activation on the NMe group of the bridging diamido ligand occurred.

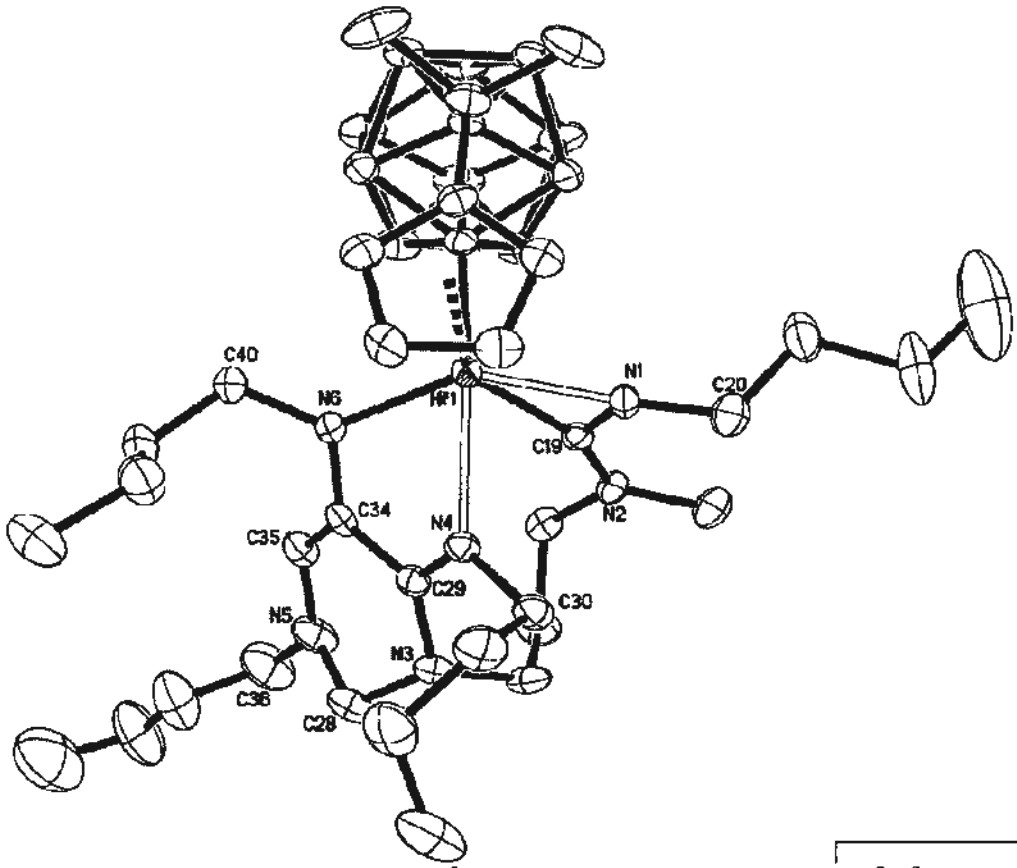


Figure 2.18. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}\{N^nBu\}\text{-}\{N^nBu\}[(=C)\text{-}C{=}CHN(^nBu)CH_2N[(CH_2)_3N(Me)N\text{-}C{=}N(^nBu)]]$ (**13b**).

As indicated in Table 2.3, the key structural features in **13a** and **13b** are comparable well with the literature data. The Zr-N(1)/C(19) distances of 2.154(4)/2.245(6) Å are close to the 2.236(3)/2.162(3) Å in **4a**, 2.190(3)/2.212(2) Å in **12a**, 2.174/2.271 Å in $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2\text{-}\eta\text{-}N^tBu)_2\}\text{-}\{\eta^2\text{-}C(CH_2Ph){=}N(2,6\text{-}Me_2C_6H_3)\}]$.[59a] The Hf(1)-N(1)/C(19) distances of 2.146(4)/2.230(5) Å are comparable to the 2.193(4)/2.176(4) Å in **12b** and 2.207(5)/2.269(6) Å in $[Hf(TC\text{-}3,5)\{\eta^2\text{-}(Cy)N{=}C(CH_2Ph)\}_2]$ (TC = Tropocoronand).[59b] A much shorter Zr-N(6)/Hf-N(6) distances of 2.126(4)/2.117(4) Å over the Zr-N(5)/Hf-N(5) distances of 2.374(4)/2.361(4) Å and the planar geometry of N(6) suggest that N(6) is the amido nitrogen and N(5) is the amino

nitrogen. The planar geometry of C(29), C(34) and C(35) atoms suggest that they are sp^2 hybridized carbon and the short N(4)-C(29) and C(34)-C(35) distances of 1.307(6)/1.376(6) Å in **13a**, and 1.298(6)/1.376(7) Å in **13b** represent a typical double bond. The planarity of the N(4)=C(29)(-N(3))-C(34)(-N(6))=C(35)-N(5) fragment indicates some electron delocalization over such a unit. All the spectroscopic data confirmed the formation of metal-bound amino-imino-tetrahydropyrimidine structures of complexes **13a** and **13b**.

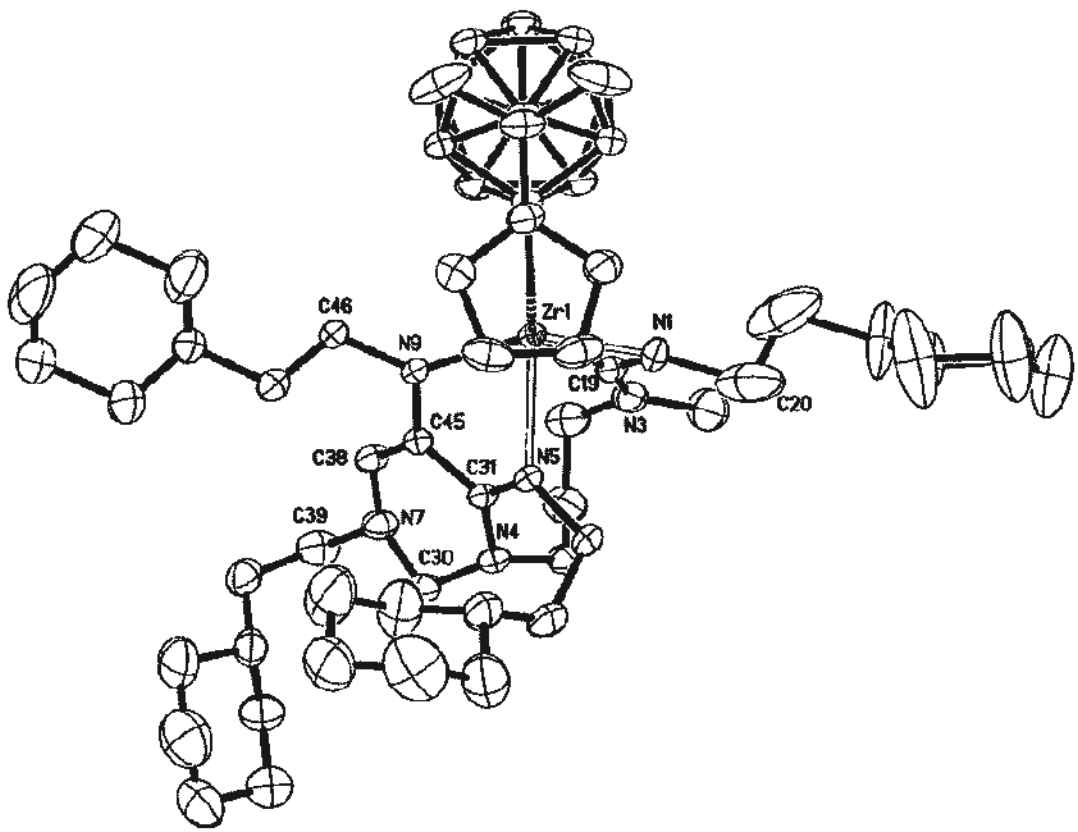


Figure 2.19. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}\{NR\}\{NR\}[(=C)\text{-}C{=}CHNRCH_2N[(CH_2)_3N(Me)N\text{-}C{=}NR]]$ (R = 2-morpholinethyl) (**14a**).

Under similar reaction conditions, reactions of **3a** or **3b** with 2-morpholinethylisocyanide afforded $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M\text{-}[\eta^2{:}\eta^2\text{-}\{NR\}\{NR\}[(=C)\text{-}C{=}CHNRCH_2N[(CH_2)_3N(Me)N\text{-}C{=}NR]]$ (R =

2-morpholinethyl) as red crystals in 59% isolated yield (M = Zr, **14a**) or orange red crystals in 70% isolated yield (M = Hf, **14b**). Both ^{1}H and ^{13}C NMR spectra of complexes **14a** and **14b** showed similar patterns as those of complexes **13a** and **13b**. A singlet at about 6.0 ppm assignable to the characteristic olefinic hydrogen and two doublets in the region 4.0 – 3.6 ppm corresponding to the two diastereotopic NCH_2N protons were observed in the ^{1}H NMR spectra in each case. The unique M-N(R)=C-C and N(R)C=CH resonances at ~164 and ~130 ppm were found in their ^{13}C NMR spectra, suggesting the formation of a metal-bound amino-imino-tetrahydropyrimidine moiety.

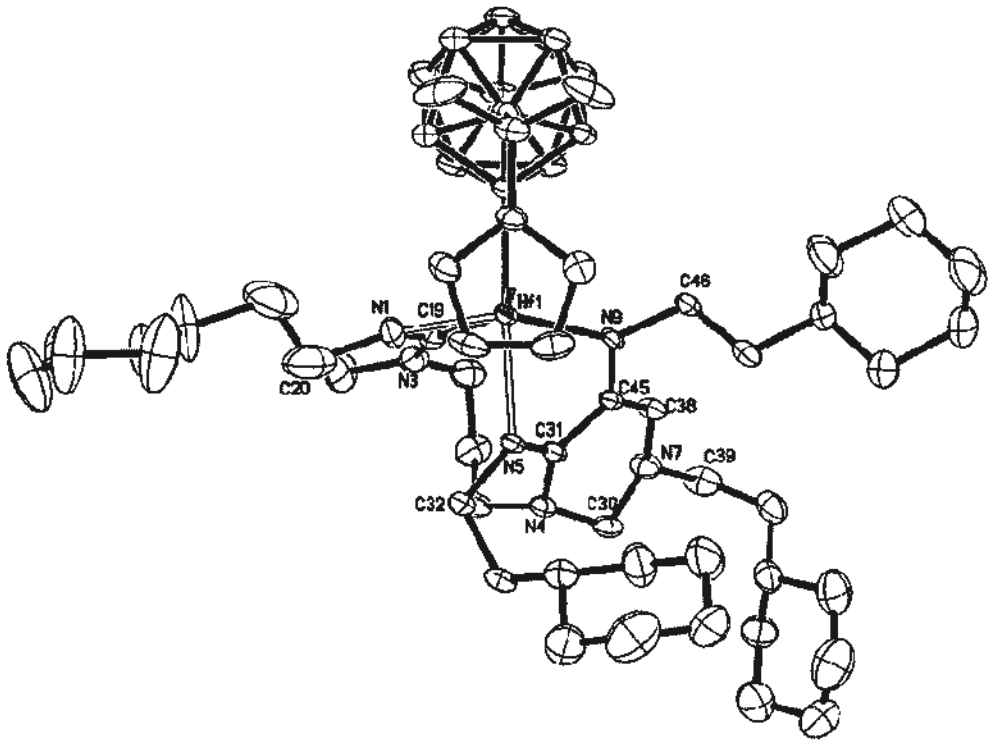


Figure 2.20. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}\{NR\}\text{-}\{NR\}[(=C)\text{-}C{=}CHNRCH_2N[(CH_2)_3N(Me)N\text{-}C{=}NR]]$ (R = 2-morpholinethyl) (**14b**).

The structures of **14a** and **14b** were further confirmed by single-crystal X-ray analyses and shown in Figures 2.19 and 2.20, respectively. The corresponding bond

distances are comparable and similar to those in **13a** and **13b** and those found in literatures.[59] The Zr-N(1)/C(19) and Hf-N(1)/C(19) distances of 2.155(4)/2.232(5) Å and 2.151(5)/2.236(6) Å are close to that of 2.154(4)/2.245(6) Å and 2.146(4)/2.230(5) Å in **13a** and **13b**, respectively. The short N(5)-C(31) and C(38)-C(45) distances of 1.294(5)/1.363(5) Å in **14a**, and 1.303(7)/1.357(8) Å in **14b**, in addition to the planarity of C(31), C(38) and C(45) atoms, suggest that N(5)-C(31) and C(38)-C(45) are two double bonds. Similar to complexes **13a** and **13b**, the N(5)=C(31)(-N(4))-C(45)(-N(9))=C(38)-N(7) atoms are in coplanar rearrangement, indicative of some electron delocalization among this unit.

On the other hand, different reaction patterns were observed if there is no β-hydrogen in the isocyanides. The reaction between **3a** or **3b** and benzyl isocyanide at afforded complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2{:}\eta^2\text{-}\{NCH_2Ph\}\{NCH_2Ph\}\text{-}[\text{-}C(=CH_2Ph)N(Me)(CH_2)_3N(Me)C=N(CH_2Ph)]$ (M = Zr, **15a**; M = Hf, **15b**) in 50% and 44% isolated yields, respectively. Although conversion was almost quantitative as monitored by NMR, the isolated yield was comparatively low in each case, which may be caused by the loss in purification and recrystallization processes. Complexes **15a** and **15b** were characterized by various spectroscopic techniques as well as elemental analyses.

In addition to the peaks derived from the phenyl ring, carbon-bridged cyclopentadienyl-carboranyl and diamido ligand, a peak at about 5.9 ppm attributable to the characteristic olefinic proton, and three sets of diastereotopic protons assignable to the three PhCH_2 groups were observed in the ^{1}H NMR spectra of both **15a** and **15b**. The unique M-N(CH$_2$Ph)=*C*-C, M-N(CH$_2$Ph)=C-*C* and C=*C*HPh resonances at ~166, ~153 and ~110 ppm were observed in their ^{13}C NMR spectra, suggesting the formation of a amino-acrylimidamide structure.

Table 2.3. Selected bond distances (Å) and angles (°)[a]

Complex (M)	**12a** (Zr)	**12b** (Hf)	**13a** (Zr)	**13b** (Hf)	**14a** (Zr)	**14b** (Hf)	**15b** (Hf)	**16a** (Zr)	**16b** (Hf)
av M-C_{ring}	2.515(3)	2.500(5)	2.559(6)	2.542(5)	2.548(5)	2.535(7)	2.533(8)	2.555(3)	2.540(11)
av M-Cent	2.214	2.196	2.258	2.240	2.249	2.239	2.228	2.257	2.242
av M-C_{cage}	2.425(3)	2.387(4)	2.397(6)	2.376(5)	2.422(4)	2.401(6)	2.425(8)	2.401(2)	2.375(8)
av M-N_{amide}			2.126(4)	2.117(4)	2.140(3)	2.127(4)	2.195(6)	2.151(2)	2.148(7)
av M-N_{imine}	2.212(2)	2.193(4)	2.153(4)	2.146(4)	2.155(4)	2.151(5)	2.157(6)	2.179(2)	2.186(7)
av M-N_{imide}			2.374(4)	2.361(4)	2.348(3)	2.321(4)	2.418(7)	2.330(2)	2.322(7)
C=C			1.374(7)	1.376(7)	1.363(5)	1.357(8)	1.359(10)	1.367(3)	1.339(13)
C_{cent}-M-C_{cage}	100.1	100.1	97.5	98.0	97.1	97.9	97.3	97.7	98.2
C_{ring}-C-C_{cage}	110.9(2)	110.6(4)	111.5(4)	110.1(4)	110.4(3)	110.7(5)	110.0(6)	110.9(2)	110.3(8)
N-M-N	116.9(1)	116.8(1)							

[a] Cent: the centroid of the cyclopentadienyl ring.

The molecular structure of **15b** was further confirmed by X-ray analyses and showed half DME of solvation. As shown in Figure 2.21, the central Hf atom is η^5-bound to the cyclopentadienyl ring, σ-bound to a cage carbon atom, η^2-bound to an iminocarbamoyl ligand and η^2-bound to the amino-acrylimidamide group in a five-legged piano stool geometry. The short N(4)-C(32) and C(40)-C(41) distances of 1.308(9) Å and 1.359(10) Å and the planarity of C(32), C(40) and C(41) atoms show that N(4)-C(32) and C(40)-C(41) are typical double bonds. The N(4), C(32), C(40) and C(41) atoms are not in the same plane, which may be due to the bulky CH_2Ph and C=CHPh groups preventing the coplanar rearrangement of these atoms.

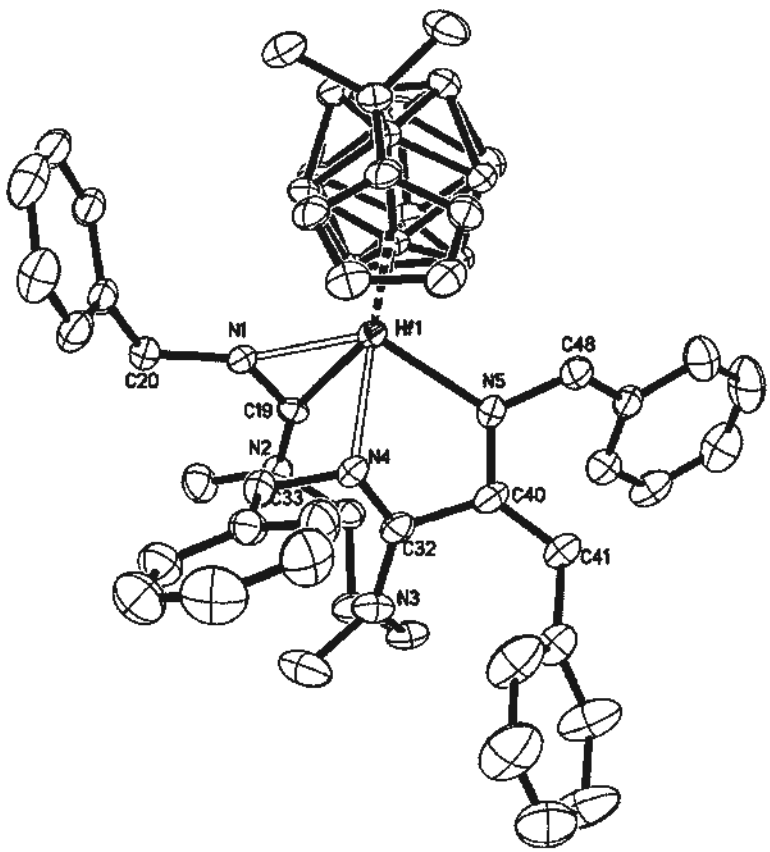


Figure 2.21. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2:\eta^2\text{-}\{NCH_2Ph\}\{NCH_2Ph\}[\text{-}C(=CH_2Ph)N(Me)(CH_2)_3N(Me)C=N(CH_2Ph)]$ (**15b**).

Treatment of **3a** or **3b** with 6 equiv of $TMSCH_2NC$ at 70 °C for 3 days afforded

the multiple insertion products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^2$:$\eta^2$-{$NCH_2TMS$}=C{CNCH(Me)Si($Me_2$)N($CH_2TMS$)C=}N(Me)($CH_2$)$_3$N(Me)C=$NCH_2TMS$] (M = Zr, **16a**; M = Hf, **16b**) in 57 ~ 64% isolated yields. These two complexes were fully characterized by various spectroscopic techniques as well as single-crystal X-ray analyses.

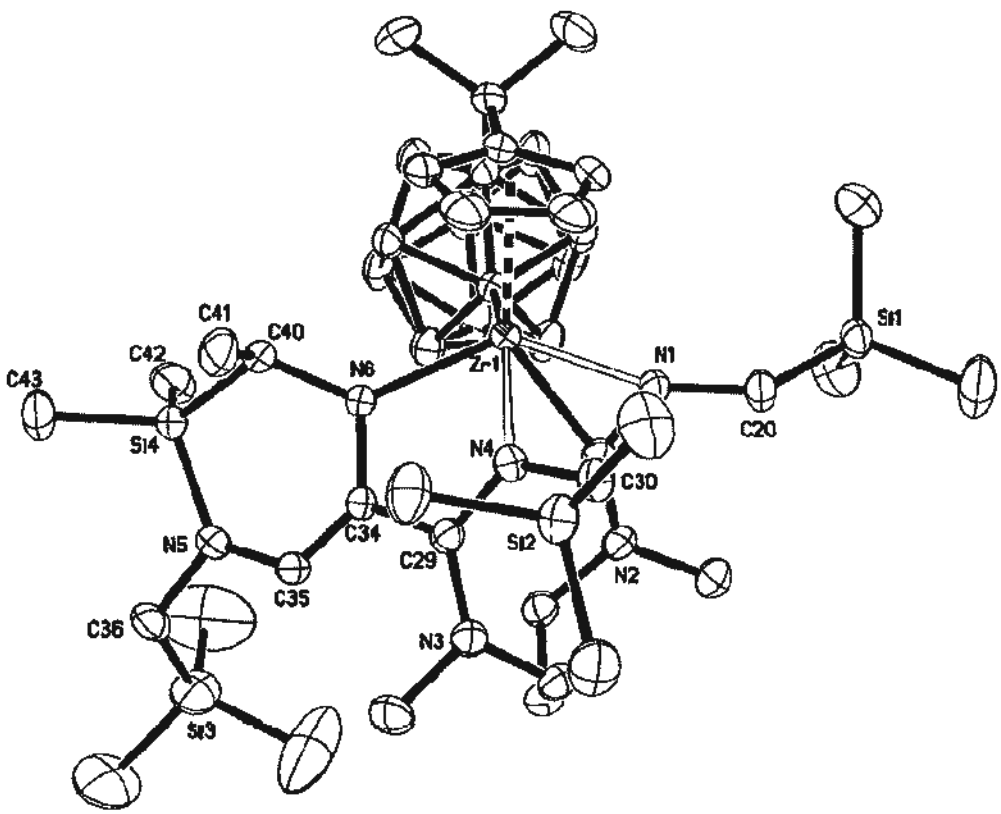


Figure 2.22. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{$NCH_2TMS$}=C{CNCH(Me)Si($Me_2$)N($CH_2TMS$)C=}N(Me)($CH_2$)$_3$N(Me)C=$NCH_2TMS$] (**16a**).

A singlet at ~6.0 ppm assignable to the characteristic C=C*H*NCH_2TMS resonance, a quartet at about 3.9 ppm attributable to the Si(Me)$_2$C*H*Me proton, a doublet at ~1.2 ppm corresponding to the Si(Me)$_2$CHCH_3 group, two singlets in the region 0.7 – 0.0 ppm for the two diastereotopic $SiMe_2$ groups and three sets of diastereotopic

CH_2TMS protons were observed in the ^{1}H NMR spectra of **16a** and **16b**. The unique M-N(CH$_2$TMS)=*C*-NMe, M-N(CH$_2$TMS)=C-*C*=CH, M-N(CH$_2$TMS)=C-C=*C*H resonances at ~168, ~134 and ~133 ppm were found in their ^{13}C NMR spectra.

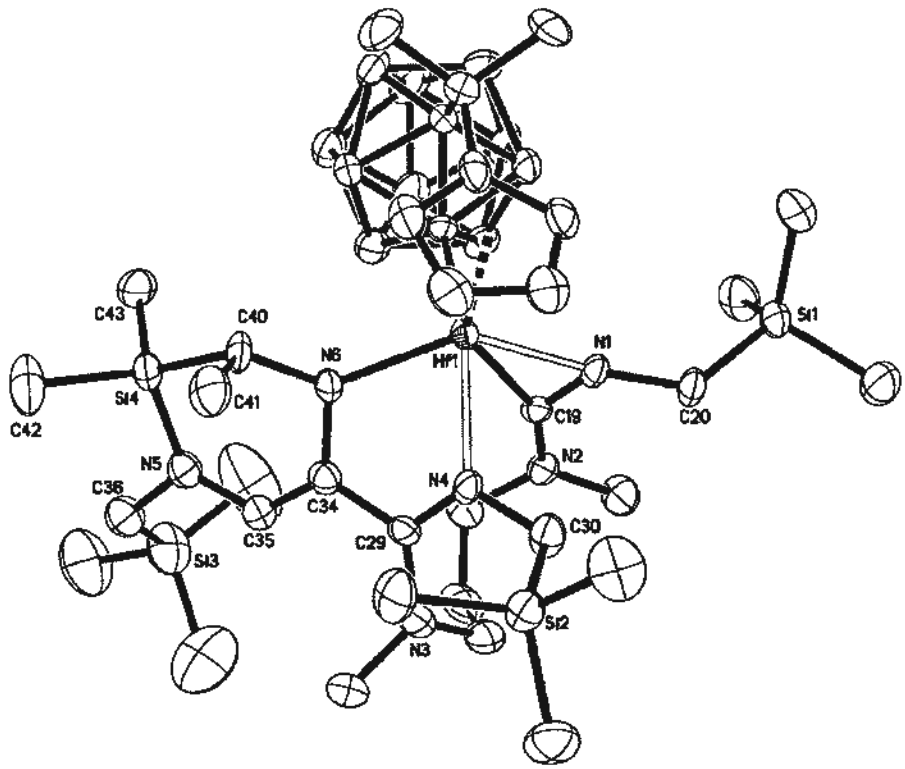


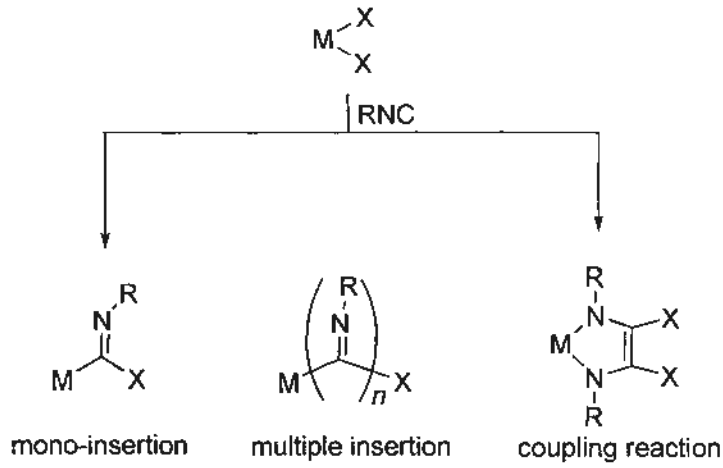
Figure 2.23. Molecular structure of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Hf[η^2:η^2-{NCH$_2$TMS}=C{CNCH(Me)Si(Me$_2$)N(CH$_2$TMS)C=}N(Me)(CH$_2$)$_3$N(Me)C=NCH$_2$TMS] (**16b**).

As shown in Figures 2.22 and 2.23, the coordination environments of the central metal atoms are very similar to that observed in the above multiple insertion products, in which the central metal atom is η^5-bound to the cyclopentadienyl ring, σ-bound to a cage carbon atom, η^2-bound to an iminocarbamoyl ligand and η^2-bound to the tetrahydrodiazasilinylmethanimino group in a five-legged piano stool geometry. The short N(4)-C(29) and C(34)-C(35) distances of 1.304(3)/1.367(3) Å in **16a**, and 1.296(12)/1.339(13) Å in **16b**, show that they are two double bonds. The planarity of

the N(4)=C(29)(-N(3))-C(34)(-N(6))=C(35)-N(5) fragment indicates some electron delocalization over such a unit, which further confirms the structures.

The reaction between **1b** and $TMSCH_2NC$, did not afford a pure product, as monitored by NMR techniques. This result shows that the bridging amido ligands have some influences on the multiple insertion reactions.

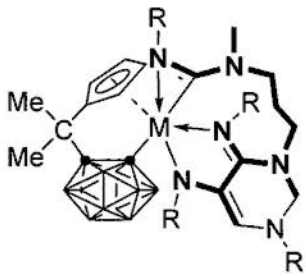
Scheme 2.8. Three types of isocyanide insertion reactions



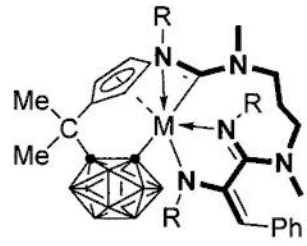
Isocyanides are isoelectronic analogue of CO, and insertion of these compounds into M-C or M-N bonds has been extensively studied.[60-63] Generally, these reactions can be classified into three types: monoinsertion,[64] multiple insertion,[65] and coupling reactions[66] (Scheme 2.8). Although these reactions seem simple, tandem reactions with migration of these inserted species or intermediate can construct complicate organometallic framework and provide useful synthetic routes to nitrogen-containing organic compounds.[60-63] For examples, reaction of $[PdCl_2(PPh_3)_2]$ with excess XylNC in the presence of H_2SiMe_2 afforded multiple insertion product [Pd{[C(=NXyl)]$_4$CH(=NXyl)}(C=NXyl)Cl], which reacted further with RNC (R = Xyl or Mes), CO or PhC≡CPh to give diazabicyclooctadiene derivatives or pyrrole derivatives, respectively.[65b] Reaction of iminotitanium complex $[(\kappa^3\text{-}N_2Npy)Ti(=N^tBu)(py)]$ $[(N_2Npy) = (2\text{-}C_5H_4N)C(Me)(CH_2NSiMe_3)_2]$ with

isocyanides bearing one α-H afforded metal bound heterocycles $[(\kappa^3\text{-}N_2Npy)Ti\{N^tBu\}\{\eta^2\text{-}NR\}[\text{-}C{=}NCH(R)N(R)CHC\text{-}]]$ (R = H, CH_3, C_3H_7 or Ph).[67]

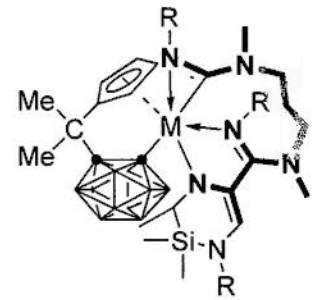
Chart 2.1. Common structures in the isocyanide multiple insertion products.



M = Zr, R = ^{n}Bu (**13a**),
R = 2-morpholinethyl (**14a**)
M = Hf, R = ^{n}Bu (**13b**),
R = 2-morpholinethyl (**14b**)

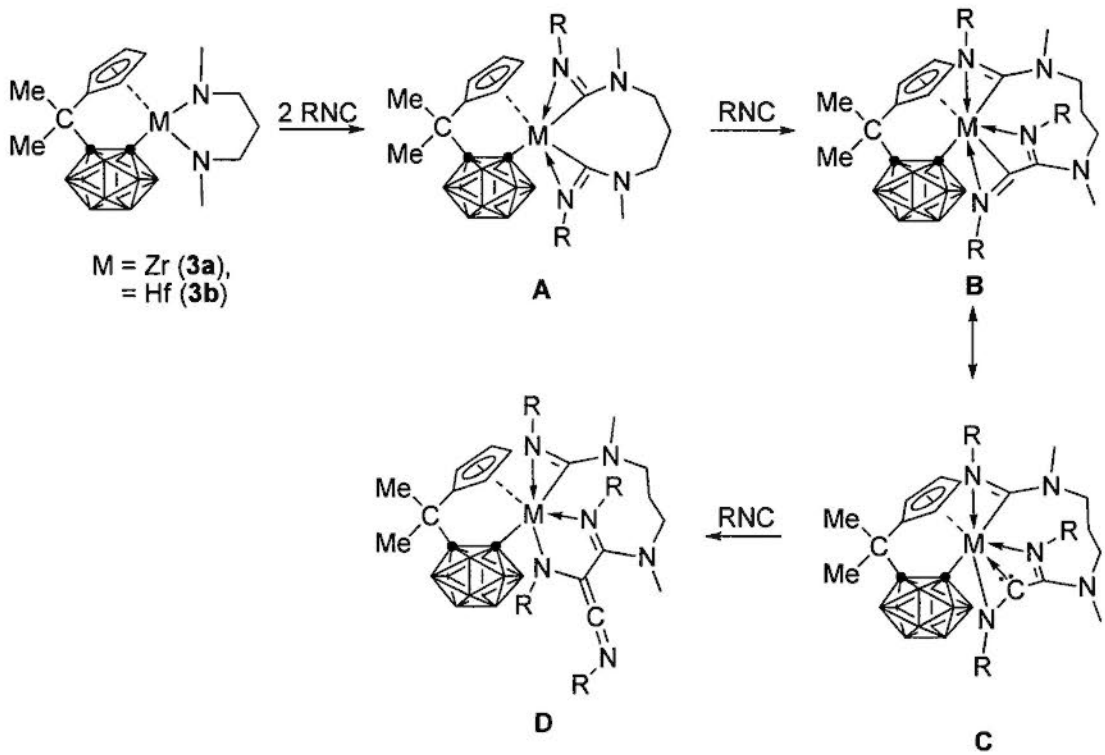


M = Zr (**15a**)
M = Hf (**15b**)



M = Zr (**16a**)
M = Hf (**16b**)

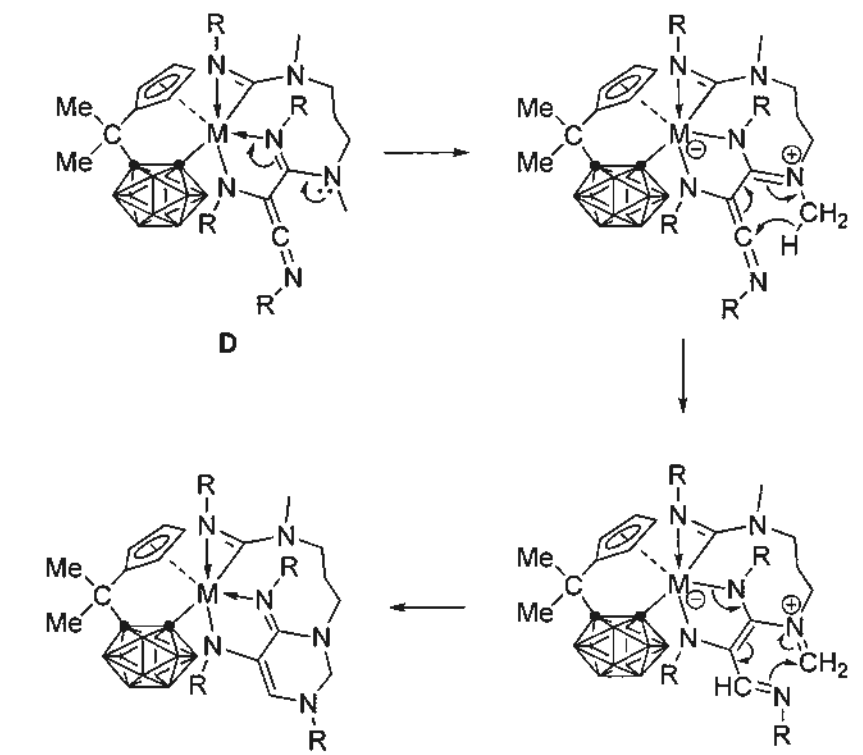
Scheme 2.9. Proposed mechanism for the formation of heterometallacycles.



In current cases, different isocyanides gave different products. They share the

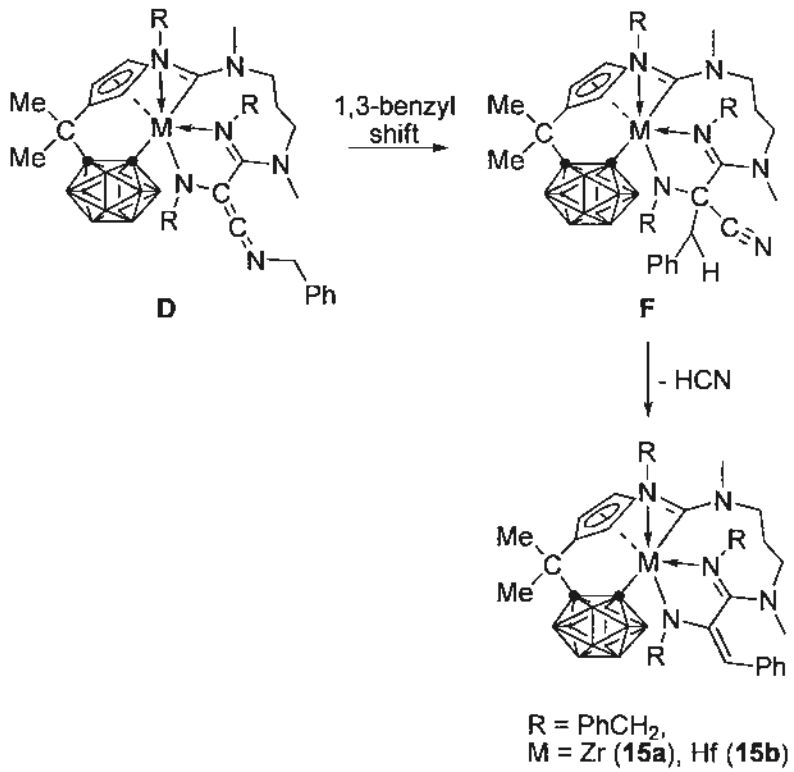
same structural motif as high-lighted in Chart 2.1. Based on these, we proposed a possible mechanism for the formation of these heterometallacycles (Scheme 2.9). Simple insertion of two equiv of isocyanides into two M-N bonds forms the diinsertion intermediate **A**.[55a,59a,64] The reaction of **3a** or **3b** with XylNC stops at this stage mainly because of the steric hindrance of the bulky Xyl groups, which prevent further reactions. The second step is insertion of an isocyanide into the newly formed M-C bond gives the triinsertion species **B**,[68] which is in resonance with a carbene intermediate **C** with a new M-N σ bond. Consequence coupling of the fourth equiv of isocyanide gives the iminoketene derivative **D**.[67,69] Although **D** cannot be isolated or detected by NMR techniques, the reaction of carbenes or carbenoids with isocyanides to give iminoketenes is well established.[70]

Scheme 2.10. Proposed mechanism for the formation of **13a**, **13b**, **14a** and **14b**.



This intermediate **D** can undergo different migratory processes depending on the R groups. For R = ^{n}Bu, an 1,5-H sigmatropic reaction occurs at the NMe group to give the Eschenmoser's salt intermediate **E**.[67] Intramolecular ring closure gives the final products **13a**, **13b** or **14a**, **14b**, as shown in Scheme 2.10.

Scheme 2.11. Proposed mechanism for the formation of **15a** and **15b**.



When R = Bn, a 1,3-benzyl migration gives the corresponding intermediate propionitriles **F**.[71] This type of conversion via thermal arrangement of the benzyl groups is well known as a radical mechanism.[71] Elimination of HCN from **F** gives complexes **15a** or **15b** (Scheme 2.11). It is noted that decyanation reactions of isocyanides in the presence of transition metal to afford metal bound cyanides have been previously reported.[72] From the reaction mixtures, we also got few crystals characterized as $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}\{NCH_2Ph\}\{NCH_2Ph\}\text{-}[\text{-}C(\text{-}C{\equiv}N)CN(Me)(CH_2)_3N(Me)C{=}NCH_2Ph]$ (**17a**) by X-ray analyses with half

toluene of solvation (Figure 2.24). Unfortunately, its spectroscopic data cannot be obtained due to a very small quantity of the crystals. Nevertheless, the structural characterization of **17a** supports the proposed decyanation process.

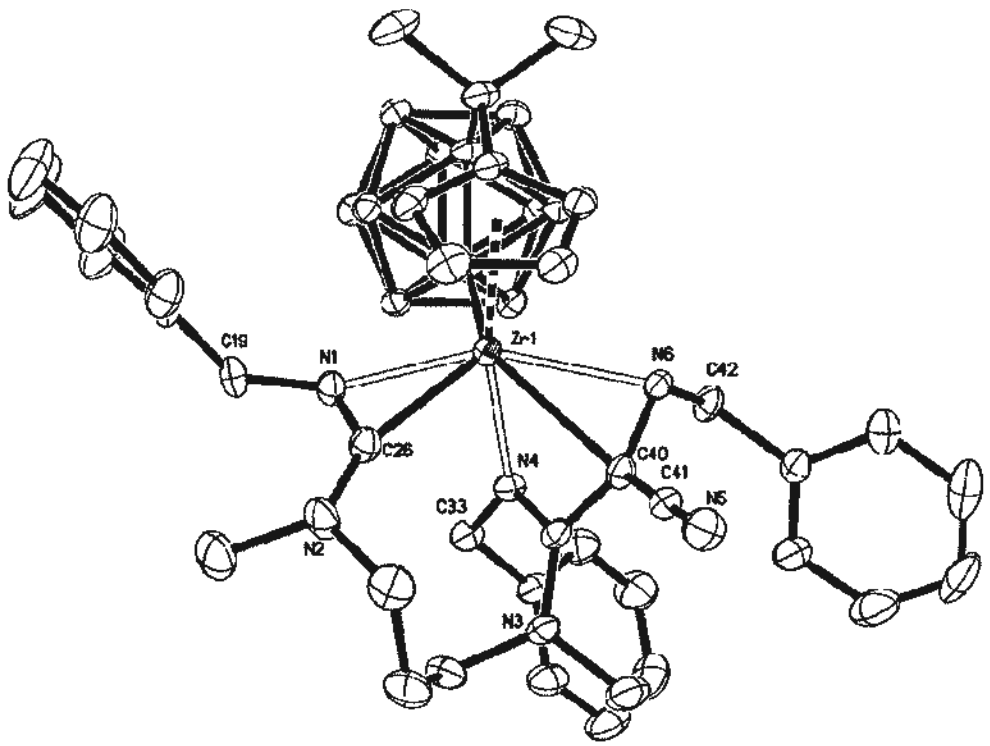


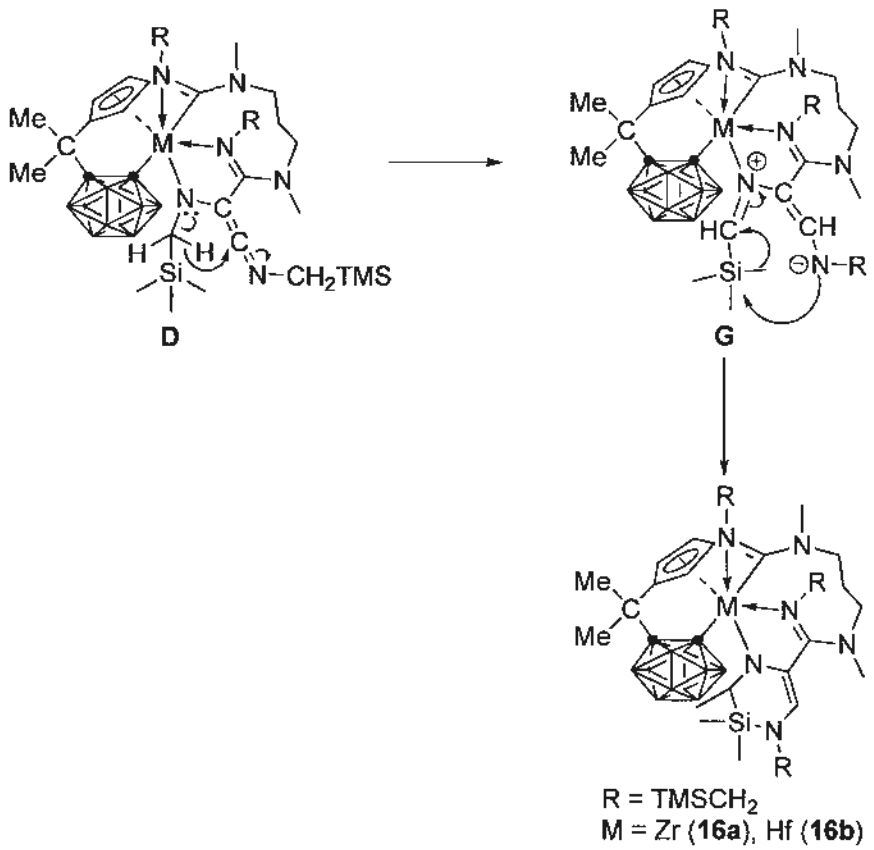
Figure 2.24. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2{:}\eta^2\text{-}\{NCH_2Ph\}\{NCH_2Ph\}[\text{-}C(\text{-}C{\equiv}N)CN(Me)(CH_2)_3N(Me)C{=}NCH_2Ph]$ (**17a**).

When $TMSCH_2NC$ was used, the α-H in the intermediate **D** can be transferred to the *sp*-C of the iminoketene group to form the intermediate **G**.[66b,67] Attack of the amide on the Si atom followed by the Me group migration gives the final product **16a** or **16b** (Scheme 2.12).

These reactions involve several bond-breaking and -forming processes. Although the rearrangement of imidoylketimines to dihydropyrimidines is a known conversion,[73] selective C-H bond activation at NMe group is not very common.[21,74] Meanwhile, Si-C bond activation on TMS group is comparatively rare,[75] and is

usually involved in late transition metal organometallic or organolithium compounds.[76] It is clear that the electronic effects of the R groups play important roles in these intramolecular bond activation and migratory processes, although exact reasons for the different product formation are not known yet.

Scheme 2.12. Proposed mechanism for the formation of **16a** and **16b**.



2.5. Summary

Group 4 metallacycles can be conveniently prepared via amine exchange reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ with diamines $HN(Me)(CH_2)_nN(Me)H$ (n = 2, 3) in toluene. The formation of volatile $HNMe_2$ and the chelating effect of the diamido ligands are the driving forces of the reactions. Reactivity studies show that unsaturated molecules insert exclusively into the M-N bonds to give the ring

expansion products, and the M-C_{cage} bond remains intact. These results suggest that the inertness of the M-C_{cage} bond toward unsaturated molecules is best ascribed to the steric effect of the cage, and the mobility of the migratory groups may not play a role in the insertion reactions. Also, the insertion of unsaturated molecules into the M-N bonds in metallacycles is a useful and effective method for the construction of large ring systems. The reaction with isocyanides gives different insertion products depending on the substituent groups. The sterically demanding isocyanide, XylNC, gives diinsertion products. For less bulky isocyanides, multiple insertion products are obtained with the C-H, C-C or C-Si bond activation. The carbon-bridged cyclopentadienyl-carboranyl and bridging amido ligand both play important roles in the multiple insertion reactions. The presence of a carbon-bridged cyclopentadienyl-carboranyl ligand leads to the unique insertion patterns, whereas the bridging amido ligand may restrict the reaction site.

Chapter 3. Insertion and Deinsertion Reaction of Carbodiimide and Isocyanide. Synthesis and Structure of Group 4 Metallacycles Bearing a Cyclopentadienyl-Carboranyl Ligand

3.1. Reaction of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^3\text{-}N(Me)(CH_2)_3\text{-}N(Me)C(=NR)N\text{-}R]$ with Unsaturated Molecules

3.1.1. Introduction

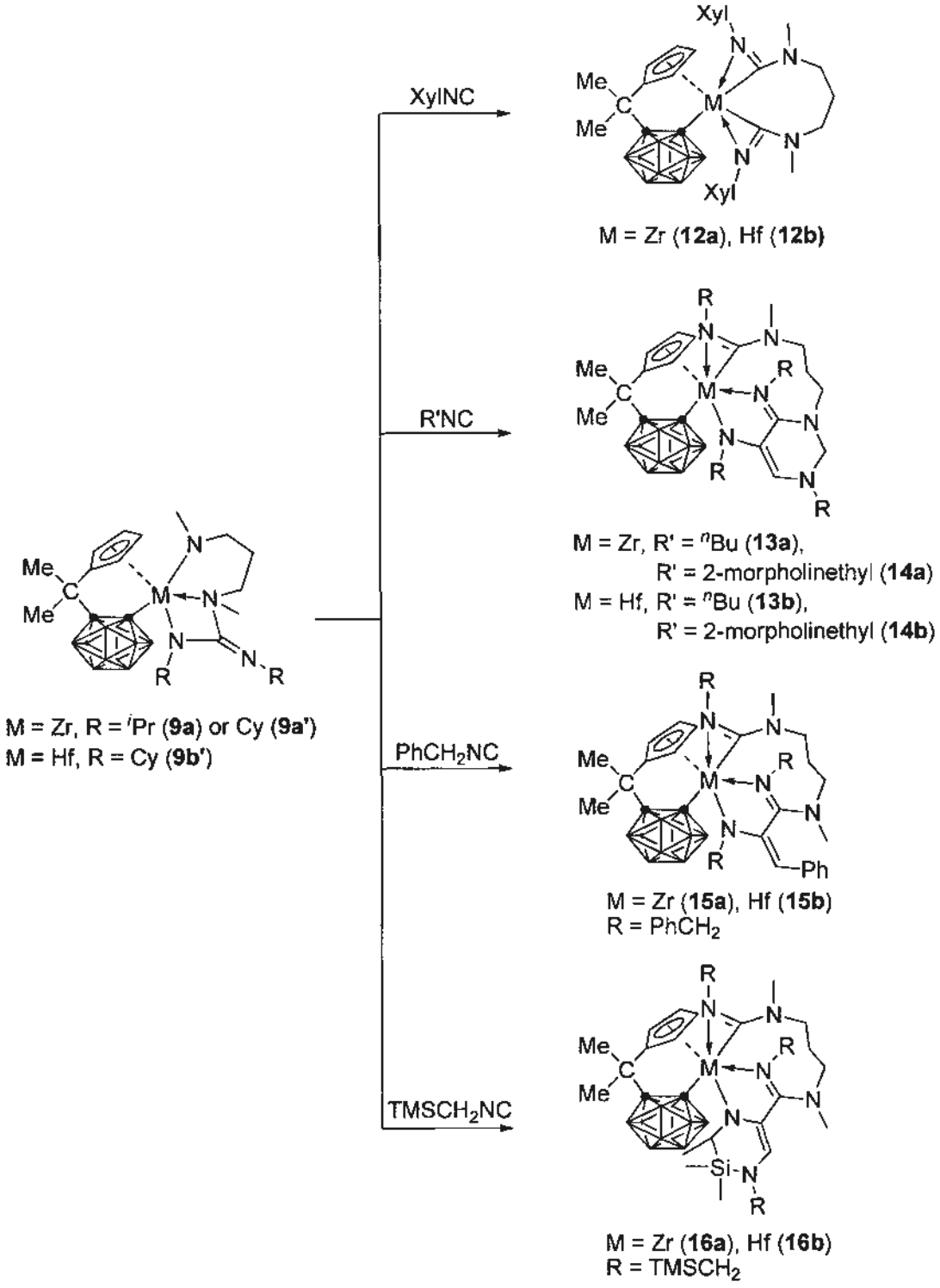
Guanidinates, as commonly used ligands in organometallic chemistry, can stabilize transition metal complexes due to their coordination flexibility and easily modifiable steric and electronic properties.[55o,57,77,78] Salt metathesis,[79] acid-base reaction[80] and insertion of carbodiimide into M-N bond[81] are useful methods to synthesize guanidinato metal complexes. The inert nature of guanidinates was observed in many of these compounds[55o,57,77,78,82] and deinsertion of carbodiimides is rare but would proceed in some cases. Our group have recently investigated the reaction of $[\sigma:\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Zr(NMe_2)(DME)$ with carbodiimides, and unprecedented zirconacarboranes $[\eta^5:\sigma:\eta^5\text{-}\{2\text{-}[C=N^iPr(NH^iPr)]C_2B_9H_{10}]Zr\text{-}[\eta^2\text{-}(^iPrN)_2C(NR_2)]$ (R = Me, Et) were isolated. Mechanistic studies showed that dissociation of carbodiimide from the Zr-N bond occurred.[83] In literature, reversible insertion of carbodiimide into Zr-C[84] and Zr=N[85] bond had been studied kinetically. Moreover, dissociation of carbodiimide from the M-N bond was reported to be involved in the transamination of guanidine using metal amido or imido

species.[78c,e,86] But it was hard in the case of metal amides and most of which are high-temperature thermolysis.[87] The insertion of carbodiimide into the M-N bond in [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M[$\eta^2$-N(Me)$(CH_2)_3$N(Me)] (M = Zr (**3a**), Hf (**3b**)) and their reverse reaction were studied. The carbodiimide insertion species reacted with other unsaturated molecules, leading to the dissociation of carbodiimide and affording mono-, di- and multi-insertion products.

3.1.2. Reactivity

Reaction with isocyanides. Treatment of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^3$-N(Me)$(CH_2)_3$N(Me)C(=NR)NR] (M = Zr, R = ^{i}Pr (**9a**), Cy (**9a'**), M = Hf, R = Cy (**9b'**)) with 2 equiv of XylNC in toluene at 60 °C afforded the unexpected isocyanide diinsertion products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^4$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C=N(Xyl)] (M = Zr (**12a**), Hf (**12b**)) almost quantitatively as monitored in situ in C_6D_6 (Scheme 3.1). The characteristic C=NC*H* resonance at 3.11 or 3.33 ppm and N=*C*=N resonance at 140.0 or 140.4 ppm of DCC or DIC, respectively, were clearly observed in the ^{1}H and ^{13}C NMR spectra, which confirmed dissociation of DCC or DIC from **9a**, **9a'** and **9b'**.These results show that carbodiimide would be deinserted from the M-N bond to afford complex **3a** or **3b**, thus insertion of carbodiimides into the M-N bond was reversible. It is noted that heat is needed as the reaction proceeded very slowly at room temperature. Complexes **12a** and **12b** can also be synthesized from the direct reactions of complexes **3a** or **3b** with XylNC.

Scheme 3.1. Reaction of complexes **9a**, **9a'** or **9b'** with isocyanides.



Besides XylNC, complexes **9a'** and **9b'** also reacted with other isocyanides bearing α-CH_2 to afford multiple insertion products in 50 to 78% isolated yields

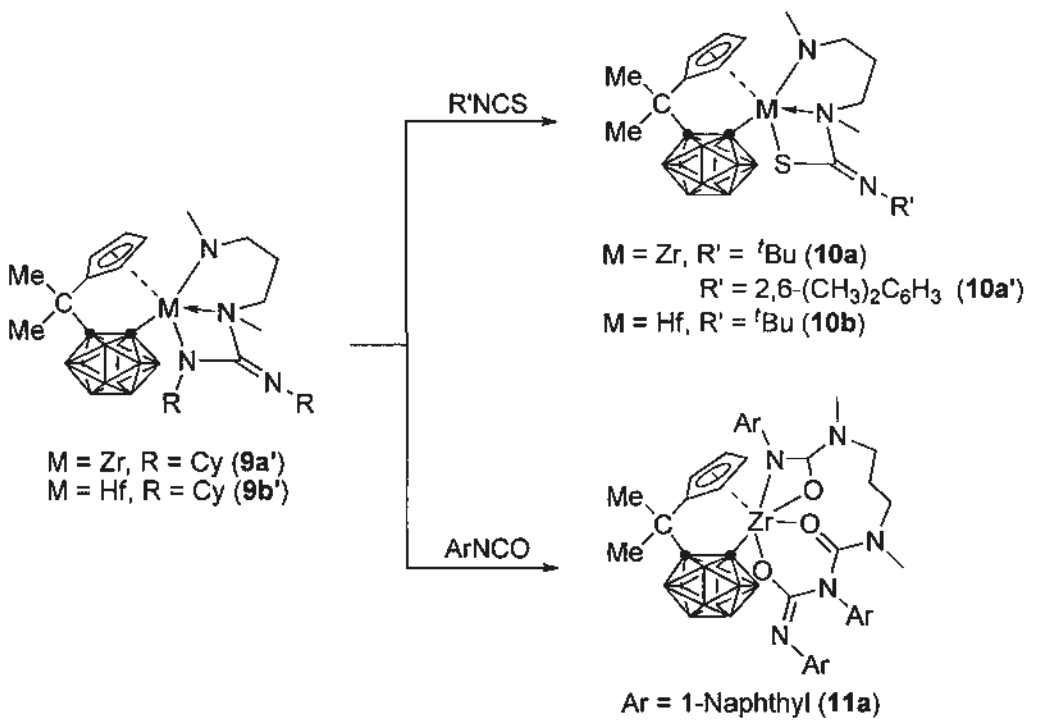
(Scheme 3.1). The reactions of **9a'** or **9b'** with isocyanides were monitored in situ in C_6D_6. These reactions were completed within three days at 60 °C, with the appearance of DCC. They were fully characterized by ^1H and ^{13}C NMR spectroscopy. As discussed in chapter 2, complexes **12 – 16** were also prepared from direct reaction of **3a,b** with the corresponding RNC.

Reaction with isothiocyanates. Reaction of **9a'** and **9b'** with 2 equiv of ^{t}BuNCS or XylNCS in toluene at 60 °C afforded the isothiocyanate monoinsertion products $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NR')S]$ (M = Zr, R' = ^{t}Bu (**10a**), or Xyl (**10a'**), M = Hf, R = ^{t}Bu (**10b**)) in 72 ~ 95% isolated yields with the dissociation of DCC (Scheme 3.2). Their ^{13}C NMR spectra exhibited unique N=*C*-S resonances at about 160 ppm. Only one isothiocyanate was inserted into the M-N bond, regardless of the amount of isothiocyanate was used, which might be due to the presence of the bridging diamido ligand. These results further confirmed the dissociation of carbodiimide from the guanidinato metal unit.

Reaction with isocyanate. In addition to isocyanides and isothiocyanates, isocyanates also reacted with guanidinato metal complexes, resulting in the deinsertion of carbodiimide. Interaction between **9a'** and PhNCO or XylNCO gave a mixture of products, which might be due to the trimerization of isocyanates at the reaction temperature. If a less reactive isocyanate was used, the insertion product could be isolated. Treatment of **9a'** with 3 equiv of 1-naphthylisocyanate in toluene at 60 °C afforded a triinsertion product $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2:\eta^2\text{-}\{OC(=NC_{10}H_7)N(C_{10}H_7)C(=O)\}N(Me)(CH_2)_3N(Me)C(NC_{10}H_7)O]$ (**11a**) in 68%

isolated yield with the release of DCC (Scheme 3.2). Four isomers were observed in its ^{1}H spectrum, which was presumably owing to the steric effect imposed by carborane and the bulky naphthalene ring, which restricts the rotation of the naphthalyl substituents.

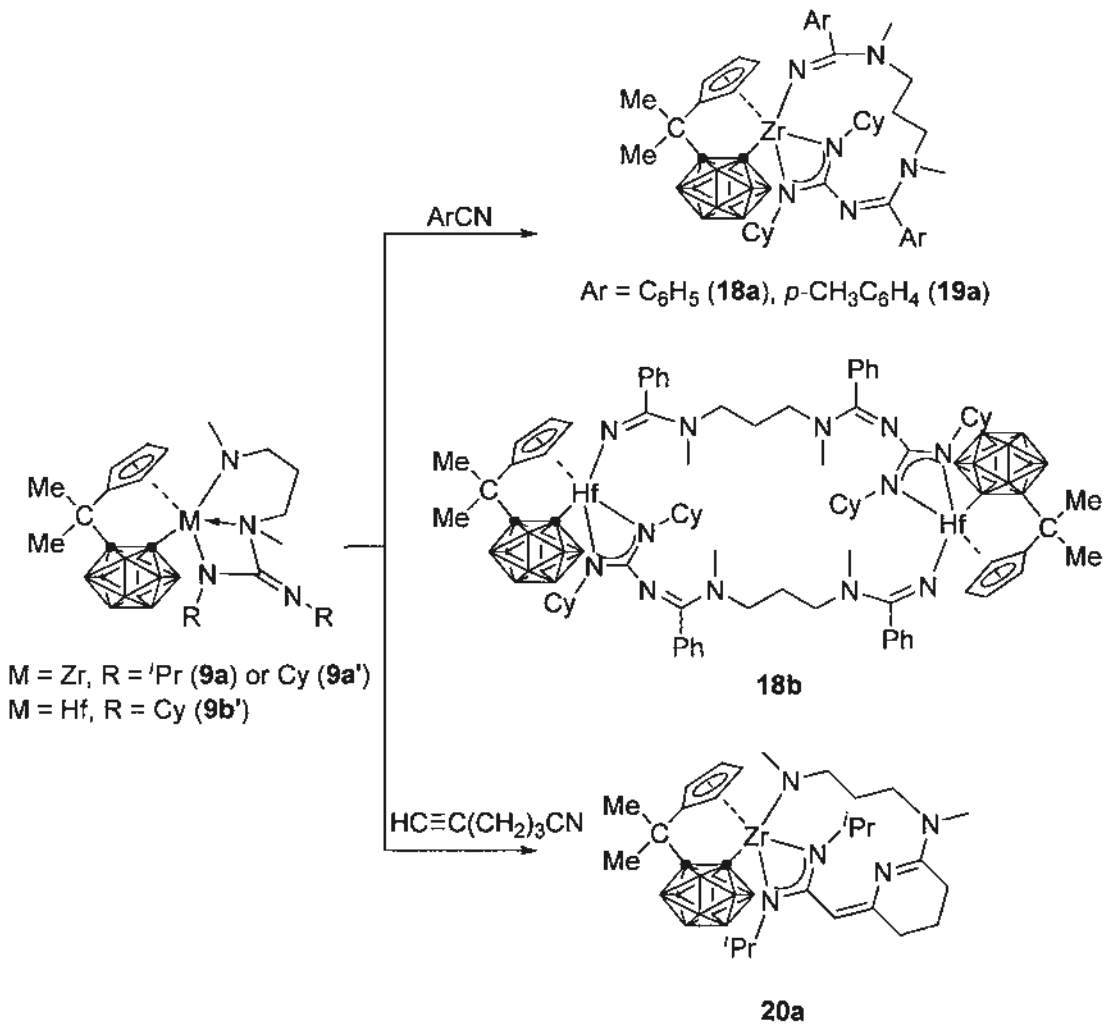
Scheme 3.2. Reaction of complexes **9a'** or **9b'** with isothiocyanates and isocyanate.



Reaction with nitriles. On the other hand, treatment of **9a'** with excess PhCN and *p*-$CH_3C_6H_4CN$ in toluene at 60 °C gave unexpected products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\sigma$:$\eta^2$-N(Ar)=CN(Me)$(CH_2)_3$N(Me)C=N(Ar)C(NCy)NCy] (Ar = Ph (**18a**) or *p*-$CH_3C_6H_4$ (**19a**)) in 57 ~ 79% isolated yields (Scheme 3.3). They were characterized by spectroscopic techniques and elemental analyses. Their ^{13}C NMR spectra exhibited unique resonances of Zr-N=*C* and N-*C*-N at ~168 and ~153 ppm, respectively. The structures of **18a** and **19a** (with a toluene of solvation)

were further confirmed by single-crystal X-ray analyses. As shown in Figures 3.1 and 3.2, the central Zr atom is coordinated by an η^5-cyclopentadienyl ring, a cage carbon atom, a nitrogen atom of nitrile, and η^2-guanidinato ligand. The $Zr\text{-}N_{imido}$ distances of 1.968(3) Å in **18a** and 1.961(4) Å in **19a** are close to the corresponding value of 1.958(9) Å observed in **8a**, and the average $Zr\text{-}N_{guanidinato}$ distances of 2.233(2) Å in **18a** and 2.232(4) Å in **19a** are also close to the corresponding value of 2.206(2) Å observed in $(guan)_2ZrMe_2$ (guan = η^2-(^{i}PrN)$_2$C(NMe$_2$)).[78b]

Scheme 3.3. Reaction of complexes **9a**, **9a'** or **9b'** with nitriles.



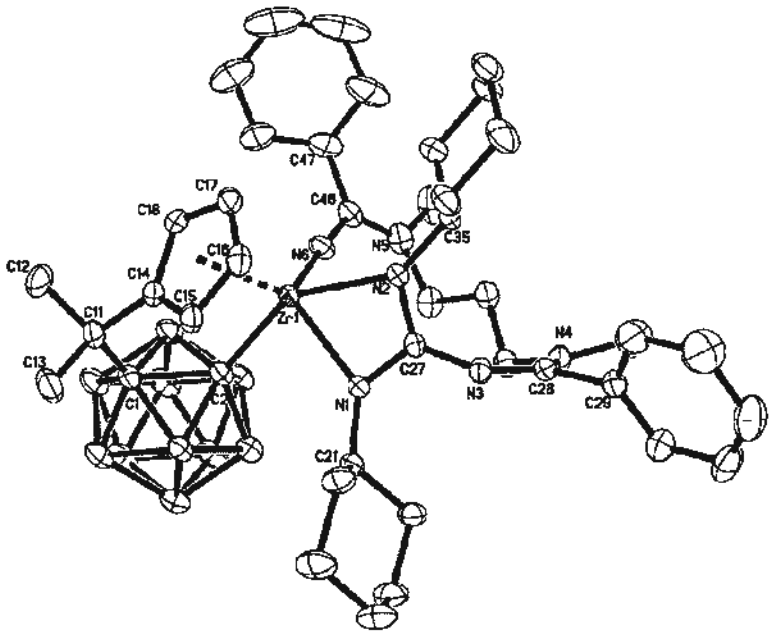


Figure 3.1. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\sigma{:}\eta^2\text{-}N(Ph)=CN(Me)(CH_2)_3N(Me)C=N(Ph)C(NCy)NCy]$ (**18a**).

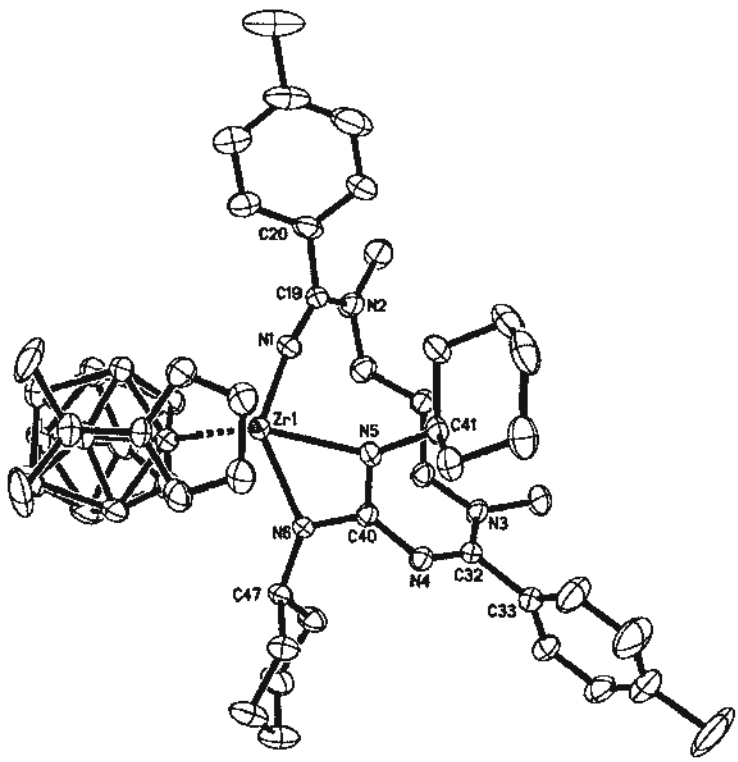
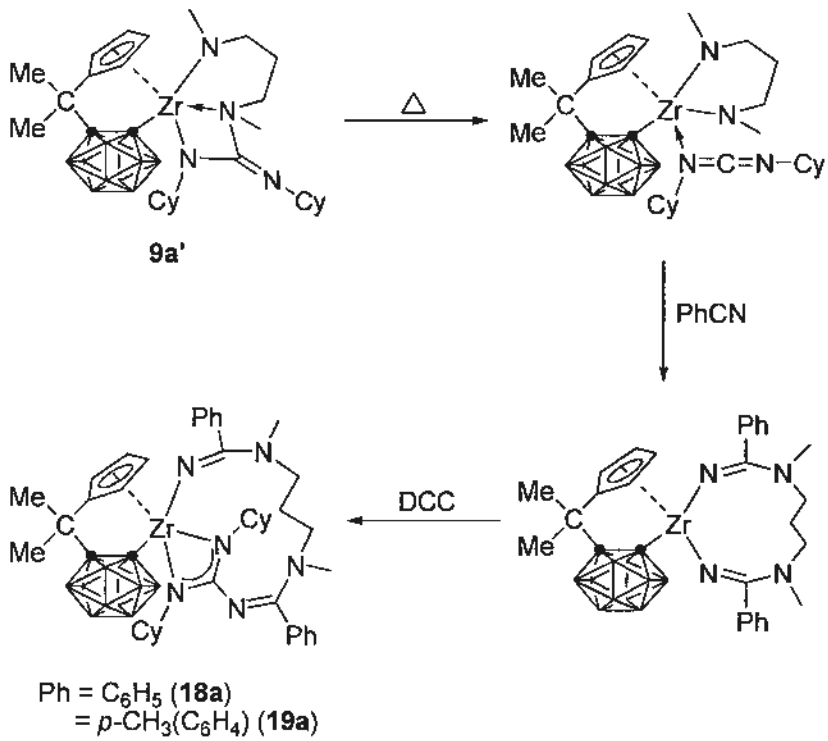


Figure 3.2. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\sigma{:}\eta^2\text{-}N(Ar)=CN(Me)(CH_2)_3N(Me)C=N(Ar)C(NCy)NCy]$ (Ar = $p\text{-}CH_3C_6H_4$) (**19a**).

Scheme 3.4 shows the possible reaction pathway for the formation of **18a** and **19a**. The deinsertion of DCC from **9a'**, followed by the insertion of PhCN into the Zr-N bonds give the metallacycles. Re-insertion of the released DCC into the newly formed Zr-N bond afforded the final product. It is not clear yet whether this insertion proceeds before the insertion of the second equiv of PhCN into the Zr-N bond or vice versa.

Scheme 3.4. Proposed mechanism for the formation of complexes **18a** and **19a**.



In the case of Hf complex **9b'**, re-insertion of DCC was also observed and a dimeric complex $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\sigma{:}\eta^2\text{-}N(Ph)=CN(Me)(CH_2)_3\text{-}N(Me)C=N(Ph)C(NCy)NCy]\}_2$ (**18b**) was isolated in 71% yield (Scheme 3.3). Such a ring expansion reaction led to the formation of a macro metallacycle. The unique resonances of Hf-N=*C* and N-*C*-N at 166.5 and 153.2 ppm were also observed in its

^{13}C NMR spectrum, which are well consistent with those of complexes **18a** and **19a**. The molecular structure of **18b** was further confirmed by single-crystal X-ray analyses and showed two toluene of solvation (Figure 3.3).

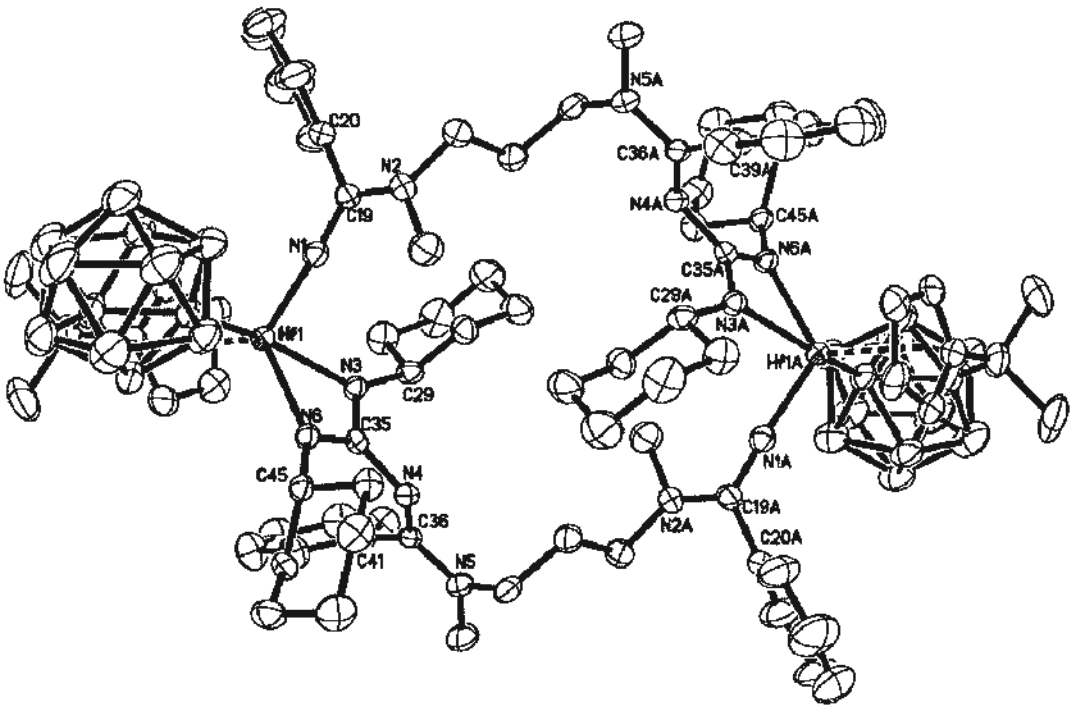


Figure 3.3. Molecular structure of {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf-[$\sigma$:$\eta^2$-N(Ph)=CN(Me)$(CH_2)_3$N(Me)C=N(Ph)C(NCy)NCy]}$_2$ (**18b**).

Complex **9a** reacted with a bifunctional unsaturated molecule 5-hexynenitrile in toluene at 60 °C, affording the cyclization product [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\sigma$:$\eta^2$-N(Me)$(CH_2)_3$N(Me)C=N$(CH_2)_3$C=C(N^{i}Pr)N^{i}Pr] (**20a**) in 44% isolated yield (Scheme 3.3). Although conversion was almost quantitative as monitored in situ, the loss in purification and recrystallization led to the low yield. Complex **20a** was fully characterized by various spectroscopic methods and single-crystal X-ray analyses. As shown in Figure 3.4, the Zr atom is coordinated to an η^5-cyclopentadienyl ring, a

cage carbon atom, an amido group and an η^2-guanidinato ligand in a four-legged piano stool geometry. The average Zr-$N_{guanidinato}$ distance of 2.248(2) Å is well comparable to the 2.233(2) Å and 2.232(4) Å in complexes **18a** and **19a**. The short C(28)-C(29) distance of 1.331(4) Å confirmed the formation of C=C bond. The unique C=C*H* and C=*C*H resonances of 5.08 and 112.4 ppm were observed in its ^{1}H and ^{13}C NMR spectra, respectively, further supporting the insertion of alkyne. The resonance at 158.6 ppm was corresponding to the N-*C*-N moiety confirming the presence of the DIC unit. Similar to complexes **18a** and **19a**, re-insertion of carbodiimide proceeded, but insertion of nitrile only took place at one M-N bond, it may be due to the steric effects of the six-membered ring. A possible reaction pathway for the formation of **20a** is shown in Scheme 3.5. Deinsertion of carbodiimide from **9a** affords the carbodiimide coordinated species **A**. The nitrile group of 5-hexynenitrile inserts into one M-N bond to give nitrile mono-insertion product **B**. Intramolecular insertion of terminal alkyne into the Zr-N bond (ring-closure) to forms a six-membered ring. Re-insertion of the released DIC into the Zr-C bond generates the final product **20a**.

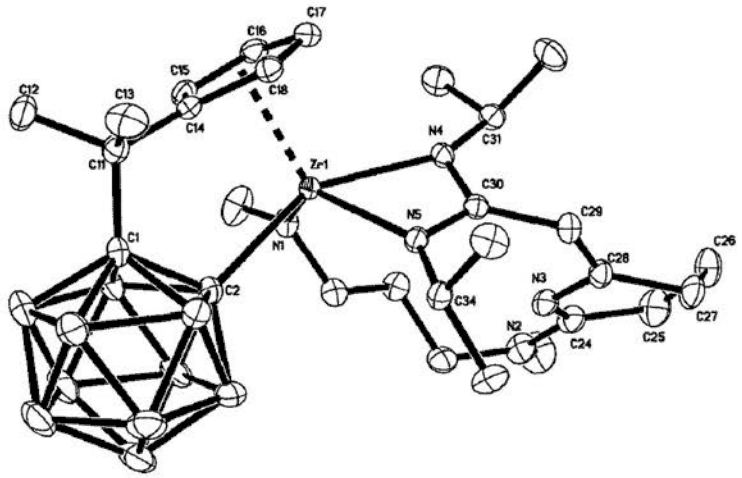
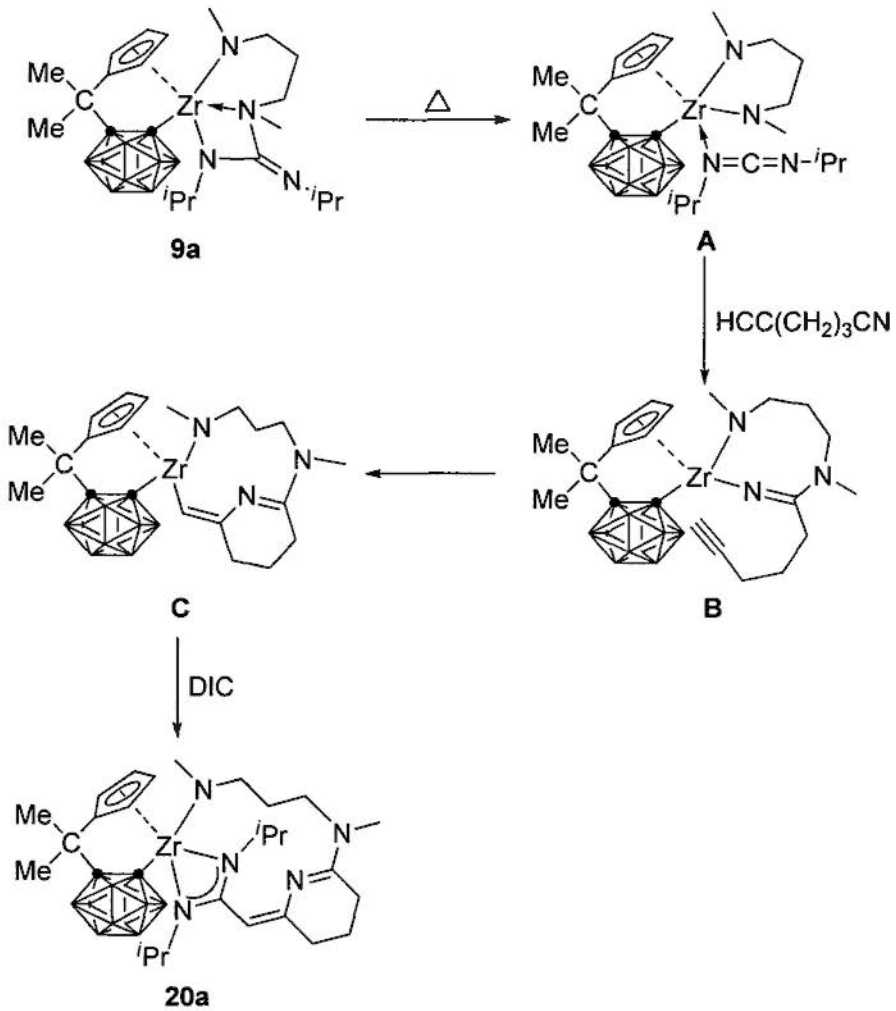


Figure 3.4. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^3\text{-}N(Me)(CH_2)_3N(Me)\overline{C{=}N(CH_2)_3C}{=}C(N^iPr)N^iPr]$ (**20a**).

Scheme 3.5. Proposed mechanism for the formation of complex **20a**.



3.1.3. Summary

Reactions of **9** with various unsaturated molecules were investigated which showed the insertion of carbodiimides into M-N bond is reversible in the presence of other unsaturated molecules. The reactions with XylNC afforded diinsertion species **12a** or **12b**. For other isocyanides bearing α-CH_2, multiple insertion species were obtained. In both cases, deinsertion of carbodiimides occurred. Besides isocyanides, complexes **9a'** and **9b'** also reacted with ^{t}BuNCS or XylNCS to give isothiocyanate monoinsertion products **10a**, **10a'** and **10b**, with the release of carbodiimide. 2-Naphthylisocyanate reacted with **9a'**, leading to the deinsertion of carbodiimide and triinsertion of isocyanate complex **11a**. These insertion products were also obtained from the reaction of **3a** or **3b** with unsaturated molecules. Re-insertion of carbodiimide was observed in the reactions with nitriles.

3.2. Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2{:}\eta^2\text{-}N(Xyl)=CN(Me)(CH_2)_3\text{-}N(Me)C=N(Xyl)N]$ with Unsaturated Molecules

3.2.1. Introduction

Insertion of carbon monoxide into the M-N or M-C bond affords η^2-acyl compounds,[63] which are very reactive and readily undergo a variety of interesting reactions[63] such as deinsertion reaction,[88] uptake of the second equiv of CO to give enediolate species,[89] or insertion of alkyl groups to generate an η^2-ketone.[90] Isocyanides, which are isoelectronic analogues of carbon monoxide, typically insert into early transition metal M-C or M-N bonds, producing η^2-iminoacyl moieties.[63]

Similar to η^2-acyl compounds, isocyanide insertion species are reactive towards the second equiv of isocyanide to generate enediamine moiety,[66] or undergo alkyl insertion to give η^2-imine.[63,66a,91] Moreover, multiple insertion reactions[65] are often observed in the reaction of metal alkyls with isocyanide, which provides useful synthetic route to nitrogen containing organic compounds.[60-63] Unlike η^2-acyl functionality, η^2-iminoacyls are more stable and migratory deinsertion of isocyanide is comparatively rare.[63]

Examples of isocyanide deinsertion reactions were reported.[92] Reversible insertion of XylNC into the metal carbon bond of Cp*FvMCl (M = Ti, Zr) (Fv $=\eta^6$-$C_5Me_4CH_2$) was observed at room temperature by NMR techniques. An equilibrium strongly favorable for the insertion product was found.[92b] Insertion of ^{t}BuNC into the Ti-C bond of titanacyclobutane Cp*$_2$Ti[η^2-$CH_2CH(^iPr)CH_2$] produced η^1-iminoacyltitanocyclopentane Cp*$_2$Ti[η^2-$CH_2CH(^iPr)CH_2C(=N^tBu)$], which underwent thermolysis at 65 °C either in the presence or absence of ethylene, leading to the deinsertion of isocyanide and the formation of the titanacyclobutane species.[66c] In late transition metal complexes, deinsertion of XylNC from the platinacyclopentane was observed.[92k] Moreover, the reversible insertion of ^{t}BuNC into the Ni-C bond took place in the formation of nickel complex *trans*-$(Me_3P)_2Ni[C(N^tBu)C_6H_4$-*o*-$CH_2]NiBr(PMe_3)$.[92d]

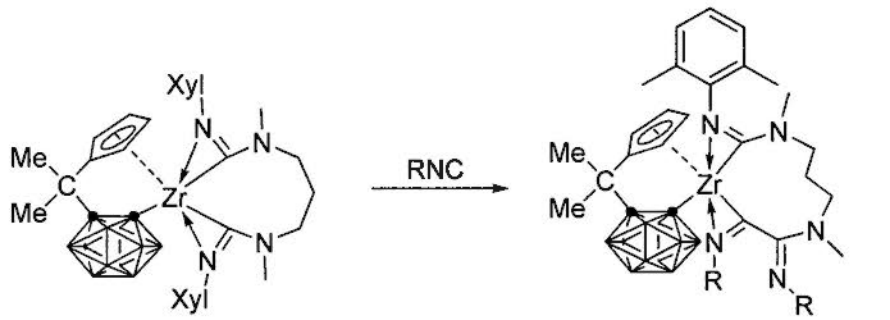
In current case, the XylNC diinsertion species [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M-[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=NXyl)] (M = Zr (**12a**), Hf (**12b**)) reacted with other unsaturated molecules, affording the isocyanide deinsertion species

depending on the metal atoms and the substrates used.

3.2.2. Reactivity

Reaction with isocyanide. Treatment of **12a** with an excess amount of ^{n}BuNC in toluene at 60 °C for 7 days afforded the unexpected product [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N(^{n}Bu))C=N(^{n}Bu)] (**21a**) as white crystals in 72% isolated yield (Scheme 3.6). It was characterized by various spectroscopic techniques as well as single-crystal X-ray analyses. Only one XylNC was deinserted from the **12a**, although excess ^{n}BuNC was added. When this reaction was monitored in C_6D_6, the characteristic $C_6H_3(CH_3)_2$ resonance at 2.06 ppm was clearly observed from ^{1}H NMR spectrum, which confirmed the dissociation of XylNC from **12a**. This result showed that the insertion of isocyanide into the M-N bond was reversible. It also indicated that heat was necessary for the reaction to occur.

Scheme 3.6. Reaction of complex **12a** with isocyanides.



12a

R = ^{n}Bu (**21a**)
= 2-Morpholinethyl (**22a**)
= $TMSCH_2$ (**23a**)

There were two multiplets in the region 7.2 – 7.0 ppm assignable to the aryl protons, and two singlets at 2.22 and 1.78 ppm attributable to the $C_6H_3(CH_3)_2$

protons were observed in the ^{1}H NMR spectrum of **21a**. The unique Zr-*C*=N(Xyl), Zr-*C*=N(^{n}Bu) and N-*C*=N(^{n}Bu) resonances at 205.8, 247.1 and 159.1 ppm were observed in its ^{13}C NMR spectrum.

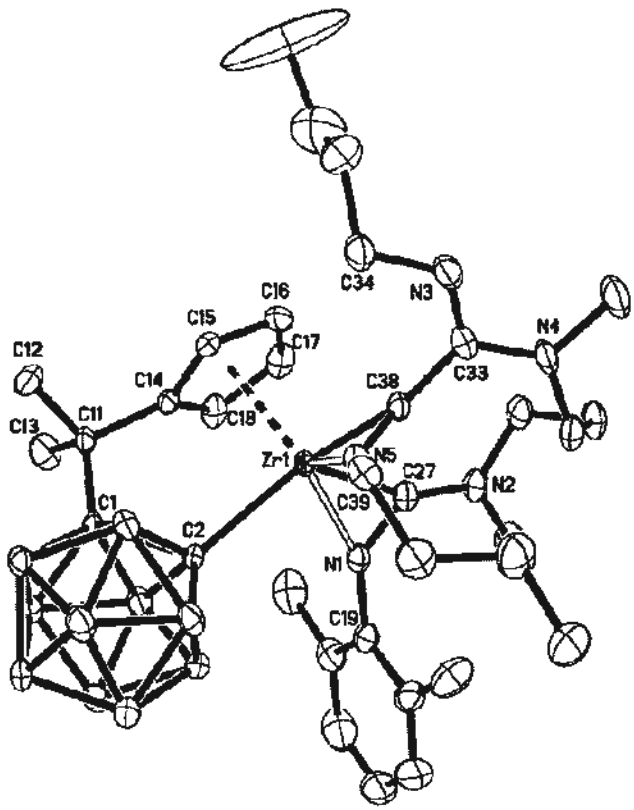


Figure 3.5. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N(^{n}Bu))C=N(^{n}Bu)] (**21a**).

As shown in Figure 3.5, the central Zr atom is η^5-bound to the cyclopentadienyl ligand, σ-bound to a cage carbon, and η^2-bound to two iminocarbamoyl group in a five-legged piano stool geometry. It clearly shows two ^{n}Bu groups in this structure, indicating that the second equiv of ^{n}BuNC was inserted into the newly formed Zr-C bond. The Zr-N(1)/C(27) distances of 2.195(5)/2.190(6) Å are very close to the 2.210(4)/2.192(5) Å in its parent complex **12a**, showing that the insertion of ^{n}BuNC

into the Zr-N bond does not obviously affect the coordination environment of the metal atoms. The Zr-N(5)/C(38) distances of 2.233(5)/2.204(6) Å are comparable well to 2.259(4)/2.221(3) Å in $Zr(NMeCy)_2[C(NXyl)NMeCy]_2$,[56a] 2.209(8)/2.143(6) Å in $(\eta^5\text{-}C_9H_6)Zr[C(NMe_2)=N(2,6\text{-}Me_2C_6H_3)]_2Cl$,[56b] 2.174/2.271 Å in $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}[SiMe_2\text{-}\eta\text{-}N^tBu)]_2\}\{\eta^2\text{-}C(CH_2Ph)=N(2,6\text{-}Me_2C_6H_3)\}]$[59a] and other η^2-bound iminocarbamoyl zirconium complexes in literature.[66a,d-f]

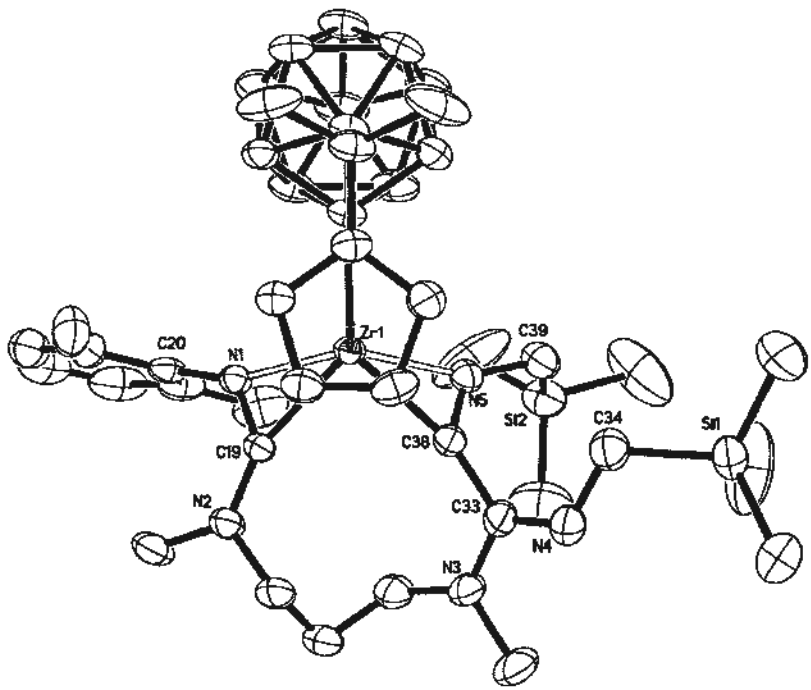


Figure 3.6. Molecular structure of $[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{:}\eta^2\text{-}N(Xyl)=CN(Me)(CH_2)_3N(Me)C(=N(CH_2TMS))C=N(CH_2TMS)]$ **(23a)**, showing one of the two crystallographically independent molecules in the unit cell.

Besides ^{n}BuNC, **12a** also reacted with other isocyanides such as 2-morpholinethyl- or trimethylsilylmethyl-isocyanide to afford the products $[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{:}\eta^2\text{-}N(Xyl)=CN(Me)(CH_2)_3N(Me)C(=NR)C=NR]$

(R = 2-morpholinethyl) (**22a**) as a white solid in 47% isolated yield, or $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}N(Xyl){=}CN(Me)(CH_2)_3N(Me)C(=N(CH_2TMS))C{=}N(CH_2TMS)]$ (**23a**) as colorless crystals in 64% isolated yield, respectively (Scheme 3.6). They were fully characterized by various spectroscopic techniques as well as elemental analyses. The unique Zr-*C*=N(Xyl), Zr-*C*=N(R) and N-*C*=N-R resonances at ~206, ~245 and ~159 ppm were observed in their ^{13}C NMR spectra. The molecular structure of **23a** was further confirmed by single-crystal X-ray analyses. There are two crystallographically independent molecules in the unit cell and a representative one is shown in Figure 3.6. The geometry of complex **23a** is the same as that found in **21a**. The Zr-N(1)/C(19) and Zr-N(5)/C(38) distances of 2.199(3)/2.193(4) Å and 2.243(4)/2.203(4) Å in **23a** are very close to 2.195(5)/2.190(6) Å and 2.233(5)/2.204(6) Å in **21a**.

The Hf analogue **12b** reacted with *n*-butyl- and 2-morpholinethyl-isocyanides at 90 °C to afford the substitution products. The reactions proceeded much faster than the Zr one and finished within 3 days as monitored by ^1H NMR spectra. There were two sets of cyclopentadienyl resonances in the ^1H NMR spectra, suggesting the presence of two possible products. After fractional recrystallization, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}N(Xyl){=}CN(Me)(CH_2)_3N(Me)C(=N(^nBu))C{=}N(^nBu)]$ (**21b**) and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}\{N^nBu\}\text{-}\{N^nBu\}[(=C)\text{-}C{=}CHN(^nBu)CH_2N[(CH_2)_3N(Me)N\text{-}C{=}N(^nBu)]]$ (**13b**) were isolated in 34% and 31% isolated yield, and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}N(Xyl){=}CN(Me)(CH_2)_3N(Me)C(=NR)C{=}NR]$

(**22b**) and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}\{NR\}\{NR\}\text{-}[(=C)\text{-}C{=}CHNRCH_2N[(CH_2)_3N(Me)N\text{-}C{=}NR]]$ (R = 2-morpholinethyl) (**14b**) were isolated in 35% and 23% yield, respectively (Scheme 3.7). The spectroscopic data of **21b** and **22b** were very similar to those of **21a** and **22a**. X-ray analyses revealed that **21a** and **21b** are isostructural and isomorphous (Figure 3.7). The Hf-N(1)/C(27) distances of 2.174(3)/2.180(4) Å are very close to the average Hf-N/C distances of 2.194(4)/2.176(4) Å in the parent complex **12b**. The Hf-N(5)/C(38) distances of 2.211(3)/2.192(4) Å are comparable well to the 2.222(5)/2.199(5) Å in $Cp_2Hf(N(CMe_3)C\text{-}C(=NCMe_3)CH_2SiMe_2CH_2)$,[68a] and 2.212(5)/2.269(6) Å in $[Hf(TC\text{-}3,5)\{\eta^2\text{-}(n\text{-}Bu)N{=}C(CH_2Ph)\}_2]$[59b] (TC = Tropocoronand).

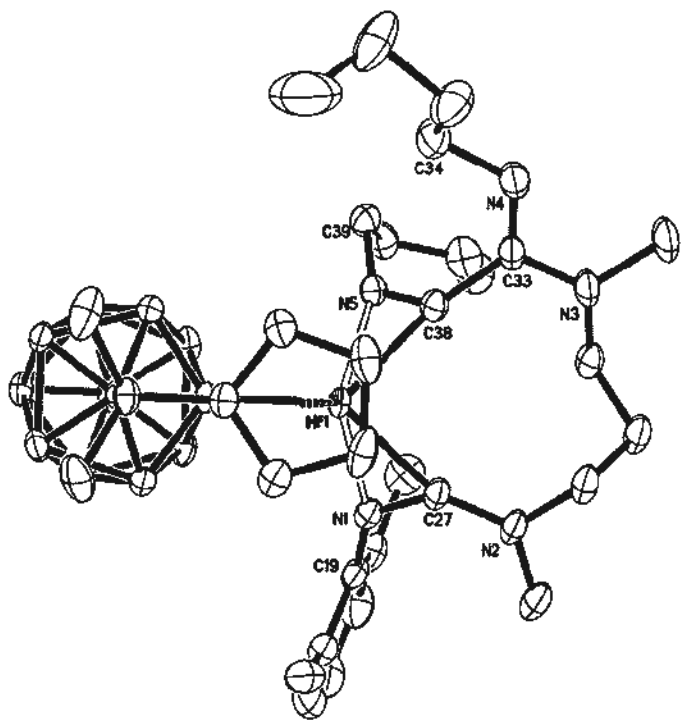
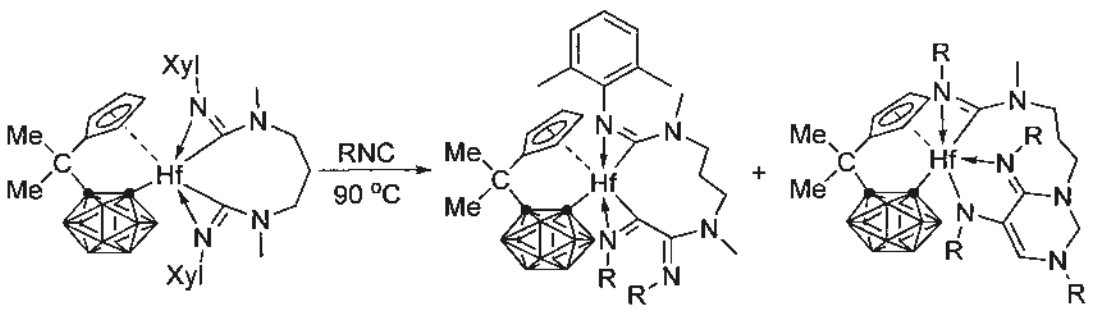


Figure 3.7. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf\text{-}[\eta^2{:}\eta^2\text{-}N(Xyl){=}CN(Me)(CH_2)_3N(Me)C(=N(^nBu))CN(^nBu)]$ (**21b**).

Scheme 3.7. Reaction of complex **12b** with isocyanides.



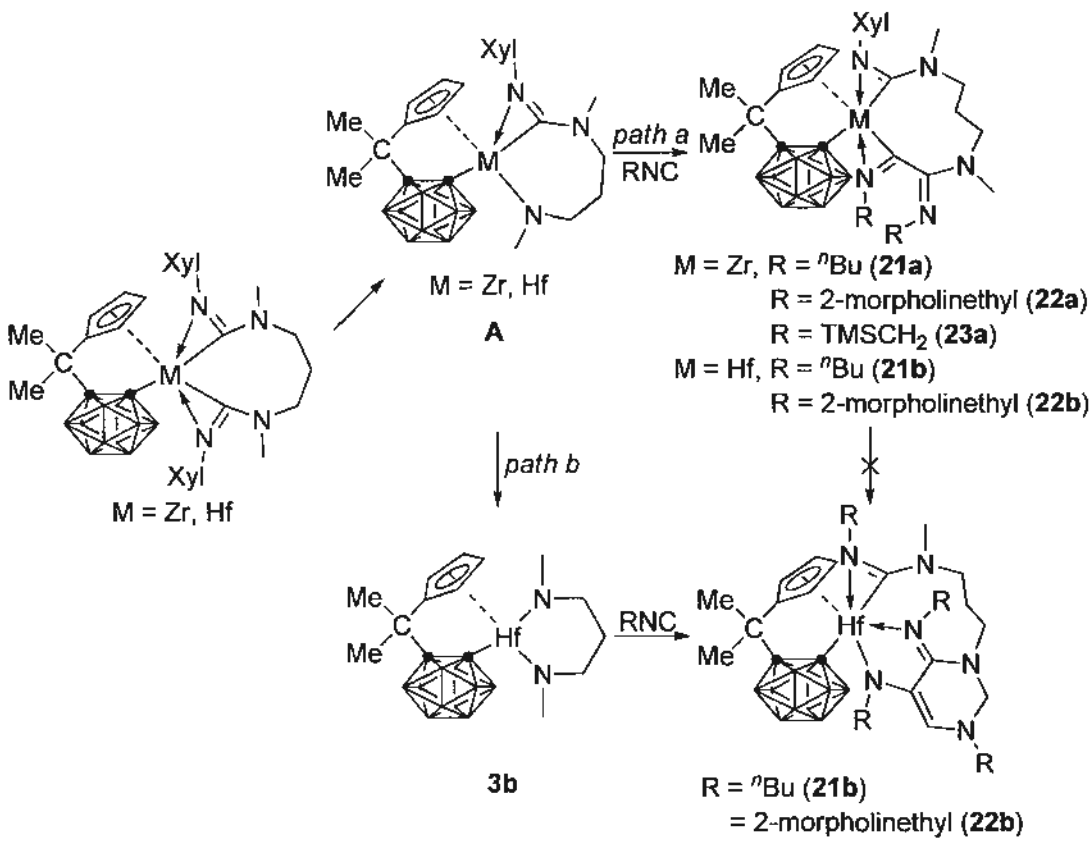
12b R = ^{n}Bu (**21b**) = 2-Morpholinethyl (**22b**) R = ^{n}Bu (**13b**) = 2-Morpholinethyl (**14b**)

Complexes **13b** and **14b** do not contain any η^2-XylNC unit, which were not observed in the reaction of the zirconium analogue **12a** with *n*-butyl- or 2-morpholinethyl-isocyanide. On the other hand, they were directly synthesized from the reaction of **3b** with *n*-butyl- or 2-morpholinethylisocyanide. To gain insights into the formation of **13b/14b**, complex **21b** was treated with excess ^{n}BuNC at 90 °C for 3 days. No reaction occurred as monitored by ^{1}H NMR in C_6D_6. If the reaction temperature was increased to 110 °C, the formation of **13b** was not detected by NMR either, rather the decomposition of **21b** was observed. Thus, **13b** or **14b** would not likely be formed from **21b** or **22b**. A possible explanation is that two pathways co-exist in the deinsertion reaction of isocyanides as shown in Scheme 3.8. The first step is the deinsertion of one XylNC group from the complex affording the key intermediate **A**. Other isocyanides inserted into the newly formed M-N bond to afford isocyanide diinsertion product (*path a*). As *n*-butyl, 2-morpholinethyl, and trimethylsilylmethyl groups are less sterically demanding than Xyl one; further

insertion of another equiv of these isocyanides into the M-C bond is allowed, affording the final products. The second pathway (*path b*) is the deinsertion of another XylNC from **A**, and affording the Hf diamide species **3b**. Reaction of **3b** with four equiv of isocyanides gives the multiple insertion species **13b** or **14b**.

It is noted that complexes **12a** reacted very slowly with ^{t}BuNC at 90 °C, and only ~10% conversion was observed after 5 days as monitor by ^{1}H NMR spectra.

Scheme 3.8. Proposed mechanism for the formation of isocyanide mono- and di-deinsertion products.



To explore the generality of the reversible insertion of isocyanide, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Xyl){=}CNMe_2]_2$ (**24a**) was synthesized by treatment of **1a** with 2 equiv of XylNC at room temperature (Scheme 3.9). It was

isolated as colorless crystals in 54% yield after recrystallization. In addition to the peaks of the carbon-bridged cyclopentadienyl-carboranyl ligand, two multiplets in the region 7.12 – 7.04 ppm corresponding to the aryl protons, one singlet at 2.41 ppm and two singlets at 2.19 and 2.12 ppm assignable to $N(CH_3)_2$ and $C_6H_3(CH_3)_2$ groups were observed in the ^{1}H NMR spectrum of **24a**. The unique Zr-*C*=N resonance at 206.7 ppm was observed in its ^{13}C NMR spectrum. The molecular structure of **24a** was further confirmed by single-crystal X-ray analyses and showed half THF of solvation. As shown in Figure 3.8, the central Zr atom is coordinated to an η^5-cyclopentadienyl ring, a cage carbon atom and two η^2-iminocarbamoyl ligands in a five-legged piano stool geometry.

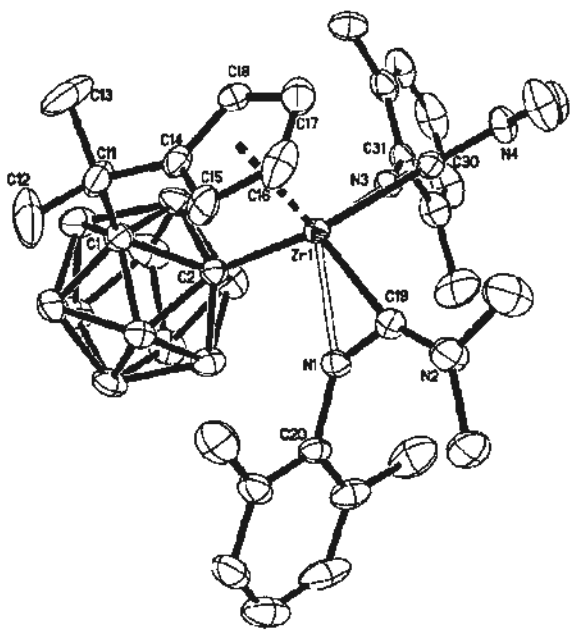
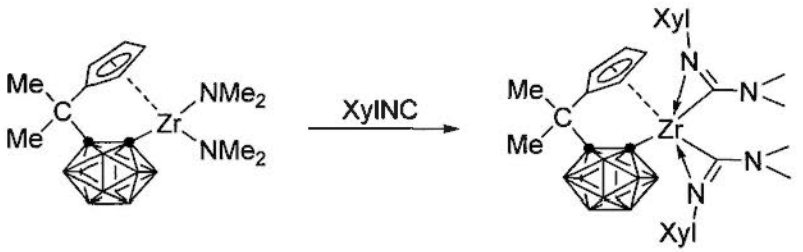


Fig 3.8. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}N(Xyl){=}CNMe_2]_2$ (**24a**).

Reaction of **24a** with excess ^{n}BuNC at 90 °C in C_6D_6 was monitored by ^{1}H NMR

spectra for one week. Although free XylNC was observed in the ^{1}H NMR spectra, the reaction was very complicated. This control experiment indicated that the bridging amido ligand should play a role in the reversible insertion reaction of isocyanide.

Scheme 3.9. Reaction of complex **1a** with XylNC.

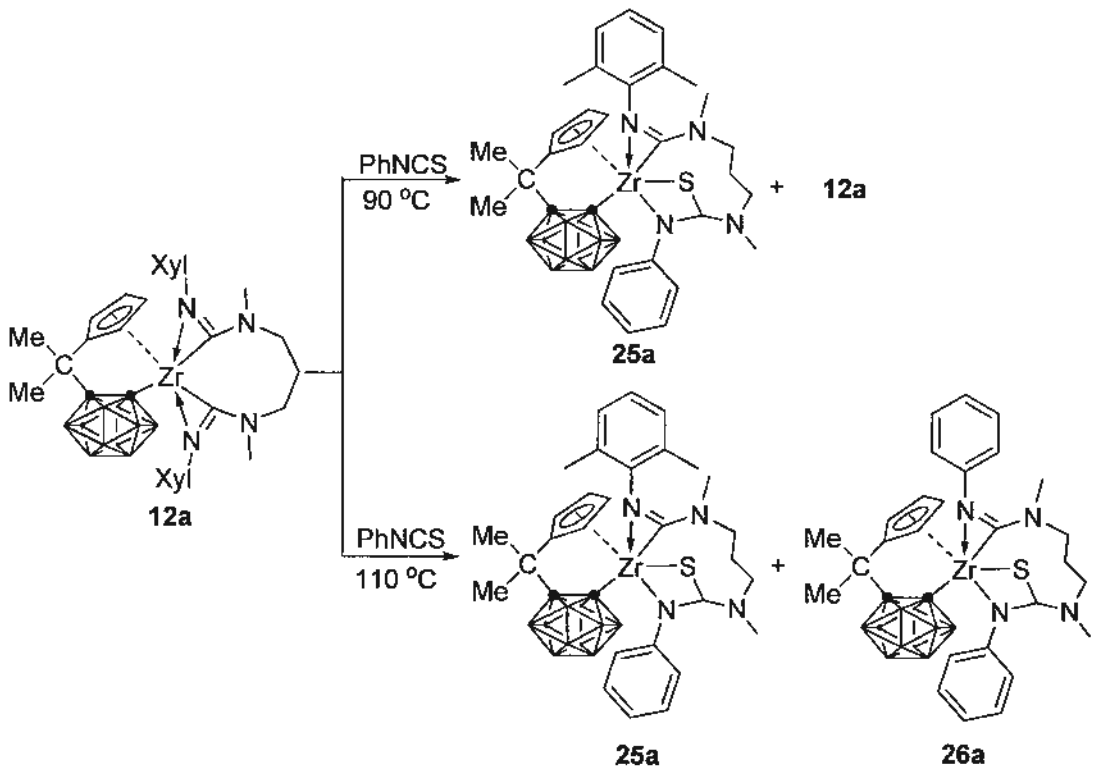


1a **24a**

Reaction with isothiocyanate. Treatment of **12a** with excess PhNCS at 90 °C in toluene for 7 days afforded [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (**25a**) as yellow crystals in 27% isolated yield and 38% of starting material (Scheme 3.10). **25a** was confirmed by various spectroscopic techniques as well as single-crystals X-ray analyses. In addition to the peaks derived from the carbon-bridged cyclopentadienyl-carboranyl ligand and the diamido moiety, five multiplets in the region 7.01 to 6.53 ppm assignable to the aryl protons, two singlets at 2.58 and 1.62 ppm attributable to the diastereotopic methyl groups on Xyl substituent were observed in the ^{1}H NMR spectrum of **25a**. The unique Zr-*C*=N and N-*C*-S resonances at 212.7 and 185.7 ppm were observed in its ^{13}C NMR spectrum, which confirmed the formation of **25a**. As shown in Figure 3.9, the Zr atom in **25a** adopts a five-legged piano stool geometry by one η^5-cyclopentadienyl ring, a cage carbon atom, an η^2-iminocarbamoyl ligand and

an η^2-NCS moiety.

Scheme 3.10. Reaction of complex **12a** with PhNCS.



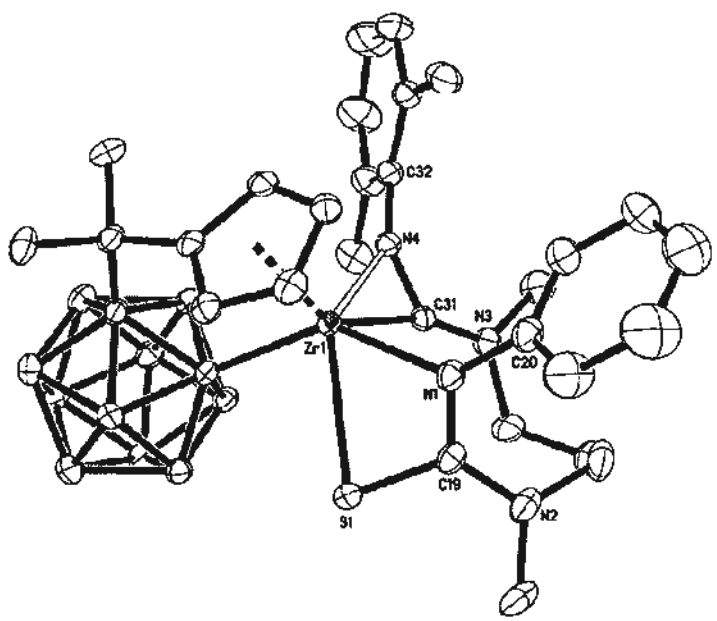


Figure 3.9. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (**25a**).

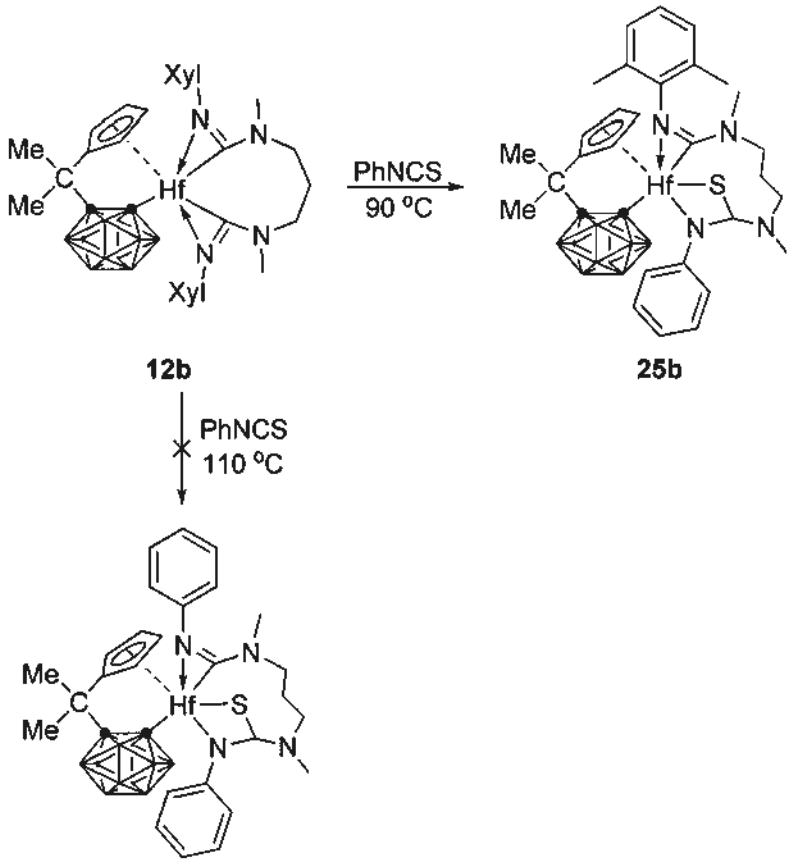
As this reaction proceeded very slowly at 90 °C with lots of starting material remaining, the reaction temperature was increased to 110 °C. It was found that such a reaction was completed within 4 days as monitored by ^{1}H NMR spectroscopy. Two sets of cyclopentadienyl signals with ~1:1 molar ratio were observed in the range 7.01 – 6.02 ppm, indicating the presence of two products. Indeed, fractional recrystallization from THF, afforded **25a** and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$:$\eta^2$-N(Ph)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (**26a**) in 14% and 21% isolated yields, respectively (Scheme 3.10). The isolated yields were very low, as most of the products were isolated as a 1:1 mixture in 49% yield.

In addition to the peaks of the bridging ligand and diamido moiety, there were four multiplets in the region 7.33 – 6.94 ppm assignable to the two aryl rings in the ^{1}H NMR spectrum of **26a**. The unique Zr-*C*=N and N-*C*-S resonances at 212.7 and 183.3 ppm were also observed in its ^{13}C NMR spectrum. The molecular structure of **26a** was further confirmed by single-crystal X-ray analyses. The coordination environment in **26a** is very similar to that in **25a** (Figure 3.10). It shows clearly two phenyl rings, instead of one Xyl and one Ph units. The Zr-N(4)/C(31) distances of 2.128(2)/2.215(3) Å are close to the values in the parent complex **12a**. The Zr-N(1)/S(1) distances of 2.263(2)/2.661(1) Å are close to the 2.268(2)/2.621(1) Å in [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Zr($NMe_2$)[$\eta^2$-SC($NMe_2$)N^{n}Bu][34] and 2.270(5)/2.606(2) Å in [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Zr($NMe_2$)[$\eta^2$-SC($NMe_2$)N^{n}Bu].[34]

The Hf complex **12b** also reacted with excess PhNCS at 90 °C in toluene to give [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)]

(**25b**) as colorless crystals in 83% isolated yield (Scheme 3.11). The reaction proceeded faster than the Zr analogue and finished within 2 days. Unlike Zr complex, only complex **25b** was observed and isolated when the reaction was performed at 110 °C. Complex **25b** showed similar ^{1}H and ^{13}C patterns to those of **25a**. The molecular structure of **25b** was further confirmed by single-crystal X-ray analyses, in which complexes **25a** and **25b** are isostructural and isomorphous (Figure 3.11). The Hf-N(1)/C(27) distances of 2.162(4)/2.198(5) Å are similar to the corresponding values of 2.194(4)/2.176(4) Å in the parent complex **12b**.

Scheme 3.11. Reaction of complex **12b** with PhNCS.



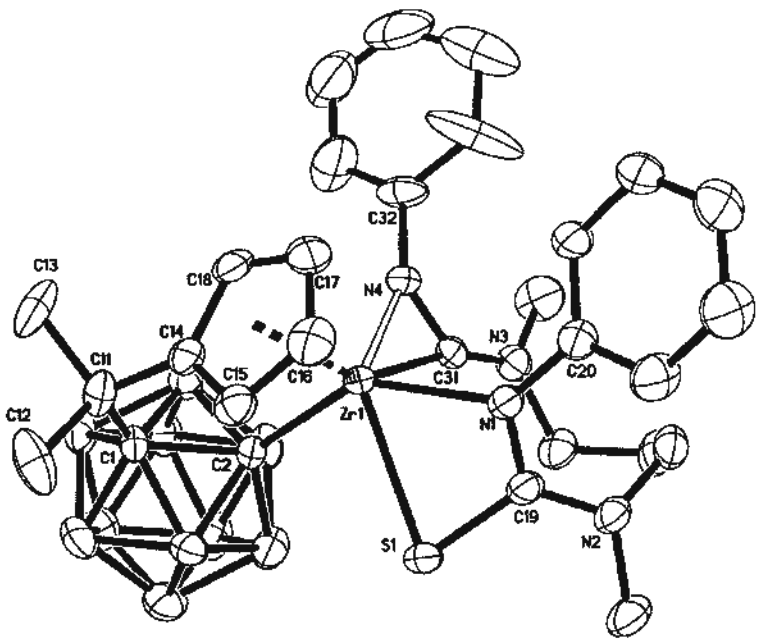


Figure 3.10. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr-[$\eta^2$:$\eta^2$-N(Ph)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (**26a**).

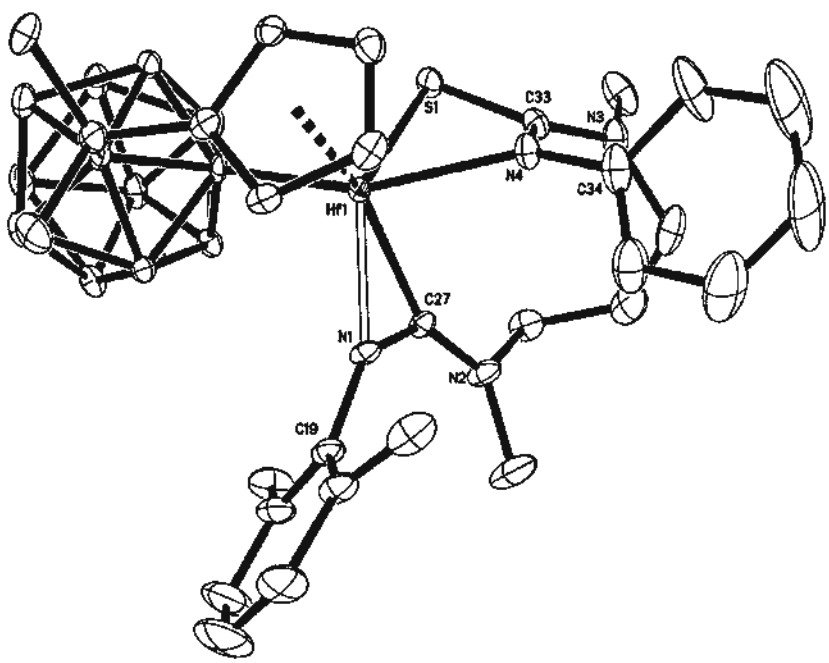
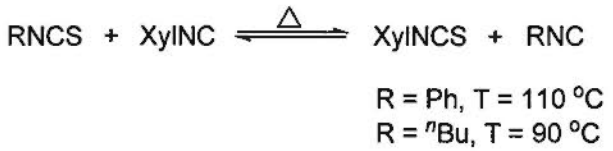


Fig 3.11. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf-[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (**25b**).

The formation and isolation of **26a** is totally unexpected. We wondered how it is formed. As monitored by ^{1}H NMR spectra in C_6D_6, only **25a** was observed at 90 °C besides the starting material, and **26a** appeared when the temperature was increased to 110 °C. Control experiments indicated that XylNC and PhNCS can undergo exchange to form PhNC and XylNCS at 110 °C. This process, however, cannot take place at 90 °C (Scheme 3.12). Thus, it is likely for the newly formed PhNC to formally substitute the XylNC unit in **25a**.

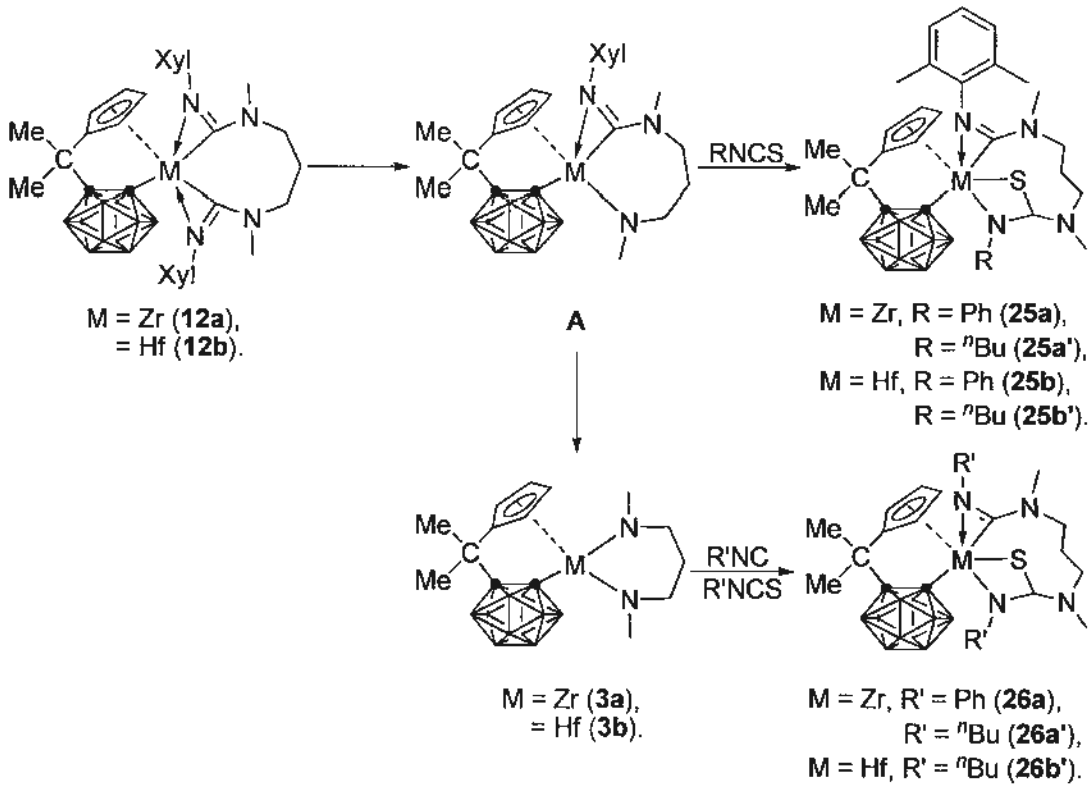
Scheme 3.12. Thermal exchange between isothiocyanates and isocyanide.



We further examined the reactions of complex **12a** or **12b** with ^{n}BuNCS. Interaction of **12a** with excess ^{n}BuNCS at 110 °C in C_6D_6 for four days, also two products with a molar ratio of ~1:1 as evidence from ^{1}H NMR spectra, which were assigned as $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}N(Xyl)=CN(Me)(CH_2)_3N(Me)C\text{-}N(^n Bu)(\text{-}S)]$ (**25a'**) and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2{:}\eta^2\text{-}N(^n Bu)=CN(Me)(CH_2)_3N(Me)C\text{-}N(^n Bu)(\text{-}S)]$ (**26a'**) (Scheme 3.13). The Hf species **12b** reacted with ^{n}BuNCS at 110 °C for 1 day also afforded two products in a molar ratio of about 5:1 as measured by ^{1}H NMR spectra, which are probably $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}N(Xyl)=CN(Me)(CH_2)_3N(Me)C\text{-}N(^n Bu)(\text{-}S)]$ (**25b'**) and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2{:}\eta^2\text{-}N(^n Bu)=CN(Me)(CH_2)_3N\text{-}(Me)C\text{-}N(^n Bu)(\text{-}S)]$ (**26b'**). Note that this ratio did not change upon heating for

another 3 days at 110 °C. Two products were observed at 90 °C by the ^{1}H NMR spectra.

Scheme 3.13. Proposed mechanism for the formation of complexes **25** and **26**.



Interaction of **12b** with ^{n}BuNCS at 110 °C for one day afforded after fractional recrystallization **25b'** as colorless crystals in 59% isolated yield and a mixture of **25b'** and **26b'** in a molar ratio of 1:3 in 10% yield. The unique Hf-*C*=N and N-*C*-S resonances at 222.3 and 185.1 ppm were observed in the ^{13}C NMR spectrum of **25b'**. The molecular structure of **25b'** was confirmed by an single-crystal X-ray analysis. As shown in Figure 3.12, the coordination environment of the central Hf atom is very similar to that of **25b**, with one η^5-cyclopentadienyl ring, a cage carbon atom, an η^2-iminocarbamoyl moiety and an η^2-NCS group in a five-legged piano stool geometry.

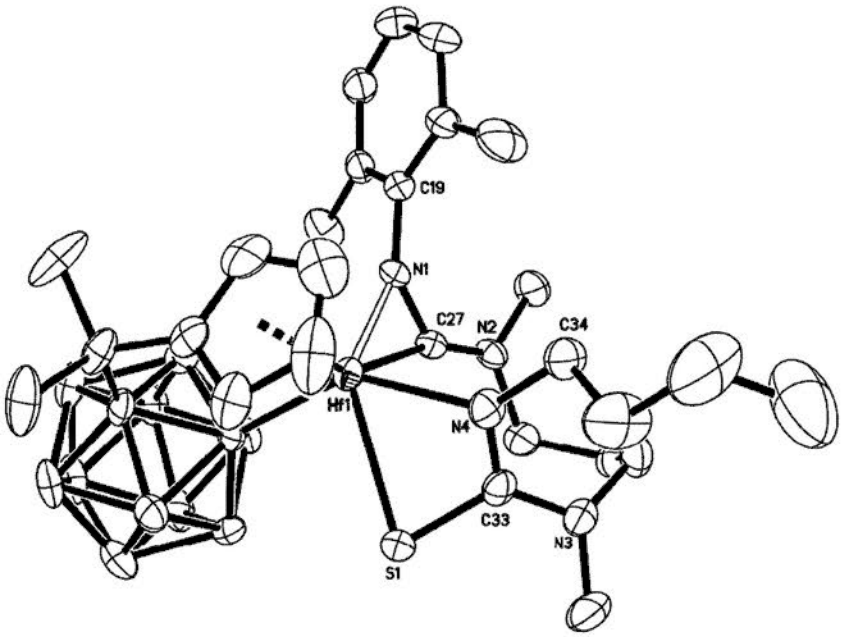


Fig 3.12. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf-[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(^{n}Bu)(-S)] (**25b'**).

A control experiment showed that metathesis of ^{n}BuNCS with XylNC would take place at 90 °C, while no reaction was observed for XylNC and PhNCS at the same temperature. **25b'** was isolated in pure form, which did not react with ^{n}BuNC to give **26b'**. Thus, the formation of **26b'** most likely results from the reaction of **12b** with ^{n}BuNCS and ^{n}BuNC. A plausible pathway for the formation of complex **25** and **26** is shown in Scheme 3.13. Complexes **12** eliminate one XylNC to form the intermediate **A**. Insertion of a RNCS molecule into the M-N bond to afford product **25**. Intermediate **A** can further eliminate another XylNC to form complexes **3**, which can react with 1 equiv of RNCS and RNC to give another product **26**. The reactivity of RNC and the reaction rate are two key factors dominating the reaction pathways. For R = Ph, the reaction of the Hf species **12b** is fast and maybe completed before PhNC

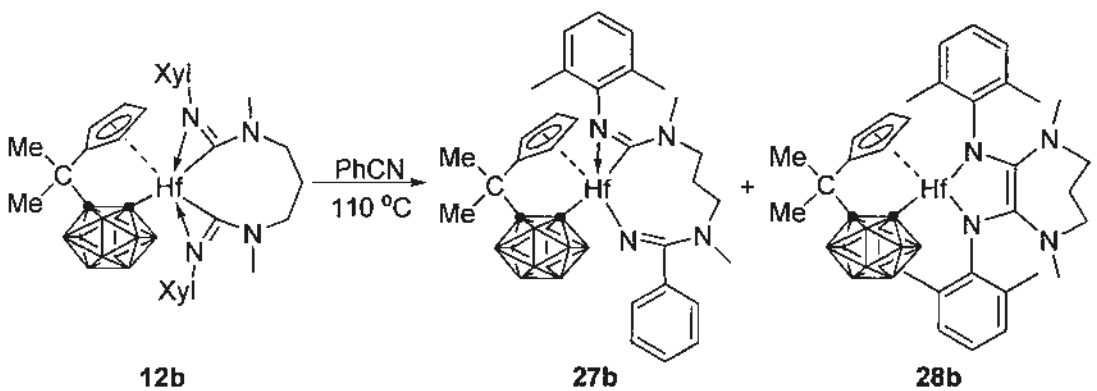
is formed. Thus, no product **26b** was observed. When R = ^{n}Bu, the isocyanide/isothiocyanate exchange reaction is much quicker, enabling the proceeding of the second step and affording complex **26b'**.

Reaction with Benzonitrile. Treatment of Hf species **12b** with excess PhCN at 110 °C in toluene for 5 days afforded [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf-[$\eta^2$:$\sigma$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(Ph)=N] (**27b**) and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$-(Xyl)NC[N(Me)$(CH_2)_3$N(Me)]=CN(Xyl)] (**28b**) in 26% and 33% isolated yields, respectively (Scheme 3.14). The reaction proceeded very slowly as evidenced by ^{1}H NMR spectroscopy. Although the structure of **27b** was not determined by X-ray analyses, the spectroscopic data together with elemental analyses confirmed its composition. Besides peaks due to the carbon-bridged cyclopentadienyl-carboranyl and diamido ligand, four multiplets in the region 7.30 to 6.86 ppm corresponding to the aryl protons and two singlets at 2.14 and 2.06 ppm attributable to the two diastereotopic methyl groups on Xyl units were observed in the ^{1}H NMR spectrum of **27b**. The unique Zr-*C*=N(Xyl) and Zr-N=*C*-Ph resonances at 217.2 and 164.3 ppm were also observed in its ^{13}C NMR spectrum. This result further confirmed the reversible insertion of isocyanide in the presence of other unsaturated molecules.

The formation of **28b** was confirmed by spectroscopic techniques as well as single-crystal X-ray analyses (Figure 3.13). Two multiplets in the region 5.81 to 5.12 ppm assignable to the cyclopentadienyl protons, a singlet at 1.35 ppm attributable to the bridging methyl groups, two multiplets in the region 7.12 to 6.97 ppm

corresponding to the aryl protons, a singlet at 2.65 ppm of NCH_3, a singlet at 2.12 ppm of $C_6H_3(CH_3)_2$ and two multiplet at 2.86 and 1.26 ppm of the three methylene groups were observed in the ^1H NMR spectrum of **28b**. The absence of the iminocarbamoyl carbon resonance at ~200 ppm, and appearance of an alkene resonance at 124.7 ppm confirmed the structure of **28b**. The NMR data also suggested that **28b** is a symmetrical species in solution. There are two crystallographically independent molecules in the unit cell and a representative one is shown in Figure 3.13. The average Hf-N(1)/N(4) distances of 2.025(6)/2.038(6) Å are corresponding to the 2.081(4) Å in $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2\text{:}\eta^2\text{-}N_2)$.[58c] The short C(27)-C(37) distance of 1.404(10) Å suggests a double bond. Complex **28b** would be formed by intramolecular coupling of the two η^2-iminocarbamoyl functionality, which is very common for isocyanide diinsertion species.[67] Complexes **28b** can also be obtained by heating **12b** in toluene at 110 °C for one week. Total conversion of **12b** to **28b** was observed with 69% isolated yield.

Scheme 3.14. Reaction of complex **12b** with PhCN.



12b **27b** **28b**

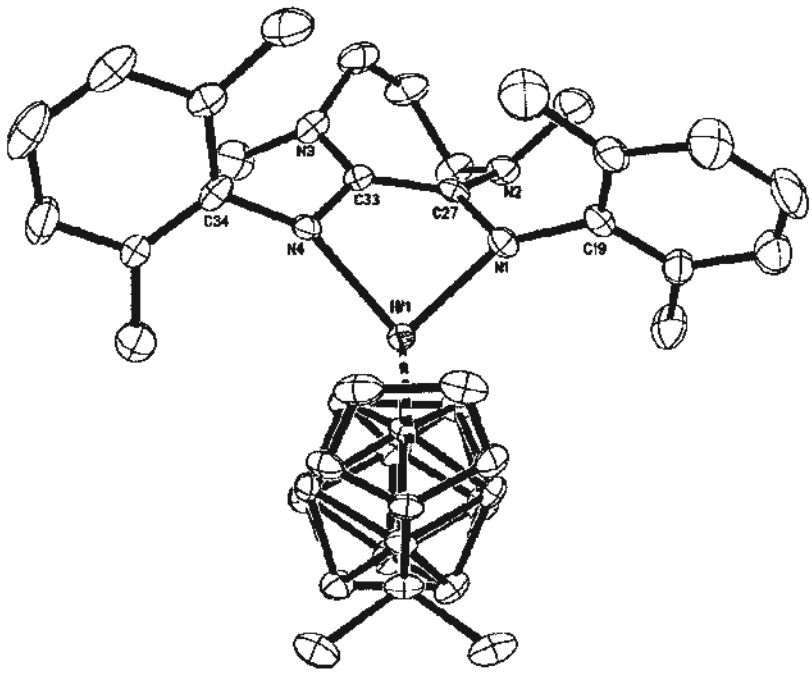


Figure 3.13. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf-[$\eta^2$-(Xyl)NC[N(Me)$(CH_2)_3$N(Me)]=CN(Xyl)] (**28b**), showing one of the two crystallographically independent molecules in the unit cell.

The yield of **27b** is low compared to the reactions of **12a** or **12b** with isocyanides or isothiocyanates, and may be ascribed to the low reactivity of PhCN. When XylNC was dissociated from **12b**, two possible pathways would be followed. The released XylNC inserts back to the M-N bond, or the other unsaturated molecules in the reaction system insert into the M-N bond. In the case of isocyanides, the reactivities are similar among these reagents, so the probability for the XylNC and RNC (R = *n*-butyl, 2-morpholinethyl, trimethylsilylmethyl) are almost the same. However, RNC was in large excess and the second equiv of RNC can insert into the M-C bond to get the more stable products. Isothiocyanates are also very reactive, and the formation of the η^2-NCS moiety can stabilize the final product. Therefore, the

reactions of **12a** or **12b** with isocyanides or isothiocyanates all gave the desired products in high yield. On the other hand, the low reactivity of benzonitrile makes the insertion of PhCN less comparable, so that isocyanide coupling occurs to give **28b** as the main product.

3.2.3. Summary

In this study, we have established that the insertion of XylNC into the M-N bond (M = Zr, Hf) is reversible in the presence of other unsaturated molecules. These reactions provide a useful method for the generation of new metallacycles containing different functionalities. In the reaction with isocyanides bearing α-CH_2, only one XylNC unit was substituted in the Zr complexes, whereas one or two XylNC moieties were replaced in the Hf complexes. Complexes **12a** and **12b** also reacted with isothiocyanates to give the isothiocyanates substituted products, in which the different isothiocyanates gave different results. The reaction of **12b** with PhCN resulted in the formation of both substituted and coupling products.

Chapter 4. Synthesis, Structure, Reactivity and Catalytic Property of Carbon-Bridged Cyclopentadienyl-Carboranyl Group 4 Metal Complexes Incorporating the $[S_2C_2B_{10}H_{10}]^{2-}$ Ligand

4.1. Introduction

1,2-Dicarba-*closo*-dodecaborane-1,2-dithiolate ([1,2-S_2-1,2-$C_2B_{10}H_{10}$]$^{2-}$), a kind of organic and inorganic hybrid moiety, can be easily synthesized from the reaction of carborane dilithium salt with elemental sulphur.[93] Metal complexes containing this ligand have been extensively studied and their synthesis and reactivities toward metal fragments and organic substrates have been reported.[94-100]

Late transition metal 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate complexes have been extensively studied. The 16e half-sandwich complexes M(η^5-Cp*)($S_2C_2B_{10}H_{10}$) (M = Rh,[97a] Ir[97b]), M(η^6-*p*-cymene)($S_2C_2B_{10}H_{10}$) (M = Ru, Os)[98] and CpCo($S_2C_2B_{10}H_{10}$)[95] were synthesized from reactions of [1,2-S_2-1,2-$C_2B_{10}H_{10}$]$^{2-}$ with proper MCl_2 reagents. They can undergo alkyne addition reactions to give stable 18e products, in which the metal center and the reaction conditions strongly influence the reactivity of these compounds. For example, the rhodium complex Cp*Rh($S_2C_2B_{10}H_{10}$) reacted with acetylene methyl carboxylate to give B(3,6)-substituted 16e product Cp*Rh(1,2-S_2-3,6-(*cis*-CH=CHCOOMe)$_2$-1,2-$C_2B_{10}H_{10}$) or with acetylene dimethyl dicarboxylate to afford Rh-S bond insertion product (Cp*)SC(COOMe)=C(COOMe)Rh($SC_2B_{10}H_{10}$), respectively.[96] On the other hand, the iridium species gave two geometrical isomers in the reaction with methyl

acetylene methyl carboxylate, in which an Ir-B bond was formed in these complexes.[99]

Besides the strong tendency to undergo addition reactions with electron donors at the metal centers, these carboranyl dithiolate-based metal complexes exhibit additional attributes for predesigned supramolecular entities. Synthesis of homo- and hetero-multinuclear clusters were achieved by using this ligand.[102]

Bimetallic complexes $(LRh)_2[S_2C_2B_{10}H_{10}]$ (L = COD, CO) (COD = 1,5-cyclooctadiene) with direct metal-metal bond was obtained in the reaction of dimerized rhodium complex $[Rh(COD)(\mu\text{-Cl})]_2$ or $[Rh(CO)2(\mu\text{-Cl})]_2$ with $Li_2S_2C_2B_{10}H_{10}$.[103] Direct hetero-metal bonding between ruthenium or group 9 metals (Co, Rh, Ir) and transition metals (Mo, W, Fe, Co) can be achieved by reaction of the 16e precursor $CpM(S_2C_2B_{10}H_{10})$ (Cp = η^5-C_5Me_5, M = Co, Rh, Ir; Cp = η^5-1,3-^{t}Bu$_2$C$_5$H$_3$, M = Co, Rh; Cp = C_5H_4, M = Co, Rh; Cp = *p*-cymene, M = Ru)[95a,97,98,104] with carboranyl transition metal reagents.[102]

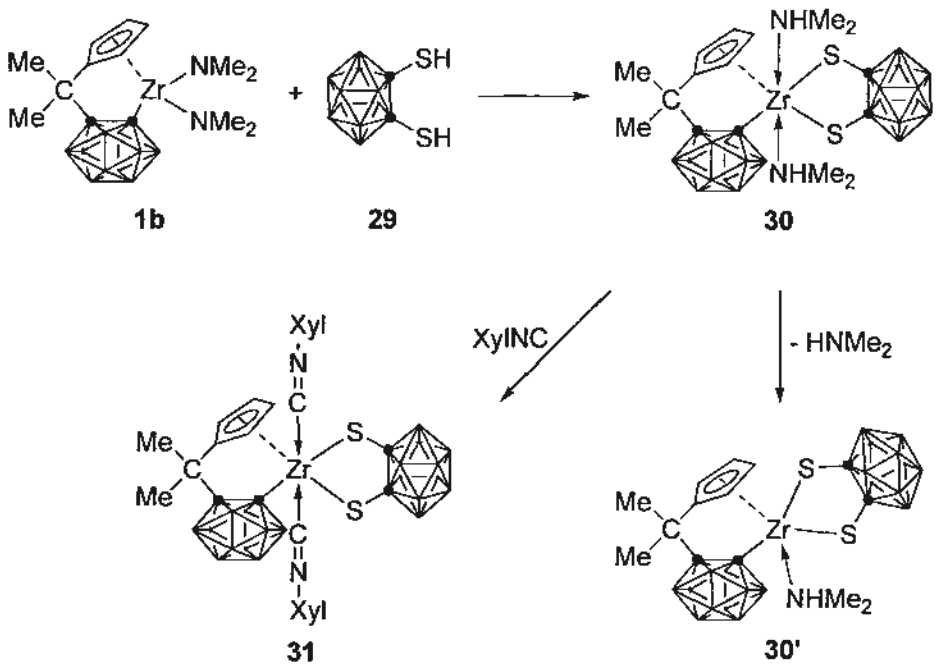
On the other hand, group 4 metal complexes bearing this 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligand are less studied. It was reported that group 4 metallocene complexes Cp'_2MCl_2 (Cp' = η^5-C_5H_5, η^5-^{t}BuC$_5$H$_4$, η^5-1,3-^{t}Bu$_2$C$_5$H$_3$; M = Ti, Zr, Hf) reacted with $Li_2S_2C_2B_{10}H_{10}$ affording ionic half-sandwich complexes $[Cp'M(S_2C_2B_{10}H_{10})_2][Li(THF)_4]$, in which one of the cyclopentadienyl ring is lost. Attempts to synthesize neutral group 4 metallocene complexes failed.[101]

On the basis of our own studies on the group 4 metal complexes and carboranes, we are interested in the chemistry of group 4 metal complexes bearing this 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligand. The carbon-bridged cyclopentadienyl-carboranyl zirconium species incorporating $[1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10}]^{2-}$ ligand was synthesized and the reaction towards unsaturated molecules was studied.

4.2. Synthesis and Structure of Carbon-Bridged Cyclopentadienyl-Carboranyl Group 4 Metal Sulphido Complexes

Similar to the synthesis of carbon-bridged cyclopentadienyl-carboranyl group 4 metal diamides, acid-base reaction is also very useful in the preparation of group 4 metal sulphido complexes. Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**1b**) with 1 equiv of 1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$ (**29**) in toluene at room temperature gave $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}](NHMe_2)_2$ (**30**) as a yellow solid in 71% isolated yield (Scheme 4.1).

Scheme 4.1. Synthesis of carbon-bridged cyclopentadienyl-carboranyl group 4 metal sulphido complexes



The ^{1}H NMR spectrum showed four multiplets in the region 6.64 – 5.90 ppm assignable to the cyclopentadienyl protons, two singlets at 1.60 and 1.55 ppm attributable to the CMe_2 methyl groups and a singlet at 2.83 ppm corresponding to the NMe_2 unit and a singlet at 9.18 ppm for the N-*H* proton. Its ^{13}C NMR spectrum exhibited five peaks in the region 145.9 to 107.3 ppm assignable to the Cp ring and

two peaks at 34.3 and 31.9 ppm attributable to the CMe_2 methyl carbons. The ^{11}B NMR spectrum exhibited a 5:4:11 patterns spanning a range from –3.4 to –9.4 ppm, in which signal overlapping of the two carborane cages was observed.

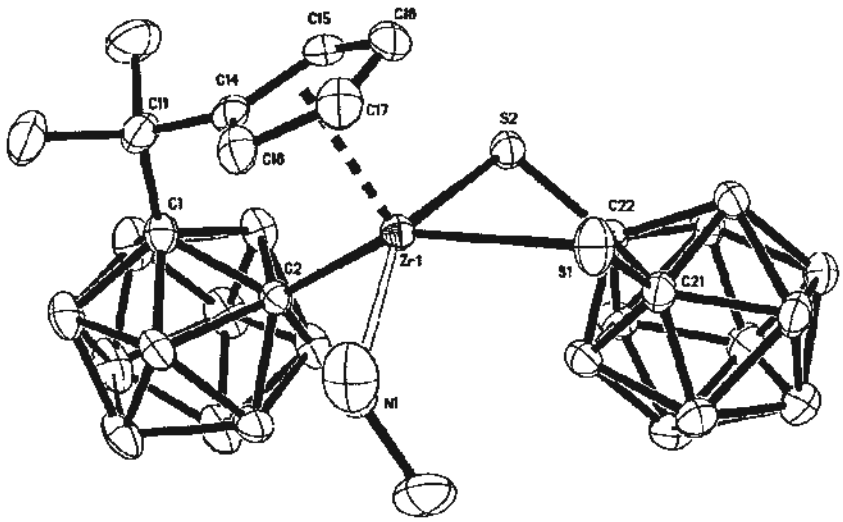


Figure 4.1. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}](NHMe_2)$ (**30'**).

Although the structure of complex **30** was not confirmed by X-ray analyses due to the poor crystallinity, the mono $HNMe_2$ coordinated species $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}](NHMe_2)$ (**30'**) was obtained as yellow crystals after recrystallization from toluene. Its spectroscopic data cannot be obtained due to the very small quantity of the crystals. Figure 4.1 shows the molecular structure of **30'**. The central Zr atom is coordinated to an η^5-cyclopentadienyl ring, a cage carbon atom, an η^2-disulphido ligand and one dimethylamine in a four-legged piano stool geometry. The average Zr-S distance of 2.559(1) Å is well comparable with 2.518(2) Å in $Cp^*_2Zr(SH)_2$,[105a] 2.544(1) Å in $[Zr(\eta^5\text{-}C_5Me_5)_2(SC(tBu)PSe)]$[105b] and 2.513(3) Å in $Cp^{tt}_2Zr(\mu^3\text{-}S)_2[Ir(CO)_2][Rh(CO)_2]$[105c] ($Cp^{tt} = \eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$). The average Zr-$C_{ring}$ and Zr-C_{cage} distances of 2.468(4) Å and 2.379(4) Å are close to the 2.543(2) Å and 2.384(2) Å in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NEt_2)_2$,[35] 2.519(5) Å

and 2.353(4) Å in $[\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$,[35] 2.502(4) Å and 2.394(3) Å in **4a**. The Zr-N(1) distance of 2.418(3) Å is comparable well with 2.360(3) Å in $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(NHEt_2)$.[15]

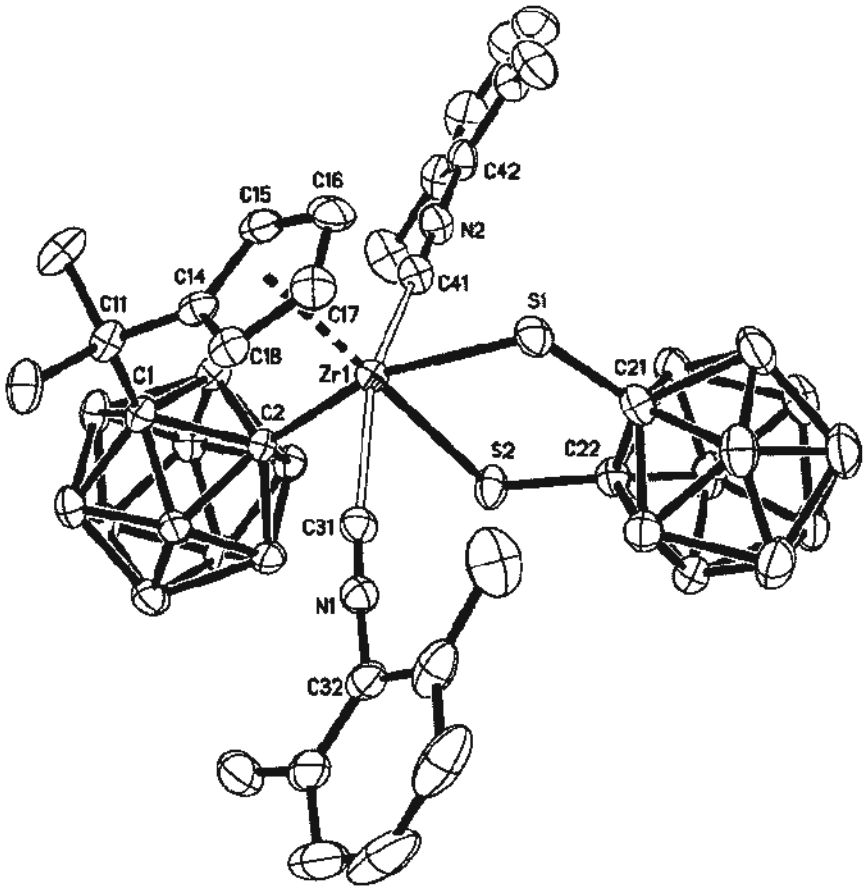


Figure 4.2. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}S_2C_2B_{10}H_{10}][2,6\text{-}(CH_3)_2C_6H_3N{=}C]_2$ (**31**)

Complex **30** can undergo ligand exchange reaction and the $HNMe_2$ can be substituted by isocyanide. Treatment of **30** with 2 equiv of XylNC in toluene at room temperature gave $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][2,6\text{-}(CH_3)_2C_6H_3N{=}C]_2$ (**31**) as yellow crystals in 73% isolated yield (Scheme 4.1). Six multiplets in the region 7.26 to 6.59 ppm assignable to the aryl and cyclopentadienyl protons, two singlets at 2.60 and 2.24 ppm attributable to the two methyl groups of XylNC, two singlets at 1.63 and 1.48 ppm corresponding to the bridging methyl

groups were observed in the ^{1}H NMR spectrum of **31**. The unique Zr-*C*=N and C_{cage}-S resonance at ~169 and ~95 ppm were observed in its ^{13}C NMR spectrum. The ^{11}B NMR spectrum exhibited a 17:3 pattern spanning the range from –9.1 to –13.5 ppm.

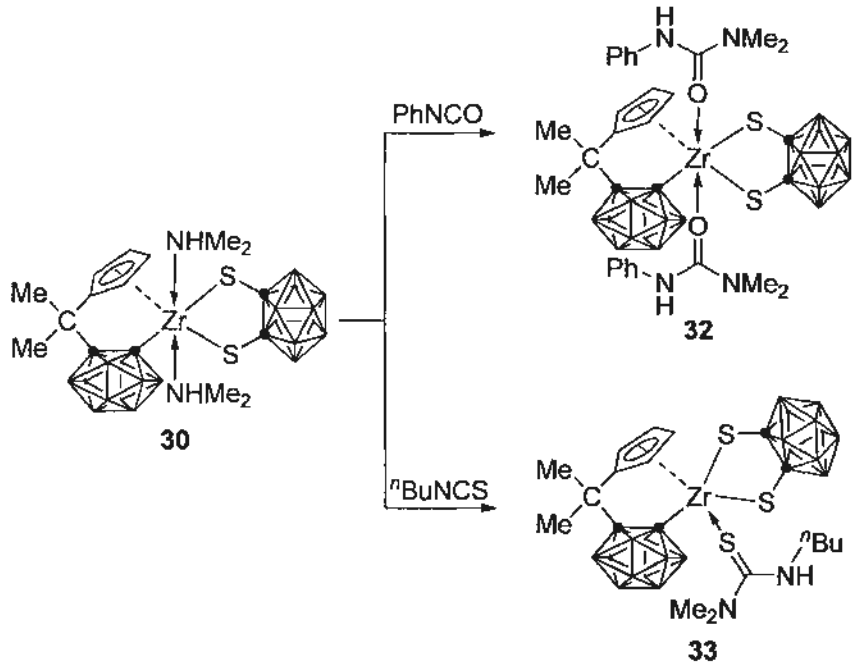
The molecular structure of **31** was further confirmed by single crystal X-ray analyses and showed half toluene of solvation (Figure 4.2). Complex **31** adopts a distorted octahedral geometry by one η^5-cyclopentadienyl ring, a cage carbon atom, an η^2-disulphido ligand and two coordinated isocyanides. The Zr-C(31)/C(41) distances of 2.381(4)/2.378(4) Å are very similar to that of 2.376(3) Å in [(η^7-C_7H_7)(η^5-C_5H_5)Zr(CN^{t}Bu)],[106a] 2.372(10) Å in [(η^8-C_8H_8)(η^4-C_8H_8)Zr(CN^{t}Bu)],[106b] and 2.350(4) Å in [Cp_2Zr(-C≡CCH_3)(CN^{t}Bu)][BPh_4].[106c]

4.3. Stoichiometric Reaction of Group 4 Metal Complex 30 with Unsaturated Molecules

The $HNMe_2$ unit in complex **30** can react with unsaturated molecules, leading to the formation of new carbon-bridged cyclopentadienyl-carboranyl zirconium sulphido complexes. Complex **30** reacted with 2 equiv of PhNCO in toluene at room temperature, afforded after recrystallization, [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][O=C($NMe_2$)NHPh]$_2$ (**32**) as pale yellow crystals in 87% isolated yield (Scheme 4.2). In addition to the peaks derived from the carbon-bridged cyclopentadienyl-carboranyl ligand, three multiplets in the region 7.86 to 7.12 ppm assignable to the aryl protons, two singlets at 2.93 and 2.50 ppm attributable to the two dimethylamido groups were observed in the ^{1}H NMR spectrum of **32**. The unique *C*=O resonances at 165.7 and 156.2 ppm were also observed in its ^{13}C NMR spectrum. Its ^{11}B NMR showed a 6:6:8 pattern spanning the range from –3.7 to –9.3 ppm. The structure of complex **32** is shown in Figure 4.3. The Zr atom is η^5-bound to

the cyclopentadienyl ring, σ-bound to a cage carbon atom, η^2-bound to the disulphido ligand and coordinated to two oxygen atoms in a distorted octahedral geometry.

Scheme 4.2. Reaction of **30** with PhNCO and ^{n}BuNCS.



In a similar manner, **30** reacted with 2 equiv of ^{n}BuNCS in toluene at room temperature to give $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}]$-$[S{=}C(NMe_2)NH^nBu]$ (**33**) as orange yellow crystals in 76% isolated yield (Scheme 4.2). In addition to the peaks of the carbon-bridged cyclopentadienyl-carboranyl ligand, a board singlet at 7.73 ppm corresponding to the N-H proton, four multiplets of the ^{n}Bu group in the region 3.87 to 0.78 ppm and a singlet at 3.23 ppm of NMe_2 were observed in the ^{1}H NMR spectrum of **33**. The unique *C*=S and C_{cage}-S resonances at 183.0 and 94.4 ppm were observed in its ^{13}C NMR spectrum. The molecular structure of **33** was further confirmed by single crystal X-ray analyses. As shown in Figure 4.4, the central Zr atom was η^5-bound to the cyclopentadienyl ring, σ-bound to a cage carbon atom, η^2-bound to the disulphide ligand and coordinated to a sulphur atom in a four-legged piano stool geometry. The formation of **33**, in which

the Zr atom is coordinated to only one 3-butyl-1,1-dimethylthiourea, is probably due to the larger atomic size of sulphur over the oxygen atom.

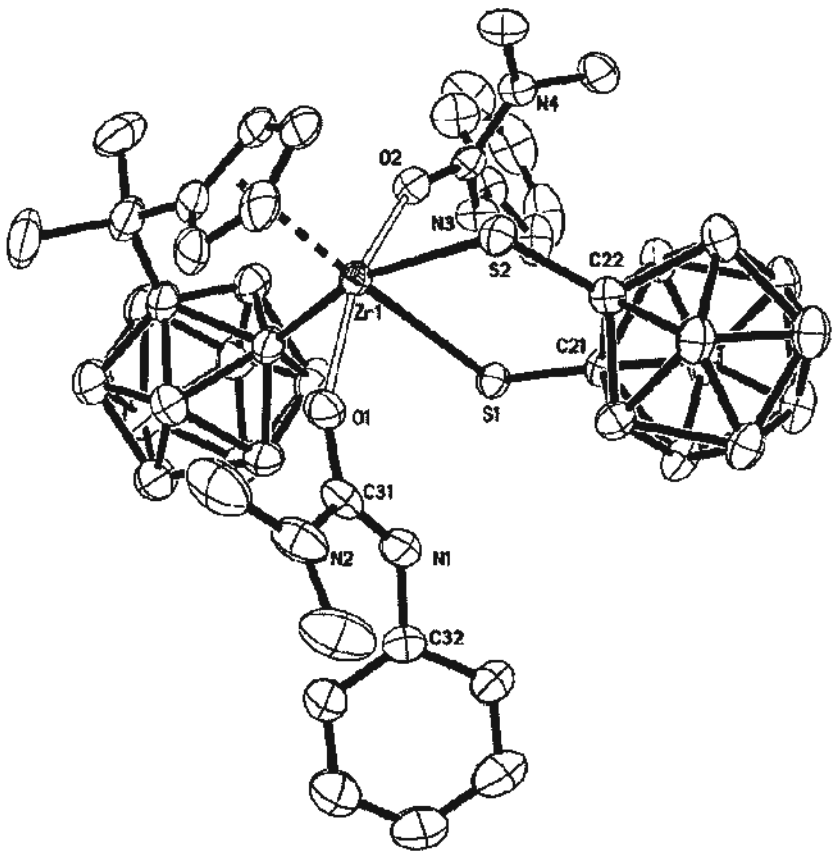


Figure 4.3. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}S_2C_2B_{10}H_{10}][O{=}C(NMe_2)NHPh]_2$ (**32**).

Whether these two reactions are promoted by the Zr center is not clear as PhNCO or ^{n}BuNCS can react with free $HNMe_2$ in the absence of any metal complex.[107] Since the isolated yields of **32** and **33** are very high, the Zr atom and sulphido groups may play a role to enhance the reaction efficiency (vide infra).

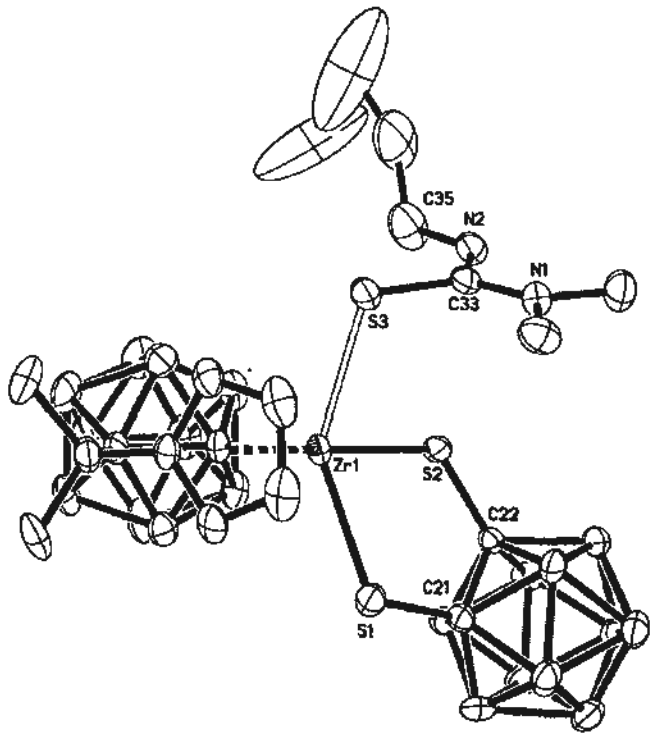


Figure 4.4. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][S=C($NMe_2$)NH^{n}Bu] (**33**).

Reaction of **30** with an equimolar amount of THF in refluxing toluene afforded the THF ring opening product [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][$\sigma$-$O(CH_2)_4NHMe_2$] (**34**) as orange crystals in 60% isolated yield (Scheme 4.3). In addition to the peaks derived from the carbon-bridged cyclopentadienyl-carboranyl ligand, four multiplets in the region 4.27 to 1.67 ppm assignable to the eight methylene protons, one singlet at 3.04 ppm attributable to the N(CH_3)$_2$ group, and a singlet at 11.37 ppm corresponding to the N-*H* resonance were observed in the ^{1}H NMR spectrum of **34**. The unique C_{cage}-S resonance at 99.1 ppm was also observed in its ^{13}C NMR spectrum, indicating the presence of the dithiolate carborane ligand. Single crystal X-ray analyses revealed that **34** is a zwitterionic species and showed a toluene of solvation. The geometry in **34** is very similar to that in **30'**, except that an alkoxide group replaces the dimethylamine (Figure 4.5). The S(2)···N(1) distance of

3.245 Å and the longer Zr-S(2) distance of 2.686(2) Å over Zr-S(1) distance of 2.593(2) Å suggest the presence of a hydrogen bonding between S(2) and N(1) in the solid state.[108] The average Zr-S distance of 2.639(1) Å is much longer than the 2.559(1) Å in complex **30'**, 2.518(2) Å in $Cp^*_2Zr(SH)_2$,[106a] 2.544(1) Å in $[Zr(\eta^5\text{-}C_5Me_5)_2(SC(tBu)PSe)]$[106b] and 2.513(3) Å in $Cp^{tt}_2Zr(\mu^3\text{-}S)_2[Ir(CO)_2][Rh(CO)_2]$ (Cp^{tt} = η^5-1,3-di-*tert*-butylcyclopentadienyl).[106c]

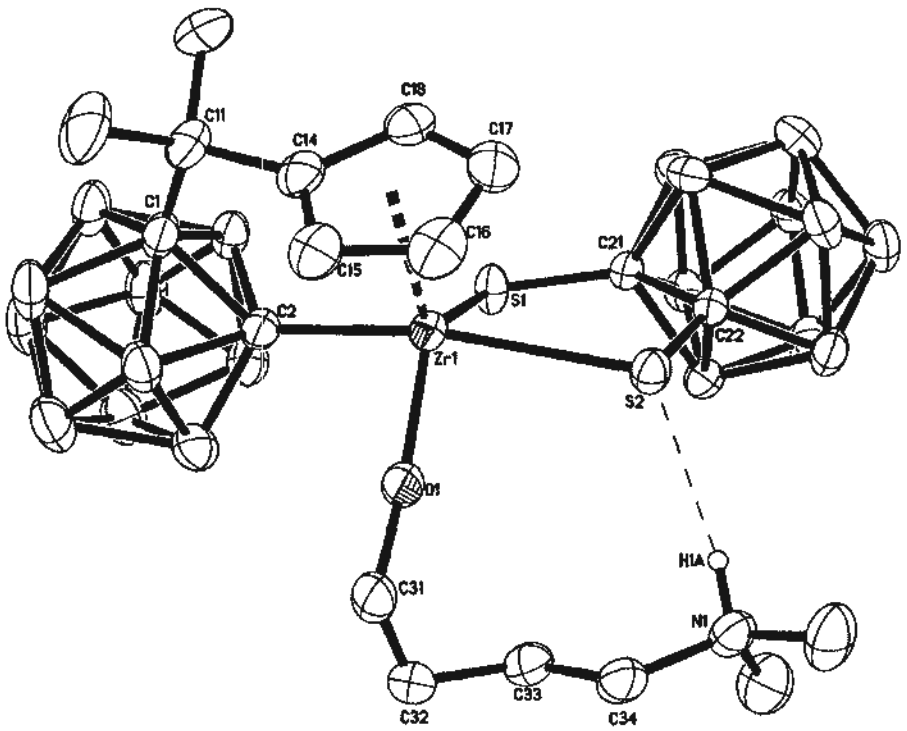


Figure 4.5. Molecular structure of $[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}S_2C_2B_{10}H_{10}][O(CH_2)_4NHMe_2]$ (**34**).

Reaction of **30** with 2 equiv of PhCN in toluene at room temperature, gave after recrystallization, $[\eta^5\text{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][NH{=}C(NMe_2)Ph]_2$ (**35**) as yellow crystals in 78% isolated yield (Scheme 4.3). The spectroscopic data were well consistent with the formation of amidine coordinated species. In addition to the peaks derived from the carbon-bridged cyclopentadienyl-carboranyl ligand,

three multiplets in the region 8.18 to 7.52 ppm due to the two phenyl rings, two singlets at 3.27 and 2.63 ppm corresponding to the two dimethylamido groups, and a board singlet at 3.02 ppm assignable to the two N-H protons were observed in the ^{1}H NMR of **35**. The unique *C*=N resonance at 166.7 ppm was observed in its ^{13}C NMR spectrum. Its ^{11}B NMR exhibited a 7:13 pattern. An X-ray diffraction study revealed that the coordination environment in **35** is very similar to **32**, with two oxygen atoms being replaced by two nitrogen atoms (Figure 4.6).

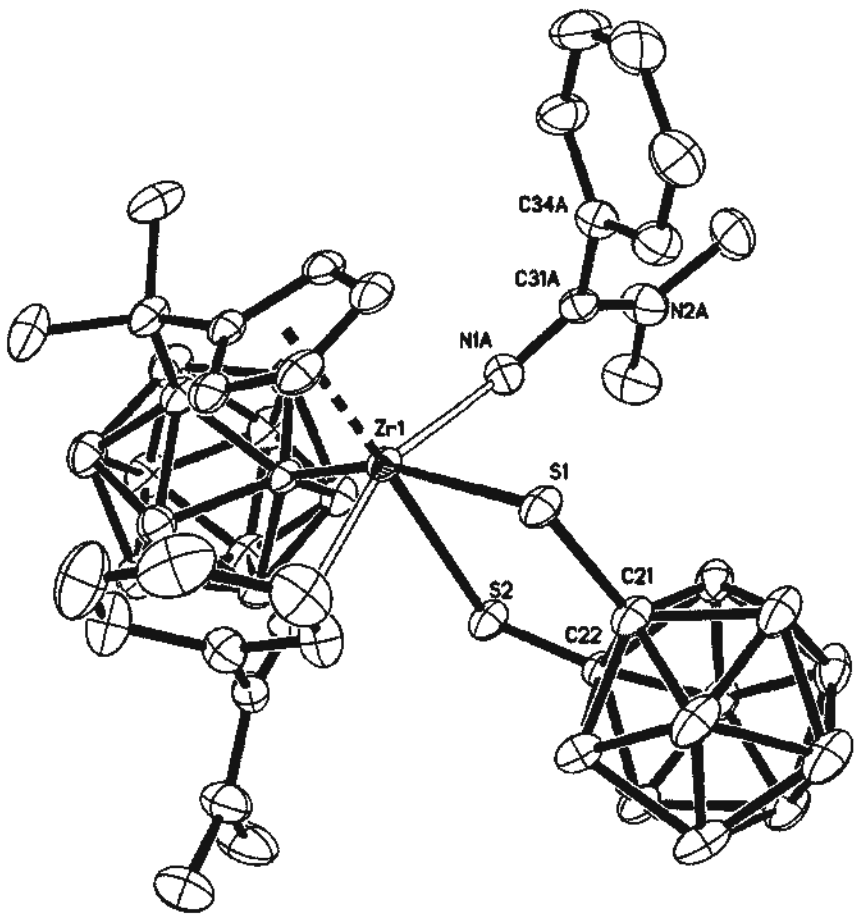
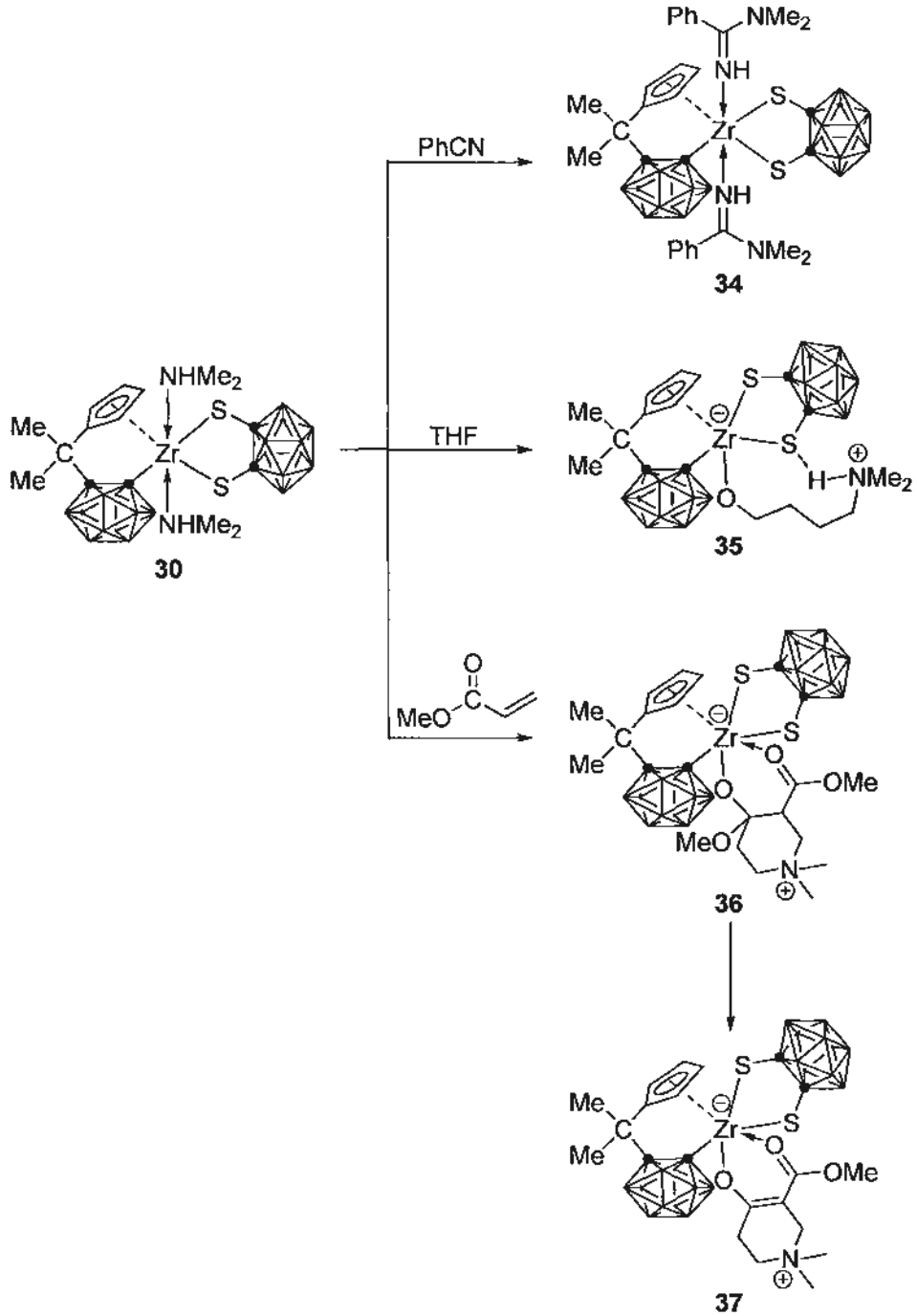


Figure 4.6. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr\text{-}[\eta^2\text{-}S_2C_2B_{10}H_{10}][NH{=}C(NMe_2)Ph]_2$ (**35**).

One $HNMe_2$ unit in complex **30** can also interact with two equiv of methyl acrylate to give the cyclization product. Treatment of **30** with three equiv of methyl

acrylate in toluene at room temperature led to immediate precipitation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][$\eta^2$-O=C(OMe)CH($CH_2NMe_2CH_2CH_2$)-C(OMe)-O] (**36**) as a white solid in 63% isolated yield. Recrystallization of **36** from THF afforded [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][$\eta^2$-O=C(OMe)-C($CH_2NMe_2CH_2CH_2$)=C-O] (**37**) as colorless crystals in 56% isolated yield.

Scheme 4.3. Reaction of **30** with THF, PhCN and MA.



As recrystallization of **36** only led to the isolation of **37**, a possible structure of **36** could be deduced from its NMR data. The unique chemical shifts of the CH group were found at 5.60 ppm in the ^{1}H NMR and 45.5 ppm in the ^{13}C NMR spectrum, which were further confirmed by ^{1}H-^{13}C HSQC technique. The peaks of *C*(OMe)=O and *C*(OMe)-O unit were observed at 174.3 and 67.8 ppm in the ^{13}C NMR spectrum. They were both in correlation with the CH unit in ^{1}H-^{13}C HMBC spectrum, indicating the C-C bond formation of the C(OMe)-O and CH groups.

Single-crystal X-ray analyses further confirmed the zwitterionic nature of **37** (Figure 4.7) and showed three THF molecules of solvation. The central Zr atom is coordinate to an η^5-cyclopentadienyl ring, a cage carbon atom, an η^2-disulphido ligand, and an η^2-oxalato moiety in a distorted octahedral geometry.

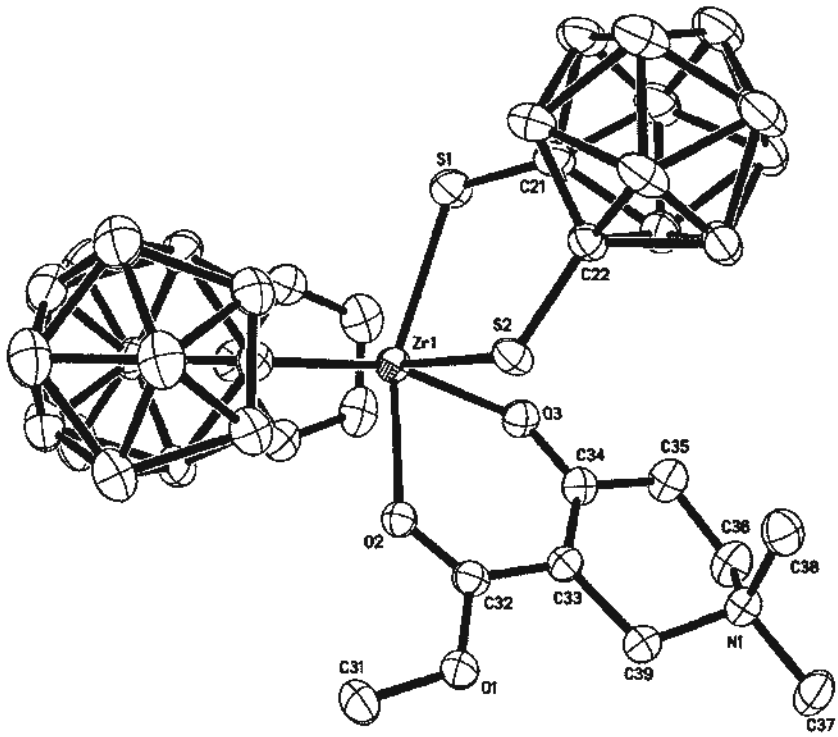
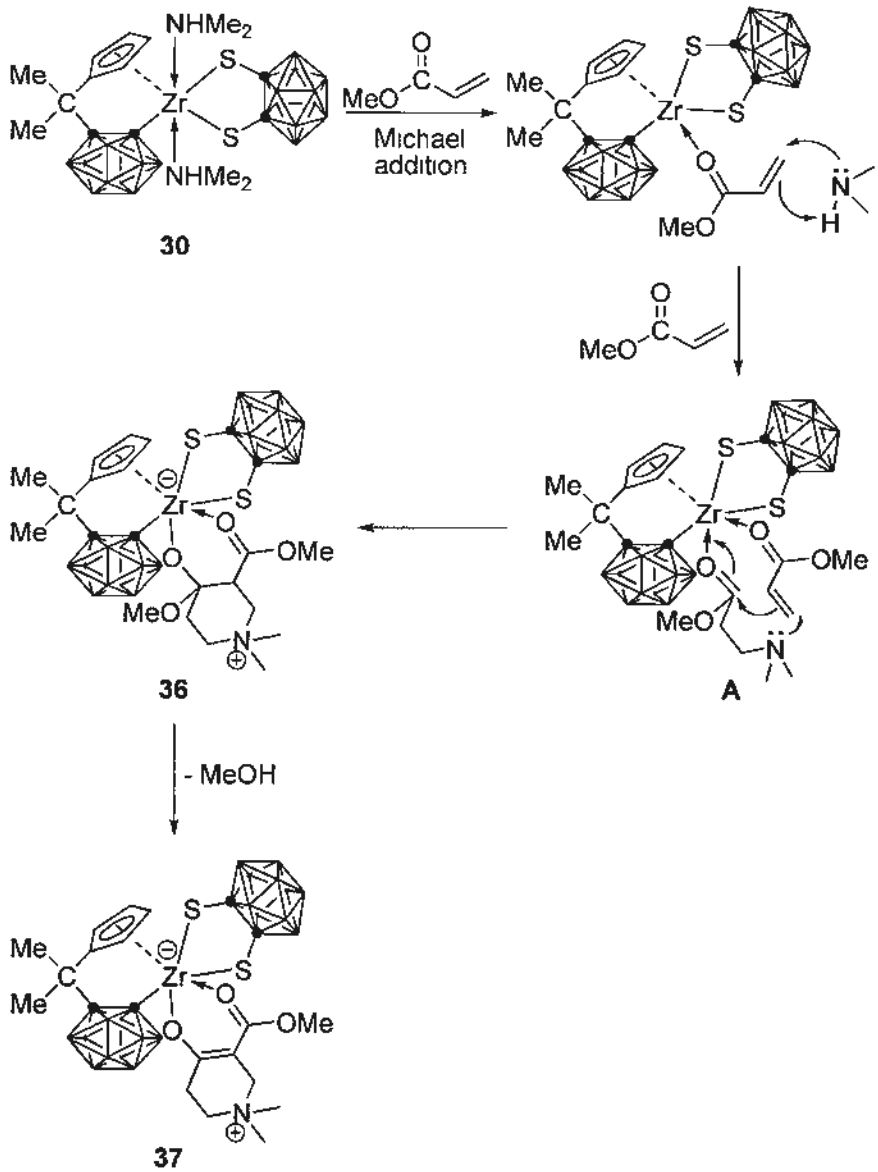


Figure 4.7. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][\eta^2\text{-}O{=}C(OMe)\overline{C(CH_2NMe_2CH_2CH_2){=}CO}]$ (**37**).

Both ^{1}H and ^{13}C NMR data suggested that **37** is a mixture of two regio-isomers in a molar ratio of about 1.7:1 in solution, which may result from the different coordination sites of the oxalate moiety. The two isomers were distinguished by ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and DEPT-135 NMR techniques. The major product exhibited four multiplets in the region 6.52 – 6.14 ppm assignable to the cyclopentadienyl protons, two doublets in the region 4.63 – 4.35 ppm assignable to the diastereotopic NCH_2 group, a singlet at 3.77 ppm of the OCH_3 resonance, a singlet at 3.55 ppm corresponding to the NMe_2 group, two multiplets of NCH_2CH_2 and NCH_2CH_2 in the region 3.85 – 2.81 ppm, and two singlets at 1.64 and 1.36 ppm attributable to the bridging $C(CH_3)_2$ unit in the ^{1}H NMR spectrum. The minor product showed a similar spectroscopic pattern. In the ^{1}H NMR spectrum, four multiplets in the region 6.51 – 5.73 ppm attributable to the cyclopentadienyl protons, two singlets at 1.62 and 1.54 ppm assignable to the bridging $C(CH_3)_2$ groups, two doublets at 4.52 and 4.40 ppm of the diastereotopic NCH_2 protons, a singlet at 3.92 ppm for the OCH_3 resonance, a singlet at 3.54 ppm corresponding to the NMe_2 group and two multiplets of NCH_2CH_2 and NCH_2CH_2 in the region 3.92 – 2.92 ppm were observed. The unique Zr-O-*C* resonances at 177.6, 168.7 ppm and the O-C=*C* resonances at 101.1 ppm of the major product and 177.8, 170.3 ppm and 109.6 ppm of the minor product, respectively, were observed in the ^{13}C NMR spectrum.

The possible pathway for the formation of **37** is shown in Scheme 4.4. The Michael addition of the coordinated dimethylamine with MA gives the intermediate **A**.[109] The lone-pair electrons of the tertiary amine attacks another molecule of MA to undergo intramolecular cyclization affording complex **36**. Eliminate of one molecule of MeOH gives **37**.[110]

Scheme 4.4. Proposed mechanism for the formation of complex **37**.



The above results suggest that, the Zr atom participates in the reaction of **30** with unsaturated molecules. THF and PhCN do not directly react with $HNMe_2$ in the absence of any promoter. The coordination of the substrates to the metal seems to be crucial for the reaction. The downfield signal at 9.18 ppm of N*H* in the ^{1}H NMR spectrum of **30** indicated a strong S···$HNMe_2$ hydrogen bonding interaction would be present, thus may enhance the nucleophilicity of the N atom and play a very important role in the above reactions.

4.4. Catalytic Hydroamination of Nitrile

Amidinates are of interest as structural units with a wide utility in drug design and as synthons for the synthesis of heterocyclic compounds.[111] Catalytic synthesis of amidines can be achieved by insertion-elimination process of a M-N bond. For example, the efficient one-step synthesis of mono-substituted N-arylamidines was reported by Shen and coworkers using [η^2:η^2-$N(SiMe_3)C(Ph)N(CH_2)_3NC(Ph)N(SiMe_3)$]Yb(ArNH)(DME) (Ar = 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$) as catalyst.[112] Another method is the Lewis acid catalyzed process, in which trivalent lanthanide triflates are used as catalyst.[113] Given the Lewis acidic property of complex **30** and its stoichiometric reaction with PhCN to form amidine coordinated species **35**, we wondered if the reaction could be carried out in a catalytic manner.

A possible catalytic cycle was proposed and shown in Scheme 4.5. RCN reacts with HNR_2 in the presence of a catalytic amount of **30** to afford amidine $PhC(NR_2)$=NH (R = Me (**38**), Et (**39**), ^{n}Pr (**40**)). Preliminary results were compiled in Table 4.1. Complex **30** showed no catalytic reactivity toward CH_3CN. This might be ascribed to the acidic proton of CH_3CN, which would quench the Zr-C_{cage} bond and prohibit the catalytic cycle. Catalytic hydroamination of PhCN with $HNMe_2$ proceeded at 90 °C in toluene in the presence of 3 mol % catalyst **30**, and compound **38** was isolated in 34% isolated yield after distillation. As the hydroamination of nitrile is a reversible reaction, using PhCN as solvent can shift the equilibrium to the product side and the yield was improved to 62%. However, if diethylamine was used, the yield was dramatically dropped to 20%. The yield was 19% when HN^nPr_2 was employed. These preliminary experiment data showed that complex **30** was able to

catalyze the hydroamination of PhCN, but the yield was not good and the substrate scope was very limited.

Scheme 4.5. Proposed mechanism for the catalytic reaction of nitriles with amines.

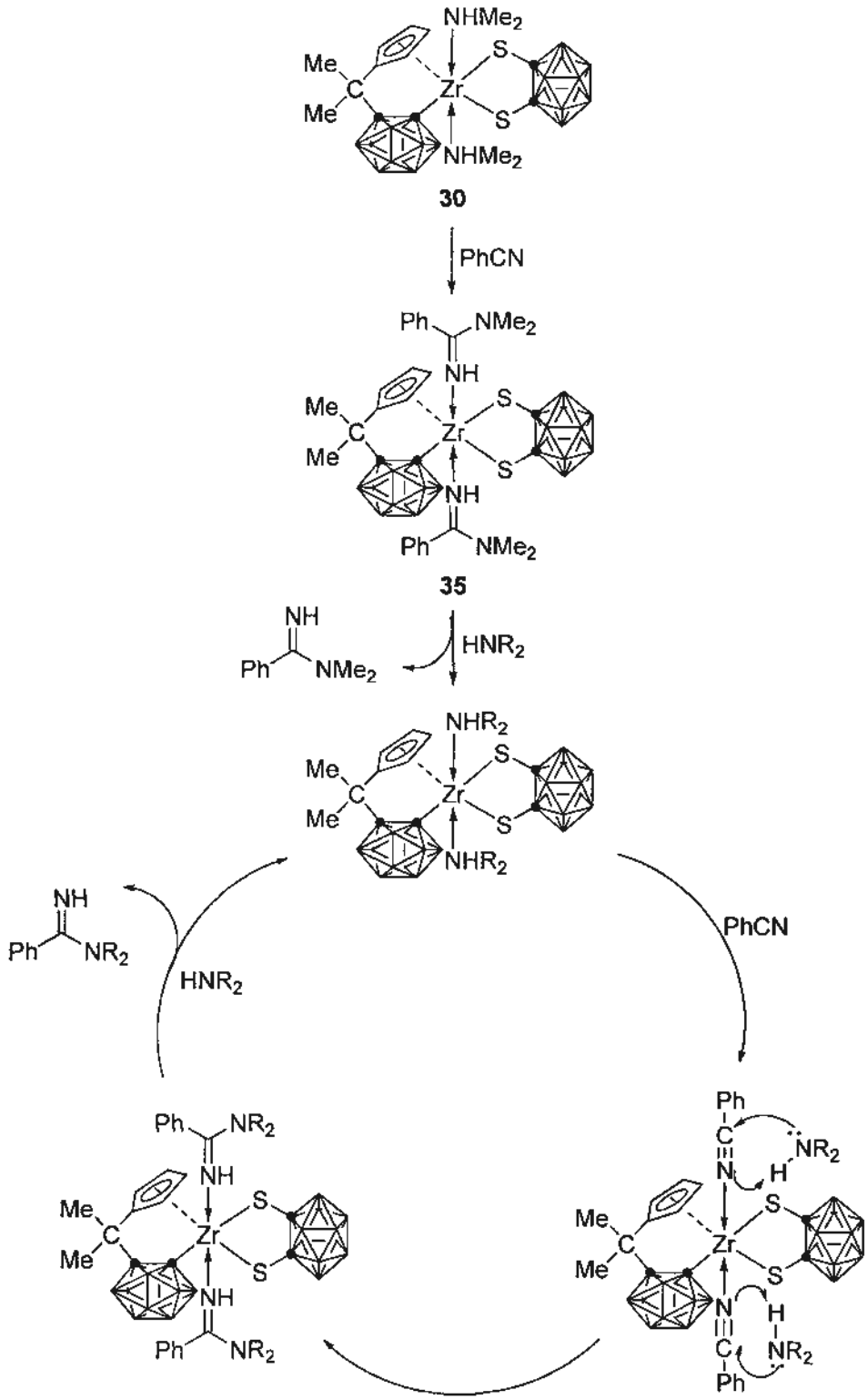


Table 4.1. Lewis acid promoted hydroamination of nitriles.

Entry	Nitrile : Amine (Molar ratio)	Temp.	Solvent	Time (hr)	Cat. (mole %)	Isolated yield (%)
1	PhCN : $HNMe_2$ (1:1.1)	30	Tol	24	3	0
2	PhCN : $HNMe_2$ (1:1.1)	90	Tol	24	3	34
3	PhCN : $HNMe_2$ (1:1.1)	120	Tol	24	3	35
4	PhCN : $HNMe_2$	30	PhCN	24	3	0
5	PhCN : $HNMe_2$	90	PhCN	24	3	62
6	PhCN : $HNMe_2$	120	PhCN	24	3	61
7	PhCN : $HNMe_2$ (1:1.1)	30	CH_2Cl_2	24	3	0
8	PhCN : $HNMe_2$ (1:1.1)	90	Tol	24	1	0
9	PhCN : $HNMe_2$	90	PhCN	24	5	60
10	CH_3CN : $HNEt_2$	90	CH_3CN	24	3	0
11	PhCN : $HNEt_2$	90	PhCN	24	3	20
12	PhCN : $HNPr_2$	90	PhCN	24	3	19

4.5. Summary

The carbon-bridged cyclopentadienyl-carboranyl zirconium disulphide complex **30** was synthesized by acid-base reaction between [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (**1a**) and 1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$ (**29**). It can undergo ligand exchange reaction with XylNC to afford the isocyanide coordinated species **31**. Reaction of **30** with unsaturated molecules such as PhNCO, ^{n}BuNCS, THF, PhCN, and MA, did not afford the Zr-S bond insertion products, rather gave the nucleophilic addition products **32-37**. The results suggested that these reactions could be viewed as Lewis-acid promoted nucleophilic addition reactions. Complex **30** could catalyze the hydroamination reaction of nitriles, but the efficiency was low and substrate scope was limited.

Chapter 5. Synthesis, Structure, and Reactivity of Group 4 Metal Complexes Bearing a Carbon-Bridged Cyclopentadienyl-Dicarbollyl Ligands

5.1. Introduction

The dicarbollide ion (*nido*-$C_2B_9H_{11}^{2-}$), an inorganic analogue of cyclopentadienide, was first prepared from the deboration of *o*-$C_2B_{10}H_{12}$ by Hawthorne and later introduced to transition metal chemistry.[4] Since then, a large number of metal complexes bearing dicarbollyl ligand have been prepared, which makes *nido*-$C_2B_9H_{11}^{2-}$ the most popular inorganic π ligand.[53,114] These metal complexes are finding many applications in catalysis,[5a,9,17,23,29,33,115] materials science,[116] medicine,[117] and extraction of f-block metal ions from nuclear wastes.[118] In fact, these metallacarboranes were generally prepared from the deboration/capitation (-B/+M) process as *o*-carboranes can be easily deborated by several inorganic or organic bases in high yield.[4,119-121] Our group recently reported the synthesis of carbon-bridged cyclopentadienyl-dicarbollyl ligand using piperidine as deboration reagent. Subsequent reactions with group 4 metal chlorides afforded the corresponding metal dicarbollides. The overall yield was not good.[28] On the other hand, an inverse +M/-B route for the synthesis of metal dicarbollide can be envisaged—synthesis of metal carboranyl complexes followed by the deboration with a proper reagent. Indeed, some examples were reported in literature such as deboration of $[\eta^5\text{-}(C_2B_{10}H_{10})C_9H_6]M(NMe_2)_3$ (M = Zr, Hf) and

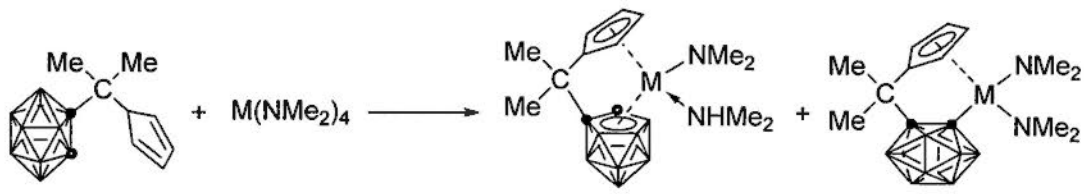
[σ:σ-($C_{13}H_8$)(^{i}Pr_2N)P(-O)($C_2B_{10}H_{10}$)]Zr(NMe_2)$_2$ by $HNMe_2$ to afford the corresponding metallacarboranes [η^5-(C_9H_6)$C_2B_9H_{10}$]M(NMe_2)$_2$($NHMe_2$) (M = Zr, Hf) and [η^1:η^5-($C_{13}H_9$)(^{i}Pr_2N)P(=O)($C_2B_9H_{10}$)]Zr(NMe_2)$_2$, respectively.[32,33] Another example for late transition metal complex is Ru(*o*-dppc)(*nido*-dppc)(H) (*o*-dppc = 1,2-(Ph_2P)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$, *nido*-dppc = 7,8-(Ph_2P)$_2$-7,8-*nido*-$C_2B_9H_{10}^-$), which was prepared from *trans*-Ru(*o*-dppc)$_2$(H)Cl in the presence of aniline.[122] This chapter reports the efficient synthesis of cyclopentadienyl-dicarbollyl zirconium amides by direct deboration of the corresponding cyclopentadienyl-carboranyl zirconium complexes using amines as deboration reagents. Their reactivities toward unsaturated molecules, Lewis acids and reducing reagents were studied.

5.2. Direct Deboration of Cyclopentadienyl-Carboranyl Metal Complexes by Amine

Our previous work showed that interaction of group 4 metal amides M(NMe_2)$_4$[123] (M = Zr, Hf) with Me_2C(C_5H_5)($C_2B_{10}H_{11}$) (**41**)[39] led to the clean formation of the corresponding constrained geometry metal complexes [η^5:σ-Me_2C(C_5H_4)($C_2B_{10}H_{10}$)]M(NMe_2)$_2$ (M = Zr, **1a**; M = Hf, **1b**).[35] However, when the reaction mixtures were stirred at room temperature for two days and then heated in refluxing toluene for 12 hrs, **1a** and [η^5:η^5-Me_2C(C_5H_4)($C_2B_9H_{10}$)]Zr(NMe_2)($NHMe_2$) (**42a**) were afforded in 63% and 33% isolated yields, and **1b** and [η^5:η^5-Me_2C(C_5H_4)($C_2B_9H_{10}$)]Hf(NMe_2)($NHMe_2$) (**42b**) in 43% and 53% isolated yields, respectively (Scheme 5.1). It was assumed that the

$HNMe_2$, generated in-situ from the amine elimination reaction, served as deboration reagent.

Scheme 5.1. Reaction of $M(NMe_2)_4$ with $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (**41**).



41 M = Zr, Hf M = Zr (**42a**), Hf (**42b**) M = Zr (**1a**), = Hf (**1b**)

Both **42a** and **42b** were fully characterized by ^1H, ^{13}C and ^{11}B NMR spectroscopy as well as elemental analyses. There were four doublets in the region 6.8 – 6.0 ppm assignable to the cyclopentadienyl protons and two singlets at high field attributable to the two diastereotopic methyl groups of the bridging CMe_2 unit, a broad singlet of cage C-*H* and two singlets of NMe_2 groups in the ^1H NMR spectra of **42a** and **42b**. Their ^{11}B NMR spectra exhibited a 1:2:2:2:1:1 pattern spanning a range from 2.1 to –22.5 ppm, which differs significantly from complexes **1a** and **1b**.

The molecular structure of **42a** was further confirmed by single-crystal X-ray analyses with a toluene of solvation (Figure 5.1). The central Zr atom is η^5-bound to the cyclopentadienyl ring, η^5-bound to the C_2B_3 open face, and coordinated to two nitrogen atoms in a distorted tetrahedral geometry. The corresponding bond distances are similar to those found in literature and listed in Table 5.1. The average Zr-C_{ring} distance of 2.530(5) Å in **42a** is comparable well to the 2.516(3) Å in $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$.[28] The average Zr-cage atom distance of 2.598(5) Å in **42a** is very close to the 2.585(3) Å in

$[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr'_2)(THF)$,[28] 2.523(5) Å in $[\eta^1:\eta^5\text{-}Me_2NCH_2(C_2B_9H_{10})]_2Zr$,[124] 2.538(5) Å in $[\eta^1:\eta^5\text{-}(C_5H_4N)CH_2(C_2B_9H_{10})]Zr(NMe_2)_2$,[125] 2.601(5) Å in $[\eta^1:\eta^5\text{-}('Pr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$[31], 2.544(6) Å in $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}Zr(CH_2SiMe_3)(THF)$,[21] 2.579(3) Å in *trans*-$[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$[29] and 2.554(8) Å in *trans*-$[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(O(CH_2)_3CH_3)(THF)$[29]

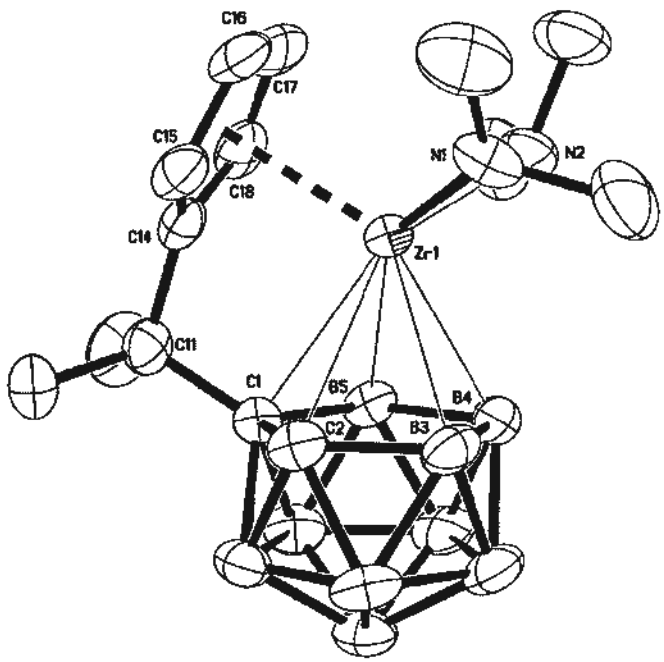
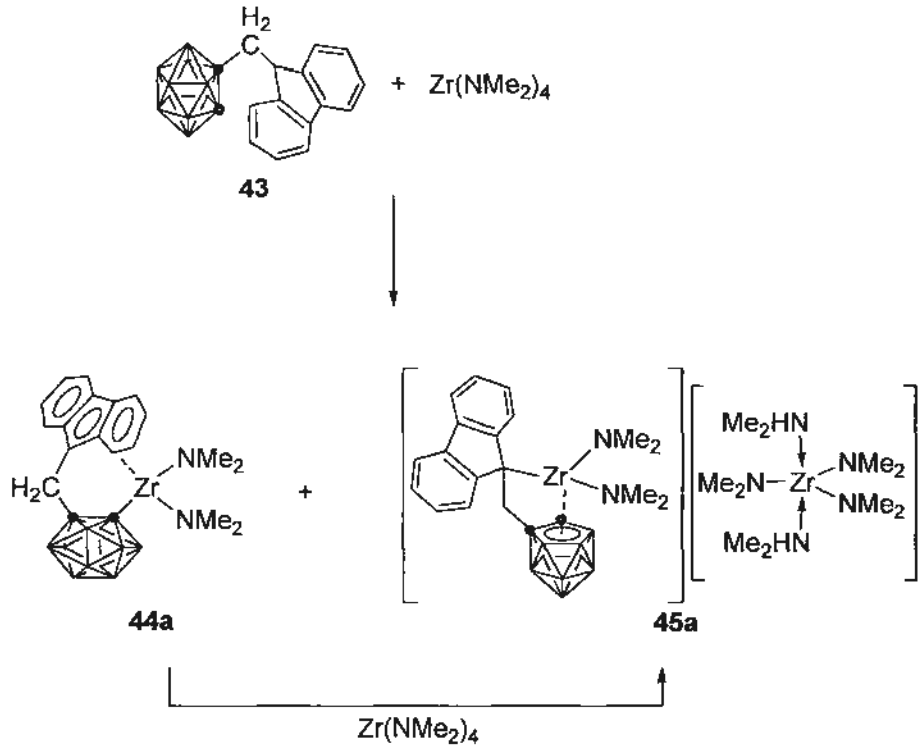


Figure 5.1. Molecular structure of $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (**42a**).

In a very similar manner, treatment of $H_2C(C_{13}H_9)(C_2B_{10}H_{11})$ (**43**)[126] with 1 equiv of $Zr(NMe_2)_4$ in toluene at room temperature afforded $[\eta^5:\sigma\text{-}H_2C(C_{13}H_8)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**44a**) in 25% isolated yield, $[\{\sigma:\eta^5\text{-}H_2C(C_{13}H_8)(C_2B_9H_{10})\}Zr(NMe_2)_2][Zr(NMe_2)_3(NHMe_2)_2]$ (**45a**) in 25%

isolated yield, and **43** in 27% yield (Scheme 5.2). The NMR tube reaction showed that complex **44a** was stable at 110 °C in C_6D_6, but was converted to **45a** in the presence of $Zr(NMe_2)_4$.

Scheme 5.2. Reaction of $Zr(NMe_2)_4$ with $H_2C(C_{13}H_9)(C_2B_{10}H_{11})$ (**43**).



Four multiplets in the region 7.47 to 6.83 ppm assignable to fluorenyl protons, a singlet at 3.70 ppm attributable to bridged CH_2 unit, and a singlet at 2.05 ppm corresponding to the NMe_2 group were observed in the ^1H NMR spectrum of **44a**. Its ^{11}B NMR spectrum exhibited a 1:3:2:2:2 pattern spanning a range from –1.4 to –11.0 ppm, which is similar to that of complex **1a**. These spectroscopic data were consistence with the formation of carbon-bridged fluorenyl-carboranyl zirconium amide. In contrast, the ^{11}B NMR spectrum of **45a** exhibited a 1:3:2:1:1:1 pattern spanning a range from –0.5 to –22.1 ppm, which differs significantly from that of

complex **44a**. These data were similar to those found in complexes **42a** and **42b**. Figures 5.2 and 5.3 show the molecular structures of complexes **44a** and **45a**, respectively. The central Zr atom in **44a** is η^5-bound to the cyclopentadienyl ring, σ-bound to the carboranyl ligand and two nitrogen atoms in a distorted tetrahedral geometry. Complex **45a** is an ionic species consisting of well-separated, alternating layers of discrete trigonal bipyramidal cations $[Zr(NMe_2)_3(NHMe_2)_2]^+$ and anions $[\{\sigma{:}\eta^5\text{-}H_2C(C_{13}H_8)(C_2B_9H_{10})\}Zr(NMe_2)_2]^-$. In the anion, the Zr atom is σ-bound to fluorenyl ring, η^5-bound to the dicarbollyl ligand, and σ-bound to two nitrogen atoms in a distorted tetrahedral geometry.

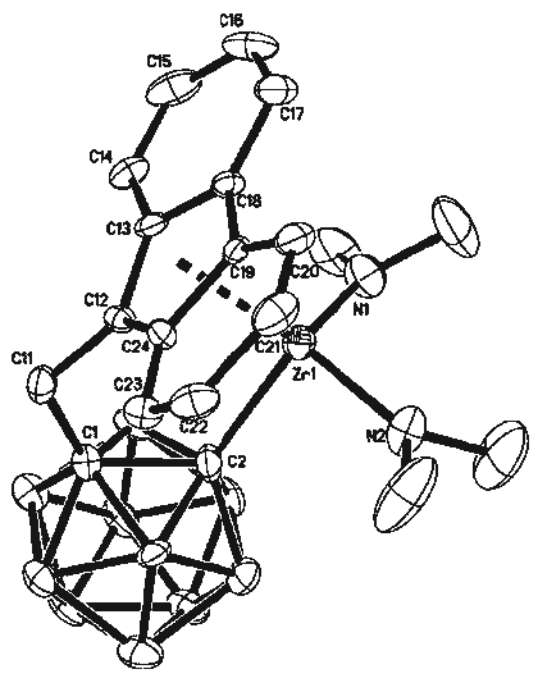


Figure 5.2. Molecular structure of $[\eta^5{:}\sigma\text{-}H_2C(C_{13}H_8)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**44a**), showing one of the two crystallographically independent molecules in the unit cell.

It is found that diamines DMEDA and DMPDA are very good deboration reagents for the carboranyl zirconium or hafnium amides **1a** or **1b**. Treatment of **1a** with an

excess amount of DMEDA in toluene at room temperature for 2 days gave $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)]$ (**46a**) as red crystals in 67% isolated yield. Similarly, reactions of **1a** or **1b** with DMPDA in toluene at refluxing temperature for 2 days also gave the group 4 metallacarboranes $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]M[\eta^2\text{-}N(Me)(CH_2)_3NH(Me)]$ (M = Zr, **47a**; M = Hf, **47b**) as a yellow solid in 73% and 43% isolated yields (Scheme 5.3). These reactions were closely monitored by ^{11}B NMR spectra and found to be completed within 2 days in quantitative yields with the formation of $HB[N(Me)(CH_2)_nN(Me)]$ (n = 1, 2). The deboration reaction using DMEDA as an agent is much faster than that using DMPDA. It is noted that direct reaction of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ ligand with DMEDA did not afford the deboration product even at 110 °C, indicating that the metal atom plays a role in the deboration process.[122,127]

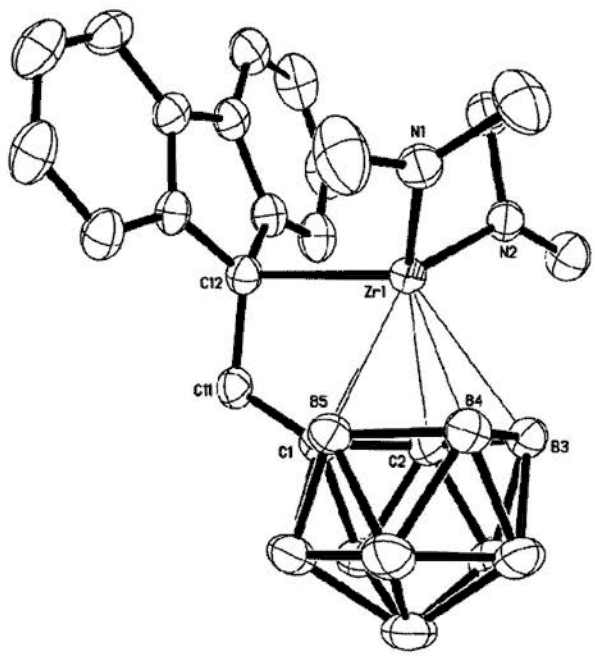


Figure 5.3. Molecular structure of the anion in

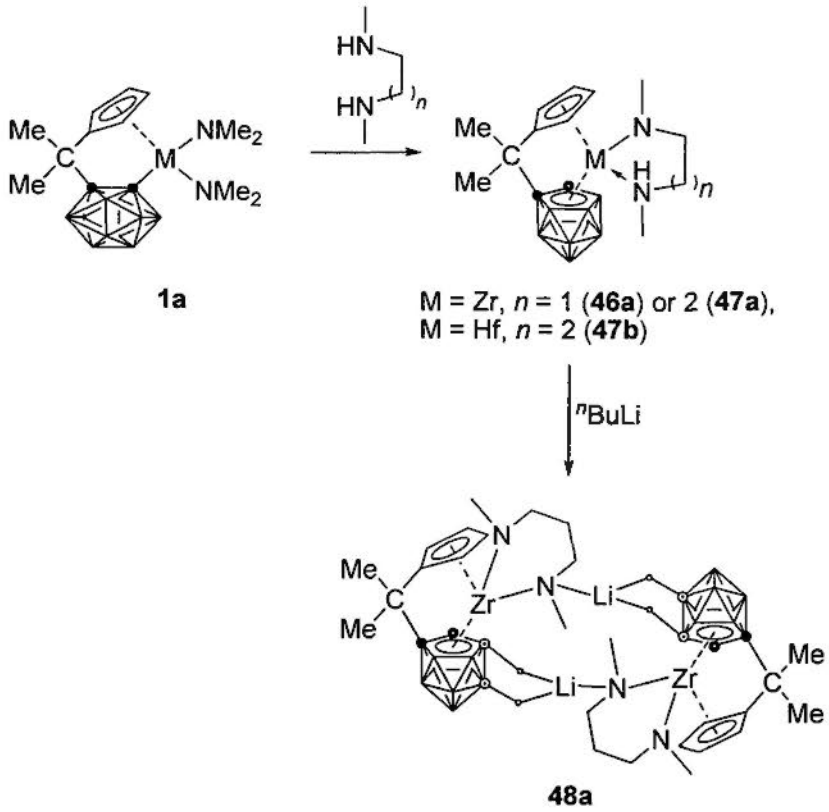
$[\{\sigma:\eta^5\text{-}H_2C(C_{13}H_8)(C_2B_9H_{10})\}Zr(NMe_2)_2][Zr(NMe_2)_3(NHMe_2)_2]$ (**45a**).

Table 1 Selected bond distances (Å)

Complex	av Zr-C_{ring}	av Zr-Cage	av Zr-N	Zr-C
42a	2.530(5)	2.598(5)	2.034(4)	
45a		2.535(4)	2.040(3)	2.440(4)
46a	2.545(8)	2.579(10)	2.020(6)	
48a	2.522(8)/2.544(8)	2.648(8)/2.670(8)	2.095(6)	
50a	2.588(4)	2.590(4)	2.041(3)	
53a	2.522(2)	2.553(2)	2.164(2)	
54a	2.519(4)	2.576(3)	2.047(2)	
$[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$[28]	2.516(3)	2.585(3)	2.055(2)	
$[\eta^1:\eta^5\text{-}Me_2NCH_2(C_2B_9H_{10})]_2Zr$[124]		2.523(5)		
$[\eta^1:\eta^5\text{-}(C_5H_4NCH_2(C_2B_9H_{10})]Zr(NMe_2)_2$[125]		2.538(5)	2.017(3)	
$[\eta^1:\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$[31]		2.601(5)	2.040(4)	

$[\eta^1{:}\sigma{:}\eta^5$-{MeN($CH_2$)$CH_2CH_2$}$C_2B_9H_{10}Zr(CH_2SiMe_3)(THF)$[21]		2.544(6)		2.242(6)
trans-$[\eta^5{:}\eta^5$-$Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$[29]	2.599(3)	2.579(3)	2.057(2)	
trans-$[\eta^5{:}\eta^5$-$Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(O(CH_2)_3CH_3)(THF)$[29]	2.580(7)	2.554(8)		
rac-$[Me_2Si(C_9H_6)_2]Zr(NMe_2)_2$[143]	2.610(2)		2.078(2)	
meso-$[Me_2C(C_9H_6)_2]ZrCl_2$[144]	2.515(4)/2.514(4)			
$[\eta^5{:}\sigma$-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$[34]	2.541(5)		2.016(8)	
$[\eta^5{:}\sigma$-$Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$[34]	2.521(8)		2.019(4)	

Scheme 5.3. Reaction of complexes **1a** and **1b** with DMEDA or DMPDA.



Four multiplets in the region 6.38 – 6.18 ppm assignable to the cyclopentadienyl protons and two singlets at 1.68 and 1.58 ppm attributable to the two diastereotopic methyl groups of the bridging CMe_2 unit, a broad singlet at 3.31 ppm of cage C-*H*, two singlets of NMe groups at 2.89 and 2.73 ppm and three multiplets of the methylene NCH_2 groups in the range 3.35 – 3.31 ppm were observed in the ^{1}H NMR spectrum of **46a**. Its ^{11}B NMR spectrum exhibited a 1:2:1:2:1:1:1 pattern spanning a range from –0.2 to –22.2 ppm, which differs significantly from its parent complex **1a**. The molecular structure of **46a** was further confirmed by single-crystal X-ray analyses and showed half $HNMe_2$ of solvation (Figure 5.4). The composition of **47a** and **47b** were characterized by various spectroscopic techniques and elemental analyses. Many attempts to grow single crystals suitable for X-ray analyses failed.

The ^{1}H and ^{13}C NMR data suggested that both **47a** and **47b** were a mixture of two regio-isomers in a molar ratio of about 1:1.6, which might result from asymmetric environments of dicarbollyl ligand and M-N bonds. To confirm the structure of **47a**, deprotonation of **47a** by 1.2 equiv of ^{n}BuLi in toluene afforded, after recrystallization, $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3N(Me)Li]_2$ (**48a**) as orange crystals in 62% isolated yield (Scheme 5.3). The molecular structure of **48a** was shown in Figure 5.5. As both nitrogen atoms are σ-bound to the Zr atom in **48a**, only one isomer was observed by NMR spectra.

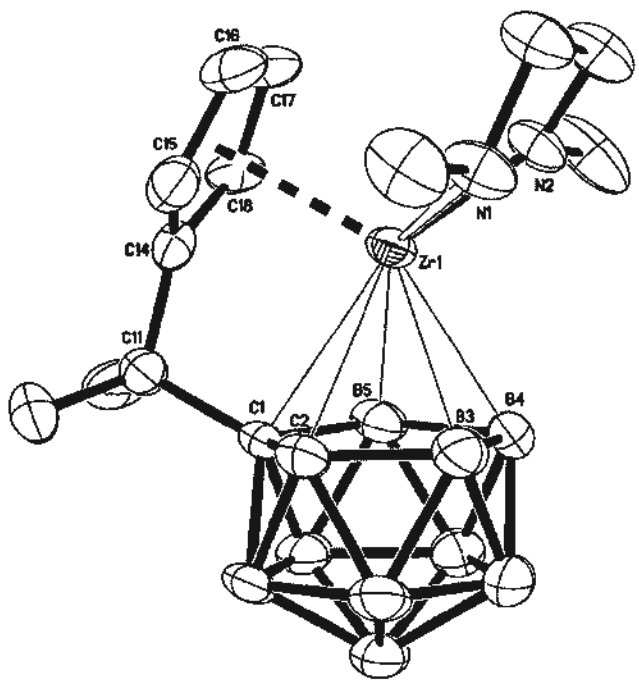


Figure 5.4. Molecular structure of

$[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)]$ (**46a**).

Similarly, the indenyl analogue $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**49a**)[34] reacted with an excess amount of DMPDA in toluene to give $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3NH(Me)]$ (**50a**) in quantitative

conversion as observed by ^{11}B NMR. This product was isolated as orange yellow crystals in 62% yield (Scheme 5.4). Its ^{1}H and ^{13}C NMR data suggested that complex **50a** is a mixture of isomers which might result from asymmetric environment of dicarbollyl ligand, indenyl ring and Zr-N bonds. The molecular structure of one of the isomers was confirmed by single-crystal X-ray analyses and shown in Figure 5.6. DMEDA also gave the corresponding deborated species as suggested by ^{11}B NMR.

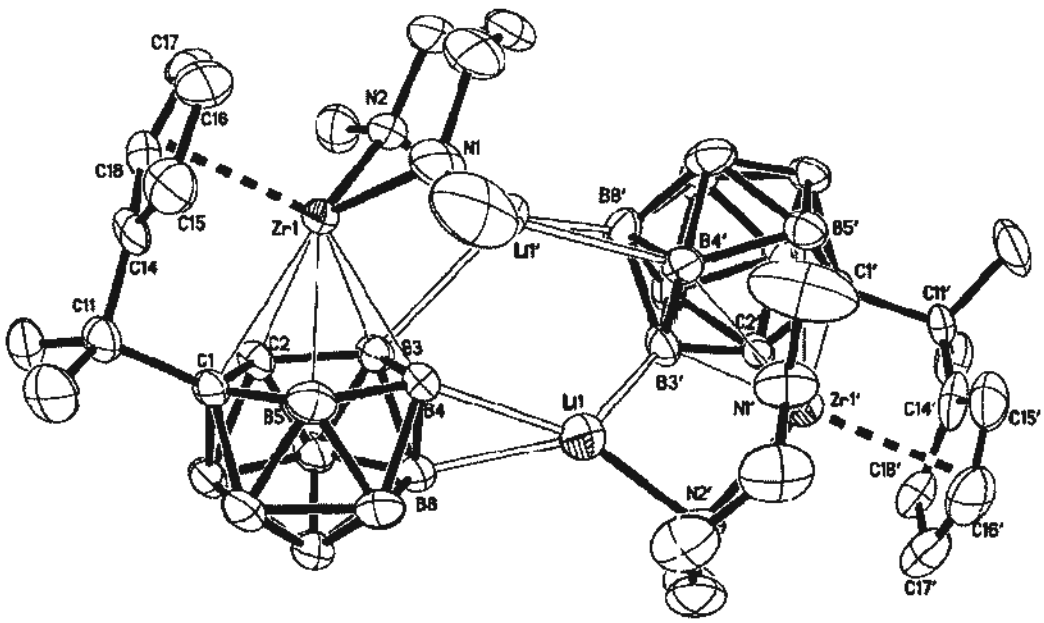
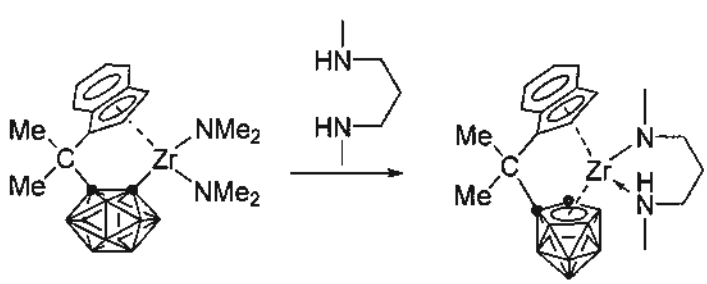


Figure 5.5. Molecular structure of

$\{[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2N(Me)Li]\}_2$ (**48a**).

Scheme 5.4. Reaction of complex **49a** with DMPDA.



49a **50a**

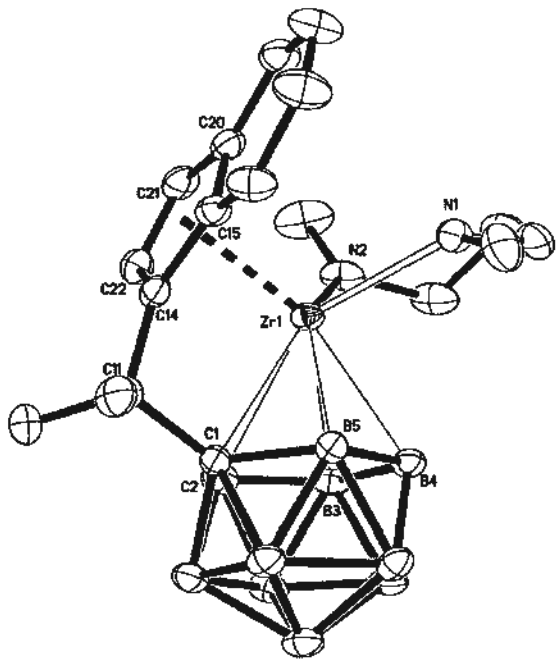


Figure 5.6. Molecular structure of

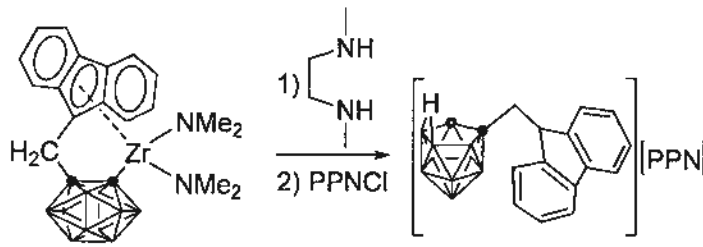
$[\eta^5{:}\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_3NH(Me)]$ (**50a**).

These zirconium dicarbollides bear similar structural features. In each case, the Zr atom is η^5-bound to both the cyclopentadienyl ring and the dicarbollyl ligand, η^2-bound to the diamine moiety in a distorted tetrahedral geometry. The corresponding bond distances are comparable to each other and similar to complex **42a** and those found in literature as listed in Table 5.1.

Reaction of $[\eta^5{:}\sigma\text{-}H_2C(C_{13}H_8)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**44a**) with 4 equiv of DMEDA resulted in the formation of deborated species $[H_2C(C_{13}H_9)(C_2B_9H_{11})]^-$ but not $[H_2C(C_{13}H_8)(C_2B_9H_{10})]^{3-}$ as indicated by ^{11}B NMR, which was hard to isolate. Further treatment with an equimolar amount of [PPN]Cl (PPN = bis(triphenylphosphine)iminium cation) in DME afforded, after recrystallization, $[H_2C(C_{13}H_9)(C_2B_9H_{11})][PPN]$ (**51**) as colorless crystals in 61% isolated yield (Scheme 5.5). The molecular structure of **51** was further confirmed by single-crystal

X-ray analyses and shown in Figure 5.7. The protonation of the fluorenyl group by the diamine is not surprising, which may be due to the less acidic and more sterically demanding fluorenyl group. Similar result was observed in the reaction of $Zr(NMe_2)_4$ with $(C_{13}H_9)(^iPr_2N)P(C_2B_{10}H_{11})$, in which the fluorenyl, and the cage C-H proton are not acidic enough to react with $Zr(NMe_2)_4$.[32]

Scheme 5.5. Reaction of complex **44a** with DMEDA.



44a **51**

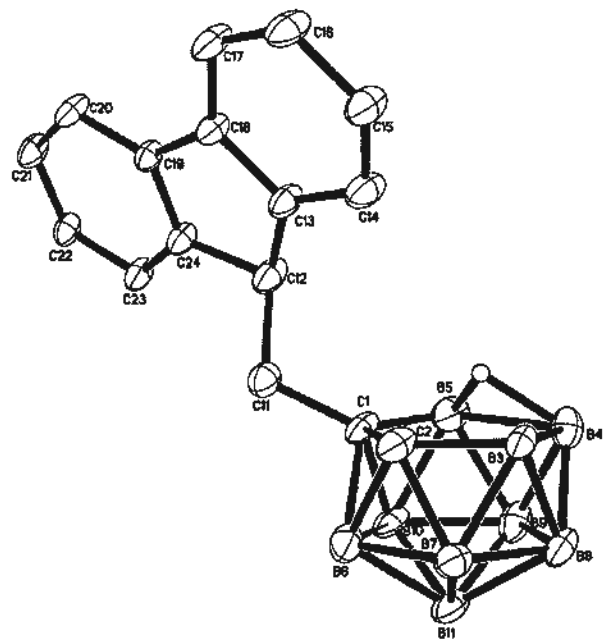
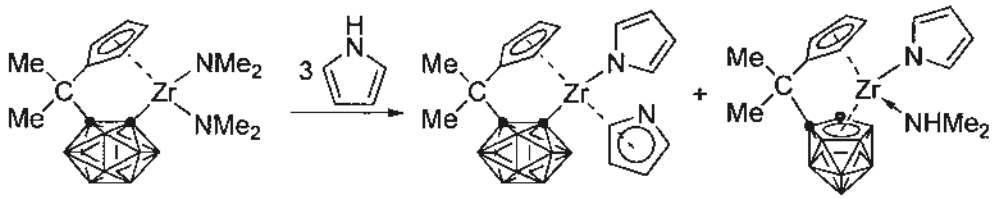


Figure 5.7. Molecular structure of the anion in $[H_2C(C_{13}H_9)(C_2B_9H_{11})][PPN]$ (**51**).

Complex **1a** also reacted with 3 equiv of pyrrole in toluene at room temperature to give $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NC_4H_4)_2$ (**52a**) and

$[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NC_4H_4)(NHMe_2)$ (**53a**) in 66% and 13% isolated yields, respectively (Scheme 5.6).

Scheme 5.6. Reaction of complex **1a** with pyrrole.



1a **52a** **53a**

They were fully characterized by various spectroscopic techniques as well as single-crystal X-ray analyses as shown in Figures 5.8 and 5.9, respectively. Both ^1H and ^{13}C NMR of **52a** indicated a symmetric species in solution, which would result from fast exchange between the η^1- and η^5-bound $NC_4H_4^-$ ligands. In addition to the resonances of the bridged ligand, two multiplets in the region 7.57 – 6.51 ppm corresponding to the pyrrole were observed in the ^1H NMR spectrum of **52a**. The solid-state structure of **52a** showed half toluene of solvation. It shows an asymmetric coordination of two pyrroles, in which one is η^1- and the other is η^5-bound to the Zr atom. The ^{11}B NMR spectrum of **52a** exhibited a 3:2:5 pattern spanning a range from –3.8 to –8.5 ppm, which is very similar to that observed in carbon-bridged cyclopentadienyl carboranyl group 4 metal complexes. In contrast, the ^{11}B NMR spectrum of **53a** exhibited a 1:2:1:1:2:1:1 pattern spanning a range from 5.0 to -17.6 ppm, which differs significantly from that of complex **52a**, but is comparable well to other dicarbollyl metal complexes. The coordination environment of **53a** is very similar to that of **42a**. The Zr-N(2)/N(1) distances of 2.164(2)/2.414(2) Å in **53a**

indicate that N(2) is an amido nitrogen and N(1) is an amino nitrogen. The deborated species **53a** was probably generated by direct deboration of **52a** by dimethylamine, but the yield was very low.

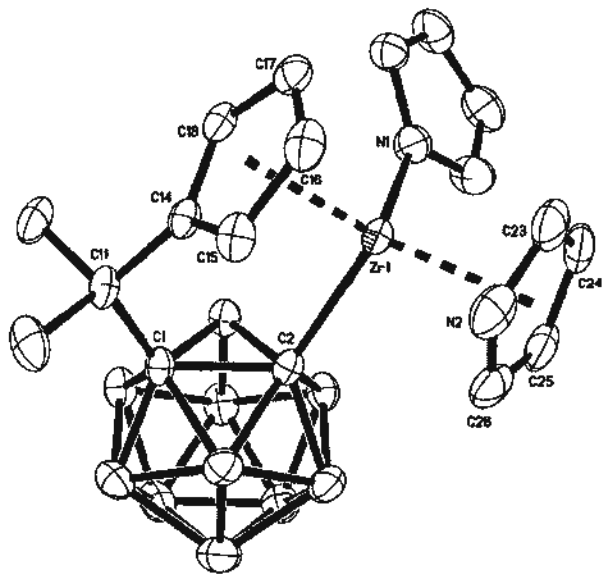


Figure 5.8. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NC_4H_4)_2$ (**52a**).

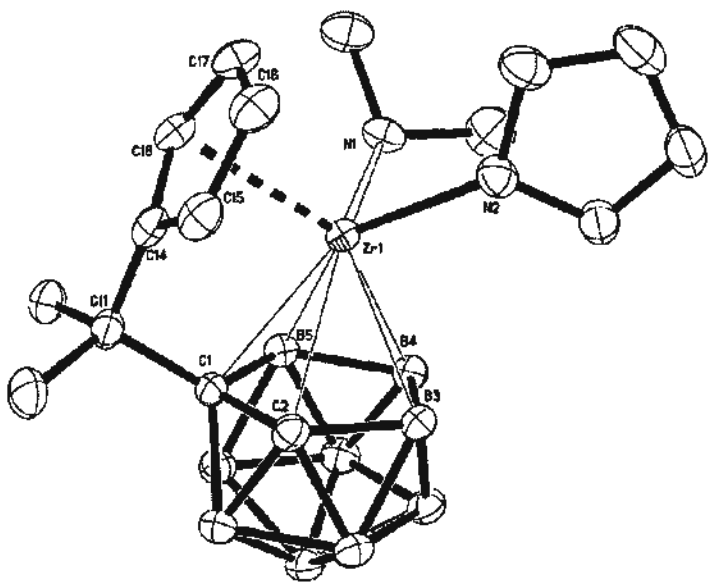
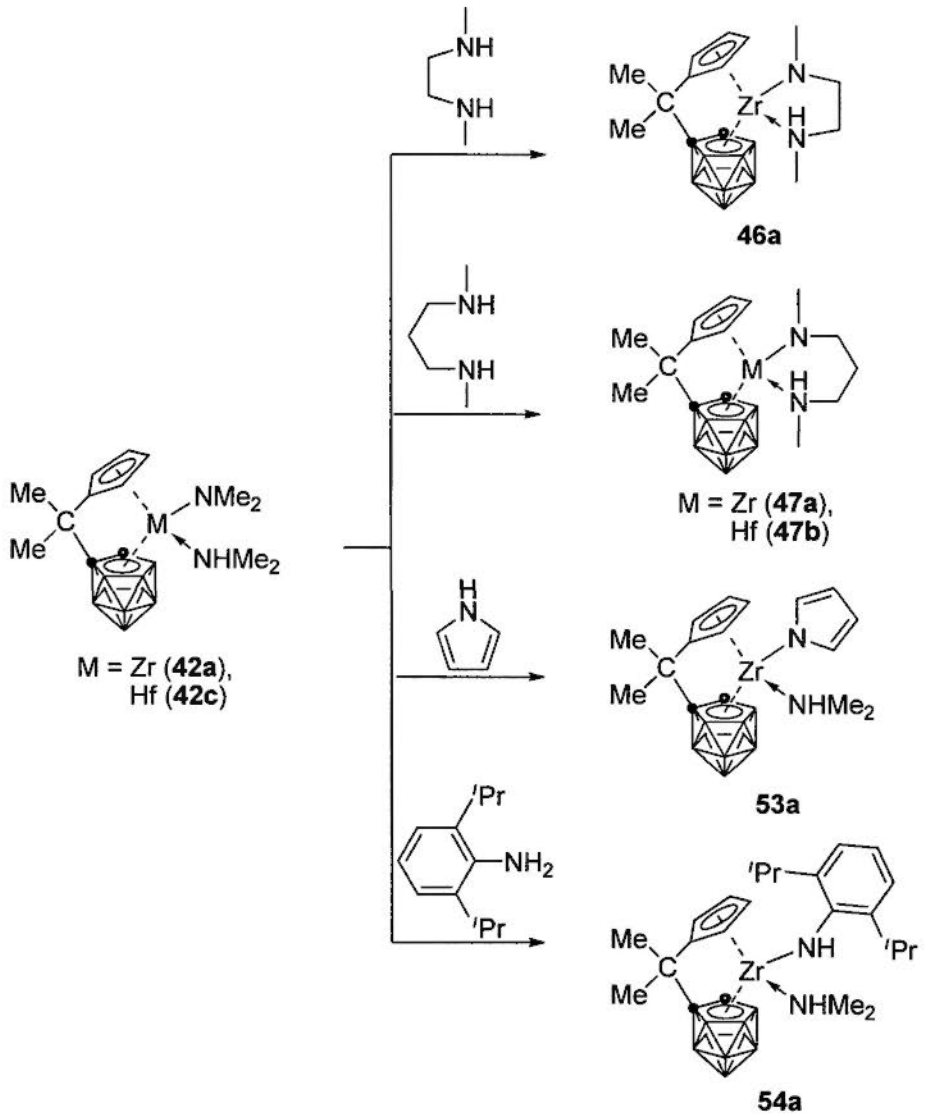


Figure 5.9. Molecular structure of $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NC_4H_4)(NHMe_2)$ (**53a**).

5.3. Amine exchange reaction

Scheme 5.7. Reaction of complexes **42a** and **42b** with amines.



A series of carbon-bridged cyclopentadienyl-dicarbollyl metal amides can be prepared in moderate to good yields by interaction of **42a** or **42b** with amines. The reaction of **42a** or **42b** with DMEDA and DMPDA in toluene afforded **46a** as red crystals in 86% isolated yields, and **47a** and **47b** as a yellow solid in 82% and 76% isolated yields, respectively. Interaction of **42a** with pyrrole or 2,6-diisopropylaniline afforded amine exchange product **53a** as yellow crystals in 90% isolated yield, or

[η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr[NH(2,6-$^i Pr_2C_6H_3$)](NHMe$_2$) (**54a**) as yellow crystals in 85% isolated yield, respectively (Scheme 5.7). The molecular structure of **54a** was confirmed by single-crystal X-ray analyses and shown in Figure 5.10. The central Zr atom is η^5-bound to both the cyclopentadienyl ring and the dicarbollyl ligand, and coordinated to two nitrogen atoms in a distorted tetrahedral geometry. A much shorter Zr-N(2) distance of 2.047(2) Å over the Zr-N(1) distance of 2.392(2) Å and the planar geometry of N(2) suggest that N(2) is the amido nitrogen and N(1) is the amino nitrogen. The ^{1}H, ^{13}C and ^{11}B NMR suggested that complex **54a** was formally in equilibrium with **42a** in pyridine, indicating a proton exchange between two nitrogen atoms.

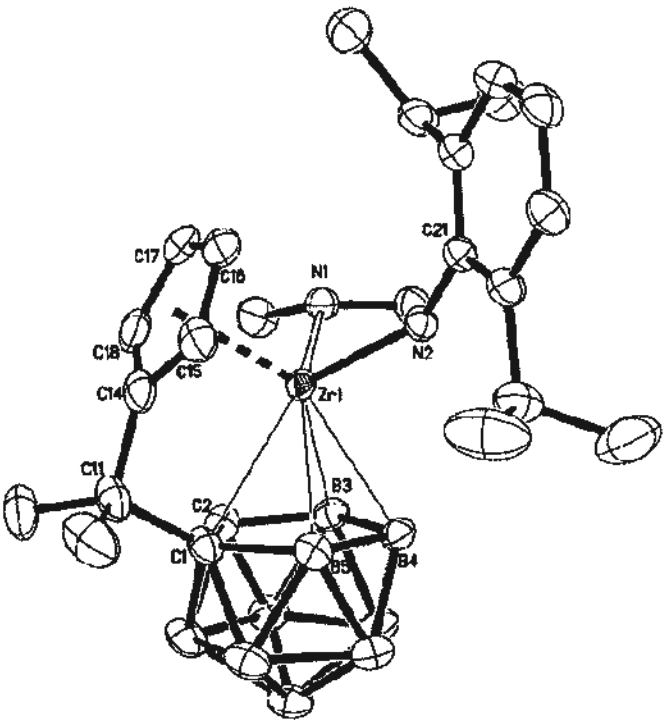


Figure 5.10. Molecular structure of

[η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr[NH(2,6-$^i Pr_2C_6H_3$)](NHMe$_2$) (**54a**).

5.4. Reactivity of Cyclopentadienyl-Dicarbollyl Group 4 Metal Amides

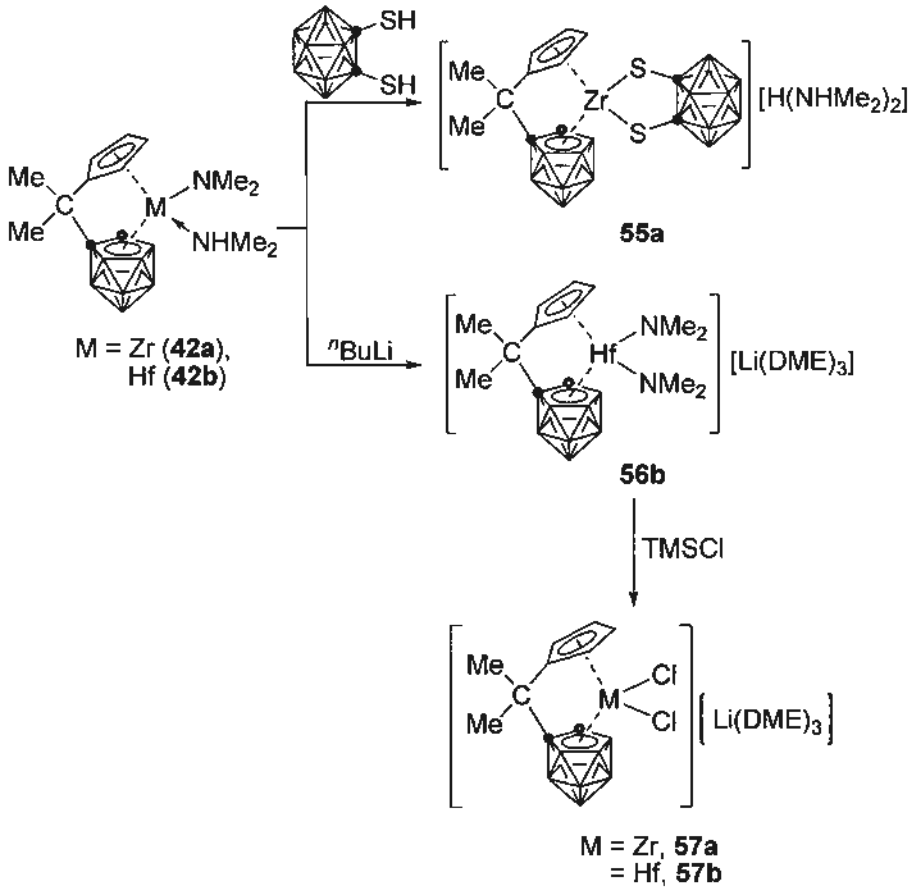
Group 4 metal alkyl or amide species are active toward various reagents. The bent-metallocene η^5-dicarbollide species of general type $(\eta^5\text{-}C_2B_9H_{11})(C_5R_5)MR$ and $\eta^5\text{-}C_2B_9H_{11})(C_5R_5)M(R)(L)$ (M = Ti, Zr, Hf; L = labile ligand) can undergo a variety of reactions, including ligand exchange, ligand C-H bond activation of electrophilic metal alkyls, or insertion of unsaturated molecules like alkene, alkynes, etc..[5a,9-13] The mono-dicarbollide amide complexes $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(NHEt_2)$ which undergoes facile ligand substitution reaction with THF or 4-picoline, and react with $[H_2NEt_2]Cl$, yielding group 4 metal dichloride species $(\eta^5\text{-}C_2B_9H_{11})ZrCl_2(NHEt_2)_2$.[15] Moreover, constrained-geometry titanacarborane complex $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti(NR_2)$ (R = Me, Et) reacted with various unsaturated molecules to afford Ti-N mono-insertion products, and can catalyze guanylation of amines.[24,25]

5.4.1. Acid-Base Reaction

Reaction of **42a** with 1 equiv of $(HS)_2C_2B_{10}H_{10}$ in toluene/benzene afforded $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr\{\eta^2\text{-}S_2C_2B_{10}H_{10}\}][H(HNMe_2)_2]$ (**55a**) as orange crystals in 70% isolated yield (Scheme 5.8). Four multiplets in the region 7.52 – 6.93 ppm assignable to the cyclopentadienyl protons and two singlets at high field attributable to the two diastereotopic methyl groups of the bridging CMe_2 unit, a broad singlet at 2.92 ppm corresponding to the cage C-*H*, a singlet at 2.66 ppm of NMe_2 group were observed in the ^{1}H NMR spectrum. The unique C_{cage}-S resonance at 98.7 ppm was also observed in its ^{13}C NMR spectrum. The ^{11}B NMR spectrum

exhibited a 1:2:5:10:1 pattern spanning a range from 7.8 to –20.4 ppm, in which signal overlapping of two carboranes was observed.

Scheme 5.8. Reaction of **42a** and **42b** with base and acid.



The molecular structure of **55a** was further confirmed by single-crystal X-ray analyses and showed a benzene of solvation. As shown in Figure 5.11, the central Zr atom is η^5-bound to both the cyclopentadienyl ring and the dicarbollyl ligand, η^2-bound to two sulphur atoms in a distorted tetrahedral geometry. The charge is then compensated with a $[H(HNMe_2)_2]^+$ cation. The Zr-C_{ring} and Zr-C_{cage} distances of 2.521(3) Å and 2.538(3) Å are comparable well to its parent complex **42a** and others in literature.[21,28,29,31,34,124,125,143,144] The average Zr-S bond distance of 2.610(2) Å is

much longer than the 2.518(2) Å in $Cp^*_2Zr(SH)_2$[105a] and 2.513(3) Å in $Cp^{tt}_2Zr(\mu^3\text{-}S)_2[Ir(CO)_2][Rh(CO)_2]$[105c] ($Cp^{tt} = \eta^5\text{-}1,3\text{-}{}^t Bu_2C_5H_3$), which may be due to the negatively charged Zr center.

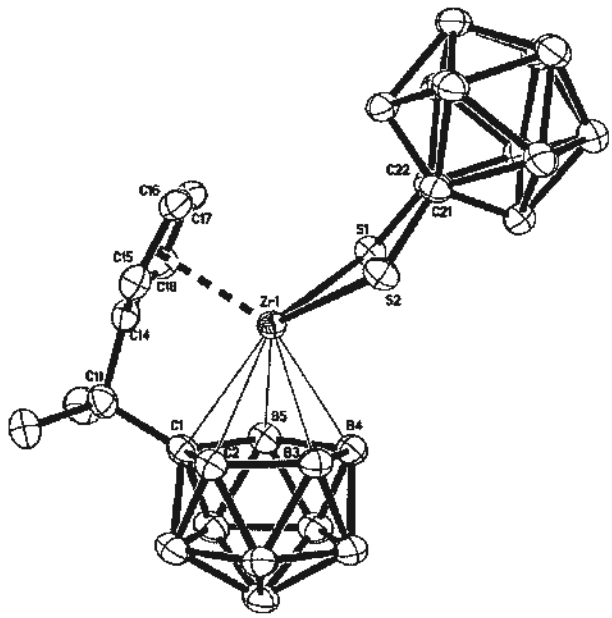


Figure 5.11. Molecular structure of the anion in $[\{\eta^5\text{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr\{\eta^2\text{-}S_2C_2B_{10}H_{10}\}][H(HNMe_2)_2]$ (**55**).

Treatment of **42b** with 1.2 equiv of ^{n}BuLi in DME afforded $[\{\eta^5\text{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Hf(NMe_2)_2][Li(DME)_3]$ (**56b**) as colorless crystals in 89% isolated yield. In addition to the peaks of the bridging ligand, two singlets at 3.39 and 3.36 ppm attributable to NMe_2 groups, and two singlets of DME molecules were observed in the ^{1}H NMR spectrum of **56b**. Despite of poor resolution of single-crystal X-ray analyses for **56b**, the preliminary diffraction results together with NMR and elemental analyses data are enough to confirm the connectivity pattern for **56b** (Figure 5.12). Further treatment of **56b** with 4 equiv of TMSCl in toluene gave hafnium dichloride species $[\{\eta^5\text{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}HfCl_2]$

[Li(DME)$_3$] (**57b**) as a white solid in 76% isolated yield (Scheme 5.8).

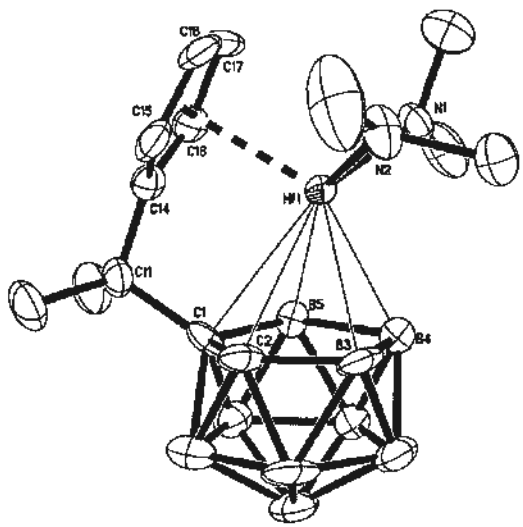


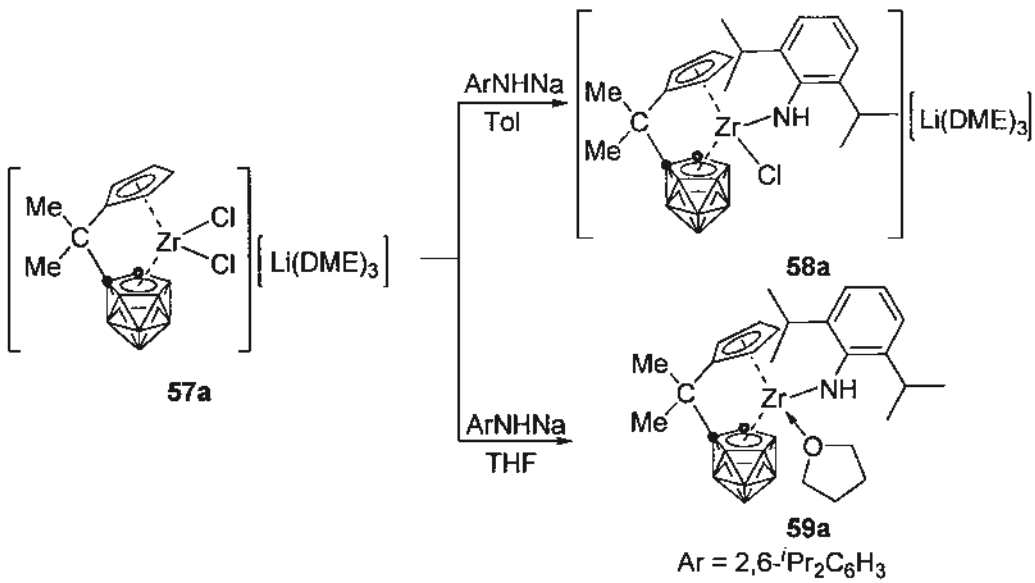
Figure 5.12. Molecular structure of the anion in

[{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$Hf(NMe_2)_2$][Li(DME)$_3$] (**56**).

Similarly, deprotonation of **42a** with ^{n}BuLi followed by treatment of 4 equiv of TMSCl in toluene afforded zirconium dichloride species [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][Li(DME)$_3$] (**57a**) as a white solid in 77% yield. This dichloro species **57a** can react with 2,6-^{i}Pr$_2$C$_6$H$_3$NHNa in toluene or THF to give [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Zr(2,6-^{i}Pr$_2C_6H_3$NH)Cl][Li(DME)$_3$] (**58a**) or [$\eta^5$:$\eta^5$-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr(2,6-^{i}Pr$_2C_6H_3$NH)(THF) (**59a**) in 79% and 63% isolated yields, respectively (Scheme 5.9). Single-crystal X-ray analyses revealed that **58a** has an ionic structure, consisting of well-separated, alternating layers of discrete tetrahedral anion [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Zr(2,6-^{i}Pr$_2C_6H_3$NH)Cl]$^-$, and octahedral cations [Li(DME)$_3$]$^+$. In the anion, the Zr atom is η^5-bound to both the cyclopentadienyl ring and the dicarbollyl ligand, σ-bound to a chlorine atom and an amido group in a distorted tetrahedral geometry (Figure 5.13). The molecular

structure of complex **59a** was confirmed by single-crystal X-ray analyses and showed a toluene of solvation. The coordination environment of Zr atom in **59a** is very similar to that found in **58a**, except that one chlorine atom was replaced by a THF molecule (Figure 5.14).

Scheme 5.9. Reaction of complex **57a** with ArNHNa.



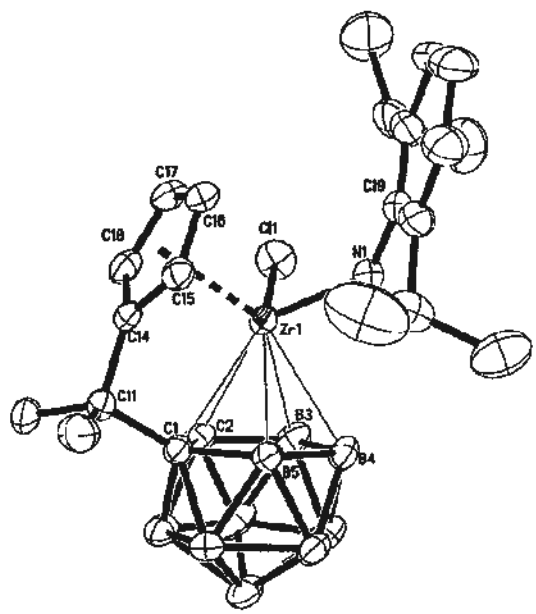


Figure 5.13. Molecular structure of the anion in

$[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr(2,6\text{-}{}^iPr_2C_6H_3NH)Cl][Li(DME)_3]$ (**58**).

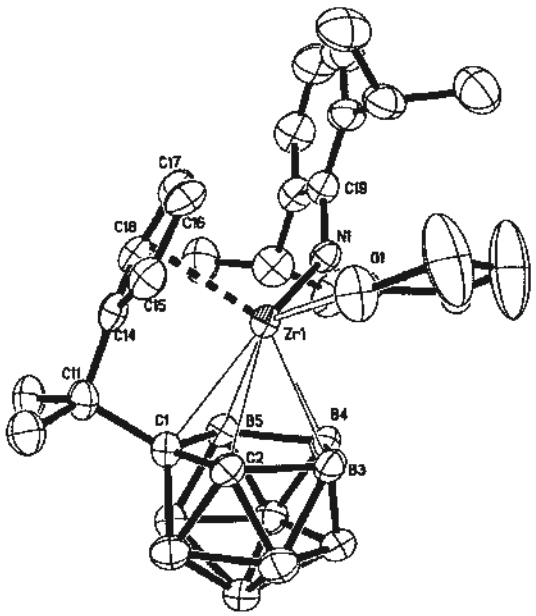


Figure 5.14. Molecular structure of

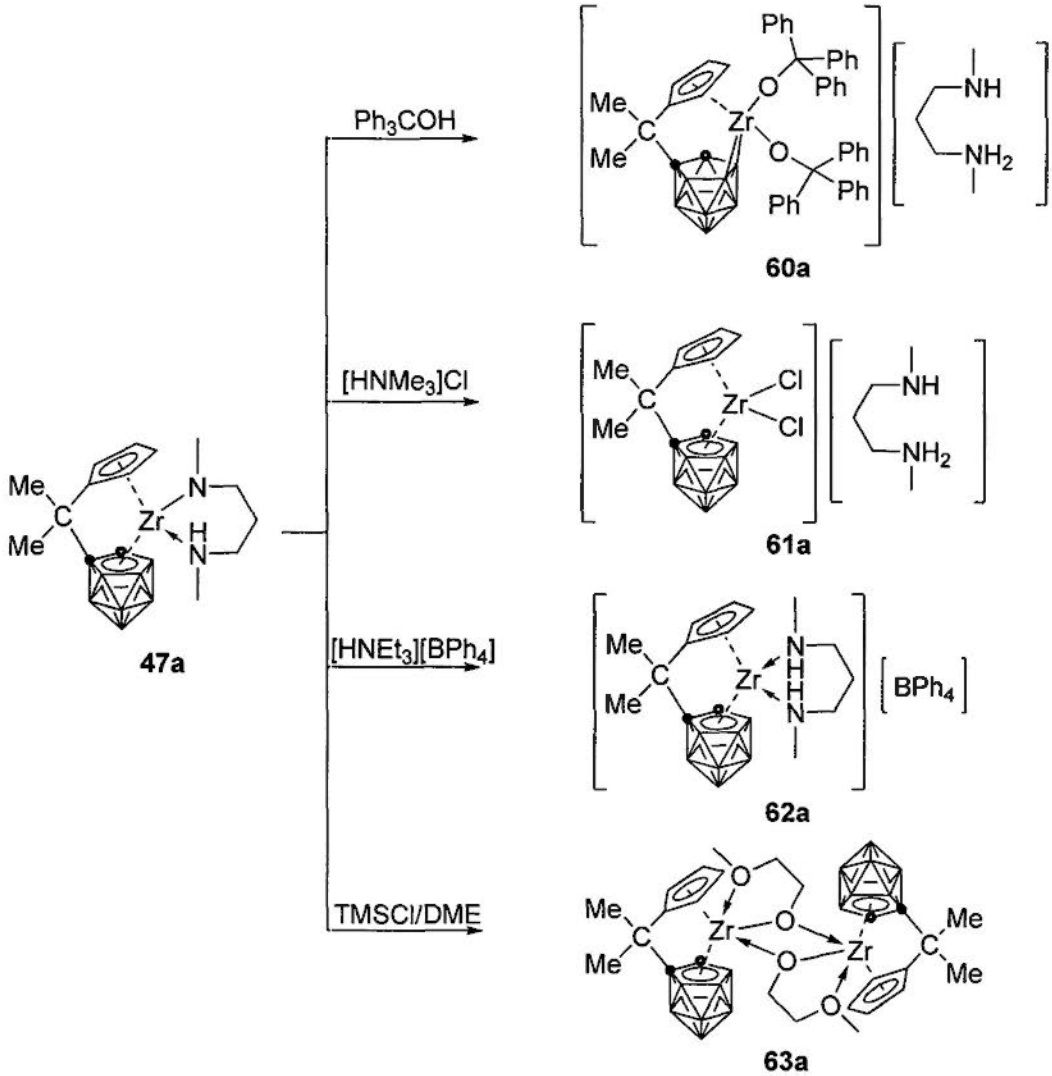
$[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(2,6\text{-}{}^iPr_2C_6H_3NH)(THF)$ (**59**).

On the other hand, interaction of **47a** with Ph_3COH, $[HNMe_3]Cl$ and $[HNMe_3][BPh_4]$ in toluene at room temperature afforded acid-base reaction products (Scheme 5.10). They were fully characterized by various spectroscopic techniques as well as single-crystal X-ray analyses.

$[\{\eta^5{:}\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr(OCPh_3)_2][HN(Me)(CH_2)_3N(Me)H_2]$ (**60a**) was isolated as colorless crystals in 68% yield from the reaction of **47a** with Ph_3COH in toluene at room temperature for 2 days (Scheme 5.10). Only dioxide species **60a** was obtained in the presence of 1 or 2 equiv of Ph_3COH. The unique Ph_3CO resonance at 107.1 ppm was observed in the ^{13}C NMR spectrum. As shown in Figure 5.15, **60a** is an ionic species with a THF of solvation, in which the anion part adopts a distorted-tetrahedral geometry coordinated by one η^5-cyclopentadienyl ring, one unsymmetrical η^2-dicarbollyl ligand and two oxygen atoms. The charge is

compensated by the $[H_2N(Me)(CH_2)_3NH(Me)]^+$ cation. The elongated Zr-C(1)/C(2)/B(3) distances of 3.055/3.215/2.891 Å is perhaps due to the presence of the two bulky Ph_3CO groups, thus the coordination of dicarbollyl ligand is changed from η^5 to η^2.

Scheme 5.10. Reaction of complex **47a** with acids



Attempt to obtain the neutral cyclopentadienyl-dicarbollyl zirconium monochloride species failed. Treatment of **47a** with 2 equiv of $[HNMe_3]Cl$ in toluene afforded $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][HN(Me)(CH_2)_3N(Me)H_2]$ (**61a**) as

colorless crystals in 59% isolated yield. Similar to the previous reaction, the dichloride species was always isolated in the presence of 1 or 2 equiv of $[HNMe_3]Cl$. Single-crystal X-ray analyses revealed that **61a** is an ionic species consisting of well-separated, alternating layers of discrete anion $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2]^-$ and cations $[H_2N(Me)(CH_2)_3NH(Me)]^+$. In the anion, the Zr atom is η^5-bound to both of the cyclopentadienyl ring and the dicarbollyl ligand, σ-bound to two terminal chlorine atoms in a distorted tetrahedral geometry (Figure 5.16).

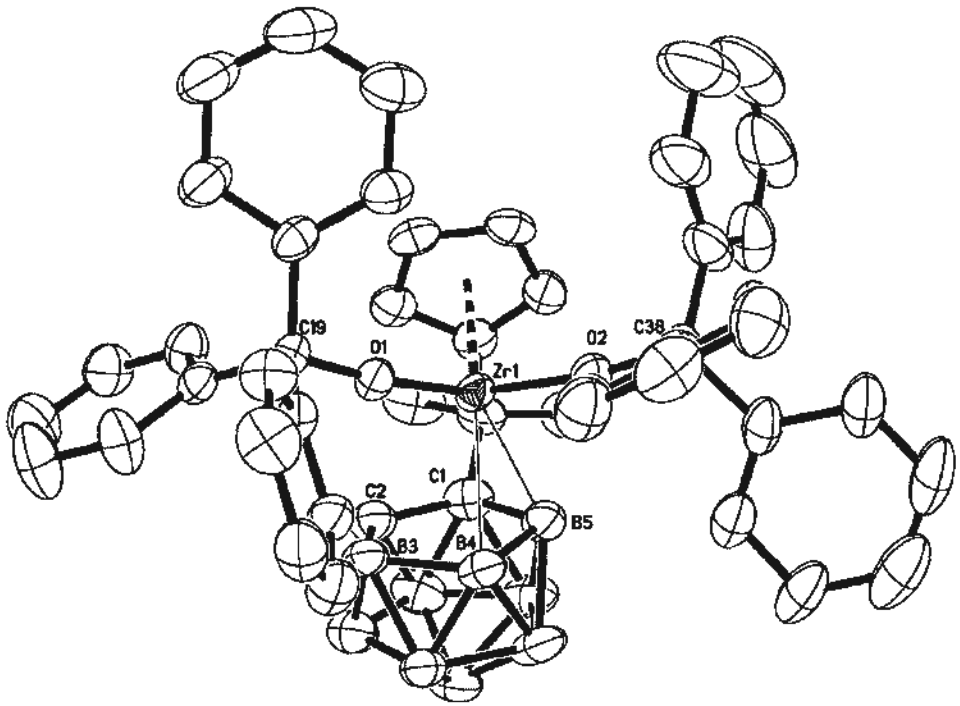


Figure 5.15. Molecular structure of the anion in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr(OCPh_3)_2][HN(Me)(CH_2)_3N(Me)H_2]$ (**60a**).

Reaction of **47a** with $[HNEt_3][BPh_4]$ in toluene afforded, after recrystallization in DME, $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr\{\eta^2\text{-}NH(Me)(CH_2)_3NH(Me)\}][B(C_6H_5)_4]$

(**62a**) as yellow crystals in 56% isolated yield (Scheme 5.10). In addition to the resonances of the bridged ligand, the ^{1}H NMR spectrum showed three multiplets in the region 8.06 to 7.12 ppm corresponding to the four phenyl rings, one triplet at 3.00 ppm assignable to the NCH_2 unit, and one singlet at 2.50 ppm attributable to the NMe groups. A pattern of 1:1:1:6:1 was observed in its ^{11}B NMR spectrum. The ionic nature of **62a** was further confirmed by a single-crystal X-ray diffraction study and showed a DME of solvation. As shown in Figure 5.17, the geometry of the anion is similar to that found in **61a**, with the two Cl atoms being replaced by two nitrogen atoms.

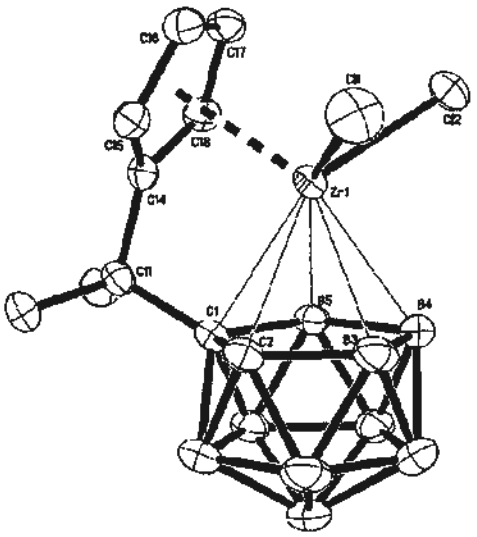


Figure 5.16. Molecular structure of the anion in

$[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][HN(Me)(CH_2)_3N(Me)H_2]$ (**61a**).

Reaction of **47b** with excess TMSCl in toluene at room temperature gave, after recrystallization from DME, an unexpected C-O bond cleavage product $\{[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\mu:\eta^1\text{-}O(CH_2)_2OMe]\}_2$ (**63a**) as colorless crystals in 21% isolated yield (Scheme 5.10). In addition to the peaks derived from the bridged

ligand, two multiplets in the region 4.60 to 3.60 ppm assignable to the OCH_2 units, and one singlet at 3.33 ppm attributable to the OMe group were observed in the ^1H NMR spectrum of **63a**. Its ^{11}B NMR spectrum showed a 1:1:2:1:2:1:1 pattern. The molecular structure of **63a** was further confirmed by single-crystal X-ray analyses and showed a DME of solvation. As shown in Figure 5.18, complex **63a** is a dimeric species bearing a bent sandwich structural motif, in which each Zr atom is η^5-bound to both the cyclopentadienyl and the dicarbollyl ligand, and three oxygen atoms in a distorted trigonal bipyramidal geometry. A possible reaction pathway for the formation of **63a** is shown in Scheme 5.11. Replacement of NMe by Cl, followed by σ-bond metathesis and dimerization, gives **63a**. The C-O bond activation by group 4 metallacarborane amides is known.[21,26]

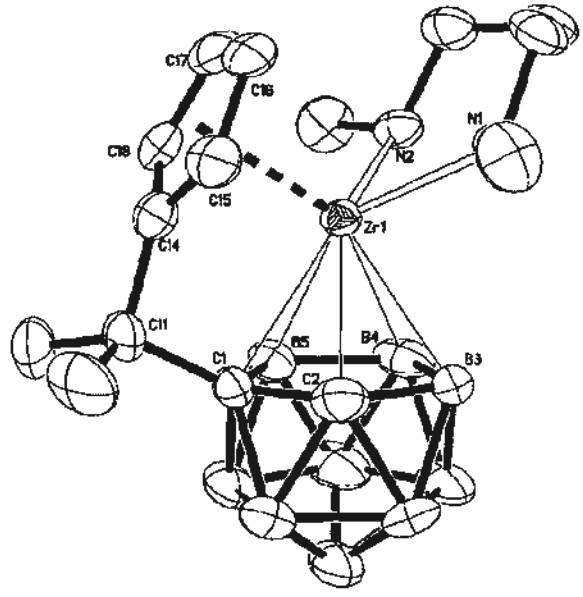


Figure 5.17. Molecular structure of the cation in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Zr\{\eta^2\text{-}NH(Me)(CH_2)_3NH(Me)\}][B(C_6H_5)_4]$ (**62a**), showing one of the two crystallographically independent molecules in the unit cell.

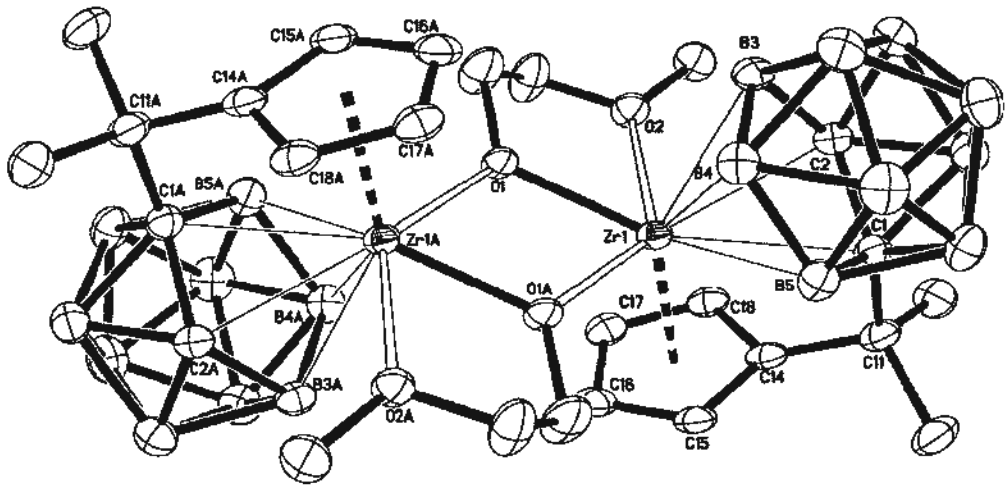
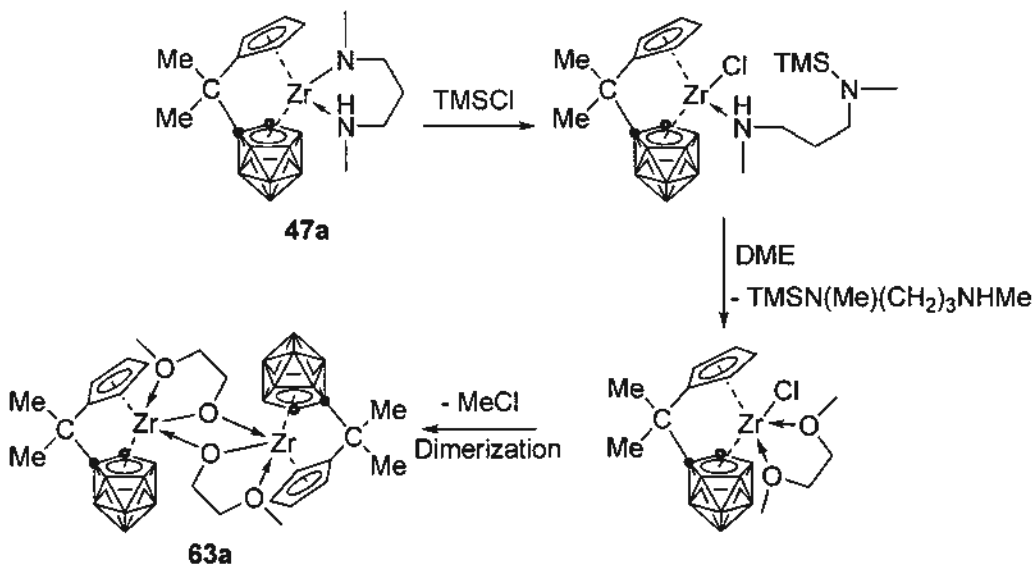


Figure 5.18. Molecular structure of

$\{[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\mu{:}\eta^1\text{-}O(CH_2)_2OMe]\}_2$ (**63a**).

Scheme 5.11. Proposed mechanism for the formation of complex **63a**.

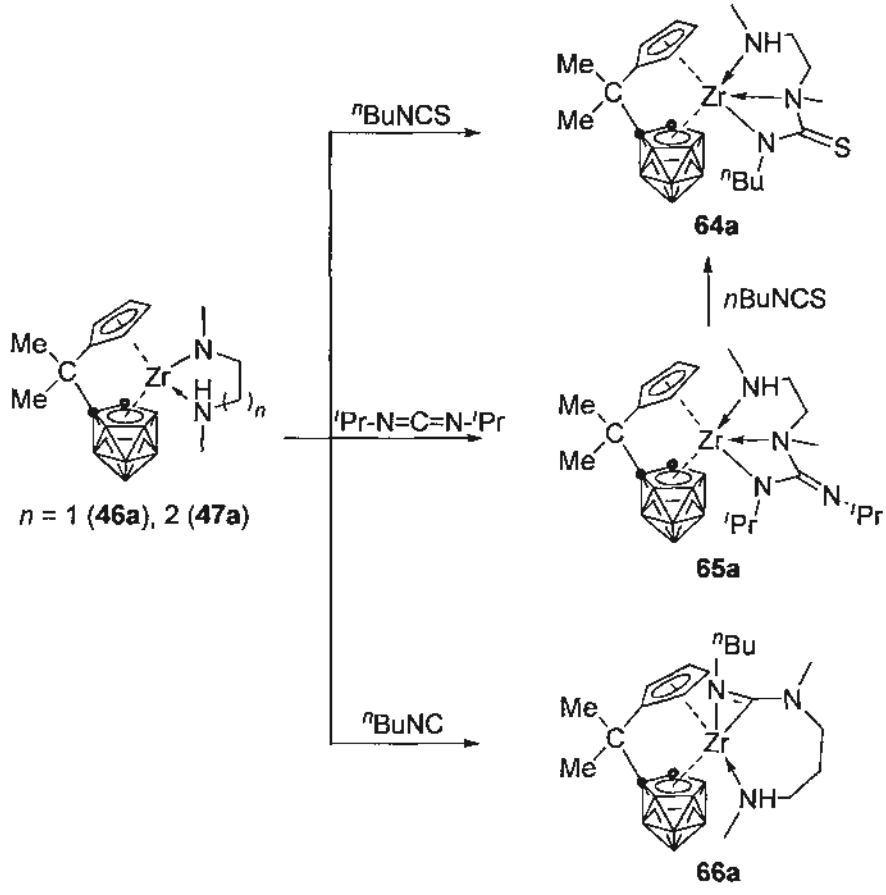


5.4.2. Insertion Reaction

Like other group 4 metal amide species, complexes **46a** and **47a** reacted with polar unsaturated molecules to afford mono-insertion products (Scheme 5.12). Treatment of **46a** with 1 equiv of ^{n}BuNCS in toluene afforded mono-insertion species $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta{:}\eta{:}\eta\text{-}NH(Me)(CH_2)_2N(Me)C(=S)N^nBu]$

(**64a**) as colorless crystals in 58% isolated yield. The ^{13}C NMR spectrum exhibited a unique resonance of N=*C*-S at about 190 ppm. Its ^{11}B NMR showed a 1:1:2:1:3:1 pattern spanning a range from 3.1 to –17.2 ppm. The molecular structure of **64a** is confirmed by single-crystal X-ray analyses and shown in Figure 5.19. The central Zr atom was η^5-bound to both the cyclopentadienyl ring and the dicarbollyl ligand and coordinated to three nitrogen atoms in a distorted trigonal bipyramidal geometry. A much shorter Zr-N(1) distance of 2.273(4) Å over the Zr-N(3) distance of 2.416(4) Å and the planar geometry of N(1) suggest that N(1) is the amido nitrogen and N(3) is the amino nitrogen.

Scheme 5.12. Reaction of **46a** or **47a** with unsaturated molecules.



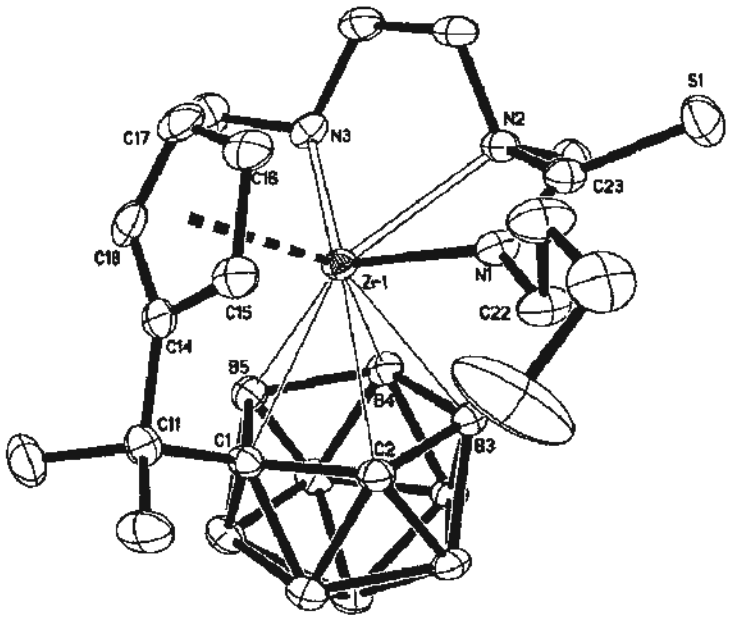


Figure 5.19. Molecular structure of

$[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta{:}\eta{:}\eta\text{-}NH(Me)(CH_2)_2N(Me)C(=S)N^nBu]$ (**64a**).

An equimolar reaction of **46a** with DIC in toluene at room temperature gave $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta{:}\eta{:}\eta\text{-}NH(Me)(CH_2)_2N(Me)C(=N^iPr)N^iPr]$ (**65a**) in 58% isolated yield. The ^1H and ^{13}C NMR spectra showed that **65a** is a mixture of two regioisomers in a molar ratio of ~1:1.2, which might result from asymmetric environment of dicarbollyl ligand and Zr-N bonds.

The molecular structure of one of the regioisomers was confirmed by single-crystal X-ray analyses and showed half toluene of solvation. As shown in Figure 5.20, the coordination environment in **65a** is very similar to that in complex **64a**. As complex **65a** is a carbodiimide insertion product, we wonder if it has similar reactivities in the deinsertion reaction of carbodiimide in the carboranyl complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NR)NR]$ (R = ^{i}Pr (**9a**),

Cy (**9a'**)). Reaction of **65a** with excess ^{n}BuNCS at room temperature showed the appearance of free DIC as evidenced by the ^{1}H NMR spectrum. The reaction proceeded much faster at 70 °C, and showed a total conversion of complex **65a** to the ^{n}BuNCS mono-insertion product **64a** within one day.

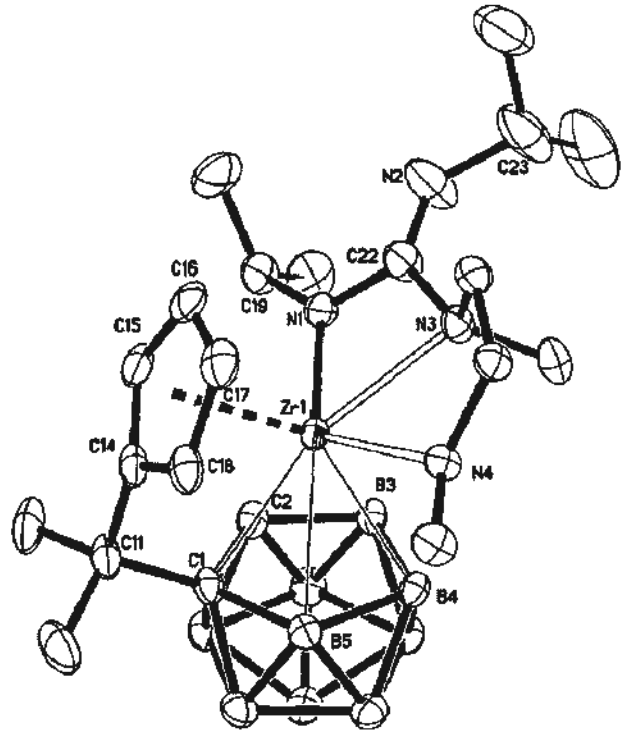


Figure 5.20. Molecular structure of

$[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta{:}\eta{:}\eta\text{-}NH(Me)(CH_2)_2N(Me)C(=N^iPr)N^iPr]$ (**65a**).

Interaction of **47a** with 1 equiv of ^{n}BuNC gave the mono-insertion product $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta{:}\eta^2\text{-}NH(Me)(CH_2)_2N(Me)C{=}N^nBu]$ (**66a**) as colorless crystals in 68% isolated yield. Only mono-insertion product was obtained in the presence of one or more equiv of ^{n}BuNC. Similar to **65a**, the spectroscopic data shows **66a** is a mixture of isomers, which might result from asymmetric environment of dicarbollyl ligand and Zr-N bonds

An X-ray study revealed that the central Zr atom is coordinated by an η^5-cyclopentadienyl ring, η^5-dicarbollyl ligand, an η^2-iminocarbamoyl ligand and amino group in a distorted trigonal bipyramidal geometry (Figure 5.21). The Zr-N(3)/C(24) distances of 2.136(3)/2.238(3) Å are similar to the 2.259(4)/2.221(3) Å in $Zr(NMeCyc)_2[C(NXy)NMeCyc]_2$,[56a] 2.174/2.271 Å in $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}[SiMe_2\text{-}\eta\text{-}N^tBu)]_2\}\text{-}\{\eta^2\text{-}C(CH_2Ph)=N(2,6\text{-}Me_2C_6H_3)\}]$[59a] and other η^2-iminocarbamoyl Zr complexes in literatures.[66a,d-f]

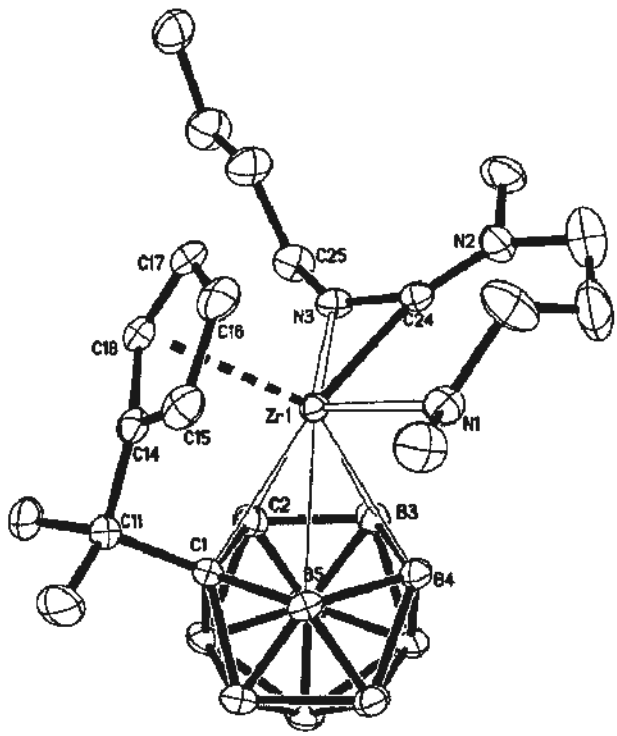


Figure 5.21. Molecular structure of

$[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta:\eta^2\text{-}NH(Me)(CH_2)_2N(Me)C=N^nBu]$ (**66a**).

5.4.3. Reduction

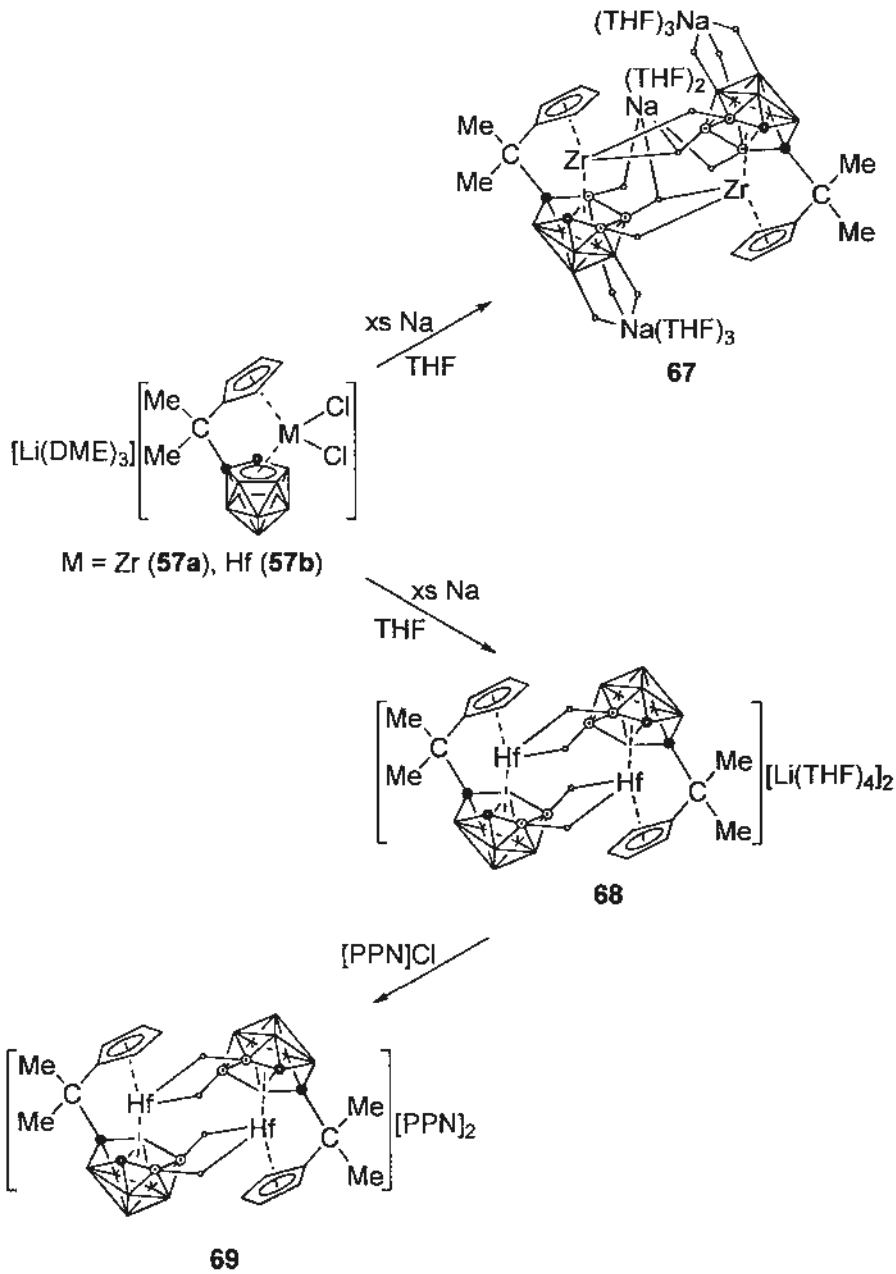
The dicarbollyl ligand in most metallacarboranes is very stable and inert under redox conditions.[128] For examples, in a recent study on molecular motor, reduction of

nickel(IV) bisdicarbollide only takes place at the nickel center, resulting in the formation of corresponding nickel(III) bisdicarbollide.[129] On the other hand, it has been documented that the *nido*-η^5-$C_2B_9H_{11}^{2-}$ can be reduced by group 1 metals to form *arachno*-η^6:η^6-$C_2B_9H_{11}^{4-}$ moiety bearing two open six-membered faces in 13-vertex bimetallacarboranes of late transition metals.[130] Such an *arachno* ligand is also observed in late transition metal complex $\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\eta^6\text{:}\eta^6\text{-}C_2B_9H_{11})$, formed by direct electrophilic insertion of $[(\eta^5\text{-}C_5Me_5)Ru(MeCN)_3]^+$ into $[(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_2B_9H_{11})]$.[131] In view of the impact of d^n/f^n metal ions on the formation of *arachno*-$C_2B_{10}H_{10}R_2^{4-}$ units,[50,132] we wondered if the electronic configurations of transition metal ions would have an effect on the geometries of the resultant *arachno*-C_2B_9 moieties. During the reduction of group 4 metal dicarbollides by group 1 metal, we discovered a new type of *arachno*-η^6-$C_2B_9H_{10}R^{4-}$ ligand bearing only one open six-membered face.

The reactions of mixed sandwich complexes **57a** or **57b** with an excess amount of Na metal in THF at room temperature for a week gave a mixed valent Zr(III)/Zr(IV) complex $\{[\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr\}_2\{Na_3(THF)_8\}$ (**67**) as brown crystals in 52% isolated yield and high valent Hf(IV) complex $[\{\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Hf]_2[Li(THF)_4]_2$ (**68**) as orange crystals in 45% isolated yield, respectively. Treatment of **68** with an equimolar amount of [PPN]Cl (PPN = bis(triphenylphosphine)iminium cation) in THF afforded, after recrystallization, $[\{\eta^5\text{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Hf]_2[PPN]_2$ (**69**) as yellow crystals in 51% isolated yield (Scheme 5.13). Complexes **67**, **68** and **69** are extremely air-

and moisture-sensitive, but remain stable for months at room temperature under an inert atmosphere.

Scheme 5.13. Reduction of **57a** or **57b** with Na metal.



Complex **67** is a paramagnetic species and does not offer any useful NMR information. It shows an EPR signal at 77 K in solid-state with g = 1.99 (line width = 36 G), which is in accordance with that of Zr(III) nucleus reported in the literature.[133]

In contrast, four doublets in the region 7.2 – 5.2 ppm assignable to the cyclopentadienyl protons and two singlets at the high field attributable to the two diastereotopic methyl groups of the bridging CMe_2 unit are observed in the ^1H NMR spectra of both **68** and **69**. Their ^{11}B NMR spectra exhibit a 1:1:2:3:1:1 pattern spanning a range from 0.4 to –43.3 ppm, which differ significantly from their parent complex **57**. The J_{BH} values fall in the range of 77 – 144 Hz. The significantly reduced J_{BH} values may suggest some B-H···M interactions in solution.[134] Furthermore, the solid-state IR spectra (KBr) exhibit two ν_{B-H} stretching bands at ca 2500 and 2465 cm^{-1}, respectively, supporting some B-H···M interactions in **67**, **68** and **69**.[135] Such interactions are further confirmed by single-crystal X-ray analyses and shown in Figures 5.22, 5.23 and 5.24, respectively. It is noted that despite of poor resolution of single-crystal X-ray analyses for **68**, the preliminary diffraction results together with NMR and elemental analyses data are enough to confirm the connectivity pattern for **68**.

The complex anions in **67** and **69** are dimeric species bearing a bent sandwich structural motif, in which each metal atom is η^5-bound to the cyclopentadienyl ring, η^6-bound to the *arachno*-C_2B_9 ligand, and coordinate to two B-H bonds of the neighboring C_2B_4 bonding face in a distorted-tetrahedral geometry. The charge is then compensated by three coordinated complex cations $[Na(THF)_x]^+$ in **67** or two PPN^+ cations in **69**, respectively. As **67** has a crystallographically imposed inversion center, the two Zr atoms are indistinguishable (Figure 5.22). The Zr-cage-carbon distances of 2.280(6)/2.258(6) Å are significantly shorter than those of

2.618(6)/2.583(6) Å in its parent complex **57a**,[28] and 2.491(5)/2.567(5) Å in the *nido*-C_2B_{10} system $[\eta^5:\eta^6:\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10}CH_2NMe)]Zr(NC_5H_5)$,[46] but are very close to those observed in the *arachno*-C_2B_{10} system such as 2.271(3)/2.266(3) Å in $[\{(\mu\text{-}\eta^5):\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$[46] and 2.249(7)/2.203(8) Å in $[\eta^1:\eta^1:\eta^7\text{-}(Me_2NCH_2CH_2)_2C_2B_{10}H_{10}]Zr(\mu\text{-}Cl)Na(THF)_3$.[132c] The average Zr-cage-boron distance of 2.568(7) Å in **67** is about 0.3 Å longer than that of Zr-cage-carbon one. This measured value compares that of 2.674(7) Å in $[\eta^5:\eta^6:\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10}CH_2NMe)]Zr(NC_5H_5)$, 2.624(4) Å in $[\{(\mu\text{-}\eta^5):\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$ and 2.545(10) Å in $[\eta^1:\eta^1:\eta^7\text{-}(Me_2NCH_2CH_2)_2C_2B_{10}H_{10}]Zr(\mu\text{-}Cl)Na(THF)_3$. The observed Zr···Zr distance of 3.659(6) Å in **67** is almost identical with that of 3.654(6) Å observed in the mixed valent Zr(III)/Zr(IV) complex $[Cp_2Zr(\mu\text{-}PPh)]_2^{\cdot-}$.[136] Similarly, the average Hf-cage-carbon distances of 2.271(6)/2.234(5) Å are also significantly shorter than those of 2.515(6)/2.533(7) Å in the *nido*-C_2B_9 system of $[(C_5Me_5)(C_2B_9H_{11})HfMe]_2$,[9] and 2.489(4)/2.674(4) Å in the *nido*-C_2B_{10} system of $[\eta^1:\eta^6\text{-}(Me_2NCH_2CH_2)(C_2B_{10}H_{11})]Hf(CH_2SiMe_3)_2$,[48] but are very comparable to the Hf-C σ bond distances of 2.239(6)/2.228(6) Å in $[(C_5Me_5)(C_2B_9H_{11})HfMe]_2$ and 2.173(4)/2.163(5) Å in $[\eta^1:\eta^6\text{-}(Me_2NCH_2CH_2)(C_2B_{10}H_{11})]Hf(CH_2SiMe_3)_2$. The average Hf-cage-boron distance of 2.560(7) Å in **69** is about 0.3 Å longer than that of Hf-cage-carbon one. In view of these experimental data, it is best to describe that the two electrons from the reducing agent are formally added to the dicarbollyl ligand, leading to the formation of *arachno*-η^6-$C_2B_9H_{10}R^{4-}$ moiety with the cage C···C

separation of 2.809(7) Å in **67** and 2.783(7) Å in **69**, respectively. The high electron density on the cage carbon atoms[137] results in the significantly shorter M-cage-carbon distances in both **67** and **69** than those observed in *nido*-C_2B_9 and *nido*-C_2B_{10} systems. Accordingly, the formal oxidation state of the Hf atom in **69** should be 4+, and that of each Zr atom in **67** should be 3.5+, rather than 1.5+.[138]

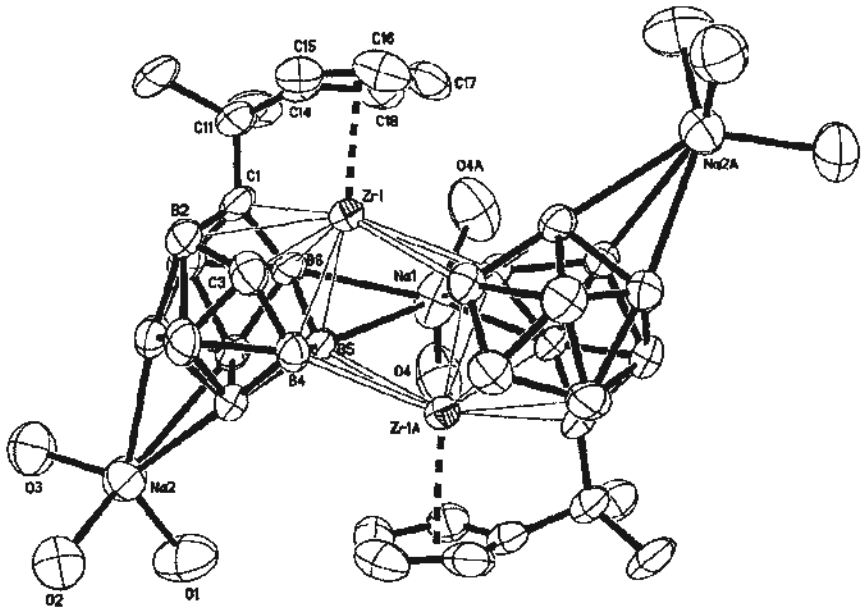


Figure 5.22. Molecular structure of $\{[\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr\}_2\{Na_3(THF)_8\}$ **(67)** (only oxygen atoms of the coordinated THF molecules are shown for clarity).

Several kinds of cage geometries have been predicted for 11-vertex *arachno* clusters, derived by removal of two vertices from a 13-vertex docosahedron, and two typical ones are shown in Chart 5.1.[1b,139] Geometry **A** is observed in 13-vertex bimetallacarboranes $M_2C_2B_9$,[130,131] whereas geometry **B** is found in current group 4 metallacarboranes MC_2B_9 (**67** – **69**) and in *arachno*-$S_2B_9H_{10}^-$.[139b] The latter resemble the so-called *hypercloso* MC_2B_9 clusters reported in literature,

$PtW(CO)_2(PEt_3)_2\{\eta^6\text{-}Me_2C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\}$[140a,b] and $[NEt_4][W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)\{\eta^6\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\}]$,[140c] in which the cage C···C separation is 2.88 Å in $PtW(CO)_2(PEt_3)_2\{\eta^6\text{-}Me_2C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\}$ and 2.917 Å in $[NEt_4][W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)\{\eta^6\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\}]$. Complex $PtW(CO)_2(PEt_3)_2\{\eta^6\text{-}Me_2C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\}$ is prepared from the equimolar reaction of $[PtH(Me_2CO)(PEt_3)_2][BF_4]$ with $[PPN][W\{\equiv C(C_6H_4Me\text{-}4)\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, and $[NEt_4][W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)\{\eta^6\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\}]$ is generated by treatment of $[NEt_4][W\{\equiv C(C_6H_4Me\text{-}4)\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with 0.5 equiv of HBF_4. No reducing agents are added to the reactions. The $W(\eta^6\text{-}C_2B_9H_9R_2)$ fragment in $[PPN][W\{\equiv C(C_6H_4Me\text{-}4)\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ and $[NEt_4][W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)\{\eta^6\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\}]$ is regarded as a 12-vertex cluster with only 12 skeletal electron pairs, which has been termed *hypercloso* cluster.[140] Thus, the $\eta^6\text{-}C_2B_9H_9R_2$ moiety in these complexes could be viewed as a formally dianionic ligand. Alternatively, it could also be visualized as a formally tetraanionic *arachno* species contributing 13 skeletal electron pairs to the 12-vertex $W(\eta^6\text{-}C_2B_9H_9R_2)$ unit, resulting in an *iso-closo* cluster.[141] The formation of complexes **67** – **69** support the latter description.

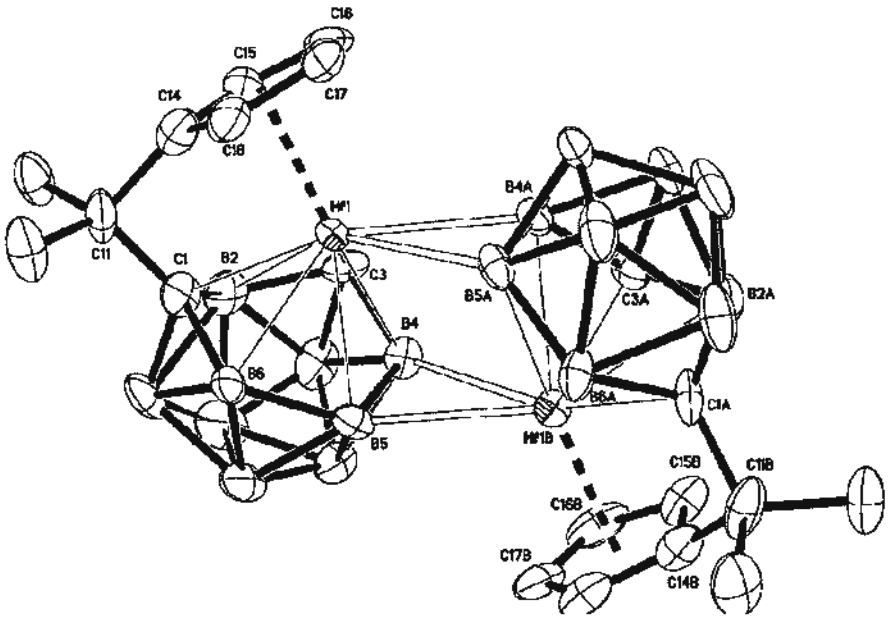


Figure 5.23. Molecular structure of the anion in $[\{\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Hf]_2[Li(THF)_4]_2$ **(68)**, showing one of the two crystallographically independent molecules in the unit cell.

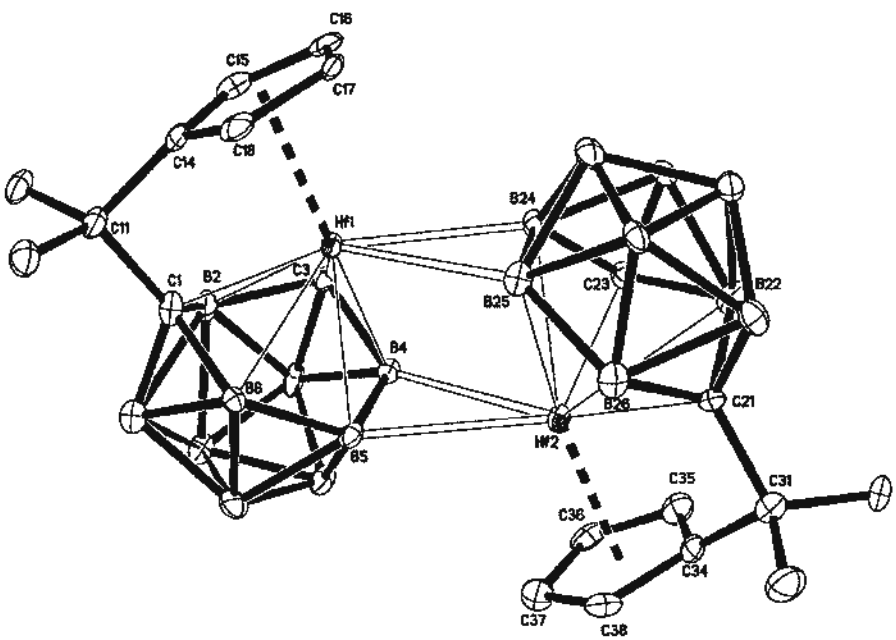
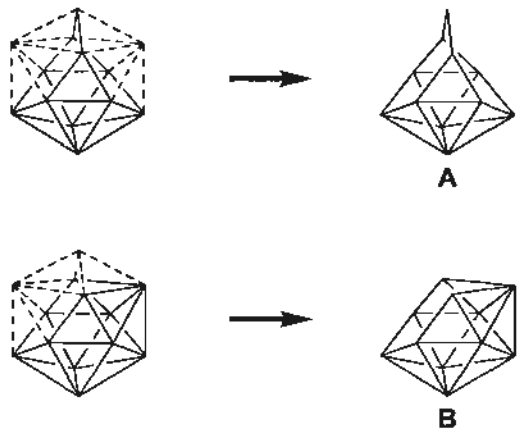


Figure 5.24. Molecular structure of the anion in $[\{\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}Hf]_2[PPN]_2$ **(69)**.

Chart 5.1. Relationship between 13-vertex *closo* and 11-vertex *arachno* clusters.



5.5. Summary

A series of carbon-bridged cyclopentadienyl-dicarbollyl group 4 metal amide complexes were synthesized by direct deboration of the carbon bridged cyclopentadienyl-carboranyl group 4 metal amides using different amines as deboration agents, which provides a new synthetic route for the generation of group 4 metallacarboranes. These results showed that diamines are more efficient in the deboration reaction of metal carboranyl complexes than $HNMe_2$. These metal dicarbollides can also be obtained by amine-exchange reactions between complexes **42** and amines. The acid-base reactions can also take place using other Brønsted acids, leading to the corresponding metallacarboranes. The group 4 metal amides are reactive towards unsaturated molecules like ^{n}BuNCS, DIC and ^{n}BuNC to afford mono-insertion products. The carbodiimide mono-insertion product reacted with ^{n}BuNCS to result in deinsertion of carbodiimide. Deprotonation of complexes **42** followed by reaction with TMSCl afforded the mixed sandwich complexes $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Li(DME)_3]$ (M = Zr (**57a**), Hf (**57b**)), which

were reduced by Na metal to give metallacarboranes bearing an *arachno*-$C_2B_9H_{10}R^{4-}$ tetraanion.

Chapter 6. Conclusion

This thesis describes (1) the synthesis and characterization of carbon-bridged cyclopentadienyl-carboranyl group 4 metal diamides and dithiolate, (2) the direct deboration of carbon-bridged cyclopentadienyl-carboranyl group 4 metal amide complexes using amines as deboration reagents, and (3) the reactivity and catalytic activity of the resultant group 4 metal complexes.

Several carbon-bridged cyclopentadienyl-carboranyl metal diamides [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M[$\eta^2$-N(Me)$(CH_2)_2$N(Me)] (M = Zr (**2a**), Ti (**2c**)) and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M[$\eta^2$-N(Me)$(CH_2)_3$N(Me)] (M = Zr (**3a**), Hf (**3b**) and Ti (**3c**)) were prepared and characterized from the reaction of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M$(NMe_2)_2$ (M = Zr (**1a**), Hf (**1b**), Ti (**1c**)) with diamine reagents (DMEDA or DMPDA). The M-N bonds in these metal amides were active toward a series of unsaturated molecules such as RNC, RCN, RNCS, RNCO and RN=C=NR. The reaction of **3a** or **3b** with different isocyanides afforded different insertion products. Di-insertion product was obtained in the reaction with XylNC, whereas other isocyanides bearing α-CH_2 gave multiple insertion products. These results indicated that the inertness of the M-C_{cage} bond toward unsaturated molecules is best ascribed to the steric effect of the carborane cage, and the mobility of the migratory groups may not play a role in the insertion reactions.

Both carbodiimide and 2,6-dimethylphenylisocyanide inserted products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M[$\eta^3$-N(Me)$(CH_2)_3$N(Me)C(=NR)NR] (M = Zr, R = ^{i}Pr (**9a**), Cy (**9a'**), M = Hf, R = Cy (**9b'**)) and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M[$\eta^2$:$\eta^2$-(Xyl)N=CN(Me)$(CH_2)_3$N(Me)C=N(Xyl)] (M = Zr, **12a**; M = Hf, **12b**) were active towards other unsaturated molecules, leading to the deinsertion reactions of

carbodiimide and isocyanide. The Zr and Hf carbodiimide mono-insertion products **9** showed similar reactivities toward RNC, RNCS and RNCO, resulting in the deinsertion of carbodiimide and affording the RNC, RNCS and RNCO insertion products. The XylNC inserted products **12** showed different reactivities toward RNC and RNCS in the deinsertion reaction of XylNC. Both mono- and di-deinsertion species were observed. These reactions provide a useful method for the generation of new metallacycles containing different functionalities.

The zirconium dithiolate complex $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}](HNMe_2)_2$ (**30**) was synthesized by amine elimination reaction. Reactions of **30** with unsaturated molecules did not afford the Zr-S bond insertion products. Instead, nucleophilic addition products were obtained. Interaction of **30** with PhCN generated $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][NH{=}C(Ph)NMe_2]_2$ (**35**), which is a Lewis acid promoted nucleophilic addition product. Complex **30** was able to catalyze the hydroamination of PhCN with dialkylamine, but the efficiency was usually low.

A series of carbon-bridged cyclopentadienyl-dicarbollyl group 4 metal amides were prepared by direct deboration of the corresponding carbon-bridged cyclopentadienyl-carboranyl metal amides using amines as deboration reagents. These metal complexes were active towards polar unsaturated molecules, such as ^{n}BuNCS, DIC and ^{n}BuNC, to afford the mono-insertion species. The DIC insertion product $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta{:}\eta{:}\eta\text{-}NH(Me)(CH_2)_2N(Me)C(=N^iPr)N^iPr]$ (**65**) also react with ^{n}BuNCS, resulting in the deinsertion of carbodiimide. Moreover, the metal dichloride species $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Li(DME)_3]$ (M = Zr (**57a**), Hf (**57b**)) was able to be reduce by Na metal to give the corresponding metallacarboranes bearing the *arachno*-C_2B_9 tetra-anions.

Chapter 7. Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except CH_2Cl_2) were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. CH_2Cl_2 was refluxed over CaH_2 for several days and distilled immediately prior to use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$M(NMe_2)_2$ (M = Zr (**1a**), Hf (**1b**), Ti(**1c**)),[35] 1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$ (**29**),[93] $Me_2C(C_{13}H_9)C_2B_{10}H_{11}$ (**41**),[39] $H_2C(C_{13}H_9)C_2B_{10}H_{11}$ (**43**),[125] [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (**49**),[35] $M(NMe_2)_4$ (M = Zr, Hf)[123] were prepared according to literature methods. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.1 MHz or a Bruker 400 spectrometer at 400.1 MHz. ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 75.5 MHz or a Bruker DPX 400 spectrometer at 100.6 MHz. ^{11}B NMR spectra were recorded on a Bruker DPX 300 spectrometer at 96.3 MHz, a Bruker 400 spectrometer at 128.4 MHz or a Varian Inova 400 spectrometer at 128.3 MHz. All chemical shifts were reported in δ units with reference to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, China or MEDAC Ltd., Brunel University, Middlesex, U.K.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-N(Me)$(CH_2)_2$N(Me)](NH$Me_2$) (2a). To a toluene (15 mL) solution of **1a** (214 mg, 0.50 mmol) was added dropwise a toluene (8 mL) solution of DMEDA (49 mg, 0.60 mmol) at -30 °C with stirring. The mixture was warmed to room temperature and stirred for 20 min. After filtration, the resulting orange-red solution was concentrated under vacuum to about 5 mL. *n*-Hexane (5 mL) vapor diffusion gave **2a** as orange solid over a period of 2 days at -30 °C (173 mg, 73%). ^{1}H NMR (300 MHz, benzene-d_6): δ 5.98 (d, J = 1.8 Hz, 1H, C_5H_4), 5.59 (brs, 1H, C_5H_4), 5.44 (brs, 1H, C_5H_4), 5.34 (brs, 1H, C_5H_4), 2.88 (s, 6H, NCH_3), 2.67 (m, 4H, NCH_2), 1.73 (d, J = 6.0 Hz, 6H, $HN(CH_3)_2$), 1.44 (s, 3H, $C(CH_3)_2$), 1.42 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 146.2, 113.4, 110.4, 107.5 (C_5H_4), 56.4, 52.4 (NCH_2), 46.9, 42.8 (NCH_3), 41.7 ($C(CH_3)_2$), 37.9, 32.2 ($C(CH_3)_2$), 33.4 ($NH(CH_3)_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ –2.1 (1B), –3.1 (1B), –4.6 (1B), –5.2 (1B), –9.0 (3B), –11.1 (3B). IR (KBr, cm^{-1}): ν_{BH} 2552 (vs). Anal. Calcd for $C_{14}H_{30}B_{10}N_2Zr$ (**2a** – $HNMe_2$): C, 39.50; H, 7.10; N, 6.58. Found: C, 39.76; H, 7.62; N, 6.68.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti[$\eta^2$-N(Me)$(CH_2)_2$N(Me)] (2c). To a toluene (15 mL) solution of **1c** (191 mg, 0.50 mmol) was added dropwise a toluene (8 mL) solution of DMEDA (220 mg, 2.50 mmol) at 0 °C with stirring. The mixture was warmed to room temperature and then heated at 60 °C for 2 days. After filtration, the resulting red solution was concentrated under vacuum to about 5 mL. Complex **2c** was isolated as red crystals after this solution stood at room temperature for 1 day (129 mg, 68%). ^{1}H NMR (300 MHz, benzene-d_6): δ 5.55 (brs, 2H, C_5H_4), 5.43 (brs, 2H, C_5H_4), 3.49 (d, J = 9.0 Hz, 2H, NCH_2), 3.25 (d, J = 9.0 Hz, 2H, NCH_2), 2.62 (s, 6H, NCH_3), 1.44 (s, 6H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ

135.4, 112.2, 109.2 (C_5H_4), 57.6 (NCH_2), 50.4 (NCH_3), 42.4 ($C(CH_3)_2$), 31.9 ($C(CH_3)_2$), the cage carbons were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ –3.2 (2B), –6.2 (2B), –9.7 (4B), –12.3 (2B). IR (KBr, cm^{-1}): ν_{BH} 2576 (vs). Anal. Calcd for $C_{14}H_{30}B_{10}N_2Ti$ (**2a**): C, 43.97; H, 7.91; N, 7.33. Found: C, 43.88; H, 8.34; N, 7.10.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-N(Me)$(CH_2)_3$N(Me)] (3a). To a toluene (15 mL) solution of **1a** (214 mg, 0.50 mmol) was added dropwise a toluene (8 mL) solution of DMPDA (56 mg, 0.55 mmol) at 0 °C with stirring. The mixture was warmed to room temperature and stirred overnight. After filtration, the resulting yellow solution was concentrated under vacuum to about 8 mL. Complex **3a** was isolated as yellow crystals after this solution stood at room temperature for 2 days (179 mg, 82%). ^1H NMR (300 MHz, benzene-d_6): δ 5.66 (d, J = 2.7 Hz, 2H, C_5H_4), 5.61 (d, J = 2.7 Hz, 2H, C_5H_4), 2.90 (m, 4H, NCH_2), 2.66 (s, 6H, NCH_3), 1.97 (m, 2H, $NCH_2CH_2CH_2N$), 1.40 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 146.4, 113.0, 109.3 (C_5H_4), 57.3 (NCH_2), 46.0 (NCH_3), 42.5 ($C(CH_3)_2$), 32.6 ($C(CH_3)_2$), 27.4 ($NCH_2CH_2CH_2N$), the cage carbons were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ –2.3 (2B), –5.1 (2B), –8.6 (2B), –9.2 (2B), –11.9 (2B). IR (KBr, cm^{-1}): ν_{BH} 2562 (vs). Anal. Calcd for $C_{15}H_{32}B_{10}N_2Zr$ (**3a**): C, 40.97; H, 7.33; N, 6.37. Found: C, 40.99; H, 7.74; N, 6.13.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$-N(Me)$(CH_2)_3$N(Me)] (3b). This complex was prepared as yellow crystals from **1b** (258 mg, 0.50 mmol) and DMPDA (56 mg, 0.55 mmol) in toluene using the identical procedure reported for **3a**: yield 214 mg (82%). ^1H NMR (300 MHz, benzene-d_6): δ 5.59 (d, J = 2.1 Hz, 2H, C_5H_4), 5.57 (d, J = 2.1 Hz, 2H, C_5H_4), 3.01 (m, 4H, NCH_2), 2.75 (s, 6H, NCH_3), 1.78 (m, 2H, $NCH_2CH_2CH_2N$), 1.38 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-

d_6): δ 145.8, 112.0, 108.7 (C_5H_4), 57.8 (NCH_2), 45.1 (NCH_3), 42.0 ($C(CH_3)_2$), 32.5 ($C(CH_3)_2$), 28.2 ($NCH_2CH_2CH_2N$), the cage carbons were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ –1.4 (1B), –2.1 (1B), –4.9 (2B), –8.9 (4B), –12.0 (2B). IR (KBr, cm^{-1}): ν_{BH} 2566 (vs). Anal. Calcd for $C_{15}H_{32}B_{10}HfN_2$ (**3b**): C, 34.18; H, 6.12; N, 5.32. Found: C, 34.11; H, 6.57; N, 4.78.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti[$\eta^2$-N(Me)$(CH_2)_3$N(Me)] (3c). To a toluene (15 mL) solution of **1c** (191 mg, 0.50 mmol) was added dropwise a toluene (8 mL) solution of DMPDA (153 mg, 1.50 mmol) at 0 °C with stirring. The mixture was warmed to room temperature and heated at 90 °C for 2 days. After filtration, the resulting red solution was concentrated under vacuum to about 8 mL. Complex **3c** was isolated as orange-red crystals after this solution stood at room temperature for 3 days (124 mg, 64%). ^1H NMR (300 MHz, benzene-d_6): δ 5.47 (m, 4H, C_5H_4), 3.12 (m, 2H, NCH_2), 2.86 (m, 2H, NCH_2), 2.69 (s, 6H, NCH_3), 1.59 (m, 2H, $NCH_2CH_2CH_2N$), 1.43 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 149.5, 112.4, 110.0 (C_5H_4), 62.6 (NCH_2), 48.7 (NCH_3), 42.0 ($C(CH_3)_2$), 31.9 ($C(CH_3)_2$), 31.2 ($NCH_2CH_2CH_2N$), the cage carbons were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ –2.6 (2B), –5.6 (2B), –8.9 (4B), –11.7 (2B). IR (KBr, cm^{-1}): ν_{BH} 2598, 2565, 2540 (vs). Anal. Calcd for $C_{15}H_{32}B_{10}N_2Ti$ (**3c**): C, 45.45; H, 8.14; N, 7.07. Found: C, 44.92; H, 7.95; N, 7.26.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-(Xyl)N=CN(Me)$(CH_2)_2$N(Me)C=N(Xyl)] (4a). To a toluene (15 mL) solution of **2a** (235 mg, 0.50 mmol) was added dropwise a toluene (8 mL) solution of XylNC (131 mg, 1.00 mmol) at -30 °C with stirring. The mixture was warmed to room temperature and stirred overnight. After filtration, the white solid was collected and redissolved in THF (20 mL). The resulting colorless solution was concentrated to

about 8 mL. Complex **4a** was isolated as colorless crystals after this solution stood at room temperature for 2 days (225 mg, 66%). Single crystal suitable for X-ray analyses were grown from a benzene/THF solution at room temperature as **4a•C$_6$H$_6$**. ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.08 (m, 6H, C$_6H_3$(CH$_3$)$_2$), 6.05 (m, 4H, C$_5H_4$), 3.87 (m, 2H, NCH_2), 3.36 (m, 2H, NCH_2), 2.51 (s, 6H, NCH_3), 2.29 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 1.91 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 1.71 (s, 6H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 207.4 (*C*=N), 146.8, 146.7, 130.9, 130.7, 128.9, 127.5, 127.3, 124.0, 121.4 (*C*$_6$H$_3$(CH$_3$)$_2$), 105.5, 102.4 (*C*$_5$H$_4$), 54.7 (NCH$_2$), 42.0 (*C*(CH$_3$)$_2$), 35.1 (NCH$_3$), 32.6 (C(*C*H$_3$)$_2$), 19.6, 18.8 (C$_6$H$_3$(*C*H$_3$)$_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ –3.3 (2B), –5.3 (2B), –9.1 (5B), –13.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2554 (vs). Anal. Calcd for C$_{32}$H$_{48}$B$_{10}$N$_4$Zr (**4a**): C, 55.86; H, 7.03; N, 8.14. Found: C, 55.40; H, 7.39; N, 7.86.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ti[η^2:η^2-(Xyl)N=CN(Me)(CH$_2$)$_2$N(Me)C=N(Xyl)] (4c). This complex was prepared as yellow crystals from **2c** (190 mg, 0.50 mmol) and XylNC (131 mg, 1.00 mmol) in toluene using the identical procedure reported for **4a**: yield 247 mg (68%). Single crystal suitable for X-ray analyses were grown from a benzene/THF solution at room temperature as **4c•C$_6$H$_6$**. ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.09 (m, 6H, C$_6H_3$(CH$_3$)$_2$), 5.85 (d, J = 2.4 Hz, 2H, C$_5H_4$), 5.83 (d, J = 2.4 Hz, 2H, C$_5H_4$), 3.81 (m, 2H, NCH_2), 3.38 (m, 2H, NCH_2), 2.53 (s, 6H, NCH_3), 2.27 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 1.94 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 1.72 (s, 6H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 203.9 (*C*=N), 148.2, 147.5, 133.0, 132.6, 129.0, 128.4, 125.4 (*C*$_6$H$_3$(CH$_3$)$_2$), 105.4, 103.0 (*C*$_5$H$_4$), 53.7 (NCH$_2$), 42.3 (*C*(CH$_3$)$_2$), 36.8 (NCH$_3$), 33.2 (C(*C*H$_3$)$_2$), 21.3, 20.5 (C$_6$H$_3$(*C*H$_3$)$_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, pyridine-d_5): δ –3.9 (2B), –5.9 (2B), –9.2 (3B), –10.3 (2B), –13.4 (1B). IR (KBr, cm^{-1}): ν_{BH}

2598, 2538 (vs). Anal. Calcd for $C_{32}H_{48}B_{10}N_4Ti$ (**4c**): C, 59.61; H, 7.50; N, 8.69. Found: C, 59.88; H, 7.65; N, 8.40.

Preparation of {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\mu$-$\eta^2$:$\eta^2$-OCN(Ph)N(Me)$(CH_2)_2$(Me)N(Ph)NCO]}$_2$ (5a). To a DME (30 mL) solution of **2a** (235 mg, 0.50 mmol) was added dropwise a DME (10 mL) solution of PhNCO (112 mg, 1.00 mmol) at -30 °C with stirring. The mixture was warmed to room temperature and stirred for 10 min. After filtration, the resulting pale yellow solution was concentrated under vacuum to about 30 mL. Complex **5a** was isolated as colorless crystals after this solution stood at room temperature for 2 days (228 mg, 69%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 9.13 (brs, 2H, C_6H_5), 7.98 (d, J = 7.8 Hz, 6H, C_6H_5), 7.64 (m, 8H, C_6H_5), 7.03 (m, 4H, C_6H_5), 6.40 (m, 8H, C_5H_4), 3.57 (brs, 8H, NCH_2), 3.06 (s, 12H, NCH_3), 1.44 (s, 12H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 156.1 (N-*C*=O), 140.9, 132.0, 129.1, 128.7, 128.3, 128.0, 121.9, 120.1 (C_6H_5 + C_5H_4), 57.9 (NCH_2), 46.9 (NCH_3), 40.7 ($C(CH_3)_2$), 34.9, 29.9 ($C(CH_3)_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ –3.7 (6B), –9.0 (4B), –11.2 (4B), –13.3 (6B). IR (KBr, cm^{-1}): ν_{BH} 2549 (vs). Anal. Calcd for $C_{56}H_{80}B_{20}N_8O_2Zr_2$ (**5a**): C, 50.65; H, 6.07; N, 8.44. Found: C, 50.42; H, 6.40; N, 8.24.

Preparation of {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-N(Me)$(CH_2)_2$NH(Me)][$\mu$-NHC$(CH_3)$=CHC≡N]}$_2$ (6a). This complex was prepared as yellow crystals from **2a** (235 mg, 0.50 mmol) and CH_3CN (62 mg, 1.50 mmol) in DME using the identical procedure reported for **5a**: yield 106 mg (42%). NMR data were not obtainable since the crystals were not redissolved in any organic solvents. IR (KBr, cm^{-1}): ν 3788 (w), 3719 (w), 3272 (w), 2903 (m), 2550 (vs) (B-H), 2328 (w), 2166 (s), 1625 (w), 1521

(s), 1048 (m), 1005 (m), 803 (m). Anal. Calcd for $C_{36}H_{72}B_{20}N_8Zr_2$ (**6a**): C, 42.57; H, 7.15; N, 11.03. Found: C, 42.95; H, 7.32; N, 10.61.

Preparation of {[η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^2-N(Me)(CH$_2$)$_2$NH(Me)][μ-TMSN=C=N]}$_2$ (7a). To a toluene (15 mL) solution of **2a** (235 mg, 0.50 mmol) was added dropwise a toluene (8 mL) solution of TMSN=C=NTMS (170 mg, 1.00 mmol) at -30 °C with stirring, and the mixture was warmed to room temperature and stirred overnight. After filtration, the resulting clear orange solution was concentrated under vacuum to about 10 mL. Complex **7a** was isolated as yellow crystals after this solution stood at room temperature for 5 days (142 mg, 53%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 6.65 (d, J = 2.7 Hz, 1H, C$_5H_4$), 6.46 (d, J = 2.7 Hz, 1H, C$_5H_4$), 5.88 (d, J = 2.7 Hz, 1H, C$_5H_4$), 5.18 (d, J = 2.7 Hz, 1H, C$_5H_4$), 3.61 (m, 2H, NCH_2), 3.18 (m, 2H, NCH_2), 3.40 (s, 6H, NCH_3), 2.64 (m, 4H, NHCH_2), 2.33 (d, J = 5.7 Hz, 6H, NHCH_3), 1.59 (s, 6H, C(CH_3)$_2$), 1.45 (s, 6H, C(CH_3)$_2$), 0.44 (s, 18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 144.1 (*C*$_5$H$_4$), 125.1 (N=*C*=N), 117.6, 113.0, 112.1, 110.0 (*C*$_5$H$_4$), 103.8, 102.4 (Cage *C*), 59.6 (NCH$_2$), 51.9 (NHCH$_2$), 50.6 (NCH$_3$), 39.5 (NHCH$_3$), 40.7 (*C*(CH$_3$)$_2$), 27.6, 26.3 (C(*C*H$_3$)$_2$), 2.0 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ –3.4 (6B), –6.3 (6B), –9.2 (8B). IR (KBr, cm^{-1}): ν_{BH} 2556 (vs). Anal. Calcd for $C_{32}H_{70}B_{20}N_6Si_2Zr_2$ (**7a** – $C_4H_{12}N_2$): C, 38.75; H, 6.91; N, 8.47. Found: C, 39.18; H, 6.94; N, 7.95.

Preparation of {[η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[μ-N=C(Ph)N(Me)(CH$_2$)$_3$N(Me)C(Ph)=N]}$_2$•0.75THF (8a•0.75THF). This complex was prepared as pale-yellow crystals from **3a** (220 mg, 0.50 mmol) and PhCN (104 mg, 1.00 mmol) in DME using the identical procedure reported for **5a**: yield 206 mg (61%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.42 (m, 12H, C$_6H_5$), 6.82 (brs, 8H, C$_6H_5$), 6.16 (brs, 4H, C$_5H_4$), 4.92 (brs, 4H, C$_5H_4$), 2.98 (m, 8H, NCH_2), 2.77 (s, 12H,

NCH_3), 1.98 (m, 4H, $NCH_2CH_2CH_2N$), 1.56 (s, 12H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 163.4 (N-*C*=N), 144.5, 140.6, 140.4, 127.9, 126.4, 110.1, 109.2, 108.8, 106.5 (C_6H_5) + C_5H_4), 103.2, 100.6 (Cage *C*), 71.4 (NCH_2), 57.9 ($N(CH_3)$), 41.6 ($C(CH_3)_2$), 32.5 ($C(CH_3)_2$), 26.6 ($NCH_2CH_2CH_2N$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.2 (6B), –5.5 (6B), –9.2 (8B). IR (KBr, cm^{-1}): ν_{BH} 2558 (vs). Anal. Calcd for $C_{61}H_{90}B_{20}N_8O_{0.75}Zr_2$ (**8a** + 0.75THF): C, 54.76; H, 6.78; N, 8.37. Found: C, 54.75; H, 6.62; N, 8.14.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^3$-N(Me)$(CH_2)_3$N(Me)C(=N^{i}Pr)N^{i}Pr] (9a). To a toluene (20 mL) solution of **3a** (220 mg, 0.50 mmol) was added dropwise a toluene (6 mL) solution of DIC (64 mg, 0.50 mmol) at -30 °C with stirring. The mixture was warmed to room temperature and stirred overnight. After filtration, the resulting clear yellow solution was concentrated under vacuum to about 10 mL. *n*-Hexane vapor diffusion (10 mL) gave **9a** as a yellow solid over a period of 2 days at room temperature (153 mg, 54%). ^1H NMR (300 MHz, pyridine-d_5): δ 6.52 (brs, 1H, C_5H_4), 6.48 (brs, 1H, C_5H_4), 6.10 (brs, 2H, C_5H_4), 4.11 (brs, 1H, $(CH_3)_2CH$), 3.79 (brs, 1H, $(CH_3)_2CH$), 3.66 (m, 2H, NCH_2), 3.22 (s, 3H, NCH_3), 2.85 (m, 2H, NCH_2), 2.70 (s, 3H, NCH_3), 1.72 (brs, 2H, $NCH_2CH_2CH_2N$), 1.62 (s, 6H, $C(CH_3)_2$), 1.59 (s, 6H, $(CH_3)_2CH$), 1.51 (s, 6H, $(CH_3)_2CH$). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 150.9 (N-*C*=N), 114.8, 110.3, 108.5 (C_5H_4), 103.5, 101.9 (Cage *C*), 59.1, 54.1 (NCH_2), 48.3, 48.0 ($(CH_3)_2CH$), 45.7, 44.0 (NCH_3), 41.8 ($C(CH_3)_2$), 32.2, 31.7 ($C(CH_3)_2$), 22.2 ($NCH_2CH_2CH_2N$), 22.0, 20.7, 19.0, 18.2 ($(CH_3)_2CH$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –2.9 (3B), –5.0 (2B), –9.0 (5B). IR (KBr, cm^{-1}): ν_{BH} 2564 (vs). Anal. Calcd. for $C_{22}H_{46}B_{10}N_4Zr$ (**9a**): C, 46.69; H, 8.19; N, 9.90. Found: C, 46.59; H, 8.27; N, 9.70.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NCy)NCy]\cdot C_7H_8$ ($9a'\cdot C_7H_8$). This complex was prepared as colorless crystals from **3a** (220 mg, 0.50 mmol) and DCC (108 mg, 0.50 mmol) in toluene using the identical procedure reported for **7a**: yield 251 mg (68%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.26 (m, 2H, $C_6H_5CH_3$), 7.15 (m, 3H, $C_6H_5CH_3$), 6.53 (brs, 1H, C_5H_4), 6.44 (brs, 1H, C_5H_4), 6.13 (brs, 2H, C_5H_4), 3.63 (brs, 1H, NC*H*), 3.52 (brs, 1H, NC*H*), 3.43 (m, 2H, NCH_2), 3.21 (s, 3H, NCH_3), 2.83 (brs, 2H, NCH_2), 2.73 (s, 3H, NCH_3), 2.20 (s, 3H, $C_6H_5CH_3$), 1.91 (d, J = 12.2 Hz, 3H, C_6H_{11}), 1.77 (brs, 3H, C_6H_{11}), 1.67 (brs, 4H, C_6H_{11}), 1.64 (s, 3H, $C(CH_3)_2$), 1.62 (s, 3H, $C(CH_3)_2$), 1.53 (brs, 2H, C_6H_{11}), 1.44 (m, 4H, C_6H_{11}), 1.31 (brs, 5H, C_6H_{11} + $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 151.4 (N-*C*=N), 129.1, 128.3 ($C_6H_5CH_3$), 115.2, 110.8, 108.8 (C_5H_4), 103.9 (Cage *C*), 59.7, 54.4 (NCH_2), 57.7, 53.7 (NCH), 48.4, 44.6 (NCH_3), 42.2 ($C(CH_3)_2$), 32.6, 32.1 ($C(CH_3)_2$), 35.2, 29.6, 29.2, 27.1, 26.4, 24.5 (C_6H_{11}), 26.2 ($NCH_2CH_2CH_2N$), 22.6 ($C_6H_5CH_3$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.6 (3B), –5.6 (2B), –9.3 (3B), –11.1 (1B), –13.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2568 (vs). Anal. Calcd. for $C_{28}H_{54}B_{10}N_4Zr$ (**9a'**): C, 52.05; H, 8.42; N, 8.67. Found: C, 52.52; H, 8.52; N, 8.42.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^3\text{-}N(Me)(CH_2)_3N(Me)C(=NCy)NCy]\cdot C_7H_8$ ($9b'\cdot C_7H_8$). This complex was prepared as colorless crystals from **3b** (259 mg, 0.49 mmol) and DCC (108 mg, 0.50 mmol) in toluene using a procedure identical with that reported for **7a**: yield 283 mg (69%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.26 (m, 2H, $C_6H_5CH_3$), 7.15 (m, 3H, $C_6H_5CH_3$), 6.51 (brs, 1H, C_5H_4), 6.42 (brs, 1H, C_5H_4), 6.15 (brs, 1H, C_5H_4), 6.10 (t, J = 2.7 Hz, 1H, C_5H_4), 3.72 (brs, 1H, NC*H*), 3.59 (brs, 1H, NC*H*), 3.44 (m, 2H, NCH_2), 3.34 (m, 2H, NCH_2), 3.32 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3), 2.20 (s, 3H, $C_6H_5CH_3$), 1.89 (m,

3H, C_6H_{11}), 1.80 (m, 3H, C_6H_{11}), 1.69 (m, 4H, C_6H_{11}), 1.64 (s, 3H, $C(CH_3)_2$), 1.62 (s, 3H, $C(CH_3)_2$), 1.49 (m, 2H, C_6H_{11}), 1.43 (m, 4H, C_6H_{11}), 1.30 (m, 5H, C_6H_{11} + $NCH_2CH_2CH_2N$), 1.11 (t, J = 11.4 Hz, 1H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 146.3 (N-*C*=N), 128.2, 127.0 ($C_6H_5CH_3$), 112.7, 108.7, 108.5, 102.6 (C_5H_4), 110.1, 102.6 (Cage *C*), 58.3, 54.5 (NCH_2), 56.1, 52.2 (NCH), 47.2, 43.7 (NCH_3), 40.2 ($C(CH_3)_2$), 34.0, 33.7, 31.2, 30.7, 25.6, 25.4, 24.9, 24.7 (C_6H_{11}), 28.5, 27.8 ($C(CH_3)_2$), 23.0 ($NCH_2CH_2CH_2N$), 21.6 ($C_6H_5CH_3$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –1.8 (1B), –3.4 (2B), –5.4 (2B), –9.1 (5B). IR (KBr, cm^{-1}): ν_{BH} 2591, 2560 (vs). Anal. Calcd. for $C_{28}H_{54}B_{10}N_4Hf$ (**9b'**): C, 45.86; H, 7.42; N, 7.64. Found: C, 46.24; H, 7.18; N, 7.62.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^3$-N(Me)$(CH_2)_3$N(Me)C(=N^{t}Bu)S] (10a). This complex was prepared as colorless crystals from **3a** (220 mg, 0.50 mmol) and ^{t}BuNCS (53 mg, 0.50 mmol) in toluene using the identical procedure reported for **7a**: yield 211 mg (76%). ^1H NMR (300 MHz, pyridine-d_5): δ 6.79 (t, J = 2.3 Hz, 1H, C_5H_4), 6.52 (t, J = 2.6 Hz, 1H, C_5H_4), 6.15 (t, J = 2.7 Hz, 1H, C_5H_4), 5.88 (t, J = 2.9 Hz, 1H, C_5H_4), 3.47 (m, 2H, NCH_2), 3.26 (s, 3H, NCH_3), 3.15 (m, 1H, NCH_2), 2.55 (s, 3H, NCH_3), 2.34 (m, 1H, NCH_2), 1.70 (m, 2H, $NCH_2CH_2CH_2N$), 1.62 (s, 3H, $C(CH_3)_2$), 1.57 (s, 3H, $C(CH_3)_2$), 1.44 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 157.8 (N=*C*-S), 113.9, 113.3, 113.0, 109.1 (C_5H_4), 104.0, 100.9 (Cage *C*), 58.4, 54.6 (NCH_2), 46.6 ($C(CH_3)_3$), 45.7, 44.9 (NCH_3), 42.9 ($C(CH_3)_2$), 33.4, 32.5 ($C(CH_3)_2$), 28.8 ($C(CH_3)_3$), 22.2 ($NCH_2CH_2CH_2N$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.2 (2B), –5.5 (2B), –8.9 (4B), –10.8 (2B). IR (KBr, cm^{-1}): ν_{BH} 2582, 2561 (vs). Anal. Calcd. for $C_{20}H_{41}B_{10}N_3SZr$ (**10a**): C, 43.29; H, 7.45; N, 7.57. Found: C, 43.12; H, 7.05; N, 7.77.

Alternative method. To a toluene (20 mL) suspension of **9a'•C_7H_8** (283 mg, 0.38 mmol) was added dropwise a toluene (6 mL) solution of ^{t}BuNCS (88 mg, 0.76 mmol) at room temperature. The mixture was stirred at 60 °C overnight, leading to a clear colorless solution. After removal of the solvent under vacuum, the white residue was washed with *n*-hexane (10 mL X 3). After filtration, the white solid was collected and redissolved in toluene (20 mL). The resulting colorless solution was filtered and concentrated under vacuum to about 10 mL. Complex **10a** was isolated as colorless crystals after the solution stood at room temperature for one week (152 mg, 72%).

Preparation of [η^5:σ-Me$_2$C(C_5H_4)($C_2B_{10}H_{10}$)]Zr[η^3-N(Me)(CH_2)$_3$N(Me)C(=NXyl)S]•(C_7H_8)$_{0.5}$ (10a'•(C_7H_8)$_{0.5}$). This complex was prepared as colorless crystals from **3a** (117 mg, 0.27 mmol) and XylNCS (69 mg, 0.42 mmol) in toluene using the identical procedure reported for **7a**: yield 142 mg (81%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.26 (m, 1H, $C_6H_5CH_3$), 7.17 (m, 2H, $C_6H_3(CH_3)_2$), 7.15 (m, 1.5H, $C_6H_5CH_3$), 7.04 (t, J = 7.4 Hz, 1H, $C_6H_3(CH_3)_2$), 6.88 (d, J = 2.7 Hz, 1H, C_5H_4), 6.58 (d, J = 2.4 Hz, C_5H_4), 6.30 (t, J = 2.7 Hz, 1H, C_5H_4), 6.05 (t, J = 2.7 Hz, 1H, C_5H_4), 3.60 (m, 2H, NCH_2), 3.35 (s, 3H, NCH_3), 3.26 (m, 1H, NCH_2), 2.83 (s, 3H, NCH_3), 2.69 (m, 1H, NCH_2), 2.23 (s, 6H, $C_6H_3(CH_3)_2$), 2.20 (s, 1.5H, $C_6H_5CH_3$), 1.84 (m, 2H, NCH$_2$CH_2CH$_2$N), 1.57 (s, 3H, C(CH_3)$_2$), 1.56 (s, 3H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 165.4 (N=*C*-S), 145.7 (C_5H_4), 128.7, 128.0, 127.8, 126.6, 125.1 ($C_6H_3(CH_3)_2$ + $C_6H_5CH_3$), 113.4, 112.8, 112.2, 108.7 (C_5H_4), 103.1, 99.9 (Cage *C*), 60.1, 45.3 (N*C*H$_2$), 45.1, 44.9 (N*C*H$_3$), 42.0 (*C*(CH$_3$)$_2$), 32.4, 31.4 (C(*C*H$_3$)$_2$), 23.7 (NCH$_2$*C*H$_2$CH$_2$N), 21.7 ($C_6H_5CH_3$), 17.7, 17.6 ($C_6H_3(CH_3)_2$). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ –3.3 (3B), –5.6 (2B), –9.2 (5B). IR (KBr, cm^{-1}): ν_{BH} 2594, 2552 (vs). Anal. Calcd. for $C_{27.5}H_{45}B_{10}N_3SZr$ (**10a'** + 0.5toluene): C, 50.89; H, 6.99; N, 6.47. Found: C, 50.44; H, 7.26; N, 6.38.

Alternative method. To a toluene (20 mL) suspension of **9a'•C_7H_8** (229 mg, 0.31 mmol) was added a toluene (6 mL) solution of XylNCS (101 mg, 0.62 mmol) at room temperature. The mixture was stirred at 60 °C overnight, giving a colorless solution. After filtration, the resulting clear colorless solution was concentrated under vacuum to about 10 mL. Complex **10a'•$(C_7H_8)_{0.5}$** was isolated as colorless crystals after this solution stood at room temperature for 3 days (152 mg, 76%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^3$-N(Me)$(CH_2)_3$N(Me)C(=N^{t}Bu)S] (10b). This complex was prepared as colorless crystals from **3b** (101 mg, 0.19 mmol) and ^{t}BuNCS (56 mg, 0.48 mmol) in toluene using the identical procedure reported for **7a**: yield 64 mg (52%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.73 (brs, 1H, C_5H_4), 6.47 (brs, 1H, C_5H_4), 6.10 (d, J = 2.4, 1H, C_5H_4), 5.81 (d, J = 2.4 Hz, 1H, C_5H_4), 3.52 (m, 1H, NCH_2), 3.37 (s, 3H, NCH_3), 3.32 (m, 1H, NCH_2), 2.93 (m, 1H, NCH_2), 2.59 (s, 3H, NCH_3), 2.46 (m, 1H, NCH_2), 1.62 (m, 5H, C(CH_3)$_2$+ NCH$_2$CH_2CH$_2$N), 1.58 (s, 3H, C(CH_3)$_2$), 1.44 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 156.6 (N=*C*-S), 147.2, 112.3, 112.2, 111.1, 108.1 (C_5H_4), 109.0, 103.7 (Cage *C*), 60.2, 54.2 (NCH$_2$), 45.5 (*C*(CH$_3$)$_2$), 45.0 (NCH$_3$), 44.7 (*C*(CH$_3$)$_3$), 42.0 (NCH$_3$), 32.1, 32.2 (C(*C*H$_3$)$_2$), 24.0 (NCH$_2$CH$_2$CH$_2$N). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ –3.4 (2B), –5.1 (2B), –9.2 (4B), –11.4 (2B). IR (KBr, cm^{-1}): ν_{BH} 2594 (vs). Anal. Calcd. for $C_{20}H_{41}B_{10}HfN_3S$ (**10b**): C, 37.40; H, 6.43; N, 6.45. Found: C, 37.74; H, 6.26; N, 6.53.

Alternative method. This complex was prepared as colorless crystals from **9b'•C_7H_8** (207 mg, 0.25 mmol) and ^{t}BuNCS (60 mg, 0.52 mmol) in toluene using a procedure identical with that reported for **10a**: yield 152 mg (95%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{OC(=N$C_{10}H_7$)N($C_{10}H_7$)C(=O)}]N(Me)$(CH_2)_3$N(Me)C(N$C_{10}H_7$)O] (11a). To a

toluene solution of **3a** (214 mg, 0.49 mmol) was added dropwise a toluene solution of 1-naphthylisocyanate (337 mg, 2.0 mmol) at -30 °C, the mixture was warmed to room temperature and stirred at 60 °C for 1 day. A colorless solution with a white precipitate was obtained. After removal of solvent under vacuum, the white residue was redissolved in THF (30 mL). After filtration, the resulting colorless solution was concentrated under vacuum to about 15 mL. *n*-Hexane (10 mL) vapor diffusion gave **11a** as colorless crystals over a period of 10 days at room temperature (321 mg, 69%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 8.86 (m, $C_{10}H_7$), 8.65 (t, J = 7.6 Hz, $C_{10}H_7$), 8.53 (d, J = 8.4 Hz, $C_{10}H_7$), 8.33 (d, J = 8.1 Hz, $C_{10}H_7$), 8.28 (d, J = 8.1 Hz, $C_{10}H_7$), 8.23 (m, $C_{10}H_7$), 8.03 (m, $C_{10}H_7$), 7.90 (m, $C_{10}H_7$), 7.79 (m, $C_{10}H_7$), 7.61 (m, $C_{10}H_7$), 7.44 (m, $C_{10}H_7$), 7.36 (t, J = 7.4 Hz, $C_{10}H_7$), 7.29 (t, J = 7.7 Hz, $C_{10}H_7$), 6.41 (d, J = 2.4 Hz, C_5H_4), 6.37 (d, J = 2.4 Hz, C_5H_4), 6.31 (d, J = 2.4 Hz, C_5H_4), 6.25 (dd, J = 3.1, 5.6 Hz, C_5H_4), 6.20 (d, J = 2.5 Hz, C_5H_4), 5.93 (m, C_5H_4), 5.65 (d, J = 2.1 Hz, C_5H_4), 5.51 (d, J = 2.1 Hz, C_5H_4), 5.44 (d, J = 2.2 Hz, C_5H_4), 5.31 (m, C_5H_4), 5.19 (m, C_5H_4), 4.68 (t, J = 13.6 Hz, NCH_2), 4.51 (t, J = 13.8 Hz, NCH_2), 4.31 (t, J = 13.0 Hz, NCH_2), 4.12 (t, J = 13.1 Hz, NCH_2), 3.40 (m, NCH_2), 3.05 (s, NCH_3), 3.03 (s, NCH_3), 2.90 (m, NCH_2), 2.57 (m, NCH_2), 2.47 (s, NCH_3), 2.42 (s, NCH_3), 2.37 (m, NCH_2), 2.20 (m, NCH_2), 2.10 (s, NCH_3), 2.06 (s, NCH_3), 2.01 (s, NCH_3), 1.99 (s, NCH_3), 1.66 (m, NCH$_2$CH_2CH$_2$N), 1.22 (s, C(CH_3)$_2$), 1.19 (m, NCH$_2$CH_2CH$_2$N), 1.14 (s, C(CH_3)$_2$), 1.13 (s, C(CH_3)$_2$), 1.11 (s, C(CH_3)$_2$), 1.10 (s, C(CH_3)$_2$), 1.09 (s, C(CH_3)$_2$), 1.08 (s, C(CH_3)$_2$), 0.66 (m, NCH$_2$CH_2CH$_2$N). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 169.4, 168.5, 166.6, 165.9, 165.2, 164.8, 164.4 (N-*C*-O), 147.1, 145.7, 144.8, 144.2, 143.3, 138.2, 138.0, 134.8, 134.6, 131.5, 131.1, 131.0, 130.2, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 128.9, 128.7, 128.6, 128.1, 128.0, 127.9, 127.4, 127.3, 127.0, 126.8, 126.7, 126.6, 126.3, 126.1, 126.1, 125.8, 125.7, 125.3, 124.9,

124.8, 124.7, 124.6, 122.4, 122.2, 122.0, 118.7, 118.1 ($C_{10}H_7$), 152.7, 152.3, 149.1, 120.4, 120.0, 119.4, 116.2, 115.0, 114.5, 114.4, 113.9, 113.8, 113.0, 112.8, 112.2 (C_5H_4), 106.9, 106.8, 106.3, 101.7, 101.0, 100.9 (Cage *C*), 51.6, 51.4, 49.7, 49.3, 45.0, 43.3 (NCH_2), 42.0, 41.9 ($C(CH_3)_2$), 34.7, 34.5, 34.2, 34.1, 33.8, 33.3 (NCH_3), 32.5, 32.3, 32.1, 31.9, 31.8, 31.6, 31.3 ($C(CH_3)_2$), 25.7, 23.3, 22.5 ($NCH_2CH_2CH_2N$). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): –1.8 (6B), –6.8 (24B). IR (KBr, cm^{-1}): ν_{BH} 2582, 2571, 2549 (vs). Anal. Calcd for $C_{48}H_{53}B_{10}N_5O_3Zr$ (**11a**): C, 60.86; H, 5.64; N, 7.39. Found: C, 61.35; H, 6.00; N, 7.05.

Alternative method. To a toluene (20 mL) supsension of **9a'•C_7H_8** (366 mg, 0.48 mmol) was added dropwise a toluene (6 mL) solution of 1-naphthylisocyanate (254 mg, 1.5 mmol) at room temperature. The mixture was stirred at 60 °C overnight. After removal of solvent under vacuum, the white residue was washed with *n*-hexane (10 mL X 3). The white solid was collected and redissolved in THF (30 mL). After filtration, the resulting colorless solution was concentrated under vacuum to about 15 mL. *n*-Hexane (10 mL) vapor diffusion gave **11a** as colorless crystals over a period of 8 days at room temperature (308 mg, 68%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-(Xyl)N=CN(Me)$(CH_2)_3$N(Me)C=N(Xyl)] (12a). This complex was prepared as colorless crystals from **3a** (220 mg, 0.50 mmol) and XylNC (131 mg, 1.00 mmol) in toluene solution using the identical procedure reported for **4a**: yield 222 mg (63%). ^1H NMR (300 MHz, pyridine-d_5): δ 7.08 (m, 6H, $C_6H_3(CH_3)_2$), 6.25 (brs, 2H, C_5H_4), 6.01 (brs, 2H, C_5H_4), 3.80 (m, 2H, NCH_2), 3.20 (m, 2H, NCH_2), 2.47 (s, 6H, NCH_3), 2.24 (s, 6H, $C_6H_3(CH_3)_2$), 1.99 (s, 6H, $C_6H_3(CH_3)_2$), 2.18 (m, 2H, $NCH_2CH_2CH_2N$), 1.68 (s, 6H, $C(CH_3)_2$). The ^{13}C NMR was not obtainable due to very poor solubility. $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.2 (2B), –5.4 (2B), –9.0 (6B). IR (KBr,

cm^{-1}): ν_{BH} 2593, 2547 (vs). Anal. Calcd for $C_{33}H_{50}B_{10}N_4Zr$ (**12a**): C, 56.45; H, 7.18; N, 7.98. Found: C, 56.71; H, 6.96; N, 7.62.

Alternative method. This complex was prepared as colorless crystals from **9a'•C_7H_8** (208 mg, 0.27 mmol) and XylNC (65 mg, 0.56 mmol) in toluene solution using the identical procedure reported for **11a**: yield 141 mg (75%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-(Xyl)N=CN(Me)$(CH_2)_3$N(Me)C=N(Xyl)] (12b). This complex was prepared as colorless crystals from **3b** (257 mg, 0.49 mmol) and XylNC (131 mg, 1.00 mmol) in toluene solution using the identical procedure reported for **4a**: yield 231 mg (58%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.04 (m, 6H, $C_6H_3(CH_3)_2$), 6.21 (brs, 2H, C_5H_4), 5.96 (brs, 2H, C_5H_4), 3.76 (brs, 2H, NCH_2), 3.18 (brs, 2H, NCH_2), 2.45 (s, 6H, NCH_3), 2.26 (s, 6H, $C_6H_3(CH_3)_2$), 2.15 (m, 2H, $NCH_2CH_2CH_2N$), 2.03 (s, 6H, $C_6H_3(CH_3)_2$), 1.68 (s, 6H, $C(CH_3)_2$). The ^{13}C NMR was not obtainable due to very poor solubility. ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ –3.0 (2B), –5.2 (2B), –8.9 (4B), –10.2 (2B). IR (KBr, cm^{-1}): ν_{BH} 2598, 2544 (vs). Anal. Calcd for $C_{33}H_{50}B_{10}HfN_4$ (**12b**): C, 50.21; H, 6.38; N, 7.10. Found: C, 50.55; H, 6.32; N, 6.59.

Alternative method. This complex was prepared as colorless crystals from **9b'•C_7H_8** (228 mg, 0.28 mmol) and XylNC (65 mg, 0.56 mmol) in toluene solution using the identical procedure reported for **11a**: yield 168 mg (76%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{N^{n}Bu}{N^{n}Bu}[(=C)-C=CHN(^{n}Bu)CH_2N[$(CH_2)_3$N(Me)N-C=N(^{n}Bu)]] (13a). To a toluene (20 mL) solution of **3a** (221 mg, 0.50 mmol) was added dropwise a toluene (6 mL) solution of ^{n}BuNC (168 mg, 2.00 mmol) at -30 °C with stirring. The mixture was warmed to room temperature and heated at 60 °C for 2 days. The solvent was removed under vacuum and the brown residue was redissolved in *n*-hexane (20 mL). The resulting

brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **13a** was isolated as orange-red crystals after this solution stood at room temperature for 7 days (211 mg, 55%). ^{1}H NMR (400 MHz, benzene-d_5): δ 6.52 (d, J = 2.2 Hz, 1H, C_5H_4), 6.44 (d, J = 2.4 Hz, 1H, C_5H_4), 6.40 (brs, 1H, C_5H_4), 6.01 (d, J = 2.4 Hz, 1H, C_5H_4), 5.84 (s, 1H, ZrN(^{n}Bu)C=C*H*), 4.17 (m, 1H, NCH_2), 3.95 (m, 1H, NCH_2), 3.75 (d, J = 11.6 Hz, 1H, NCH_2N^{n}Bu), 3.40 (d, J = 11.6 Hz, 1H, NCH_2N^{n}Bu), 3.52 (m, 3H, NCH_2), 3.14 (m, 1H, NCH_2), 2.87 (m, 1H, NCH_2), 2.77 (t, J = 11.6 Hz, 1H, NCH_2), 2.47 (s, 3H, NCH_3), 2.36 (m, 4H, NCH_2), 1.83 (m, 2H, NCH$_2$CH_2), 1.73 (s, 3H, C(CH_3)$_2$), 1.72 (m, 2H, NCH$_2$CH_2), 1.71 (s, 3H, C(CH_3)$_2$), 1.43 (m, 2H, NCH$_2$CH_2), 1.31 (m, 8H, NCH$_2$CH_2CH$_2$N + NCH$_2$CH_2 + NCH$_2$CH$_2$CH_2), 1.13 (m, 4H, NCH$_2$CH$_2$CH_2), 1.01 (t, J = 7.3 Hz, 3H, CH_3), 0.98 (t, J = 7.3 Hz, 3H, CH_3), 0.89 (t, J = 7.3 Hz, 3H, CH_3), 0.80 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C{H} NMR (100 MHz, benzene-d_6): δ 216.7 (Zr-N(^{n}Bu)=*C*), 164.3 (Zr-N(^{n}Bu)*C*=N), 148.1 (C_5H_4), 129.4 (Zr-N(^{n}Bu)C=*C*H), 110.9, 110.4, 108.7, 105.5 (C_5H_4), 105.2, 102.3 (Cage *C*), 66.2 (NCH$_2$N^{n}Bu), 56.8, 54.2, 52.6, 50.3, 48.6, 48.1 (NCH$_2$), 42.5 (*C*(CH$_3$)$_2$), 35.4 (NCH$_3$), 33.4, 32.9 (C(*C*H$_3$)$_2$), 32.9, 32.0, 30.2, 30.1 (NCH$_2$*C*H$_2$), 29.2, 21.4, 21.0, 20.5, 20.4 (NCH$_2$CH$_2$*C*H$_2$ + NCH$_2$CH$_2$CH$_2$N), 14.9, 14.2, 14.0, 13.9 (*C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ –3.3 (3B), –5.7 (3B), –10.6 (4B). IR (KBr, cm^{-1}): ν_{BH} 2602, 2550 (vs). Anal. Calcd. for $C_{35}H_{68}B_{10}N_6Zr$ (**13a**): C, 54.43; H, 8.87; N, 10.88. Found: C, 54.69; H, 8.90; N, 10.56.

Alternative method. To a toluene (20 mL) supension of **9a'•C$_7$H$_8$** (204 mg, 0.26 mmol) was added dropwise a toluene (6 mL) solution of ^{n}BuNC (105 mg, 1.30 mmol) at room temperature. The mixture was stirred at 60 °C overnight. After removal of solvent under vacuum, the brown residue was redissolved in *n*-hexane (30 mL). After filtration, the resulting brown solution was concentrated under vacuum to about 15

mL. Complex **13a** was isolated as orange-red crystals after this solution stood at room temperature for 7 days (100 mg, 50%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-{N^{n}Bu}{N^{n}Bu}[(=C)-C=CHN(^{n}Bu)CH_2N[$(CH_2)_3$N(Me)N-C=N(^{n}Bu)]] (13b). To a toluene (20 mL) solution of **3b** (251 mg, 0.48 mmol) was added dropwise a toluene (6 mL) solution of ^{n}BuNC (168 mg, 2.00 mmol) at -30 °C with stirring. The mixture was warmed to room temperature and heated at 60 °C for 2 days. The solvent was removed under vacuum and the brown residue was washed with *n*-hexane (10 mL X 3). After filtration, the orange residue was redissolved in ether (30 mL). The resulting clear orange solution was filtered and concentrated under vacuum to about 15 mL. Complex **13b** was isolated as orange crystals after this solution stood at room temperature for 7 days (228 mg, 55%). ^{1}H NMR (400 MHz, benzene-d_5): δ 6.51 (d, J = 2.8 Hz, 1H, C_5H_4), 6.40 (m, 2H, C_5H_4), 5.92 (d, J = 2.8 Hz, 1H, C_5H_4), 5.80 (s, 1H, HfN(^{n}Bu)C=C*H*), 4.12 (m, 1H, NCH_2), 3.98 (m, 1H, NCH_2), 3.73 (d, J = 11.6 Hz, 1H, NCH_2N^{n}Bu), 3.35 (d, J = 11.6 Hz, 1H, NCH_2N^{n}Bu), 3.57 (m, 3H, NCH_2), 3.16 (m, 1H, NCH_2), 2.85 (m, 1H, NCH_2), 2.73 (m, 1H, NCH_2), 2.51 (m, 1H, NCH_2), 2.42 (s, 3H, NCH_3), 2.33 (m, 3H, NCH_2), 1.82 (m, 2H, NCH_2CH_2), 1.73 (s, 3H, $C(CH_3)_2$), 1.72 (s, 3H, $C(CH_3)_2$), 1.60 (m, 2H, NCH_2CH_2), 1.46 (m, 5H, NCH_2CH_2 + $NCH_2CH_2CH_2N$ + $NCH_2CH_2CH_2$), 1.29 (m, 4H, NCH_2CH_2 +$NCH_2CH_2CH_2$), 1.10 (m, 5H, $NCH_2CH_2CH_2N$ + $NCH_2CH_2CH_2$), 1.02 (t, J = 7.2 Hz, 3H, CH_3), 0.97 (t, J = 7.2 Hz, 3H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3), 0.79 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C{H} NMR (100 MHz, benzene-d_6): δ 224.4 (HfN(^{n}Bu)=*C*), 165.4 (HfN(^{n}Bu)=*C*N), 146.7 (C_5H_4), 130.2 (Hf-N(^{n}Bu)C=*C*H), 129.3 ((Hf-N(^{n}Bu)C=CH), 110.6, 109.1, 108.0, 104.2 (C_5H_4), 111.4, 102.1 (Cage *C*), 66.3 (NCH_2N^nBu), 56.7, 53.6, 52.6, 49.7, 48.4, 48.2 (NCH_2), 42.0 ($C(CH_3)_2$), 35.4 (NCH_3), 33.3, 32.9

($C(CH_3)_2$), 31.1, 32.8, 30.2, 30.0 (NCH_2CH_2), 29.2, 21.4, 21.0, 20.5, 20.3 ($NCH_2CH_2CH_2$ + $NCH_2CH_2CH_2N$), 14.9, 14.1, 14.0, 13.9 (CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –0.3 (3B), –2.6 (2B), –5.9 (3B), –8.6 (1B), –10.8 (1B). IR (KBr, cm^{-1}): ν_{BH} 2603, 2552 (vs). Anal. Calcd. for $C_{35}H_{68}B_{10}HfN_6$ (**13b**): C, 48.85; H, 8.08; N, 9.77. Found: C, 48.74; H, 7.67; N, 9.47.

Alternative method. To a toluene (20 mL) supension of **9b'•C_7H_8** (370 mg, 0.45 mmol) was added dropwise a toluene (6 mL) solution of ^{n}BuNC (268 mg, 4.0 mmol) at room temperature. The mixture was stirred at 60 °C overnight. After removal of solvent under vacuum, the brown residue was washed with *n*-hexane (10 mL X 3). After filtration, the orange residue was redissolved in ether (30 mL). The resulting clear orange solution was filtered and concentrated under vacuum to about 15 mL. Complex **13b** was isolated as orange crystals after this solution stood at room temperature for 3 days (265 mg, 69%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{NR}{NR}[(=C)-C=CHNRCH$_2$N[$(CH_2)_3$N(Me)N-C=NR]] (R = 2-morpholinethyl) (14a). To a toluene (20 mL) solution of **3a** (220 mg, 0.50 mmol) was added dropwise a toluene (6 mL) solution of 2-morpholinethylisocyanide (280 mg, 2.00 mmol) at -30 °C with stirring. The mixture was warmed to room temperature and heated at 60 °C for 2 days. The solvent was removed under vacuum, and the brown residue was washed with *n*-hexane (10 mL X 3) and redissolved in toluene (20 mL). The resulting brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **14a** was isolated as orange-red crystals after this solution stood at room temperature for 11 days (293 mg, 59%). ^1H NMR (400 MHz, benzene-d_6): δ 6.69 (brs, 1H, C_5H_4), 6.55 (brs, 1H, C_5H_4), 6.49 (brs, 1H, C_5H_4), 6.04 (s, 1H, Zr-N(R)C=C*H*), 6.02 (d, J = 2.0 Hz, 1H, C_5H_4), 4.48 (m, 1H, NCH_2), 3.95 (m, 2H, NCH_2 + NCH_2N), 3.71 (m,

10H, NCH_2 + NCH_2CH_2O), 3.62 (m, 5H, NCH_2N + NCH_2CH_2O), 3.56 (m, 4H, NCH_2CH_2O), 3.44 (m, 1H, NCH_2), 2.92 (m, 1H, NCH_2), 2.79 (m, 1H, NCH_2), 2.70 (m, 1H, NCH_2), 2.58 (m, 2H, NCH_2), 2.52 (s, 3H, NCH_3), 2.44 (m, 8H, NCH_2), 2.36 (m, 4H, NCH$_2$CH_2O), 2.28 (m, 8H, NCH$_2$CH_2O), 2.04 (m, 4H, NCH$_2$CH_2O), 1.95 (m, 2H, NCH_2), 1.73 (m, 4H, C(CH_3)$_2$ + NCH$_2$CH_2CH$_2$N), 1.71 (s, 3H, C(CH_3)$_2$). ^{13}C{H} NMR (100 MHz, benzene-d_6): δ 217.4 (Zr-*C*=N), 164.6 (ZrN(R)=*C*N), 148.7 (*C*$_5$H$_4$), 130.4 (Zr-N(R)C=*C*H), 111.2, 110.9, 109.4, 105.5 (*C*$_5$H$_4$), 104.8, 102.5 (Cage *C*), 67.3, 67.2, 67.1, 67.0 (N*C*H$_2$CH$_2$O), 66.6 (N*C*H$_2$N), 61.8, 59.4, 57.7, 57.0 (N*C*H$_2$), 55.0, 54.6, 54.4, 53.9 (NCH$_2$*C*H$_2$O), 52.9, 49.0, 48.3, 47.3, 47.0 (N*C*H$_2$), 42.6 (*C*(CH$_3$)$_2$), 36.3 (N*C*H$_3$), 33.5, 32.8 (C(*C*H$_3$)$_2$), 29.2 (NCH$_2$*C*H$_2$CH$_2$N). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ –3.2 (3B), –5.6 (4B), –8.6 (3B). IR (KBr, cm^{-1}): ν_{BH} 2580 (vs). Anal. Calcd. for $C_{43}H_{80}B_{10}N_{10}O_4Zr$ (**14a**): C, 51.62; H, 8.06; N, 14.00. Found: C, 52.00; H, 8.15; N, 14.42.

Alternative method. To a toluene (20 mL) supension of **9a'•C$_7$H$_8$** (354 mg, 0.45 mmol) was added dropwise a toluene (6 mL) solution of 2-mortholinethylisocyanide (407 mg, 2.90 mmol) at room temperature. The mixture was stirred at 60 °C overnight. After removal of solvent under vacuum, the brown residue was washed with *n*-hexane (10 mL X 3). After filtration, the brown residue was redissolved in toluene (20 mL). The resulting clear brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **14a** was isolated as orange-red crystals after this solution stood at room temperature for 24 days (263 mg, 58%).

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Hf[η^2:η^2-{NR}{NR}[(=C)-C=CHNRCH$_2$N[(CH$_2$)$_3$N(Me)N-C=NR]] (R = 2-morpholinethyl) (14b). To a toluene (20 mL) solution of **3b** (251 mg, 0.48 mmol) was added dropwise a toluene (6 mL) solution of 2-morpholinethylisocyanide (280 mg, 2.00 mmol) at -30 °C with

stirring. The mixture was warmed to room temperature and heated at 60 °C for 2 days. The solvent was removed under vacuum and the brown residue was washed with *n*-hexane (10 mL X 3) and redissolved in DME (20 mL). The resulting brown solution was filtered and concentrated under vacuum to about 8 mL. Complex **14b** was isolated as orange crystals after this solution stood at room temperature for 11 days (364 mg, 70%). ^{1}H NMR (400 MHz, benzene-d_6): δ 6.65 (d, J = 2.3 Hz, 1H, C_5H_4), 6.49 (m, 2H, C_5H_4), 6.00 (s, 1H, Hf-N(R)C=C*H*), 5.96 (d, J = 2.4 Hz, 1H, C_5H_4), 4.40 (m, 1H, NCH_2), 3.97 (m, 2H, NCH_2 + NCH_2N), 3.77 (m, 2H, NCH_2), 3.69 (m, 8H, NCH_2CH$_2$O), 3.62 (m, 5H, NCH_2N + NCH_2CH$_2$O), 3.57 (m, 4H, NCH_2CH$_2$O), 3.42 (m, 1H, NCH_2), 2.93 (m, 1H, NCH_2), 2.78 (m, 1H, NCH_2), 2.64 (m, 3H, NCH_2), 2.54 (s, 3H, NCH_3), 2.45 (m, 12H, NCH_2 + NCH$_2$CH_2O), 2.36 (m, 4H, NCH$_2$CH_2O), 2.28 (m, 4H, NCH$_2$CH_2O), 2.09 (m, 4H, NCH$_2$CH_2O), 1.97 (m, 2H, NCH_2), 1.79 (m, 1H, NCH$_2$CH_2CH$_2$N), 1.73 (s, 3H, C(CH_3)$_2$), 1.71 (s, 3H, C(CH_3)$_2$). ^{13}C{H} NMR (100 MHz, benzene-d_6): δ 225.0 (Hf-*C*=N), 165.8 (HfN(R)=*C*N), 146.9 (*C*$_5$H$_4$), 131.2 (Hf-N(R)C=*C*H), 110.5, 102.3 (Cage *C*), 111.0, 109.4, 108.6, 104. (*C*$_5$H$_4$), 67.3, 67.2, 67.1, 67.0 (N*C*H$_2$CH$_2$O), 66.7 (N*C*H$_2$N), 61.9, 59.2, 57.9, 57.0 (N*C*H$_2$), 55.1, 54.6, 54.3, 53.9 (NCH$_2$*C*H$_2$O), 52.3, 49.1, 48.3, 46.7, 46.6 (N*C*H$_2$), 42.1 (*C*(CH$_3$)$_2$), 35.6 (N*C*H$_3$), 33.4, 32.8 (C(*C*H$_3$)$_2$), 29.2 (NCH$_2$*C*H$_2$CH$_2$N). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ –5.2 (10B). IR (KBr, cm^{-1}): ν_{BH} 2586, 2551 (vs). Anal. Calcd. for $C_{43}H_{80}B_{10}HfN_{10}O_4$ (**14b**): C, 47.48; H, 7.41; N, 12.88. Found: C, 47.36; H, 7.52; N, 12.85.

Alternative method. This complex was prepared as orange crystals from **9b'•C$_7$H$_8$** (377 mg, 0.47 mmol) and 2-morpholinethylisocyanide (282 mg, 2.00 mmol) in toluene solution using the identical procedure reported for **14a**: yield 378 mg (74%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{$NCH_2Ph$}{$NCH_2Ph$}[-C(=$CH_2Ph$)N(Me)$(CH_2)_3$N(Me)C=N($CH_2Ph$)] (15a). This complex was prepared as yellow crystals from **3a** (219 mg, 0.50 mmol) and $PhCH_2NC$ (257 mg, 2.20 mmol) in toluene using the identical procedure reported for **14a**: yield 220 mg (50%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.60 (d, J = 7.6 Hz, 2H, C_6H_5), 7.46 (brs, 2H, C_6H_5), 7.39 (brs, 2H, C_6H_5), 7.28 (t, J = 7.4 Hz, 4H, C_6H_5), 7.12 (m, 5H, C_6H_5), 6.83 (m, 5H, C_6H_5), 5.92 (brs, 1H, C_5H_4), 5.92 (brs, 1H, PhC*H*=C), 5.42 (brs, 1H, C_5H_4), 5.32 (brs, 1H, C_5H_4), 5.25 (brs, 2H, C_5H_4 + PhCH_2), 4.96 (brs, 1H, PhCH_2), 4.81 (d, J = 13.9 Hz, 1H, PhCH_2), 4.62 (d, J = 13.9 Hz, PhCH_2), 4.36 (brs, 2H, NCH_2 + PhCH_2), 4.17 (brs, 1H, PhCH_2), 3.89 (brs, 1H, NCH_2), 2.92 (m, 2H, NCH_2), 2.53 (s, 3H, NCH_3), 2.26 (s, 3H, NCH_3), 1.32 (s, 3H, C(CH_3)$_2$), 1.27 (s, 3H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 212.5 (Zr*C*=NCH_2Ph), 166.6 (Zr-N(CH_2Ph)=*C*-C), 153.1 (Zr-N(CH_2Ph)=C-*C*), 148.0, 142.1, 141.1, 140.0, 130.3, 129.4, 129.1, 127.6, 126.6, 126.3, 123.5 (*C*$_6$H$_5$), 139.3, 115.9, 111.4, 107.0, 98.2 (*C*$_5$H$_4$), 110.6, 103.5 (Cage *C*), 110.7 (C=*C*HPh), 60.6, 58.1 (CH_3NCH_2), 55.7, 53.3 (Ph*C*H$_2$), 42.1 (*C*(CH$_3$)$_2$), 38.3, 36.0 (N*C*H$_3$), 32.7 (C(*C*H$_3$)$_2$), 23.0 (NCH$_2$*C*H$_2$*C*H$_2$N). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ –4.8 (6B), –9.6 (4B). IR (KBr, cm^{-1}): ν_{BH} 2589, 2555 (vs). Anal. Calcd. for $C_{46}H_{59}B_{10}N_5Zr$ (**15a**): C, 62.69; H, 6.75; N, 7.95. Found: C, 62.37; H, 7.14; N, 7.64.

Alternative method. To a toluene (20 mL) supension of **9a'•C_7H_8** (641 mg, 0.82 mmol) was added dropwise a toluene (6 mL) solution of $PhCH_2NC$ (469 mg, 4.00 mmol) at room temperature. The mixture was stirred at 60 °C overnight. After removal of solvent under vacuum, the brown residue was washed with *n*-hexane (10 mL X 3). The residue was recrystallized from ether. The yellowish brown solid was redissolved in DME (20 mL). After filtration, the resulting yellow solution was

concentrated under vacuum to about 10 mL. *n*-Hexane (10 mL) vapor diffusion gave **15a** as yellow crystals over a period of 9 days at room temperature (369 mg, 51%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-{$NCH_2Ph$}{$NCH_2Ph$}[-C(=$CH_2Ph$)N(Me)$(CH_2)_3$N(Me)C=N($CH_2Ph$)] (15b). This complex was prepared as yellow crystals from **3b** (262 mg, 0.50 mmol) and $PhCH_2NC$ (257 mg, 2.20 mmol) in toluene using the identical procedure reported for **14a**: yield 211 mg (44%). Single crystal suitable for X-ray analyses were grown from a DME solution at room temperature as **15b•0.5DME**. ^{1}H NMR (400 MHz, benzene-d_6): δ 7.60 (d, J = 7.5 Hz, 2H, C_6H_5), 7.44 (t, J = 8.6 Hz, 4H, C_6H_5), 7.29 (m, 4H, C_6H_5), 7.13 (m, 4H, C_6H_5), 6.83 (m, 6H, C_6H_5), 6.48 (brs, 1H, C_5H_4), 5.93 (brs, 1H, PhC*H*=C), 5.41 (brs, 1H, C_5H_4), 5.29 (brs, 1H, C_5H_4), 5.23 (brs, 2H, C_5H_4 + $PhCH_2$), 5.03 (brs, 1H, $PhCH_2$), 4.87 (d, J = 13.8 Hz, 1H, $PhCH_2$), 4.67 (d, J = 13.8 Hz, $PhCH_2$), 4.38 (m, 2H, NCH_2 + $PhCH_2$), 4.15 (d, J = 14.0 Hz, 1H, $PhCH_2$), 3.84 (brs, 1H, NCH_2), 2.91 (d, J = 8.8 Hz, 2H, NCH_2), 2.56 (s, 3H, NCH_3), 2.24 (s, 3H, NCH_3), 1.33 (s, 3H, $C(CH_3)_2$), 1.28 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 221.4 (Hf-N(CH_2Ph)=C-C), 160.8 (Hf-N(CH_2Ph)=C-*C*), 152.8 (C=*C*HPh), 146.0, 142.1, 141.2, 140.1, 130.4, 129.5, 129.1, 127.6, 126.5, 126.2 (C_6H_5), 139.3, 115.5, 109.9, 105.7, 99.0 (C_5H_4), 113.6, 103.3 (Cage *C*), 109.5 ($PhCH_2N$=C-C=*C*HPh), 60.6, 58.3 (CH_3NCH_2), 55.2, 53.1 ($PhCH_2$), 41.6 ($C(CH_3)_2$), 38.5, 36.2 (NCH_3), 32.8, 32.6 ($C(CH_3)_2$), 22.9 ($NCH_2CH_2CH_2N$). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ –5.3 (6B), –8.3 (4B). IR (KBr, cm^{-1}): ν_{BH} 2589, 2554 (vs). Anal. Calcd. for $C_{46}H_{59}B_{10}HfN_5$ (**15b**): C, 57.04; H, 6.14; N, 7.23. Found: C, 57.11; H, 6.22; N, 6.99.

Alternative method. This complex was prepared as yellow crystals from **9b'•C_7H_8** (733 mg, 0.89 mmol) and $PhCH_2NC$ (468 mg, 4.00 mmol) in toluene using the identical procedure reported for **15a**: yield 486 mg (56%).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-{$NCH_2TMS$}=C{CNCH(Me)Si($Me_2$)N($CH_2TMS$)C=}N(Me)($CH_2$)$_3$N(Me)C=NC$H_2TMS$] (16a). To a toluene (20 mL) solution of **3a** (132 mg, 0.30 mmol) was added dropwise a toluene (6 mL) solution of $TMSCH_2NC$ (204 mg, 1.80 mmol) at -30°C with stirring. The mixture was stirred at 70 °C for 5 days. The solvent was removed under vacuum, and the red residue was redissolved in THF (20 mL). The resulting red solution was filtered and concentrated under vacuum to about 10 mL. Complex **16a** was isolated as orange-red crystals after this solution stood at room temperature for 12 days (152 mg, 57%). ^{1}H NMR (400 MHz, benzene-d_6): δ 6.63 (d, J = 2.7 Hz, 1H, C_5H_4), 6.51 (d, J = 2.4 Hz, 1H, C_5H_4), 6.27 (d, J = 2.8 Hz, 1H, C_5H_4), 5.78 (d, J = 2.5 Hz, 1H, C_5H_4), 6.30 (s, 1H, C=C*H*NCH_2TMS), 4.02 (m, 1H, NCH_2), 3.93 (q, J = 7.4 Hz, 1H, Si(Me_2)C*H*Me), 3.44 (d, J = 14.4, 1H, NCH_2TMS), 3.34 (d, J = 14.4 Hz, 1H, NCH_2TMS), 2.93 (m, 2H, NCH_2), 2.73 (d, J = 14.0 Hz, 1H, NCH_2TMS), 2.58 (d, J = 14.0 Hz, 1H, NCH_2TMS), 2.61 (s, 3H, NCH_3), 2.53 (d, J = 14.1 Hz, 1H, NCH_2TMS), 2.39 (d, J = 14.1 Hz, 1H, NCH_2TMS), 2.51 (s, 3H, NCH_3), 2.06 (d, J = 15.1 Hz, 1H, NCH_2), 1.75 (s, 3H, C(CH_3)$_2$), 1.72 (s, 3H, C(CH_3)$_2$), 1.15 (d, J = 7.4 Hz, 3H, Si(Me_2)CHCH_3), 0.75 (s, 3H, (CH_3)$_2$SiCHCH_3), 0.30 (s, 9H, Si(CH_3)$_3$), 0.07 (s, 3H, (CH_3)$_2$SiCHCH_3), 0.06 (s, 9H, Si(CH_3)$_3$), 0.01 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 218.6 (Zr-*C*=NCH_2TMS), 167.9 (Zr-N=*C*-NCH_3), 148.5 (*C*$_5$H$_4$), 133.7 (ZrN=C-*C*=CH + ZrN=C-C=*C*H), 110.6, 110.0, 109.9, 105.7 (*C*$_5$H$_4$), 105.8, 101.7 (Cage *C*), 56.4, 45.6 (N*C*H$_2$), 45.3 (Me$_2$Si*C*H(CH$_3$), 44.9 (N*C*H$_2$TMS), 43.7 (N*C*H$_3$), 42.9, 42.6 (N*C*H$_2$TMS), 41.2 (N*C*H$_3$), 36.4 (C(*C*H$_3$)$_2$), 35.0, 32.5 (C(*C*H$_3$)$_2$), 24.7 (NCH$_2$*C*H$_2$*C*H$_2$N), 18.6 ((CH$_3$)$_2$SiCH(*C*H$_3$)), 0.5 (Si(*C*H$_3$)$_2$), –0.4 (*C*H$_2$TMS), –0.8 (*C*H$_2$TMS), –1.6 (*C*H$_2$TMS). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_5): δ –3.2 (3B), –5.4 (2B), –8.7 (5B). IR (KBr, cm^{-1}): ν_{BH} 2581 (vs).

Anal. Calcd. for $C_{35}H_{76}B_{10}N_6Si_4Zr$ (**16a**): C, 47.09; H, 8.58; N, 9.41. Found: C, 47.33; H, 8.51; N, 8.94.

Alternative method. To a toluene (20 mL) supension of **9a'•C_7H_8** (194 mg, 0.25 mmol) was added dropwise a toluene (6 mL) solution of $TMSCH_2NC$ (204 mg, 1.80 mmol) at room temperature. The mixture was stirred at 60 °C for 3 days. The solvent was removed under vacuum and the red residue was redissolved in ether (20 mL). The resulting red solution was filtered and concentrated under vacuum to about 15 mL, **16a** was isolated as orange-red crystals after this solution stood at room temperature for 5 days (146 mg, 65%).

Preparation of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Hf[\eta^2:\eta^2\text{-}\{NCH_2TMS\}=C\{CNCH(Me)Si(Me_2)N(CH_2TMS)C=\}N(Me)(CH_2)_3N(Me)C=NCH_2TMS]$ (16b). To a toluene (20 mL) solution of **3b** (158 mg, 0.30 mmol) was added dropwise a toluene (6 mL) solution of $TMSCH_2NC$ (204 mg, 1.80 mmol) at -30°C with stirring. The mixture was heated at 70 °C for 4 days. The solvent was removed under vacuum and the orange residue was washed with cold *n*-hexane (-30 °C, 5 mL). After filtration, the orange solid was collected and redissolved in toluene (20 mL). The resulting orange solution was filtered and concentrated under vacuum to about 10 mL. Complex **16b** was isolated as orange crystals after this solution stood at room temperature for 5 days (188 mg, 64%). ^{1}H NMR (400 MHz, benzene-d_6) (313K): δ 6.59 (d, J = 2.6 Hz, 1H, C_5H_4), 6.43 (m, 1H, C_5H_4), 6.27 (d, J = 2.7 Hz, 1H, C_5H_4), 5.77 (m, 1H, C_5H_4), 6.33 (s, 1H, C=C*H*NCH_2TMS), 4.02 (m, 1H, NCH_2), 3.87 (q, J = 7.4 Hz, 1H, $Si(Me_2)CHMe$), 3.46 (d, J = 14.4 Hz, 1H, NCH_2TMS), 3.35 (d, J = 14.4 Hz, 1H, NCH_2TMS), 2.92 (m, 2H, NCH_2), 2.71 (d, J = 14.2 Hz, 1H, NCH_2TMS), 2.61 (d, J = 14.2 Hz, 1H, NCH_2TMS), 2.61 (s, 3H, NCH_3), 2.54 (d, J = 15.8 Hz, 1H, NCH_2TMS), 2.39 (d, J = 15.8 Hz, 1H, NCH_2TMS), 2.52 (s, 3H, NCH_3),

2.07 (d, J = 15.5 Hz, 1H, NCH_2), 1.75 (s, 3H, C(CH_3)$_2$), 1.72 (s, 3H, C(CH_3)$_2$), 1.70 (m, 1H, NCH$_2$CH_2CH$_2$N), 1.14 (d, J = 7.4 Hz, 4H, Si(Me$_2$)CHCH_3 + NCH$_2$CH_2CH$_2$N), 0.76 (s, 3H, (CH_3)$_2$SiCHCH$_3$), 0.31 (s, 9H, Si(CH_3)$_3$), 0.08 (s, 3H, (CH_3)$_2$SiCHCH$_3$), 0.07 (s, 9H, Si(CH_3)$_3$), 0.01 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6) (313K): δ 226.8 (Hf-*C*=NCH$_2$TMS), 168.8 (Hf-N=*C*-NCH$_3$), 146.8 (*C*$_5$H$_4$), 137.8 (HfN=C-*C*=CH), 134.6 (HfN=C-C=*C*H), 109.5, 109.3, 109.1, 104.8 (*C*$_5$H$_4$), 101.5 (Cage *C*), 56.3, 45.2 (N*C*H$_2$), 44.8 (Me$_2$Si*C*H(CH$_3$), 43.8 (N*C*H$_2$TMS), 43.5 (N*C*H$_3$), 42.5, 42.0 (N*C*H$_2$TMS), 41.1 (N*C*H$_3$), 35.9 (*C*(CH$_3$)$_2$), 34.2, 32.4 (C(*C*H$_3$)$_2$), 21.3 (NCH$_2$*C*H$_2$CH$_2$N), 18.4 ((CH$_3$)$_2$SiCH(*C*H$_3$)), 0.6 (Si(CH$_3$)$_2$), –0.3 (*C*H$_2$TMS), –0.8 (*C*H$_2$TMS), –1.6 (*C*H$_2$TMS). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ –3.8 (3B), –5.4 (2B), –8.7 (5B). IR (KBr, cm^{-1}): ν_{BH} 2575, 2547 (vs). Anal. Calcd. for $C_{35}H_{76}B_{10}HfN_6Si_4$ (**16b**): C, 42.90; H, 7.82; N, 8.58. Found: C, 42.85; H, 7.38; N, 8.25.

Alternative method. To a toluene (20 mL) suspension of **9b'•C$_7$H$_8$** (222 mg, 0.27 mmol) was added dropwise a toluene (6 mL) solution of TMSCH$_2$NC (204 mg, 1.8 mmol) at room temperature with stirring. The mixture was heated at 70 °C for 3 days. The solvent was removed under vacuum and the orange residue was washed with cold *n*-hexane (-30 °C, 5 mL). After filtration, the orange solid was collected and redissolved in toluene (20 mL). The resulting orange solution was filtered and concentrated under vacuum to about 10 mL. Complex **16b** was isolated as orange crystals after this solution stood at room temperature for 4 days (207 mg, 78%).

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^3-N(Ph)=CN(Me)(CH$_2$)$_3$N(Me)C=N(Ph)C(NCy)NCy] (18a). This complex was prepared as yellow crystals from **9a'•C$_7$H$_8$** (358 mg, 0.46 mmol) and PhCN (305 mg, 3.00 mmol) in toluene using a procedure identical with that reported for **10a**: yield

311 mg (79%). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.44 (d, J = 6.9 Hz, 2H, C_6H_5), 7.33 (d, J = 6.6 Hz, 2H, C_6H_5), 7.12 (m, 6H, C_6H_5), 6.33 (brs, 2H, C_5H_4), 6.25 (brs, 1H, C_5H_4), 5.84 (brs, 1H, C_5H_4), 4.55 (t, J = 11.4 Hz, 1H, NC*H*), 4.32 (t, J = 11.4 Hz, 1H, NC*H*), 3.86 (brs, 1H, NCH_2), 3.05 (brs, 1H, NCH_2), 2.43 (s, 3H, NCH_3), 2.29 (s, 3H, NCH_3), 2.22 (m, 2H, NCH_2), 1.95 (m, 4H, C_6H_{11}), 1.74 (m, 6H, C_6H_{11}), 1.58 (m, 4H, C_6H_{11}), 1.50 (s, 3H, C(CH_3)$_2$), 1.44 (s, 3H, C(CH_3)$_2$), 1.24 (m, 4H, C_6H_{11}), 1.07 (m, 2H, C_6H_{11}), 0.85 (m, 2H, NCH$_2$CH_2CH$_2$N). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 167.6 (Zr-*C*=N), 156.4 (*C*=N), 152.8 (N-*C*-N), 146.4 (C_5H_4), 139.9, 138.8, 129.3, 128.7, 128.6, 128.5, 127.3, 126.8, 125.6 (C_6H_5), 114.0, 111.1, 109.0, 107.2 (C_5H_4), 107.2, 101.7 (Cage *C*), 56.6, 55.9 (NCH), 49.0, 47.3 (NCH$_2$), 42.3 (*C*(CH$_3$)$_2$), 39.3, 38.5 (NCH$_3$), 34.9, 32.4 (C(*C*H$_3$)$_2$), 35.7, 35.2, 33.4, 32.8, 27.5, 27.2, 26.4, 26.3, 26.1 (C_6H_{11}), 26.8 (NCH$_2$*C*H$_2$CH$_2$N). ^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ –2.5 (3B), –5.0 (2B), –9.0 (5B). IR (KBr, cm^{-1}): ν_{BH} 2597, 2545 (vs). Anal. Calcd for $C_{42}H_{64}B_{10}N_6Zr$ (**18a**): C, 59.18; H, 7.57; N, 9.86. Found: C, 58.98; H, 7.50; N, 9.68.

Preparation of {[η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Hf[η^3-N(Ph)=CN(Me)(CH$_2$)$_3$N(Me)C=N(Ph)C(NCy)NCy]}$_2$•(C$_7$H$_8$)$_2$ (18b•(C$_7$H$_8$)$_2$). This complex was prepared as yellow crystals from **9b'•C$_7$H$_8$** (251 mg, 0.30 mmol) and PhCN (192 mg, 1.80 mmol) in toluene using a procedure identical with that reported for **10a**: yield 222 mg (71%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.48 (d, J = 7.2 Hz, 4H, C_6H_5), 7.31 (d, J = 7.2 Hz, 4H, C_6H_5), 7.24 (t, J = 7.2 Hz, 4H, C_6H_5), 7.12 (m, 8H, C_6H_5 + $C_6H_5CH_3$), 7.06 (m, 6H, C_6H_5 + $C_6H_5CH_3$), 7.05 (m, 4H, C_6H_5 + $C_6H_5CH_3$), 6.32 (brs, 2H, C_5H_4), 6.28 (d, J = 2.4 Hz, 2H, C_5H_4), 6.24 (brs, 2H, C_5H_4), 5.81 (d, J = 2.4 Hz, 2H, C_5H_4), 4.53 (t, J = 8.0 Hz, 2H, NC*H*), 4.33 (t, J = 12.4 Hz, 2H, NC*H*), 3.90 (t, J = 11.2 Hz, 2H, NCH_2), 3.10 (brs, 2H, NCH_2), 2.44 (s, 6H, NCH_3), 2.30 (m, 4H, NCH_2), 2.25 (s, 6H, NCH_3), 2.20 (m, 4H, C_6H_{11}), 2.10 (s, 6H,

$C_6H_5CH_3$), 1.89 (m, 8H, C_6H_{11}), 1.75 (m, 8H, C_6H_{11}), 1.58 (m, 8H, C_6H_{11}), 1.53 (s, 6H, $C(CH_3)_2$), 1.48 (s, 6H, $C(CH_3)_2$), 1.27 (m, 8H, C_6H_{11}), 1.22 (m, 4H, C_6H_{11}), 1.05 (m, 4H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 166.5 (Hf-N=*C*), 158.5 (*C*=N), 153.2 (N-*C*-N), 144.7 (C_5H_4), 141.0, 138.7, 137.8, 129.3, 129.3, 128.7, 128.5, 128.4, 127.3, 126.7, 125.6 (C_6H_5 + $C_6H_5CH_3$), 113.5, 110.3, 108.2, 106.7 (C_5H_4), 115.2, 101.3 (Cage *C*), 54.5, 55.7 (N*C*H), 49.1, 47.0 (NCH_2), 41.8 ($C(CH_3)_2$), 39.3, 38.5 (NCH_3), 33.3, 33.0 ($C(CH_3)_2$), 35.7, 35.2, 34.8, 32.4, 31.9, 27.5, 27.2, 26.7, 26.4, 26.1 (C_6H_{11}), 23.0 ($NCH_2CH_2CH_2N$), 21.4 ($C_6H_5CH_3$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –4.8 (5B), –8.6 (5B). IR (KBr, cm^{-1}): ν_{BH} 2599, 2545 (vs). Anal. Calcd for $C_{98}H_{144}B_{20}Hf_2N_{12}$ (**18b** + $(C_7H_8)_2$): C, 57.04; H, 7.03; N, 8.15. Found: C, 56.71; H, 7.44; N, 7.95.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^3$-N(Ar)=CN(Me)$(CH_2)_3$N(Me)C=N(Ar)C(NCy)NCy]•$C_7H_8$ (19a•C_7H_8) (Ar = *p*-$CH_3C_6H_4$). This complex was prepared as yellow crystals from **9a'•C_7H_8** (208 mg, 0.28 mmol) and *p*-$CH_3C_6H_4CN$ (198 mg, 1.70 mmol) in toluene using a procedure identical with that reported for **10a**: yield 154 mg (57%). ^1H NMR (400 MHz, benzene-d_6): δ 7.40 (d, J = 7.4 Hz, 2H, $C_6H_4CH_3$), 7.30 (d, J = 7.4 Hz, 2H, $C_6H_4CH_3$), 7.12 (d, J = 7.3 Hz, 2H, $CH_3C_6H_4$ + $C_6H_5CH_3$), 7.02 (m, 7H, $C_6H_4CH_3$ + $C_6H_5CH_3$), 6.38 (brs, 1H, C_5H_4), 6.34 (brs, 1H, C_5H_4), 6.32 (brs, 1H, C_5H_4), 5.90 (brs, 1H, C_5H_4), 4.58 (t, J = 12.3 Hz, 1H, NC*H*), 4.37 (t, J = 11.2 Hz, 1H, NC*H*), 3.88 (t, J = 10.4 Hz, 1H, NCH_2), 3.07 (brs, 1H, NCH_2), 2.52 (s, 3H, NCH_3), 2.40 (s, 3H, NCH_3), 2.36 (m, 2H, NCH_2), 2.23 (m, 4H, C_6H_{11}), 2.11 (s, 3H, $C_6H_4CH_3$), 2.10 (s, 3H, $C_6H_5CH_3$), 2.07 (s, 3H, $C_6H_4CH_3$), 1.95 (m, 2H, C_6H_{11}), 1.79 (m, 4H, C_6H_{11}), 1.63 (m, 2H, C_6H_{11}), 1.56 (s, 3H, $C(CH_3)_2$), 1.52 (s, 3H, $C(CH_3)_2$), 1.37 (m, 4H, C_6H_{11}), 1.28 (m, 4H, C_6H_{11}), 1.09 (m, 2H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100

MHz, benzene-d_6): δ 168.1 (Zr-N=*C*), 157.1 (*C*=N), 153.4 (N-*C*-N), 146.7 (C_5H_4), 139.6, 138.8, 138.0, 137.5, 136.3, 129.8, 129.7, 129.5, 128.9, 127.9, 127.4, 126.0 ($C_6H_4CH_3$ + $C_6H_5CH_3$), 114.3, 111.4, 109.4, 107.6 (C_5H_4), 107.9, 102.0 (Cage *C*), 57.0, 56.3 (NCH), 49.4, 47.8 (NCH_2), 42.7 ($C(CH_3)_2$), 39.7, 39.0 (NCH_3), 36.1, 33.8 ($C(CH_3)_2$), 35.7, 35.3, 33.3, 32.8, 27.9, 27.7, 27.1, 26.9, 26.7, 26.5 (C_6H_{11}), 21.8 ($NCH_2CH_2CH_2N$), 21.6, 21.5 ($C_6H_4CH_3$ + $C_6H_5CH_3$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –5.3 (5B), –9.0 (5B). IR (KBr, cm^{-1}): ν_{BH} 2595, 2549 (vs). Anal. Calcd for $C_{45.75}H_{70}B_{10}N_6Zr$ (**19a** + 0.25Toluene): C, 60.82; H, 7.81; N, 9.30. Found: C, 60.60; H, 7.96; N, 9.23.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\sigma$:$\eta^2$-N(Me)$(CH_2)_3$N(Me)C=N$(CH_2)_3$C=C($N^iPr$)$N^iPr$] (20a). This complex was prepared as yellow crystals from **9a** (203 mg, 0.36 mmol) and 5-hexynenitrile (205 mg, 2.20 mmol) in toluene using a procedure identical with that reported for **10a**: yield 104 mg (44%). ^1H NMR (300 MHz, pyridine-d_5): δ 6.47 (brs, 1H, C_5H_4), 6.40 (brs, 1H, C_5H_4), 6.32 (brs, 1H, C_5H_4), 6.07 (brs, 1H, C_5H_4), 5.08 (s, 1H, C=C*H*), 4.43 (m, 1H, C*H*$(CH_3)_2$), 3.84 (m, 1H, C*H*$(CH_3)_2$), 3.62 (t, J = 11.7 Hz, 1H, NCH_2), 3.29 (m, 1H, NCH_2), 3.16 (s, 3H, NCH_3), 2.90 (m, 1H, NCH_2), 2.71 (s, 3H, NCH_3), 2.58 (m, 1H, NCH_2), 2.33 (d, J = 6.0 Hz, 1H, CH_2), 2.17 (m, 1H, CH_2), 2.02 (m, 2H, CH_2), 1.89 (m, 2H, CH_2), 1.62 (s, 3H, $C(CH_3)_2$), 1.58 (s, 3H, $C(CH_3)_2$), 1.49 (d, J = 6.3 Hz, 3H, $CH(CH_3)_2$), 1.30 (d, J = 6.6 Hz, 3H, $CH(CH_3)_2$), 1.15 (d, J = 5.7 Hz, 3H, $CH(CH_3)_2$), 0.99 (d, J = 6.6 Hz, 3H, $CH(CH_3)_2$), 0.79 (m, 2H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 179.0 (C=*C*(CH_2)N), 158.6 (N-*C*-N), 145.5 (N=*C*-NCH_3), 144.8, 112.8, 109.4, 106.9, 105.3 (C_5H_4), 112.4 (*C*=C(CH_2)N), 101.5 (Cage *C*), 50.7, 45.8 (NCH_2), 47.2, 46.3 ($NCH(CH_3)_2$), 44.6, 36.8 (NCH_3), 42.1 ($C(CH_3)_2$), 35.0, 35.1 ($C(CH_3)_2$), 26.9, 24.2 (CH_2), 26.2, 24.0, 23.6, 23.3 ($NCH(CH_3)_2$), 21.2

($NCH_2CH_2CH_2N$). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ –3.3 (3B), –5.3 (2B), –9.7 (5B). IR (KBr, cm^{-1}): ν_{BH} 2604, 2555 (vs). Anal. Calcd for $C_{28}H_{53}B_{10}N_5Zr$ (**20a**): C, 51.02; H, 8.11; N, 10.63. Found: C, 50.42; H, 8.22; N, 10.17.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N(^{n}Bu))C=N(^{n}Bu)] (21a). To a toluene (20 mL) suspension of **12a** (458 mg, 0.65 mmol) was added dropwise a toluene (6 mL) solution of ^{n}BuNC (334 mg, 4.00 mmol) at room temperature with stirring. The mixture was stirred at 90 °C for 7 days. The solvent was removed under vacuum and the brown residue was washed with *n*-hexane (10 mL X 3). After filtration, the light brown solid was collected and redissolved in toluene (20 mL). The resulting light brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **21a** was isolated as colorless crystals after this solution stood at room temperature for 5 days (343 mg, 72%). ^1H NMR (400 MHz, pyridine-d_5): δ7.15 (m, 1H, $C_6H_3(CH_3)_2$), 7.02 (t, J = 7.4 Hz, 1H, $C_6H_3(CH_3)_2$), 6.98 (d, J = 6.9 Hz, 1H, $C_6H_3(CH_3)_2$), 6.29 (t, J = 2.3 Hz, 1H, C_5H_4), 6.17 (t, J = 2.7 Hz, 1H, C_5H_4), 5.96 (d, J = 2.6 Hz, 1H, C_5H_4), 5.56 (d, J = 2.5 Hz, 1H, C_5H_4), 4.15 (m, 1H, CH_3NCH_2), 3.91 (t, J = 13.0 Hz, 1H, CH_3NCH_2), 3.52 (m, 1H, CH_3NCH_2), 3.18 (d, J = 13.6 Hz, 1H, CH_3NCH_2), 3.10 (s, 3H, NCH_3), 2.95 (t, J = 6.9 Hz, 2H, NCH_2), 2.71 (m, 2H, NCH_2), 2.32 (s, 3H, NCH_3), 2.22 (s, 3H, $C_6H_3(CH_3)_2$), 1.78 (s, 3H, $C_6H_3(CH_3)_2$), 1.78 (m, 2H, NCH_2CH_2), 1.63 (m, 9H, $C(CH_3)_2$ + NCH_2CH_2 + $NCH_2CH_2CH_2N$), 1.44 (m, 3H, $NCH_2CH_2CH_2$ + $NCH_2CH_2CH_2N$), 1.16 (m, 2H, $NCH_2CH_2CH_2$), 1.02 (t, J = 7.3 Hz, 3H, CH_3), 0.79 (t, J = 7.3 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 247.1 (Zr-*C*=N^{n}Bu), 205.8 (Zr-*C*=NXyl), 159.1 (*C*=N^{n}Bu), 147.1 (C_5H_4), 146.6, 131.4, 131.3, 125.7, 125.1 ($C_6H_3(CH_3)_2$), 105.8, 105.4, 105.3, 104.9 (C_5H_4), 103.5, 103.4 (Cage *C*), 54.7, 53.3 (CH_3NCH_2), 50.2, 44.5 (NCH_2), 42.2 ($C(CH_3)_2$), 35.7

(NCH_2CH_2), 33.7, 33.1 (NCH_3), 32.7, 31.4 ($C(CH_3)_2$), 26.0 ($NCH_2CH_2CH_2N$), 21.2, 21.1 ($NCH_2CH_2CH_2$), 19.3, 18.8 ($C_6H_3(CH_3)_2$), 14.4, 13.7 (CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ –3.2 (3B), –5.1 (2B), –8.8 (5B). IR (KBr, cm^{-1}): ν_{BH} 2596, 2550 (vs). Anal. Calcd. for $C_{34}H_{59}B_{10}N_5Zr$ (**21a**): C, 55.39; H, 8.07; N, 9.50. Found: C, 55.62; H, 8.15; N, 9.55.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N(^{n}Bu))C=N(^{n}Bu)] (21b). To a toluene (20 mL) suspension of **12b** (295 mg, 0.37 mmol) was added dropwise a toluene (6 mL) solution of *n*-BuNC (186 mg, 2.20 mmol) at room temperature with stirring. The mixture was stirred at 90 °C for 2 days. The solvent was removed under vacuum and the brown residue was washed with ether (10 mL X 3). After filtration, the light brown solid was collected and redissolved in toluene (20 mL). The resulting brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **21b** was isolated as colorless crystals after this solution stood at room temperature for 5 days (104 mg, 34%). The ethereal solution was concentrated under vaccum to about 10 mL. Complex **13b** was isolated as orange crystals after this solution stood at room temperature for 5 days (98 mg, 31%). **21b:** ^1H NMR (400 MHz, pyridine-d_5): δ 7.14 (d, J = 7.1 Hz, 1H, $C_6H_3(CH_3)_2$), 7.02 (t, J = 7.4 Hz, 1H, $C_6H_3(CH_3)_2$), 6.97 (d, J = 7.0 Hz, 1H, $C_6H_3(CH_3)_2$), 6.22 (d, J = 2.2 Hz, 1H, C_5H_4), 6.12 (d, J = 2.3 Hz, 1H, C_5H_4), 5.92 (d, J = 2,5 Hz, 1H, C_5H_4), 5.51 (d, J = 2.4 Hz, 1H, C_5H_4), 4.17 (m, 1H, CH_3NCH_2), 3.87 (t, J = 13.0 Hz, 1H, CH_3NCH_2), 3.55 (m, 1H, CH_3NCH_2), 3.17 (d, J = 13.4 Hz, 1H, CH_3NCH_2), 3.10 (s, 3H, NCH_3), 3.00 (t, J = 6.9 Hz, 2H, NCH_2), 2.70 (m, 2H, NCH_2), 2.30 (s, 3H, NCH_3), 2.25 (s, 3H, $C_6H_3(CH_3)_2$), 1.82 (m, 2H, NCH_2CH_2), 1.81 (s, 3H, $C_6H_3(CH_3)_2$), 1.67 (m, 10H, $C(CH_3)_2$ + $NCH_2CH_2CH_2$ + $NCH_2CH_2CH_2N$), 1.41 (m, 2H, NCH_2CH_2), 1.17 (m, 2H, $NCH_2CH_2CH_2$), 1.02 (t, J =

7.3 Hz, 3H, CH_3), 0.78 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 256.5 (Hf-C=N^{n}Bu), 214.1 (Hf-C=NXyl), 159.4 (C=N^{n}Bu), 145.9 (C_5H_4), 145.9, 131.7, 128.1, 127.4, 125.2 ($C_6H_3(CH_3)_2$), 109.8, 103.5 (Cage C), 104.5, 104.2, 104.1, 103.6 (C_5H_4), 54.7, 53.1 (CH_3NCH_2), 50.1, 44.4 (NCH_2), 41.6 ($C(CH_3)_2$), 35.8 (NCH_2CH_2), 33.8, 33.7 (C(CH_3)$_2$), 32.5, 31.3 (NCH_3), 26.0 ($NCH_2CH_2CH_2N$), 21.2, 20.7 ($NCH_2CH_2CH_2$), 19.4, 18.8 ($C_6H_3(CH_3)_2$), 14.4, 13.7 (CH_3). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ –3.4 (3B), –5.1 (2B), –8.5 (5B). IR (KBr, cm^{-1}): ν_{BH} 2594, 2549 (vs). Anal. Calcd. for $C_{34}H_{59}B_{10}HfN_5$ (**13b**): C, 49.53; H, 7.21; N, 8.49. Found: C, 49.54; H, 7.36; N, 8.23.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^2:η^2-N(Xyl)=CN(Me)(CH$_2$)$_3$N(Me)C(=NR)C=NR] (R = 2-morpholinethyl) (22a). To a toluene (20 mL) suspension of **12a** (229 mg, 0.33 mmol) was added dropwise a toluene (6 mL) solution of RNC (R = 2-morpholinethyl) (280 mg, 2.00 mmol) at room temperature with stirring. The mixture was stirred at 90 °C for 5 days. The solvent was removed under vacuum and the brown residue was washed with *n*-hexane (10 mL X 3). After filtration, the light brown solid was collected and redissolved in DME (20 mL). The resulting light brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **22a** was isolated as colorless crystals after this solution stood at room temperature for 5 days (133 mg, 47%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.15 (m, 1H, $C_6H_3(CH_3)_2$), 7.03 (m, 2H, $C_6H_3(CH_3)_2$), 6.22 (m, 2H, C_5H_4), 5.98 (m, 1H, C_5H_4), 5.81 (m, 1H, C_5H_4), 4.32 (m, 1H, Zr-C=NCH_2), 3.94 (t, J = 13.0 Hz, 1H, CH_3NCH_2), 3.74 (t, J = 4.6 Hz, 4H, NCH_2CH_2O), 3.68 (m, 1H, Zr-CNCH_2), 3.63 (t, J = 5.1 Hz, 4H, NCH_2CH_2O), 3.41 (m, 1H, N=C-C=NCH_2), 3.23 (m, 1H, CH_3NCH_2), 3.11 (s, 3H, NCH_3), 2.87 (m, 4H, CH_3NCH_2 + ZrC=NCH_2 + C=NCH$_2$CH_2), 2.67 (m, 3H, C=NCH_2 + NCH$_2$CH_2O),

2.53 (m, 4H, $CNCH_2CH_2$ + NCH_2CH_2O), 2.42 (m, 2H, NCH_2CH_2O), 2.34 (s, 3H, NCH_3), 2.24 (m, 5H, $C_6H_3(CH_3)_2$ + NCH_2CH_2O), 1.79 (m, 1H, $NCH_2CH_2CH_2N$), 1.67 (s, 3H, $C(CH_3)_2$), 1.65 (s, 3H, $C(CH_3)_2$), 1.55 (m, 1H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 248.5 (ZrC=NR), 206.1 (ZrC=NXyl), 159.3 (C-C=NR), 147.0 (C_5H_4), 146.1, 131.4, 131.2, 128.1, 127.4, 125.1 ($C_6H_3(CH_3)_2$), 106.1, 103.4 (Cage *C*), 106.1, 105.7, 104.4 (C_5H_4), 67.2, 66.6 (NCH_2CH_2O), 62.0, 58.1 ($C=NCH_2CH_2$), 54.8 (CH_3NCH_2 + NCH_2CH_2O), 54.0 (NCH_2CH_2O), 50.0, 49.3 ($C=NCH_2$), 45.4 (CH_3NCH_2), 42.3 ($C(CH_3)_2$), 33.9, 32.5 ($C(CH_3)_2$), 33.7, 33.4 (NCH_3), 26.1 ($NCH_2CH_2CH_2N$), 19.4, 18.8 ($C_6H_3(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ –4.7 (5B), –9.5 (5B). IR (KBr, cm^{-1}): ν_{BH} 2562, 2540 (vs). Anal. Calcd. for $C_{38}H_{65}B_{10}N_7O_2Zr$ (**22a**): C, 53.61; H, 7.70; N, 11.52. Found: C, 53.87; H, 7.83; N, 11.45.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=NR)C=NR] (R = 2-morpholinethyl) (22b). To a toluene (20 mL) suspension of **12b** (237 mg, 0.30 mmol) was added dropwise a toluene (6 mL) solution of RNC (R = 2-morpholinethyl) (253 mg, 1.80 mmol) at room temperature with stirring. The mixture was stirred at 90 °C for 3 days. The solvent was removed under vacuum and the brown residue was washed with *n*-hexane (10 mL X 3). After filtration, the light brown solid was collected and redissolved in DME (20 mL). The resulting brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **22b** and **14b** were isolated as colorless and orange red crystals by fractional recrystallization (**22b**: 100 mg, 35%; **14b**: 76 mg, 23%). **22b:** ^1H NMR (400 MHz, pyridine-d_5): δ 7.15 (d, J = 2.7 Hz, 1H, $C_6H_3(CH_3)_2$), 7.02 (m, 2H, $C_6H_3(CH_3)_2$), 6.16 (t, J = 2.5 Hz, 2H, C_5H_4), 5.93 (d, J = 2.5 Hz, 1H, C_5H_4), 5.78 (d, J = 2.4 Hz, 1H, C_5H_4), 4.37 (m, 1H, Hf-C=NCH_2), 3.90

(t, J = 13.0 Hz, 1H, CH_3NCH_2), 3.75 (m, 5H, Hf-C=NCH_2 + NCH_2CH_2O), 3.65 (t, J = 4.5 Hz, 4H, NCH_2CH_2O), 3.44 (m, 1H, C=NCH_2), 3.22 (d, J = 13.4 Hz, 1H, CH_3NCH_2), 3.12 (s, 3H, NCH_3), 2.87 (m, 4H, CH_3NCH_2 + Hf-C=NCH_2CH_2 + C=NCH_2CH_2), 2.67 (m, 3H, C=NCH_2CH_2 + NCH_2CH_2O), 2.53 (m, 4H, C=NCH_2CH_2 + NCH_2CH_2O), 2,42 (m, 2H, NCH_2CH_2O), 2.32 (s, 3H, NCH_3), 2.26 (s, 3H, $C_6H_3(CH_3)_2$), 2.23 (m, 2H, NCH_2CH_2O), 1.81 (s, 3H, $C_6H_3(CH_3)_2$), 1.75 (m, 1H, $NCH_2CH_2CH_2N$), 1.67 (s, 3H, $C(CH_3)_2$), 1.65 (s, 3H, $C(CH_3)_2$), 1.54 (t, J = 13.6 Hz, 1H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 257.8 (Hf*C*=NR), 214.4 (Hf*C*=NXyl), 160.2 (C-*C*=NR), 146.0 (C_5H_4), 145.8, 131.7, 131.6, 128.2, 127.4, 125.2 ($C_6H_3(CH_3)_2$), 109.6, 103.5 (Cage *C*), 105.3, 104.5, 104.0, 103.7 (C_5H_4), 67.2, 66.6 (NCH_2CH_2O), 62.1, 58.1 (C=NCH_2CH_2), 54.8 (CH_3NCH_2 + NCH_2CH_2O), 54.0 (NCH_2CH_2O), 49.6, 49.0 (C=NCH_2), 45.4 (CH_3NCH_2), 41.8 ($C(CH_3)_2$), 34.0, 32.5 ($C(CH_3)_2$), 33.7, 33.3 (NCH_3), 26.1 ($NCH_2CH_2CH_2N$), 19.5, 18.8 ($C_6H_3(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ –5.1 (3B), –8.6 (7B). IR (KBr, cm^{-1}): ν_{BH} 2562, 2540 (vs). Anal. Calcd. for $C_{38}H_{65}B_{10}HfN_7O_2$ (**22b**): C, 48.63; H, 6.98; N, 10.45. Found: C, 49.19; H, 7.31; N, 10.24.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C(=N($CH_2$TMS))C=N($CH_2$TMS)] (23a). To a toluene (20 mL) suspension of **12b** (201 mg, 0.29 mmol) was added dropwise a toluene (6 mL) solution of $TMSCH_2NC$ (205 mg, 2.20 mmol) at room temperature with stirring. The mixture was stirred at 90 °C for 3 days. The solvent was removed under vacuum and the brown residue was redissolved in ether (20 mL). The resulting brown solution was filtered and concentrated under vacuum to about 10 mL. Complex **23a** was isolated as colorless crystals after this solution stood at room temperature for 3 days (148 mg, 64%). ^1H NMR (400 MHz, benzene-d_6): δ 6.98 (d, J

= 7.4 Hz, 1H, $C_6H_3(CH_3)_2$), 6.91 (t, J = 7.5 Hz, 1H, $C_6H_3(CH_3)_2$), 6.80 (d, J = 7.3, 1H, $C_6H_3(CH_3)_2$), 5.98 (t, J = 2.7 Hz, 1H, C_5H_4), 5.79 (t, J = 2.2 Hz, 2H, C_5H_4), 5.43 (d, J = 2.4 Hz, 1H, C_5H_4), 4.40 (d, J = 12.2 Hz, 1H, CH_3NCH_2), 3.25 (m, 1H, CH_3NCH_2), 3.69 (t, J = 13.0 Hz, 1H, CH_3NCH_2), 3.29 (d, J = 14.5 Hz, 1H, CH_3NCH_2), 2.83 (s, 3H, NCH_3), 2.61 (m, 4H, $(CH_3)_3SiCH_2$), 2.07 (s, 3H, $C_6H_3(CH_3)_2$), 1.95 (s, 3H, NCH_3) 1.69 (s, 3H, $C_6H_3(CH_3)_2$), 1.57 (s, 3H, $C(CH_3)_2$), 1.50 (s, 3H, $C(CH_3)_2$), 1.26 (t, J = 13.8 Hz, 1H, $NCH_2CH_2CH_2N$), 0.90 (t, J = 14.2 Hz, 1H, $NCH_2CH_2CH_2N$), 0.25 (s, 9H, $(CH_3)_3Si$), 0.03 (s, 9H, $(CH_3)_3Si$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 243.9 (Zr-*C*=$NCH_2Si(CH_3)_3$), 207.0 (Zr-*C*=NXyl), 159.6 (*C*=$NCH_2Si(CH_3)_3$), 147.7 (C_5H_4), 145.9, 131.2, 130.9, 127.8, 127.5, 125.1 ($C_6H_3(CH_3)_2$), 105.4, 104.7, 104.3, 103.7 (C_5H_4), 102.9, 102.6 (Cage *C*), 54.3, 47.8 (CH_3NCH_2), 45.1, 41.8 ($CH_2Si(CH_3)_3$), 42.2 ($C(CH_3)_2$), 33.7, 33.3 ($C(CH_3)_2$), 33.4 (NCH_3), 26.2 ($NCH_2CH_2CH_2N$), 20.6, 19.0 ($C_6H_3(CH_3)_2$), –0.9 ($CH_2Si(CH_3)_3$), –2.1 ($CH_2Si(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –2.3 (3B), –4.5 (2B), –8.1 (5B). IR (KBr, cm^{-1}): ν_{BH} 2557 (vs). Anal. Calcd. for $C_{34}H_{63}B_{10}N_5Si_2Zr$ (**23a**): C, 51.21; H, 7.96; N, 8.78. Found: C, 51.29; H, 7.68; N, 8.49.

Preparation of $[\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2$-N(Xyl)=$CNMe_2]_2$ (24a). To a toluene solution of **1a** (426 mg, 1.00 mmol)was added dropwise a toluene solution of XylNC (264 mg, 2.02 mmol) at -30 °C with stirring, the solution was stirred at room temperature overnight. After filtration and washed with toluene (5 mL) and *n*-hexane (10 mL X 3), **24a** was collected as a white solid (377 mg, 54%). Single crystal suitable for X-ray analyses were grown from a THF/toluene solution at room temperature as **24a•0.5THF**. ^1H NMR (400 MHz, pyridine-d_5): δ 7.12 (m, 2H, $C_6H_3(CH_3)_2$), 7.04 (m, 4H, $C_6H_3(CH_3)_2$), 6.34 (t, J = 2.3 Hz, 2H, C_5H_4), 5.95 (t, J = 2.6 Hz, 2H, C_5H_4), 3.27 (s, 6H, $N(CH_3)_2$), 2.41 (s, 6H, $N(CH_3)_2$), 2.19 (s, 6H,

$C_6H_3(CH_3)_2$), 2.12 (s, 6H, $C_6H_3(CH_3)_2$), 1.65 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_6): δ 206.7 (Zr-*C*=N), 147.3, 132.3, 131.2, 128.1, 127.8, 124.8 ($C_6H_3(CH_3)_2$), 146.6, 106.0, 104.5 (C_5H_4), 103.1 (Cage *C*), 46.8, 36.4 ($N(CH_3)_2$), 42.0 ($C(CH_3)_2$), 33.3 ($C(CH_3)_2$), 20.4, 19.5 ($C_6H_3(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, d-pyridine): δ –3.6 (2B), –5.6 (3B), –9.1 (5B). IR (KBr, cm^{-1}): ν_{BH} 2540 (vs). Anal. Calcd. for $C_{32}H_{50}B_{10}N_4Zr$: C, 55.69; H, 7.30; N, 8.12. Found: C, 55.61; H, 7.14; N, 7.81.

Preparation of $[\eta^5:\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2:\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (25a). To a toluene (20 mL) suspension of **12a** (342 mg, 0.49 mmol) was added dropwise a toluene (6 mL) solution of PhNCS (479 mg, 3.50 mmol) at room temperature with stirring. The mixture was stirred at 90 °C for 7 days. The solvent was removed under vacuum and the yellow residue was washed with *n*-hexane (10 mL X 3) and redissolved in THF (20 mL). The resulting yellow solution was filtered and concentrated under vacuum to about 10 mL. Complexes **12a** (131 mg, 38%) and **25a** (93 mg, 27%) were isolated as colorless crystals and pale yellow solid by fractional recrystallization. **25a**: ^1H NMR (400 MHz, benzene-d_6): δ 7.01 (m, 3H, C_6H_5), 6.93 (m, 1H, $C_6H_3(CH_3)_2$), 6.81 (m, 2H, $C_6H_3(CH_3)_2$), 6.64 (d, J = 7.9 Hz, 2H, C_6H_5), 6.53 (d, J = 2.9 Hz, 1H, C_5H_4), 6.35 (d, J = 2.6 Hz, 1H, C_5H_4), 6.00 (d, J = 2.5 Hz, 1H, C_5H_4), 5.56 (d, J = 2.4 Hz, 1H, C_5H_4), 3.88 (t, J = 13.7 Hz, 1H, NCH_2), 3.15 (m, 1H, NCH_2), 2.59 (s, 3H, $C_6H_3(CH_3)_2$), 2.58 (s, 3H, NCH_3), 2.48 (d, J = 14.4 Hz, 1H, NCH_2), 2.22 (m, 1H, NCH_2), 1.62 (s, 3H, $C_6H_3(CH_3)_2$), 1.46 (s, 3H, $C(CH_3)_2$), 1.40 (s, 3H, $C(CH_3)_2$), 1.04 (t, J = 13.9 Hz, 1H, $NCH_2CH_2CH_2N$), 0.68 (t, J = 13.9 Hz, 1H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 212.7 (Zr*C*=NXyl), 185.7 (N-*C*-S), 150.0 (C_5H_4), 147.9, 147.0, 133.3, 129.9, 129.3, 129.0, 128.7, 128.5, 127.7, 125.7, 121.5

($C_6H_3(CH_3)_2$ + C_6H_5), 115.0, 114.7, 110.0, 107.2 (C_5H_4), 104.5, 103.7 (Cage *C*), 55.1, 49.8 (NCH_2), 42.4 ($C(CH_3)_2$), 36.5, 34.4 (NCH_3), 34.1, 31.2 ($C(CH_3)_2$), 24.4 ($NCH_2CH_2CH_2N$), 21.7, 20.6 ($C_6H_3(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –2.8 (3B), –6.0 (7B). IR (KBr, cm^{-1}): ν_{BH} 2586, 2548 (vs). Anal. Calcd. for $C_{31}H_{46}B_{10}N_4SZr$ (**25a**): C, 52.73; H, 6.57; N, 7.93. Found: C, 52.69; H, 6.83; N, 7.62.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (25b). To a toluene (20 mL) suspension of **12b** (222 mg, 0.28 mmol) was added dropwise a toluene (6 mL) solution of PhNCS (184 mg, 1.41 mmol) at room temperature with stirring. The mixture was stirred at 90 °C for 2 days. The solvent was removed under vacuum and the yellow residue was washed with *n*-hexane (5 mL X 3), and redissolved in toluene (20 mL). The resulting yellow solution was filtered and concentrated under vacuum to about 10 mL. Complex **25b** was isolated as colorless crystals after this solution stood at room temperature for 6 days (184 mg, 83%). ^1H NMR (400 MHz, benzene-d_6): δ 7.04 (m, 2H, C_6H_5), 7.00 (d, J = 7.3 Hz, 1H, $C_6H_3(CH_3)_2$), 6.92 (t, J = 7.5 Hz, 1H, $C_6H_3(CH_3)_2$), 6.82 (d, J = 7.1 Hz, 1H, $C_6H_3(CH_3)_2$), 6.79 (t, J = 7.3 Hz, 1H, C_6H_5), 6.65 (d, J = 7.9 Hz, 2H, C_6H_5), 6.48 (dd, J = 2.4, 5.6 Hz, 1H, C_5H_4), 6.28 (dd, J = 2.5, 5.3 Hz, 1H, C_5H_4), 5.94 (dd, J = 3.1, 5.6 Hz, 1H, C_5H_4), 5.83 (dd, J = 2.9, 5.4 Hz, 1H, C_5H_4), 3.87 (t, J = 13.6 Hz, 1H, NCH_2), 3.12 (m, 1H, NCH_2), 2.63 (s, 3H, $C_6H_3(CH_3)_2$), 2.59 (s, 3H, NCH_3), 2.49 (m, 1H, NCH_2), 2.21 (m, 1H, NCH_2), 1.93 (s, 3H, NCH_3), 1.61 (s, 3H, $C_6H_3(CH_3)_2$), 1.46 (s, 3H, $C(CH_3)_2$), 1.43 (s, 3H, $C(CH_3)_2$), 1.02 (t, J = 13.6 Hz, $NCH_2CH_2CH_2N$), 0.69 (t, J = 13.6 Hz, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 222.7 (Hf-*C*NXyl), 185.8 (N-*C*-S), 148.3 (C_5H_4), 147.6 (C_5H_4), 146.5, 133.7, 130.2, 121.4, 119.3 ($C_6H_3(CH_3)_2$), 113.9, 113.3, 108.5, 106.3 (C_5H_4), 111.0, 103.6 (Cage *C*), 55.3, 49.8 (NCH_2), 41.9 ($C(CH_3)_2$), 36.4,

34.7 (NCH_3), 34.2, 31.1 ($C(CH_3)_2$), 24.5 ($NCH_2CH_2CH_2N$), 21.7, 20.7 ($C_6H_3(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –2.7 (3B), –4.7 (2B), –6.0 (5B). IR (KBr, cm^{-1}): ν_{BH} 2589, 2549 (vs). Anal. Calcd. for $C_{31}H_{46}B_{10}HfN_4S$ (**25b**): C, 46.93; H, 5.84; N, 7.06. Found: C, 46.79; H, 5.40; N, 6.80.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(Xyl)=CN(Me)$(CH_2)_3$N(Me)C-N(^{n}Bu)(-S)] (25b') and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\eta^2$-N(^{n}Bu)=CN(Me)$(CH_2)_3$N(Me)C-N(^{n}Bu)(-S)] (26b'). To a toluene (20 mL) suspension of **12b** (228 mg, 0.29 mmol) was added dropwise a toluene (6 mL) solution of ^{n}BuNCS (220 mg, 1.74 mmol) at room temperature with stirring. The mixture was stirred at 110 °C for 1 days. The solvent was removed under vacuum and the yellow residue was washed with cold *n*-hexane (-30 °C, 5 mL X 2), and redissolved in DME (10 mL). The resulting yellow solution was filtered and concentrated under vacuum to about 5 mL. Complex **25b'** was isolated as colorless crystals after this solution stood at room temperature for 6 days (132 mg, 59%). **26b'** cannot be purified by recrystallization, only a mixture of **25b'** and **26b'** was obtained (22 mg, 10%) in a molar ratio of 1:3.

25b': ^1H NMR (400 MHz, benzene-d_6): δ 6.96 (m, 3H, $C_6H_3(CH_3)_2$), 6.44 (m, 1H, C_5H_4), 6.14 (dd, J = 3.2, 5.6 Hz, 1H, C_5H_4), 5.92 (dd, J = 2.4, 5.3 Hz, 1H, C_5H_4), 5.77 (dd, J = 3.0, 5.5 Hz, 1H, C_5H_4), 3.92 (m, 1H, NCH_2), 3.04 (m, 1H, NCH_2), 2.79 (m, 2H, NCH_2), 2.45 (m, 1H, NCH_2), 2.57 (s, 3H, NCH_3), 2.49 (s, 3H, $C_6H_3(CH_3)_2$), 2.28 (m, 1H, NCH_2), 1.98 (s, 3H, $C_6H_3(CH_3)_2$), 1.91 (s, 3H, NCH_3), 1.45 (s, 3H, $C(CH_3)_2$), 1.44 (m, 2H, NCH_2CH_2), 1.18 (m, 3H, $NCH_2CH_2CH_2$ + $NCH_2CH_2CH_2N$), 0.89 (t, J = 7.3 Hz, 3H, CH_3), 0.72 (t, J = 14.2 Hz, 1H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 222.3 (Hf-*C*=N), 185.1 (N-*C*-S), 148.5, 148.3, 133.6, 129.9, 129.6, 125.4 ($C_6H_3(CH_3)_2$), 115.7, 110.8, 107.0, 105.1 (C_5H_4), 112.3, 103.2

(Cage *C*), 55.1, 53.8, 47.9 (NCH_2), 41.2 ($C(CH_3)_2$), 35.8 (NCH_3), 33.4, 32.7 ($C(CH_3)_2$), 32.2 (NCH_3), 32.1 (NCH_2CH_2), 23.6 ($NCH_2CH_2CH_2N$), 20.9 ($C_6H_3(CH_3)_2$ + $NCH_2CH_2CH_2$), 20.6 ($C_6H_3(CH_3)_2$), 14.2 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ –1.7 (1B), –2.8 (2B), –5.5 (3B), –8.9 (3B), –12.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2593, 2546 (vs). Anal. Calcd. for $C_{29}H_{50}B_{10}HfN_4S$ (**25b'**): C, 45.04; H, 6.52; N, 7.24. Found: C, 45.08; H, 6.62; N, 7.00.

26b': ^1H NMR (400 MHz, benzene-d_6): δ 6.57 (dd, J = 2.3, 5.7 Hz, 1H, C_5H_4), 6.34 (dd, J = 2.4, 5.3 Hz, 1H, C_5H_4), 6.08 (dd, J = 3.1, 5.6 Hz, 1H, C_5H_4), 5.89 (dd, J = 3.0, 5.4 Hz, 1H, C_5H_4), 4.05 (m, 1H, NCH_2), 3.44 (m, 2H, NCH_2), 2.88 (m, 2H, NCH_2), 2.71 (m, 1H, NCH_2), 2.57 (s, 3H, NCH_3), 2.31 (m, 1H, NCH_2), 2.28 (s, 3H, NCH_3), 2.20 (m, 1H, NCH_2), 1.53 (s, 3H, $C(CH_3)_2$), 1.51 (s, 3H, $C(CH_3)_2$), 1.47 (m, 2H, NCH_2CH_2), 1.23 (m, 6H, NCH_2CH_2 + $NCH_2CH_2CH_2$), 0.88 (m, 4H, CH_3 + $NCH_2CH_2CH_2N$), 0.84 (t, J = 7.4 Hz, 3H, CH_3), 0.72 (t, J = 14.5 Hz, 1H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 221.7 (Hf-*C*=N), 181.7 (N-*C*-S), 147.2, 114.4, 111.7, 107.4, 104.8 (C_5H_4), 56.2, 52.4, 50.6, 47.6 (NCH_2), 41.7 ($C(CH_3)_2$), 36.6, 35.3 (NCH_3), 34.1, 31.9 ($C(CH_3)_2$), 32.6, 32.2 (NCH_2CH_2), 23.5 ($NCH_2CH_2CH_2N$), 23.0, 20.9 ($NCH_2CH_2CH_2$), 14.3, 14.1 (CH_3), the cage carbons were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ –1.9 (3B), –5.3 (3B), –8.1 (3B), –12.2 (1B).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$:$\eta^2$-N(Ph)=CN(Me)$(CH_2)_3$N(Me)C-N(Ph)(-S)] (26a). To a toluene (20 mL) suspension of **12a** (300 mg, 0.43 mmol) was added dropwise a toluene (6 mL) solution of PhNCS (333 mg, 2.56 mmol) at room temperature with stirring. The mixture was stirred at 110 °C for 3 days. The solvent was removed under vacuum and the yellow residue was redissolved in THF (20 mL). The resulting yellow solution was filtered

and concentrated under vacuum to about 10 mL. Complexes **25a** and **26a** were isolated as yellow crystals by fractional recrystallization (**25a**: 44 mg, 14%; **26a**: 62 mg, 21%). A mixture of **25a** and **26a** was obtained (147 mg, 49%) in a molar ratio of ~1:1. ^{1}H NMR (400 MHz, benzene-d_6): δ 7.33 (d, J = 4.5 Hz, 4H, C_6H_5), 7.24 (m, 3H, C_6H_5), 7.14 (m, 2H, C_6H_5), 6.94 (t, J = 7.4 Hz, 1H, C_6H_5), 6.65 (dd, J = 2.3, 5.6 Hz, 1H, C_5H_4), 6.42 (dd, J = 2.4, 5.3 Hz, 1H, C_5H_4), 6.12 (dd, J = 3.0, 5.5 Hz, 1H, C_5H_4), 6.03 (dd, J = 3.1, 5.6 Hz, 1H, C_5H_4), 3.84 (t, J = 13.2 Hz, 1H, NCH_2), 3.06 (m, 1H, NCH_2), 2.70 (s, 3H, NCH_3), 2.63 (m, 1H, NCH_2), 2.09 (s, 3H, NCH_3), 2.03 (m, 1H, NCH_2), 1.53 (s, 3H, $C(CH_3)_2$), 1.42 (s, 3H, $C(CH_3)_2$), 1.07 (t, J = 15.1 Hz, 1H, $NCH_2CH_2CH_2N$), 0.60 (t, J = 14.5 Hz, 1H, $NCH_2CH_2CH_2N$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 212.7 (Zr*C*=NPh), 183.3 (N-*C*-S), 150.1 (C_5H_4), 149.5, 148.4, 129.3, 128.5, 125.6, 125.5, 123.1, 122.4 (C_6H_5), 116.3, 113.4, 110.1, 106.1 (C_5H_4), 103.8, 103.0 (Cage *C*), 55.2, 48.7 (NCH_2), 42.3 ($C(CH_3)_2$), 36.3, 35.5 (NCH_3), 33.7, 31.9 ($C(CH_3)_2$), 23.6 ($NCH_2CH_2CH_2N$). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ –2.8 (3B), –5.7 (3B), –8.1 (3B), –12.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2592, 2556 (vs). Anal. Calcd. for $C_{29}H_{42}B_{10}N_4SZr$ (**26a**): C, 51.37; H, 6.24; N, 8.26. Found: C, 51.66; H, 6.56; N, 7.90.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$:$\sigma$-(Xyl)N=CN(Me)$(CH_2)_3$N(Me)C(Ph)=N] (27b) and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$-N(Xyl)C[N(Me)$(CH_2)_3$N(Me)]=CN(Xyl)] (28b). To a toluene (20 mL) suspension of **12b** (268 mg, 0.34 mmol) was added dropwise a toluene (6 mL) solution of PhCN (357 mg, 3.40 mmol) at room temperature with stirring. The mixture was stirred at 110 °C for 7 days. The solvent was removed under vacuum and the yellow sticky residue was redissolved in ether (20 mL). After filtration, the resulting yellow solution was concentrated under vacuum to about 10

mL. Complex **27b** was isolated as pale yellow crystals after this solution stood at room temperature for 6 days and **28b** was isolated as yellow crystals after the remaining solution stood at room temperature for 2 days (**27b**: 68 mg, 26%; **28b**: 89 mg, 33%). **27b:** ^{1}H NMR (400 MHz, benzene-d_6): δ 7.30 (d, J = 7.3 Hz, 2H, C_6H_5), 7.19 (m, 2H, C_6H_5), 7.11 (m, 1H, C_6H_5), 7.00 (d, J = 7.1 Hz, 1H, $C_6H_3(CH_3)_2$), 6.91 (t, J = 7.4 Hz, 1H, $C_6H_3(CH_3)_2$), 6.86 (d, J = 7.2 Hz, 1H, $C_6H_3(CH_3)_2$), 6.05 (brs, 1H, C_5H_4), 5.91 (brs, 1H, C_5H_4), 5.85 (brs, 1H, C_5H_4), 5.54 (brs, 1H, C_5H_4), 4.15 (m, 2H, NCH_2), 3.10 (m, 2H, NCH_2), 2.43 (s, 3H, NCH_3), 2.14 (s, 6H, NCH_3 + $C_6H_3(CH_3)_2$), 2.06 (s, 3H, $C_6H_3(CH_3)_2$), 1.53 (s, 3H, $C(CH_3)_2$), 1.50 (s, 3H, $C(CH_3)_2$), 1.25 (m, 2H, $NCH_2CH_2CH_2N$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 217.2 (Hf-*C*=NXyl), 164.3 (Hf-N=*C*-Ph), 147.6, 145.8, 132.5, 131.4, 129.2, 128.7 (C_6H_5 + $C_6H_3(CH_3)_2$), 139.0, 109.4, 107.8, 105.8, 104.8 (C_5H_4), 110.7, 103.9 (Cage *C*), 54.7, 46.0 (NCH_2), 42.4 ($C(CH_3)_2$), 39.0, 36.9 (NCH_3), 33.4, 33.3 ($C(CH_3)_2$), 25.7 ($NCH_2CH_2CH_2N$), 20.1, 19.5 ($C_6H_3(CH_3)_2$). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ –3.0 (3B), –5.1 (3B), –8.3 (4B). IR (KBr, cm^{-1}): ν_{BH} 2587, 2556 (vs). Anal. Calcd. for $C_{31}H_{46}B_{10}HfN_4$ (**27b**): C, 48.91; H, 6.09; N, 7.36. Found: C, 48.79; H, 5.95; N, 6.82.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Hf[$\eta^2$-(Xyl)NC[N(Me)($CH_2$)$_3$N(Me)]=CN(Xyl)] (28b). A toluene (15 mL) suspension of **12b** (157 mg, 0.20 mmol) was heated at 110 °C in a close Schlenk flask for 7 days. After filtration, the resulting clear yellow solution was evaporated to dryness under vacuum. The yellow residue was redissolved in ether (30 mL). After filtration, the resulting yellow solution was concentrated under vacuum to about 15 mL. Complex **28b** was isolated as pale yellow crystals after this solution stood at room temperature for 2 days (108 mg, 69%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.12 (m, 2H, $C_6H_3(CH_3)_2$), 6.97 (m, 4H, $C_6H_3(CH_3)_2$), 5.81 (t, J = 2.7 Hz, 2H, C_5H_4), 5.12 (t, J =

2.6 Hz, 2H, C_5H_4), 2.86 (m, 4H, NCH_2), 2.65 (s, 6H, NCH_3), 2.12 (s, 6H, $C_6H_3(CH_3)_2$), 1.35 (s, 6H, $C(CH_3)_2$), 1.26 (m, 2H, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 149.6 (C_5H_4), 144.2, 134.1, 132.3, 129.0, 128.8, 128.6 ($C_6H_3(CH_3)_2$), 124.7 (C=C), 112.2, 109.7 (C_5H_4), 50.1 (NCH_2), 42.2 ($C(CH_3)_2$), 37.7 (NCH_3), 32.3 ($C(CH_3)_2$), 21.9 ($NCH_2CH_2CH_2N$), 20.7 ($C_6H_3(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –0.5 (1B), –2.5 (1B), –5.1 (2B), –9.8 (2B), –10.6 (4B). IR (KBr, cm^{-1}): ν_{BH} 2563 (vs). Anal. Calcd. for $C_{33}H_{50}B_{10}HfN_4$ (28b): C, 50.21; H, 6.38; N, 7.10. Found: C, 50.40; H, 6.35; N, 6.77.

Preparation of $[\eta^5:\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2$-$S_2C_2B_{10}H_{10}](NHMe_2)_2$ (30). To a toluene (20 mL) solution of **1b** (214 mg, 0.50 mmol) was added dropwise a toluene (2.0 mL) solution of **29** (0.25 M, 0.50 mmol) at -78 °C with stirring. The mixture was stirred at room temperature overnight. After filtration, the resulting clear yellow solution was concentrated to about 5 mL. *n*-Hexane (10 mL) vapor diffusion gave **30** as a yellow solid over a period of 2 days (226 mg, 71%). ^1H NMR (400 MHz, pyridine-d_5): δ 9.18 (s, 2H, $HN(CH_3)_2$), 6.64 (d, J = 2.0 Hz, 1H, C_5H_4), 6.60 (brs, 1H, C_5H_4), 6.26 (brs, 1H, C_5H_4), 5.90 (d, J = 2.1 Hz, 1H, C_5H_4), 2.83 (s, 12H, $HN(CH_3)_2$), 1.60 (s, 3H, $C(CH_3)_2$), 1.55 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (400 MHz, pyridine-d_6): δ 145.9, 114.7, 113.3, 109.8, 107.3 (C_5H_4), 103.3, 103.1 (Cage *C*), 94.5 (Cage *C*-S), 42.2 ($C(CH_3)_2$), 36.0 ($HN(CH_3)_2$), 34.3, 31.9 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.4 (5B),–5.8 (4B), –9.4 (11B). IR (KBr, cm^{-1}): ν_{BH} 2568 (vs). Anal. Cacld. for $C_{14.5}H_{38.75}B_{20}N_{1.25}S_2Zr$ (**30** – $0.75HNMe_2$): C, 28.92; H, 6.48; N, 2.91. Found: C, 29.06; H, 6.28; N, 2.45.

Preparation of $[\eta^5:\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2$-$S_2C_2B_{10}H_{10}][2,6$-$(CH_3)_2C_6H_3N{=}C]_2{\cdot}(C_7H_8)_{0.5}$ (31•$(C_7H_8)_{0.5}$). To a toluene (20 mL) solution of **1b** (214 mg, 0.50 mmol) was added dropwise a toluene (2.0 mL) solution of **29** (0.25 M,

0.50 mmol) at -78°C with stirring. The mixture was stirred at room temperature overnight. The orange yellow solution was filtered to a flask containing a toluene (5 mL) solution of XylNC (135 mg, 1.00 mmol) at -78 °C. Complex **31•(C_7H_8)$_{0.5}$** was isolated as yellow crystals after this solution stood at room temperature overnight (312 mg, 73%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.26 (m, 2H, $C_6H_3(CH_3)_2$ + C_5H_4), 7.14 (m, 2H, $C_6H_3(CH_3)_2$ + C_5H_4), 6.04 (d, J = 7.5 Hz, 2H, $C_6H_3(CH_3)_2$), 6.99 (d, J = 7.5 Hz, 2H, $C_6H_3(CH_3)_2$), 6.30 (brs, 1H, C_5H_4), 6.59 (brs, 1H, C_5H_4), 2.60 (s, 6H, $C_6H_3(CH_3)_2$), 2.24 (s, 6H, $C_6H_3(CH_3)_2$), 1.63 (s, 3H, $C(CH_3)_2$), 1.48 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 169.5 (XylN=*C*), 153.8, 117.5, 114.1, 111.7, 111.6 (C_5H_4), 106.3, 106.2 (Cage *C*), 95.1, 94.5 (Cage *C*-S), 42.2 ($C(CH_3)_2$), 34.1, 31.0 ($C(CH_3)_2$), 18.7, 18.6 ($C_6H_3(CH_3)_2$). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ –9.1 (17B), –13.5 (3B). IR (KBr, cm^{-1}): ν_{BH} 2553 (vs). Anal. Calcd. for $C_{31.75}H_{50}B_{20}N_2S_2Zr$ (**31** + 0.25Toluene): C, 45.87; H, 6.06; N, 3.37. Found: C, 45.65; H, 6.08; N, 3.43.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][O=C(NMe$_2$)NHPh]$_2$ (32). To a toluene (20 mL) solution of **1b** (214 mg, 0.50 mmol) was added dropwise a toluene (2.0 mL) solution of **29** (0.25 M, 0.50 mmol) at -78°C with stirring. The mixture was stirred at room temperature overnight. The orange yellow solution was filtered to a flask containing a toluene (5 mL) solution of PhNCO (115 mg, 1.00 mmol) at -78 °C. The solution was stirred at room temperature overnight. After filtration, the yellow solid was collected and redissolved in THF (20 mL). The resulting yellow solution was filtered and concentrated under vacuum to about 10 mL. Complex **32** was isolated as yellow crystals after this solution stood at room temperature for 5 days (382 mg, 87%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 8.82 (brs, 1H, N-*H*), 7.86 (d, J = 7.5 Hz, 2H, C_6H_5),

7.33 (m, 5H, C_6H_5 + N-*H*), 7.23 (d, J = 7.5 Hz, 3H, C_6H_5), 7.12 (m, 2H, C_6H_5 + C_5H_4), 6.67 (d, J = 2.7 Hz, 1H, C_5H_4), 5.99 (d, J = 2.7 Hz, 1H, C_5H_4), 5.44 (d, J = 2.4 Hz, 1H, C_5H_4), 2.93 (s, 6H, $N(CH_3)_2$), 2.50 (brs, 6H, $N(CH_3)_2$), 1.52 (s, 3H, $C(CH_3)_2$), 1.49 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 165.7, 156.2 (*C*=O), 147.9 (C_5H_4), 146.0, 141.1, 128.7, 128.3, 124.9, 123.3, 121.9, 120.2 (C_6H_5), 118.6, 117.1, 112.3, 112.0 (C_5H_4), 108.1 (Cage *C*), 100.0, 99.2 (Cage *C*-S). 41.3 ($C(CH_3)_2$), 37.0, 35.9 ($N(CH_3)_2$), 33.0, 31.8 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_6): δ –3.7 (6B), –6.8 (6B), –9.3 (8B). IR (KBr, cm^{-1}): ν_{BH} 2568(vs). Anal. Calcd. for $C_{30}H_{54}B_{20}N_4O_2S_2Zr$ (**32**): C, 41.21; H, 6.23; N, 6.41. Found: C, 41.21; H, 6.34; N, 6.49.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Zr[$\eta^2$-$S_2C_2B_{10}H_{10}$][S=C(NMe$_2$)NH^{n}Bu] (33). To a toluene solution of **1b** (214 mg, 0.50 mmol) was added dropwise a toluene (2.0 mL) solution of **29** (0.25 M, 0.50 mmol) at -78°C with stirring. The mixture was stirred at room temperature overnight. The orange yellow solution was filtered to a flask containing a toluene (5 mL) solution of ^{n}BuNCS (131 mg, 1.00 mmol) at -78 °C. The solution was stirred at room temperature overnight. After filtration, the resulting yellowish orange solution was concentrated under vacuum to about 5 mL. Complex **33** was isolated as yellow crystals after this solution stood at room temperature for 5 days (269 mg, 76%). ^1H NMR (300 MHz, pyridine-d_5): δ 7.73 (brs, 1H, N-*H*), 7.28 (brs, 2H, C_5H_4), 6.41 (brs, 2H, C_5H_4), 3.87 (q, J = 6.6 Hz, 2H, NCH_2), 3.23 (s, 6H, $N(CH_3)_2$), 1.68 (m, 2H, NCH_2CH_2), 1.47 (s, 6H, $C(CH_3)_2$), 1.28 (q, J = 7.4 Hz, 2H, $NCH_2CH_2CH_2$), 0.78 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 183.0 (*C*=S), 155.6, 117.6, 115.9 (C_5H_4), 110.5, 106.6 (Cage *C*), 94.4 (Cage *C*-S), 46.0 (NCH_2), 42.0 ($C(CH_3)_2$), 40.3 ($N(CH_3)_2$), 33.1 ($C(CH_3)_2$), 32.0 (NCH_2CH_2), 20.3 ($NCH_2CH_2CH_2$),

13.9 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –0.2 (3B), –3.2 (3B), –5.0 (4B), –8.1 (10B). IR (KBr, cm^{-1}): ν_{BH} 2951 (vs). Anal. Calcd. for $C_{19}H_{46}B_{20}N_2S_3Zr$ (**33**): C, 32.31; H, 6.57; N, 3.97. Found: C, 32.46; H, 6.60; N, 3.89.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][O(CH_2)_4NHMe_2]\cdot C_7H_8$ ($34\cdot C_7H_8$). To a toluene (20 mL) solution of **1b** (427 mg, 1.00 mmol) was added dropwise a toluene (4 mL) solution of **29** (0.25 M, 1.00 mmol) at room temperature with stirring. The mixture was stirred at room temperature overnight. After filtration, 0.5 mL of THF was added at room temperature, and the solution was heated at reflux for one day. After filtration, Complex $34\cdot C_7H_8$ was isolated as orange crystals via slow evaporation of solvents (454 mg, 60%). ^1H NMR (300 MHz, pyridine-d_5): δ 11.37 (brs, 1H, N-*H*), 6.71 (d, J = 2.4 Hz, 1H, C_5H_4), 6.46 (t, J = 2.4 Hz, 1H, C_5H_4), 6.30 (t, J = 2.1 Hz, 1H, C_5H_4), 5.73 (t, J = 2.7 Hz, 1H, C_5H_4), 4.27 (m, 2H, NCH_2), 3.26 (m, 2H, NCH_2CH_2), 3.04 (s, 6H, $N(CH_3)_2$), 2.11 (m, 2H, OCH_2CH_2), 1.67 (m, 2H, OCH_2), 1.60 (s, 3H, $C(CH_3)_2$), 1.56 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_6): δ 149.6, 118.4, 115.1, 113.2, 109.7 (C_5H_4), 109.7, 104.8 (Cage *C*), 99.1 (Cage *C*-S), 75.3 (OCH_2), 69.7 (OCH_2CH_2), 60.3 (NCH_2CH_2), 45.4 ($N(CH_3)_2$), 43.9 (NCH_2), 35.5 ($C(CH_3)_2$), 34.5, 32.3 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_5): δ –3.9 (4B), –8.0 (6B), –9.8 (10B). IR (KBr, cm^{-1}): ν_{BH} 2571 (vs). Anal. Calcd. for $C_{25}H_{53}B_{20}NOS_2Zr$ (**34** + Toluene): C, 39.76; H, 7.07; N, 1.85. Found: C, 39.38; H, 7.05; N, 2.08.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][NH{=}C(NMe_2)Ph]_2$ (35). This complex was prepared as colorless crystals from **1b** (220 mg, 0.50 mmol), **29** (2.0 mL, 0.50 mmol) and PhCN (103 mg, 1.00 mmol) in toluene (20 mL) solution using the identical procedure reported for **33**: yield 327 mg (78%). ^1H NMR (400 MHz, pyridine-d_5): δ 8.18 (brs, 2H, C_6H_5), 7.86

(d, J = 7.2 Hz, 2H, C_6H_5), 7.52 (m, 6H, C_6H_5), 5.92 (brs, 2H, C_5H_4), 4.18 (brs, 2H, C_5H_4), 3.27 (s, 6H, $N(CH_3)_2$), 3.02 (brs, 2H, N-*H*), 2.63 (s, 6H, $N(CH_3)_2$), 1.38 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 166.7 (*C*=N), 151.1 (C_5H_4), 132.9, 129.9, 128.8, 128.7, 128.6 128.2, 127.2, 1274.1 (C_6H_5), 116.4, 107.5 (C_5H_4), 106.6, 105.7 (Cage *C*), 97.0, 95.0 (Cage *C*-S), 41.2 ($C(CH_3)_2$), 40.5, 38.9 ($N(CH_3)_2$), 36.6, 31.9 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –5.4 (7B), –8.9 (13B). IR (KBr, cm^{-1}): ν_{BH} 2555 (vs). Anal. Calcd. for $C_{30}H_{54}B_{20}N_4S_2Zr$ (**35**): C, 42.78; H, 6.46; N, 6.65. Found: C, 43.07; H, 6.79; N, 6.29.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][\eta^2\text{-}O{=}C(OMe)CH(CH_2NMe_2CH_2CH_2)\text{-}C(OMe)\text{-}O]\cdot C_7H_8$ (36•C_7H_8) and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}S_2C_2B_{10}H_{10}][\eta^2\text{-}O{=}C(OMe)C(CH_2NMe_2CH_2CH_2)\text{=}C\text{-}O]\cdot 3THF$ (37•3THF). To a toluene (20 mL) solution of **1b** (214 mg, 0.50 mmol) was added dropwise a toluene (2.0 mL) solution of **29** (0.25 M, 0.50 mmol) at -78°C with stirring. The mixture was stirred at room temperature overnight. The orange yellow solution was filtered to a flask containing a toluene (5 mL) solution of MA (179 mg, 2.00 mol) at -78 °C. A white solid was immediately formed. The solution was stirred at room temperature overnight. After filtration, the white solid was collected and washed with toluene (5 mL X 2) and *n*-hexane (10 mL X 3) to give **36•C_7H_8** as a white solid (271 mg, 63%). Recrystallization of **36•C_7H_8** from THF (8 mL) solution gave **37•3THF** as colorless crystals over a period of 18 days at room temperature (267 mg, 56%) (Isomer A : Isomer B = 1.7:1). **36**: ^1H NMR (400 MHz, pyridine-d_5): δ 7.14 (m, 1H, C_5H_4), 6.80 (d, J = 1.8 Hz, 1H, C_5H_4), 6.06 (brs, 1H, C_5H_4), 5.80 (d, J = 2.1 Hz, 1H, C_5H_4), 5.60 (m, 1H, MeOC(=O)C*H*), 4.26 (d, J = 11.8 Hz, 1H, NCH_2), 4.04 (m, 1H, NCH_2), 4.02 (s, 3H, OCH_3), 3.68 (m, 2H, NCH_2CH_2), 3.60 (s, 3H, $N(CH_3)_2$), 3.50 (s, 3H, $N(CH_3)_2$), 3.26 (s, 3H, OCH_3), 2.23

(1H, NCH_2CH_2), 1.80 (m, 1H, NCH_2CH_2), 1.60 (s, 3H, $C(CH_3)_2$), 1.58 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_6): δ 174.3 (Zr-O=*C*), 148.0, 119.3, 115.6, 114.4, 113.5 (C_5H_4), 107.7, 102.5 (Cage *C*), 96.5 (Zr-O-*C*OMe)), 67.8 (Zr-O-*C*(OMe)-O), 61.1, 59.8 (NCH_2), 56.6 (NCH_3), 56.3, 48.2 (OCH_3), 47.7 (NCH_3), 45.5 (MeOC(=O)*C*H), 41.9 ($C(CH_3)_2$), 33.8, 31.6 ($C(CH_3)_2$), 25.7 (NCH_2CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.9 (3B), –6.5 (2B), –9.2 (5B). IR (KBr, cm^{-1}): ν_{BH} 2587 (vs). Anal. Calcd. for $C_{29}H_{57}B_{20}NO_4S_2Zr$ (**36** + Toluene): C, 40.72; H, 6.72; N, 1.64. Found: C, 40.98; H, 6.94; N, 1.71.

37: Isomer A: ^1H NMR (400 MHz, pyridine-d_5): δ 6.52 (m, 1H, C_5H_4), 6.49 (m, 1H, C_5H_4), 6.14 (dd, J = 2.3, 5.6 Hz, 1H, C_5H_4), 5.78 (dd, J = 3,2, 5.6 Hz, 1H, C_5H_4), 4.63 (d, J = 13.8 Hz, 1H, NCH_2), 4.35 (d, J = 13.8 Hz, 1H, NCH_2), 3.85 (m, 2H, NCH_2CH_2), 3.77 (s, 3H, OCH_3), 3.55 (s, 6H, $N(CH_3)_2$), 2.81 (m, 2H, NCH_2CH_2), 1.64 (s, 3H, $C(CH_3)_2$), 1.56 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 177.6, 168.7 (Zr-O-*C*), 147.5, 118.3, 115.2, 110.7, 109.1 (C_5H_4), 101.1 (O-C=*C*), 96.0, 95.5 (Cage *C*), 90.1 (Cage *C*-S), 59.3 (NCH_2), 59.0 (NCH_2CH_2), 53.5 ($N(CH_3)_2$), 52.5 (OCH_3), 40.8 ($C(CH_3)_2$), 33.5, 31.3 ($C(CH_3)_2$), 29.3 (NCH_2CH_2). Isomer B: ^1H NMR (400 MHz, pyridine-d_5): δ 6.51 (m, 1H, C_5H_4), 6.44 (dd, J = 2.4, 5.0 Hz, 1H, C_5H_4), 6.11 (dd, J = 2.4, 5.6 Hz, 1H, C_5H_4), 5.73 (dd, J = 3.28, 5.5 Hz, 1H, C_5H_4), 4.52 (d, J = 14.0 Hz, 1H, NCH_2), 4.40 (d, J = 14.0 Hz, 1H, NCH_2), 3.92 (s, 3H, OCH_3), 3.92 (m, 2H, NCH_2CH_2), 3.54 (s, 6H, $N(CH_3)_2$), 3.10 (m, 1H, NCH_2CH_2), 2.92 (m, 1H, NCH_2CH_2), 1.62 (s, 3H, $C(CH_3)_2$), 1.54 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 177.8, 170.3 (Zr-O-*C*), 147.8, 119.5, 114.3, 110.3, 109.5 (C_5H_4), 109.6 (O-C=*C*), 95.6, 95.3 (Cage *C*), 88.5 (Cage *C*-S), 59.8 (NCH_2), 59.0 (NCH_2CH_2), 53.9 (OCH_3), 48.2 ($N(CH_3)_2$), 40.8 ($C(CH_3)_2$), 33.1, 31.6 ($C(CH_3)_2$), 28.5 (NCH_2CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.6 (14B), –

6.9 (12B), −8.8 (24B). IR (KBr, cm^{-1}): ν_{BH} 2595, 2553 (vs). Anal. Calcd. for $C_{27}H_{57}B_{20}NO_{4.5}S_2Zr$ (**37** + 1.5THF): C, 38.64; H, 6.85; N, 1.67. Found: C, 38.29; H, 7.12; N, 1.56.

General Procedure for the Preparation of Amidine 38 ~ 40. PhCN and catalyst **30** (0.05 equiv) were mixed in a Schlenk flask with a Teflon valve, followed by addition of amine at -78 °C. The flask was then closed (in order to prevent evaporation of amines with low boiling point) and the resulting mixture was warmed to room temperature and stirred at 90 °C for 12 hrs. Removal of the solvent and excess amine gave the corresponding product which was purified by distillation.

Preparation of PhC(=NH)N(CH_3)$_2$) (38). This compound was prepared from PhCN (10 mL), $HNMe_2$ (0.70 mL, 10.86 mmol) and **30** (191 mg, 0.30 mmol) according to the "General Procedure for the Preparation of Amidine". Colorless oil (1.02 g, 62%). ^{1}H NMR (400 MHz, chloroform-d_1): δ 7.35 (m, 3H, C_6H_5), 7.29 (m, 2H, C_6H_5), 6.21 (brs, 1H, N-*H*), 2.90 (s, 6H, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, chloroform-d_1): δ 170.0 (*C*=N), 138.7, 128.8, 128.4, 126.6 (C_6H_5), 38.6 (N(CH_3)$_2$).

Preparation of PhC(=NH)N(CH_2CH_3)$_2$) (39). This compound was prepared from PhCN (5 mL), $HNEt_2$ (0.20 mL, 1.93 mmol) and **30** (38 mg, 0.06 mmol) according to the "General Procedure for the Preparation of Amidine". Colorless oil (69 mg, 20%). ^{1}H NMR (400 MHz, chloroform-d_1): δ 7.36 (m, 3H, C_6H_5), 7.30 (m, 2H, C_6H_5), 4.97 (brs, 1H, N-*H*), 3.31 (q, J = 7.0 Hz, 4H, NCH_2CH_3), 1.12 (t, J = 7.1 Hz, 6H, NCH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, chloroform-d_1): δ 168.6 (*C*=N), 139.1, 128.6, 128.4, 126.4 (C_6H_5), 42.0 (NCH_2CH_3), 13.2 (NCH_2CH_3).

Preparation of PhC(=NH)N($CH_2CH_2CH_3$)$_2$) (40). This compound was prepared from PhCN (5 mL), HN^{n}Pr$_2$ (0.28 mL, 2.04 mmol) and **30** (38 mg, 0.06 mmol) according to the "General Procedure for the Preparation of Amidine". Colorless oil

(78 mg, 19%). ^{1}H NMR (300 MHz, chloroform-d_1): δ 7.27 (m, 3H, C_6H_5), 7.20 (m, 2H, C_6H_5), 4.63 (brs, 1H, N-*H*), 3.13 (t, J = 7.4 Hz, 4H, $NCH_2CH_3CH_3$), 1.50 (m, 4H, $NCH_2CH_2CH_3$), 0.75 (t, J = 8.6 Hz, 6H, $NCH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (75 MHz, chloroform-d_1): δ 169.1 (*C*=N), 139.3, 128.5, 128.3, 126.5 (C_6H_5), 49.5 ($NCH_2CH_2CH_3$), 21.0 ($NCH_2CH_2CH_3$), 11.2 ($NCH_2CH_2CH_3$).

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (1a) and [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]$Zr(NMe_2)(HNMe_2)$ (42a). To a toluene (30 mL) solution of $Zr(NMe_2)_4$ (2.72 g, 10.20 mmol) was added dropwise a toluene (15 mL) solution of **41** (2.51 mg, 10.02 mmol) at room temperature with stirring. The mixture was stirred at room temperature for 2 days and refluxed overnight. After filtration, the yellow solid was collected and washed with toluene (5 mL X 2). After thoroughly dried under vacuum, complex **42a** was collected as a yellow solid (1.40 g, 33%). The remaining yellow solution was concentrated to about 8 mL, **1a** was isolated as yellow crystals after this solution stood at -30 °C for 2 days (2.68 g, 63%). Single crystal of **42a** suitable for X-ray analyses were grown from a DME/toluene solution at room temperature as **42a**•C_7H_8. **42a**: ^{1}H NMR (300 MHz, pyridine-d_5): δ 6.68 (brs, 1H, C_5H_4), 6.24 (d, J = 2.1 Hz, 1H, C_5H_4), 6.14 (brs, 2H, C_5H_4), 3.29 (s, 6H, $N(CH_3)_2$), 3.07 (brs, 1H, Cage C-*H*), 2.33 (s, 6H, $HN(CH_3)_2$), 1.60 (s, 3H, $C(CH_3)_2$), 1.51 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 117.7, 109.8, 105.2 (C_5H_4), 49.5 ($N(CH_3)_2$), 38.2 ($HN(CH_3)_2$), 36.3 ($C(CH_3)_2$), 27.5, 26.6 ($C(CH_3)_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ 2.1 (1B), –4.1 (2B), –7.6 (2B), –10.7 (2B), –13.0 (1B), –20.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2544, 2509 (vs). Anal. Calcd. for $C_{14}H_{33}B_9N_2Zr$ (**42a**): C, 40.23; H, 7.96; N, 6.70. Found: C, 40.25; H, 8.07; N, 6.44.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$Hf(NMe_2)_2$ (1b) and [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]$Hf(NMe_2)(HNMe_2)$ (42b). **1b** and **42b** were prepared as colorless crystals and white solid from **41** (2.00 g, 8.00 mmol) and $Hf(NMe_2)_4$ (2.84 g, 8.00 mmol) in toluene using a procedure identical with that reported for **1a** and **42a**. **1b**: yield 1.79 g (43%), **42b**: yield 2.12 g (53%). **42b**: ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.62 (brs, 1H, C_5H_4), 6.19 (brs, 1H, C_5H_4), 6.07 (brs, 1H, C_5H_4), 6.07 (brs, 1H, C_5H_4), 3.29 (s, 6H, $N(CH_3)_2$), 3.12 (brs, 1H, Cage C-*H*), 2.32 (s, 6H, $HN(CH_3)_2$), 1.60 (s, 3H, $C(CH_3)_2$), 1.50 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_6): δ 120.7, 117.8, 108.8, 103.5 (C_5H_4), 68.1 (Cage *C*), 49.2 ($N(CH_3)_2$), 47.1 (Cage *C*-H), 38.9 ($HN(CH_3)_2$), 37.7 ($C(CH_3)_2$), 28.1, 27.3 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ 0.2 (1B), –5.5 (2B), –8.9 (2B), –12.0 (2B), –15.0 (1B), –22.5 (1B). IR (KBr, cm^{-1}): ν_{BH} 2533 (vs). Anal. Calcd. for $C_{14}H_{33}B_9HfN_2$ (**42b**): C, 33.28; H, 6.58; N, 5.54. Found: C, 33.13; H, 6.45; N, 5.28.

Preparation of [η^5:σ-$H_2C(C_{13}H_8)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (44a) and [{σ:η^5-$H_2C(C_{13}H_8)(C_2B_9H_{10})$}$Zr(NMe_2)_2$][$Zr(NMe_2)_3(HNMe_2)_2$] (45a). To a toluene (15 mL) solution of $Zr(NMe_2)_4$ (534 mg, 2.00 mmol) was added dropwise a toluene (10 mL) solution of **43** (600 mg, 2.00 mmol) at -30 °C with stirring, the mixture was stirred at room temperature for two days. The yellow solid was collected by filtration and washed with toluene (2 mL X 3). Single crystal suitable for X-ray analyses was grown from slowly evaporation of a saturated toluene solution of **45a** (397 mg, 25%). After removal of toluene under vacuum, the residue was extracted with hot *n*-hexane (15 mL X 3). The remaining orange yellow solid was collected and recrystallization from toluene to give **44a** as orange yellow crystals (253 mg, 25%). Evaporation of the *n*-hexane solution gave **43** as pale yellow crystals (162 mg, 27%).

44a: ^{1}H NMR (300 MHz, d_6-benzene): δ 7.47 (d, J = 8.1 Hz, 2H, $C_{13}H_8$), 7.34 (d, J = 8.4 Hz, 2H, $C_{13}H_8$), 6.98 (t, J = 7.7 Hz, 2H, $C_{13}H_8$), 6.83 (t, J = 7.5 Hz, 2H, $C_{13}H_8$), 3.70 (s, 2H, CH_2), 2.05 (s, 12H, $N(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-benzene): δ 131.8, 127.5, 122.8, 122.7, 121.1, 114.0, 106.9 ($C_{13}H_8$), 100.3, 97.1 (Cage *C*), 42.0 ($N(CH_3)_2$), 34.2 (CH_2). $^{11}B\{^{1}H\}$ NMR (96 MHz, d_6-benzene): δ –1.4 (1B), –4.9 (3B), –8.4 (2B), –9.6 (2B), –11.0 (2B). IR (KBr, cm^{-1}): ν_{BH} 2569 (vs). Anal. Calcd for $C_{20}H_{32}B_{10}N_2Zr$ (**44a**): C, 48.06; H, 6.45; N, 5.60. Found: C, 48.06; H, 6.74; N, 5.72.

45a: ^{1}H NMR (400 MHz, d_5-pyridine): δ 8.21 (m, 3H, $C_{13}H_8$), 7.49 (q, J = 7.2 Hz, 2H, $C_{13}H_8$), 7.41 (d, J = 7.8 Hz, 1H, $C_{13}H_8$), 7.23 (t, J = 7.3 Hz, 1H, $C_{13}H_8$), 7.13 (t, J = 7.2 Hz, 1H, $C_{13}H_8$), 4.18 (d, J = 14.9 Hz, 1H, CH_2), 3.90 (d, J = 14.9 Hz, 1H, CH_2), 3.25 (brs, 1H, Cage C-*H*), 2.89 (s, 18 H, $Zr(N(CH_3)_2)(HN(CH_3)_2)$, 2.87 (s, 6H, $N(CH_3)_2$), 2.47 (s, 6H, $N(CH_3)_2$), 2.32 (d, J = 6.2 Hz, 12H, $Zr(N(CH_3)_2)(HN(CH_3)_2)$. $^{13}C\{^{1}H\}$ NMR (100 MHz, d_5-pyridine): δ 146.9, 134.7, 134.2, 124.2, 120.5, 120.3, 119.6, 119.4, 118.4, 118.0, 61.0 ($C_{13}H_8$), 52.1 (Cage *C*), 51.6 (Cage *C*-H), 44.7, 44.0, 42.2, 38.9 (NCH_3), 42.4 (CH_2). $^{11}B\{^{1}H\}$ NMR (96 MHz, d_5-pyridine): δ –0.5 (1B), –5.1 (3B), –8.6 (2B), –10.2 (1B), –12.7 (1B), –22.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2515 (vs). Anal. Calcd for $C_{30}H_{64}B_9N_7Zr_2$ (**45a**): C, 44.89; H, 8.04; N, 12.22. Found: C, 44.74; H, 7.97; N, 12.40.

Preparation of $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr[\eta^2\text{-}NMe(CH_2)_2NHMe]\cdot(C_2H_7N)_{0.5}$ ($46a\cdot(C_2H_7N)_{0.5}$). To a toluene solution (15 mL) of **1a** (853 mg, 1.99 mmol) was added dropwise a toluene (3 mL) solution of DMEDA (529 mg, 6.00 mmol) at -30 °C with stirring. The solution turned from yellow to red immediately and further stirred at room temperature in a closed Schlenk flask for 2 days. After filtration and washed with toluene (5 mL) and *n*-hexane (10 mL X 3),

46a•(C_2H_7N)$_{0.5}$ was collected as a red solid (588 mg, 67%). Single crystal suitable for X-ray analyses was grown from slowly evaporation of a saturated toluene solution of **46a•(C_2H_7N)$_{0.5}$**. ^{1}H NMR (400 MHz, d_5-pyridine): δ 6.83 (d, J = 2.3 Hz, 1H, C_5H_4), 6.74 (brs, 1H, C_5H_4), 6.31 (d, J = 1.8 Hz, 1H, C_5H_4), 6.18 (brs, 1H, C_5H_4), 3.55 (brs, 2H, NCH_2), 3.32 (brs, 1H, NCH_2), 3.31 (brs, 2H, NCH_2 + Cage C-*H*), 2.89 (s, 3H, NCH_3), 2.73 (s, 3H, NCH_3), 1.68 (s, 3H, $C(CH_3)_2$), 1.58 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, d_5-pyridine): δ 138.0, 118.6, 116.3, 111.2, 107.4 (C_5H_4), 67.4 (Cage *C*), 56.3, 54.0 (NCH_2), 47.9 (Cage *C*-H), 42.1 (NCH_3), 38.5 (NCH_3 + $C(CH_3)_2$), 27.8 ($C(CH_3)_2$). ^{11}B{^{1}H} NMR (96 MHz, d_5-pyridine): δ –0.2 (1B), –3.8 (2B), –5.6 (1B), –10.3 (2B), –11.3 (1B), –15.6 (1B), –22.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2522 (vs). Anal. Calcd for $C_{15}H_{34.5}B_9N_{2.5}Zr$ (**46a** + 0.5$HNMe_2$): C, 41.09; H, 7.93; N, 7.99. Found: C, 41.49; H, 7.92; N, 7.61.

Alternative method. To a toluene (8 mL) suspension of **42a** (88 mg, 0.21 mmol) was added a toluene (2 mL) solution of DMEDA (23 mg, 0.25 mmol) at room temperature, the suspension was stirred at room temperature overnight. After filtration, the residue was collected and washed with toluene (5 mL) and *n*-hexane (10 mL X 3) to give **46a•(C_2H_7N)$_{0.5}$** as a red solid (79 mg, 86%).

Preparation of [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr[$\eta^2$-$NMe(CH_2)_3NHMe$] (47a). To a toluene (15 mL) solution of **1a** (853 mg, 2.00 mmol) was added dropwise a toluene (5 mL) solution of DMPDA (612 mg, 6.00 mmol) at -30 °C with stirring. The solution remained yellow and was further stirred at 110 °C in a closed Schlenk flask for 2 days. After filtration and washing with toluene (5 mL) and *n*-hexane (10 mL X 3), **47a** was collected as a yellow solid (625 mg, 73%) (Isomer A : Isomer B = 1.6:1). Isomer A: ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.78 (brs, 1H, C_5H_4), 6.61 (brs, 1H, C_5H_4), 6.28 (brs, 1H, C_5H_4), 6.16 (brs, 1H, C_5H_4), 5.00 (brs, 1H, NCH_2), 3.30 (s, 3H,

NCH_3), 3.11 (brs, 1H, NCH_2), 2.95 (s, 1H, Cage C-*H*), 2.69 (brs, 2H, NCH_2), 2.65 (s, 3H, NCH_3), 1.62 (brs, 5H, C(CH_3)$_2$ + NCH$_2$CH_2CH$_2$N), 1.53 (s, 3H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 128.3, 118.2, 116.5, 109.3, 107.6 (C_5H_4), 67.8 (Cage *C*), 54.1, 53.7 (NCH$_2$), 46.5 (Cage *C*-H), 45.7, 39.4 (NCH$_3$), 37.8 (*C*(CH$_3$)$_2$), 27.9, 27.7 (C(*C*H$_3$)$_2$), 25.1 (NCH$_2$*C*H$_2$CH$_2$N). Isomer B: ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.95 (brs, 1H, C$_5H_4$), 6.48 (brs, 1H, C$_5H_4$), 6.31 (brs, 2H, C$_5H_4$), 5.11 (brs, 1H, NCH_2), 3.30 (s, 1H, Cage C-*H*), 3.15 (brs, 2H, NCH_2), 3.00 (s, 3H, NCH_3), 2.78 (s, 3H, NCH_3), 2.69 (brs, 1H, NCH_2), 1.62 (brs, 5H, C(CH_3)$_2$ + NCH$_2$CH_2CH$_2$N), 1.53 (s, 3H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 130.4, 118.2, 114.2, 111.6, 105.9 (C_5H_4), 69.0 (Cage *C*), 54.1, 53.7 (NCH$_2$), 51.4 (Cage *C*-H), 45.7, 41.1 (NCH$_3$), 37.8 (*C*(CH$_3$)$_2$), 28.2, 27.1 (C(*C*H$_3$)$_2$), 26.2 (NCH$_2$*C*H$_2$CH$_2$N). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ 0.2 (1.5B), –1.8 (1B), –3.6 (1.5B), –6.4 (4B), –9.5 (4B), –11.7 (8B), –22.7 (2.5B). IR (KBr, cm^{-1}): ν_{BH} 2544, 2522, 2497 (vs). Anal. Calcd. For $C_{15}H_{33}B_9N_2Zr$ (**47a**): C, 41.90; H, 7.74; N, 6.52. Found: C, 42.23; H, 7.75; N, 6.59.

Alternative method. Complex **47a** was prepared as a yellow solid from **42a** (417mg, 1.00 mmol) and DMPDA (112 mg, 1.10 mmol) in toluene using a procedure identical with that reported for **46•(C_2H_7N)$_{0.5}$**: yield 352 mg (82%).

Preparation of [η^5:η^5-Me$_2$C(C_5H_4)($C_2B_9H_{10}$)]Hf[η^2-NMe(CH$_2$)$_3$NHMe] (47b). Complex **47b** was prepared as a yellow solid from **1b** (258 mg, 0.49 mmol) and DMPDA (153 mg, 1.50 mmol) in toluene using a procedure identical with that reported for **47a**: yield 109 mg (43%) (Isomer A : Isomer B = 2:1). Isomer A: ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.75 (brs, 1H, C$_5H_4$), 6.62 (brs, 1H, C$_5H_4$), 6.12 (brs, 2H, C$_5H_4$), 4.35 (brs, 1H, NCH_2), 3.39 (s, 3H, NCH_3), 3.12 (brs, 1H, NCH_2), 2.99 (s, 1H, Cage C-*H*), 2.83 (brs, 2H, NCH_2), 2.74 (s, 3H, NCH_3), 1.62 (brs, 5H, C(CH_3)$_2$

+ $NCH_2CH_2CH_2N$), 1.51 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 116.5, 115.6, 107.5, 105.0 (C_5H_4), 68.6 (Cage *C*), 55.0 (NCH_2), 46.6 (Cage *C*-H), 48.8, 39.7 (NCH_3), 37.6 ($C(CH_3)_2$), 27.9 ($C(CH_3)_2$), 25.8 ($NCH_2CH_2CH_2N$). Isomer B: ^1H NMR (400 MHz, pyridine-d_5): δ 6.95 (brs, 1H, C_5H_4), 6.51 (brs, 1H, C_5H_4), 6.30 (brs, 1H, C_5H_4), 6.20 (brs, 1H, C_5H_4), 4.66 (brs, 1H, NCH_2), 3.39 (s, 1H, Cage C-*H*), 3.20 (brs, 2H, NCH_2), 2.99 (s, 3H, NCH_3), 2.83 (s, 4H, NCH_3 + NCH_2), 1.62 (brs, 5H, $C(CH_3)_2$ + $NCH_2CH_2CH_2N$), 1.51 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 123.2, 114.5, 109.8, 103.7 (C_5H_4), 66.4 (Cage *C*), 57.2, 54.8 (NCH_2), 51.6 (Cage *C*-H), 46.0, 40.8 (NCH_3), 37.6 ($C(CH_3)_2$), 28.4, 27.1 ($C(CH_3)_2$), 25.8 ($NCH_2CH_2CH_2N$). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ –0.7 (1.5B), –2.1 (1B), –4.0 (1.5B), –6.4 (4B), –9.2 (4B), –11.3 (8B), –23.4 (2.5B). IR (KBr, cm^{-1}): ν_{BH} 2547 (vs). Anal. Calcd. For $C_{15}H_{33}B_9HfN_2$ (**47b**): C, 34.83; H, 6.43; N, 5.42. Found: C, 35.32; H, 6.30; N, 5.52.

Alternative method. Complex **47b** was prepared as a yellow solid from **42b** (104 mg, 0.21 mmol) and DMPDA (24 mg, 0.23 mmol) in toluene using a procedure identical with that reported for **46•$(C_2H_7N)_{0.5}$**: yield 82 mg (76%).

Preparation of {[η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr[$\eta^2$-N(Me)$(CH_2)_3$N(Me)Li]}$_2$ (48a). To a toluene (30 mL) solution of **47a** (429 mg, 1.00 mmol) was added ^{n}BuLi (1.6 M in hexane) (0.80 mL, 1.28 mmol) at -78 °C with stirring. The mixture was stirred at room temperature overnight. After filtration, clear orange solution was concentrated to about 10 mL. Complex **48a** was isolated as orange crystals after this solution stood at room temperature for 4 days (270 mg, 62%). ^1H NMR (400 MHz, pyridine-d_5): δ 6.53 (q, J = 2.8 Hz, 2H, C_5H_4), 6.38 (m, 4H, C_5H_4), 6.22 (d, J = 2.4 Hz, 2H, C_5H_4), 3.90 (m, 2H, NCH_2), 3.77 (m, 2H, NCH_2), 3.33 (s, 6H, NCH_3), 3.26 (s, 6H, NCH_3), 3.14 (m, 4H, NCH_2), 2.56 (brs, 2H, Cage C-*H*), 2.52 (m, 2H,

$NCH_2CH_2CH_2N$) 1.84 (m, 2H, $NCH_2CH_2CH_2N$), 1.74 (s, 6H, $C(CH_3)_2$), 1.53 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 136.8, 113.3, 110.0, 107.4, 104.7 (C_5H_4), 67.7 (Cage *C*), 59.8, 58.6 (NCH_2), 47.1, 46.6 (NCH_3), 40.2 (Cage *C*-H), 36.2 ($C(CH_3)_2$), 28.8 ($NCH_2CH_2CH_2N$), 27.3, 25.6 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –7.6 (4B), –10.1 (2B), –12.5 (4B), –13.8 (4B), –16.5 (4B), –30.1 (2B). IR (KBr, cm^{-1}): ν_{BH} 2530, 2506 (vs). Anal. Calcd. For $C_{30}H_{64}B_{18}Li_2N_4Zr_2$ (**48a**): C, 41.33; H, 7.40; N, 6.43. Found: C, 41.74; H, 6.94; N, 6.69.

Preparation of [η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr[$\eta^2$-$NMe(CH_2)_2NHMe$] (50a). To a toluene (15 mL) solution of **49a** (239 mg, 0.50 mmol) was added DMPDA (152 mg, 1.50 mmol) at -30 °C with stirring, the mixture was stirred at 110 °C in a closed Schlenk flask for 3 days, and then cooled to room temperature. After filtration, the resulting orange solution was concentrated to about 8 mL under vacuum. Complex **50a** was isolated as orange crystals after this solution stood at room temperature for 2 days. (149 mg, 62%) Single crystal suitable for X-ray analyses was grown from slow evaporation of a saturated DME solution of **50a**. ^1H NMR (400 MHz, pyridine-d_5): δ 7.89 (m, C_9H_6), 7.69 (m, C_9H_6), 7.14 (m, C_9H_6), 6.99 (m, C_9H_6), 6.79 (m, C_9H_6), 6.55 (brs, C_9H_6), 4.72 (m, NCH_2), 4.57 (brs, NCH_2), 4.48 (brs, NCH_2), 3.38 (brs, NCH_2 + NCH_3), 3.28 (s, NCH_3 + Cage C-*H*), 3.16 (brs, NCH_2 + Cage C-*H*), 2.96 (brs, NCH_2 + Cage C-*H*), 2.87 (NCH_2 + NCH_3) 2.80 (s, NCH_3), 2.56 (brs, NCH_3 + NCH_2), 2.45 (brs, NCH_2), 2.20 (s, NCH_3), 2.17 (s, NCH_3), 2.00 (s, $C(CH_3)_2$), 1.92 (s, $C(CH_3)_2$), 1.74 (s, $C(CH_3)_2$) 1.71 (s, $C(CH_3)_2$), 1.62 (s, $C(CH_3)_2$), 1.53 (brs, $NCH_2CH_2CH_2N$), 1.41 (brs, $NCH_2CH_2CH_2N$), 1.39 (brs, $NCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 129.9, 127.3, 126.1, 125.9, 125.4, 125.2, 125.0, 120.6, 117.6, 114.3, 114.1, 113.7, 113.2, 112.2, 110.9, 110.3, 108.4, 106.7 (C_9H_6),

69.6, 66.6 (Cage *C*), 59.8, 56.9, 56.4, 55.4, 55.0, 53.9 (NCH_2), 51.7 (NCH_3), 48.8, 47.7 (Cage *C*-H), 45.1, 44.7, 42.5, 41.1, 40.1 (NCH_3), 40.9, 40.4, 40.2 ($C(CH_3)_2$), 31.6, 31.2, 30.4, 29.6 ($C(CH_3)_2$), 28.4, 26.5 ($NCH_2CH_2CH_2N$). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ 1.1 (2.5B), –0.1 (1.5B), –2.8 (2B), –5.2 (3B), –6.8 (3.5B), –9.0 (2B), –10.1 (3B), –13.3 (5.5B), –21.8 (3B). IR (KBr, cm^{-1}): ν_{BH} 2502 (vs). Anal. Calcd. For $C_{19}H_{35}B_9N_2Zr$ (**50a**): C, 47.54; H, 7.35; N, 5.84. Found: C, 47.24; H, 7.33; N, 5.65.

Preparation of $[H_2C(C_{13}H_9)(C_2B_9H_{11})][PPN]$ (51). To a toluene (15 mL) solution of **44** (100 mg, 0.20 mmol) was added dropwise a toluene (5 mL) solution of DMEDA (71 mg, 0.80 mmol) at -30°C, the mixture was stirred at room temperature for 2 days. The solution changed from yellow to colorless. The solvent was removed under vacuum. The white residue was redissolved in DME. [PPN]Cl (114 mg, 0.20 mmol) was added at -30 °C to give a white suspension. A clear solution was obtained after the solution was stirred at room temperature for one day. After filtration, the resulting colorless solution was concentrated to about 8 mL. *n*-Hexane vapor diffusion gave **51** as colorless crystals over a period of 2 days at room temperature (104 mg, 61%). ^1H NMR (400 MHz, dichloromethane-d_2): δ 7.87 (m, 1H, $C_{13}H_9$), 7.75 (m, 2H, $C_{13}H_9$), 7.67 (m, 6H, C_6H_5), 7.52 (m, 24H, C_6H_5), 7.36 (m, 2H, $C_{13}H_9$), 7.27 (m, 2H, $C_{13}H_9$), 7.19 (m, 1H, $C_{13}H_9$) 4.31 (dd, J = 4.1, 10.1 Hz, 1H, $C_{13}H_9$), 2.64 (dd, J = 4.2, 14.5 Hz, 1H, CH_2), 1.84 (brs, 1H, Cage C-*H*), 1.46 (dd, J = 10.2, 14.5 Hz, 1H, CH_2), –2.72 (brs, 1H, B-*H*-B). $^{13}C\{^1H\}$ NMR (100 MHz, dichloromethane-d_2): δ 148.9, 148.2, 129.4, 128.6, 128.0, 127.9, 125.0, 119.8 ($C_{13}H_9$), 134.2 (C_6H_5), 132.6 (m, C_6H_5), 129.9 (m, C_6H_5), 127.0 (m, C_6H_5), 51.1 ($C_{13}H_9$ + Cage *C*-H), 46.1 (CH_2), the other cage carbon was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, dichloromethane-d_2): –11.0 (1B), –11.8 (1B), –14.9 (1B), –16.4

(1B), –18.3 (2B), –21.7 (1B), –32.8 (1B), –36.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2508 (vs). Anal. Calcd. for $C_{52}H_{52}B_9NP_2$ (**51**): C, 73.46; H, 6.16; N, 1.65. Found: C, 72.87; H, 6.50; N, 1.57.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^5\text{-}C_4H_4N][\sigma\text{-}C_4H_4N]\cdot(C_7H_8)_{0.5}$ ($52a\cdot(C_7H_8)_{0.5}$) and $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(C_4H_4N)(HNMe_2)$ (53a). To a toluene (10 mL) solution of **1a** (214 mg, 0.50 mmol) was added dropwise a toluene (6 mL) solution of pyrrole (101 mg, 1.50 mmol) at -30 °C with stirring. The mixture was stirred at room temperature for 2 days. After filtration, the resulting yellow solution was concentrated to about 8 mL. Complex $52a\cdot(C_7H_8)_{0.5}$ (172 mg, 66%) and **53a** (29 mg, 13%) were isolated as yellow crystals by fractional recrystallization.

52a: ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.57 (brs, 4H, C_4H_4N), 6.51 (d, J = 1.5 Hz, 4H, C_4H_4N), 7.46 (t, J = 2.9 Hz, 2H, C_5H_4), 6.27 (d, J = 3.0 Hz, 2H, C_5H_4), 1.74 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 152.8, 119.2, 115.8 (C_5H_4), 126.1, 110.7 (C_4H_4N), 43.6 ($C(CH_3)_2$), 33.0 ($C(CH_3)_2$), the cage carbons were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ –3.8 (3B), –5.4 (2B), –8.9 (5B). IR (KBr, cm^{-1}): ν_{BH} 2599, 2557 (vs). Anal. Calcd. for $C_{21.5}H_{32}B_{10}N_2Zr$ (**52a** + 0.5Toluene): C, 49.87; H, 6.23; N, 5.41. Found: C, 49.54; H, 6.38; N, 5.03.

53a: ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.57 (d, J = 1.5 Hz, 2H, C_4H_4N), 6.46 (d, J = 1.5 Hz, 2H, C_4H_4N), 7.15 (brs, 1H, C_5H_4), 6.62 (d, J = 2.1 Hz, 1H, C_5H_4), 6.52 (d, J = 1.8 Hz, 1H, C_5H_4), 6.43 (brs, 1H, C_5H_4), 2.36 (s, 6H, $HN(CH_3)_2$), 2.13 (brs, 1H, Cage C-*H*), 1.70 (s, 3H, $C(CH_3)_2$), 1.65 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 132.2, 110.5 (C_4H_4N), 126.0, 122.0, 113.8, 109.1 (C_5H_4), 54.5 (Cage *C*-H), 39.9 ($HN(CH_3)_2$), 39.6 ($C(CH_3)_2$), 28.0 ($C(CH_3)_2$), the other cage carbon was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ 5.0 (1B), –2.2 (2B), –5.6

(2B), –9.1 (2B), –12.2 (1B), –17.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2522 (vs). Anal. Calcd. for $C_{16}H_{31}B_9N_2Zr$ (**53a**): C, 43.68; H, 7.10; N, 6.37. Found: C, 44.02; H, 7.46; N, 5.93.

Alternative method. Complex **53a** was prepared as a yellow solid from **42a** (84 mg, 0.20 mmol) and pyrrole (30 mg, 0.44 mmol) in toluene using a procedure identical with that reported for **46a•$(C_2H_7N)_{0.5}$**: yield 79 mg (90%).

Preparation of [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr[NH-2,6-^{i}$Pr_2$-$C_6H_3$]($NHMe_2$) (54a). This complex was prepared as a yellow solid from **42a** (125 mg, 0.30 mmol) and 2,6-^{i}$Pr_2C_6H_3NH_2$ (320 mg, 1.80 mmol) in toluene (10 mL) using a procedure identical with that reported for **46a•$(C_2H_7N)_{0.5}$**: yield 141 mg (85%). Single crystal suitable for X-ray analyses were grown from slow evaporation of a toluene solution of **54a** at room temperature. ^{1}H NMR (400 MHz, pyridine-d_5): δ 10.29 (s, 1H, N-*H*), 7.26 (m, 3H, C_6H_3), 6.59 (d, J = 2.4 Hz, 1H, C_5H_4), 6.47 (d, J = 2.0 Hz, 2H, C_5H_4), 6.02 (d, J = 2.3 Hz, 1H, C_5H_4), 1.56 (s, 3H, $C(CH_3)_2$), 1.51 (s, 3H, $C(CH_3)_2$), 1.25 (m, 12H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 152.6 (C_5H_4), 141.2, 125.9, 119.6, 119.4 (C_6H_3), 118.4, 111.0, 105.7 (C_5H_4), 48.6 ($CH(CH_3)_2$), 38.8 ($HN(CH_3)_2$), 37.9 ($C(CH_3)_2$) 28.1, 28.0 ($C(CH_3)_2$), 27.8, 27.2 ($CH(CH_3)_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (128 MHz, benzene-d_5): δ 2.9 (1B), 1.0 (0.5B), –2.9 (1B), –5.4 (1.5B), –6.8 (1B), –8.6 (2.5B), –12.0 (4B), –19.8 (1B), –21.5 (0.5B). IR (KBr, cm^{-1}): ν_{BH} 2525 (vs). Anal. Calcd. for $C_{24}H_{45}B_9N_2Zr$ (**54a**): C, 52.40; H, 8.24; N, 5.09. Found: C, 52.72; H, 8.21; N, 5.20.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Zr{$\eta^2$-$S_2C_2B_{10}H_{10}$}][$H(HNMe_2)_2$] •($C_6H_6$) (55a•$C_6H_6$). To a toluene (10 mL) suspension of **42a** (101 mg, 0.24 mmol) was added dropwise a benzene (2 mL) solution of **29** (51 mg, 0.24 mmol) at -30 °C, the solution became clear orange immediately. The solution was stirred at room

temperature overnight. After filtration, the resulting clear orange solution was concentrated to about 8 mL. Complex **55a•C_6H_6** was isolated as orange crystals after this solution stood at room temperature for 2 days (116 mg, 70%). Single crystal suitable for X-ray analyses were grown from a toluene/benzene solution at room temperature as **55a•C_6H_6**. ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.52 (s, 3H, N-*H*), 6.98 (m, 1H, C_5H_4), 6.67 (m, 1H, C_5H_4), 5.93 (m, 2H, C_5H_4), 2.92 (brs, 1H, Cage C-*H*), 2.66 (s, 12H, HN(CH_3)$_2$), 1.44 (s, 3H, C(CH_3)$_2$), 1.25 (s, 3H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_6): δ 139.0, 121.1, 119.9, 108.2, 107.8 (C_5H_4), 98.7 (Cage *C*-S), 74.5 (Cage *C*), 50.0 (Cage *C*-H), 38.2 ($C(CH_3)_2$ + HN(CH_3)$_2$), 29.0, 27.4 (C(CH_3)$_2$). ^{11}B NMR (128 MHz, benzene-d_6): δ 7.8 (1B), –4.5 (2B), –6.4 (5B), –9.2 (10B), –20.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2567 (vs). Anal. Calcd. for $C_{15.5}H_{39.5}B_{19}NS_2Zr$ (**55** + 0.25C_6H_6 – $HNMe_2$): C, 30.99; H, 6.63; N, 2.33. Found: C, 30.59; H, 6.33; N, 2.21.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Hf($NMe_2$)$_2$][Li(DME)$_3$] (56b). To a DME (20 mL) suspension of **42b** (748 mg, 1.48 mmol) was added dropwise ^{n}BuLi (1.6 M in hexane) (1.2 mL, 1.92 mmol) at -78°C with stirring. The mixture was stirred at room temperature overnight. The solvent was removed under vacuum, the yellow residue was washed with *n*-hexane (10 mL X 3) and redissolved in toluene (20 mL). Complex **56b** was isolated as pale yellow crystals after this solution stood at -30 °C for 3 days (1.03 g, 89%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.57 (dd, J = 3.2, 5.7 Hz, 1H, C_5H_4), 6.44 (dd, J = 3.2, 5.5 Hz, 1H, C_5H_4), 6.27 (dd, J = 2.6, 5.2 Hz, 1H, C_5H_4), 6.17 (dd, J = 2.6, 5.2 Hz, 1H, C_5H_4), 3.49 (s, 12H, OCH_2), 3.39 (s, 6H, N(CH_3)$_2$), 3.36 (s, 6H, N(CH_3)$_2$), 3.26 (s, 18H, OCH_3), 2.67 (brs, 1H, Cage C-*H*), 1.65 (s, 3H, C(CH_3)$_2$), 1.45 (s, 3H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_6): δ 113.8, 107.4, 105.8, 102.4 (C_5H_4), 72.0 (OCH_2), 68.9 (Cage *C*), 58.6

(OCH_3), 48.4, 48.0 ($N(CH_3)_2$), 41.5 ($C(CH_3)_2$), 36.2 (Cage *C*-H), 28.5, 27.4 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): δ –5.5 (1B), –8.8 (1B), –9.7 (1B), –13.1 (1B) –14.8 (2B), –16.3 (1B), –17.6 (1B), –30.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2589, 2555 (vs). Anal. Calcd. for $C_{26}H_{62}B_9HfLiN_2O_6$ (**56b**): C, 39.96; H, 8.00; N, 3.58. Found: C, 39.78; H, 7.65; N, 3.35.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][Li(DME)$_3$] (57a). To a DME solution of **42a** (856 mg, 2.05 mmol) was added dropwise ^{n}BuLi (1.6 M in hexane) (2.0 mL, 3.20 mmol) at -78 °C with stirring, the solution was stirred at room temperature overnight. After filtration, the clear yellowish orange solution was evaporated to dryness. The orange residue was redissolved in toluene. A toluene solution of TMSCl (542 mg, 4.98 mmol) was added at -30 °C, and the solution was stirred at room temperature overnight. After removal of solvent under vacuum, the pale yellow residue was washed with *n*-hexane (10 mL X 3), and redissolved in DME (20 mL). Complex **57a** was isolated as a white solid after the solution stood at -30 °C for 6 days (1.04 g, 77%). ^1H NMR (400 MHz, pyridine-d_5): δ 6.97 (m, 2H, C_5H_4), 6.40 (dd, J = 2.8, 5.3 Hz, 1H, C_5H_4), 6.20 (dd, J = 2.8, 5.1 Hz, 1H, C_5H_4), 3.48 (s, 12 H, OCH_2), 3.25 (s, 18H, OCH_3), 1.61 (s, 3H, $C(CH_3)_2$), 1.47 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 126.1, 125.5, 107.6, 105.3 (C_5H_4), 72.0 (OCH_2), 58.5 (OCH_3), 51.8 (Cage *C*-H) 38.4 ($C(CH_3)_2$), 28.5, 27.4 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ 5.0 (1B), –2.9 (1B), –5.8 (3B), –12.2 (3B), –19.2 (1B). These data are consistent with those reported in the literature.[28]

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$HfCl_2$][Li(DME)$_3$] (57b). Complex **57b** was prepared as a white solid from **42b** (492 mg, 0.97 mmol), ^{n}BuLi (1.6 M in *n*-hexane) (1.2 mL, 1.92 mmol) and TMSCl (436 mg, 4.01 mmol) in

toluene using a procedure identical with that reported for **57a**: yield 562 mg (76%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.93 (t, J = 2.2 Hz, 1H, C_5H_4), 6.88 (t, J = 2.7 Hz, 1H, C_5H_4), 6.27 (d, J = 2.3 Hz, 1H, C_5H_4), 6.11 (d, J = 2.3 Hz, 1H, C_5H_4), 3.49 (s, 12H, OCH_2), 3.26 (s, 18H, OCH_3), 1.60 (s, 3H, $C(CH_3)_2$), 1.47 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 126.0, 125.3, 121.3, 105.8, 102.9 (C_5H_4), 72.0 (OCH_2), 66.9 (Cage *C*), 58.5 (OCH_3), 50.2 (Cage *C*-H), 38.0 ($C(CH_3)_2$), 28.3, 27.7 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ 3.6 (1B), –3.8 (1B), –5.9 (2B), –7.0 (1B), –12.9 (3B), –21.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2516 (vs). Anal. Calcd. for $C_{22}H_{50}B_9Cl_2HfO_6$ (**57b**): C, 34.57; H, 6.59. Found: C, 34.62; H, 6.66.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Zr(2,6-^{i}Pr$_2C_6H_3$NH)Cl][Li(DME)$_3$] (58a). To a toluene (20 mL) suspension of **57a** (827 mg, 1.22 mmol) was added 2,6-^{i}Pr$_2$C$_6$H$_3$NHNa (243 mg, 1.22 mmol) at -30 °C with stirring. The mixture was stirred at room temperature for 2 days. After filtration, the resulting yellow solution was concentrated under vacuum to about 10 mL. Complex **58a** was isolated as yellow crystals after this solution stood at room temperature for 5 days (784 mg, 79%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 9.44 (s, 1H, N-*H*), 7.31 (d, J = 7.5 Hz, 2H, C_6H_3), 7.18 (t, J = 7.6 Hz, 1H, C_6H_3), 6.64 (m, 1H, C_5H_4), 6.25 (m, 1H, C_5H_4), 6.20 (m, 1H, C_5H_4), 6.06 (d, J = 2.5 Hz, 1H, C_5H_4), 4.58 (brs, 2H, $CH(CH_3)_2$), 3.50 (s, 12H, OCH_2), 3.27 (s, 18H, OCH_3), 2.94 (brs, 1H, Cage C-*H*), 1.59 (s, 3H, $C(CH_3)_2$), 1.43 (brs, 6H, $CH(CH_3)_2$), 1.38 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.36 (s, 3H, $C(CH_2)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 154.0, 142.2, 123.3, 123.1 (C_6H_3), 126.7, 121.2, 117.9, 106.6, 103.7 (C_5H_4), 72.0 (OCH_2), 66.7 (Cage *C*), 58.6 (OCH_3), 47.4 (Cage *C*-H), 38.0 ($C(CH_3)_2$), 29.3, 26.5 ($C(CH_3)_2$), 27.8 ($CH(CH_3)_2$), 24.8, 23.8 ($CH(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ 2.8 (1B), –3.2 (1B), –6.8 (2B), –9.1 (1B), –12.7 (3B), –20.0 (1B). IR (KBr, cm^{-1}): ν_{BH}

2523 (vs). Anal. Calcd. for $C_{34}H_{68}B_9ClLiNO_6Zr$ (**58a**): C, 49.93; H, 8.38; N, 1.71. Found: C, 50.22; H, 8.38; N, 1.45.

Preparation of [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr(2,6-^{i}Pr$_2C_6H_3$NH)(THF)•$C_7H_8$ (59a•C_7H_8). To a THF (15 mL) solution of **57a** (679 mg, 1.00 mmol) was added a THF (5 mL) solution of 2,6-^{i}Pr$_2$C$_6$H$_3$NHNa (201 mg, 1.01 mmol) at -30 °C with stirring. The mixture was stirred at room temperature for 2 days. After filtration, the resulting yellow solution was evaporated to dryness under vacuum. The yellow residue was redissolved in toluene (20 mL). After filtration, the resulting yellow solution was concentrated to about 10 mL. Complex **59a•C_7H_8** was isolated as yellow crystals after this solution stood at room temperature for 5 days (423 mg, 63%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 10.29 (N-*H*), 7.26 (m, 3H, C_6H_3), 6.59 (d, J = 2.4 Hz, 1H, C_5H_4), 6.46 (d, J = 1.5 Hz, 2H, C_5H_4), 6.02 (d, J = 2.4 Hz, 1H, C_5H_4), 3.81 (m, 1H, C*H*(CH$_3$)$_2$), 3.64 (m, 4H, OC*H*$_2$), 3.46 (m, 1H, C*H*(CH$_3$)$_2$), 3.19 (brs, 1H, Cage C-*H*), 1.59 (m, 4H, OCH$_2$C*H*$_2$), 1.56 (s, 3H, C(C*H*$_3$)$_2$), 1.51 (s, 3H, C(C*H*$_3$)$_2$), 1.26 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_6): δ 152.6, 141.1, 129.3, 128.6, 125.9 (C_6H_3), 124.2, 119.7, 119.4, 108.8, 106.5 (C_5H_4), 67.7 (O*C*H$_2$), 65.8 (Cage *C*), 48.6 (Cage *C*-H), 38.8 (*C*(CH$_3$)$_2$), 28.0, 27.8, 26.9 (C(*C*H$_3$)$_2$ + *C*H(CH$_3$)$_2$ + CH(*C*H$_3$)$_2$), 25.7 (OCH$_2$*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ –3.0 (1B), –3.1 (1B), –6.7 (3B), –12.7 (3B), –19.9 (1B). These data are consistent with those reported in the literature.[28]

Preparation of [{η^5:η^2-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Zr(OCPh$_3$)$_2$] [HN(Me)(CH$_2$)$_3$N(Me)H$_2$] (60a). To a toluene (20 mL) suspension of **47a** (216 mg, 0.50 mmol) was added Ph$_3$COH (262 mg, 1.01 mmol) at -30 °C with stirring. The mixture was stirred at room temperature for 2 days, the resulting milky solution was filtered and concentrated under vacuum to about 15 mL. Complex **60a** was isolated

as colorless crystals after this solution stood at room temperature for 3 days (321 mg, 68%). Single crystal suitable for X-ray analyses were grown from a THF/toluene solution at room temperature as **60a•THF**. ^{1}H NMR (400 MHz, pyridine-d_5): δ 8.07 (d, J = 7.4 Hz, 6H, C_6H_5), 7.85 (m, 6H, C_6H_5), 7.25 (m, 15H, C_6H_5), 7.13 (m, 3H, C_6H_5), 6.23 (m, 1H, C_5H_4), 6.06 (dd, J = 2.4, 5.0 Hz, 1H, C_5H_4), 5.78 (dd, J = 3.1, 5.5 Hz, 1H, C_5H_4), 4.68 (dd, J = 3.0, 5.6 Hz, 1H, C_5H_4), 3.01 (t, J = 6.1 Hz, 4H, NCH_2), 2.65 (brs, 1H, Cage C-*H*), 2.51 (s, 6H, NCH_3), 1.82 (m, 2H, $NCH_2CH_2CH_2N$), 1.45 (s, 3H, $C(CH_3)_2$), 1.33 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_6): δ 142.8, 129.8, 127.6, 127.5, 126.6, 126.4 (C_6H_5), 115.0, 107.2, 92.1, 91.8 (C_5H_4), 107.1 (*C*O), 50.6 (NCH_2), 41.6 (Cage *C*-H), 41.6 ($C(CH_3)_2$), 36.1 (NCH_3), 27.9, 26.4 ($C(CH_3)_2$), 24.8 ($NCH_2CH_2CH_2N$), the other cage carbon was not observed. ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ –5.6 (1B), –7.9 (1B), –10.8 (1B), –13.4 (2B), –17.2 (3B), –31.8 (1B). IR (KBr, cm^{-1}): ν_{BH} 2528, 2501 (vs). Anal. Calcd. for $C_{53}H_{65}B_9N_2O_2Zr$ (**60a**): C, 66.96; H, 6.89; N, 2.95. Found: C, 67.23; H, 7.15; N, 2.89.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][$HN(Me)(CH_2)_3N(Me)H_2$] (61a). This complex was prepared as colorless crystals from **47a** (201 mg, 0.47 mmol) and [$HNMe_3$]Cl (96 mg, 1.00 mmol) in toluene using a procedure identical with that reported for **60a**: yield 140 mg (59%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 6.97 (t, J = 2.1 Hz, 2H, C_5H_4), 6.40 (d, J = 2.4 Hz, 1H, C_5H_4), 6.22 (d, J = 2.1 Hz, 1H, C_5H_4), 3.29 (brs, 1H, Cage C-*H*), 3.06 (t, J = 6.0 Hz, 4H, NCH_2), 2.56 (s, 6H, NCH_3), 1.86 (m, 2H, $NCH_2CH_2CH_2N$), 1.62 (s, 3H, $C(CH_3)_2$), 1.49 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 126.4, 125.5, 108.0, 105.5 (C_5H_4), 67.3 (Cage *C*), 52.0 (Cage *C*-H), 50.7 (NCH_2), 38.5 ($C(CH_3)_2$), 34.6 (NCH_3), 28.5, 27.5 ($C(CH_3)_2$), 24.9 ($NCH_2CH_2CH_2N$). ^{11}B{^{1}H} NMR (400 MHz, pyridine-d_5): δ 6.0

(1B), –2.9 (1B), –5.6 (3B), –12.2 (3B), –19.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2549, 2518, 2490 (vs). Anal. Calcd. for $C_{15}H_{35}B_9Cl_2N_2Zr$ (**61a**): C, 35.83; H, 7.02; N, 5.57. Found: C, 36.05; H, 6.65; N, 5.37.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Zr{$\eta^2$-NH(Me)$(CH_2)_3$NH(Me)}][$B(C_6H_5)_4$]•DME (62a•DME). To a toluene (20 mL) suspension of **47a** (215 mg, 0.50 mmol) was added [$HNEt_3$][BPh_4] (252mg, 0.60 mmol) at -30 °C with stirring. The mixture was stirred at room temperature for 3 days. After filtration, the yellow solid was collected and redissolved in DME (20 mL). After filtration, clear yellow solution was concentrated to about 15 mL. *n*-Hexane vapor diffusion gave **62a•DME** as yellow crystals over a period of 2 days at room temperature (235 mg, 56%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 8.06 (d, J = 1.8 Hz, 8H, C_6H_5), 7.29 (t, J = 1.2 Hz, 8H, C_6H_5), 7.12 (t, J = 7.2 Hz, 4H, C_6H_5), 6.93 (brs, 2H, C_5H_4), 6.41 (brs, 1H, C_5H_4), 6.29 (brs, 1H, C_5H_4), 3.01 (t, J = 6.2 Hz, 4H, NCH_2), 2.50 (s, 6H, NCH_3), 1.82 (m, 2H, $NCH_2CH_2CH_2N$), 1.69 (s, 3H, $C(CH_3)_2$), 1.59 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 164.9, 137,1. 126.2, 122.4 (C_6H_5), 118.9, 111.3, 108.2 (C_5H_4), 68.2 (Cage *C*), 54.8 (Cage *C*-H), 49.7 (NCH_2), 38.3 ($C(CH_3)_2$) 33.7 (NCH_3), 28.1, 26.0 ($C(CH_3)_2$), 23.9 ($NCH_2CH_2CH_2N$). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ 2.3 (1B), –3.7 (1B), –5.2 (1B), –8.0 (6B), –19.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2539 (vs). Anal. Calcd. for $C_{36.5}H_{47}B_{10}NZr$ (**62a** – $0.5C_5H_{14}N_2$): C, 62.71; H, 6.78; N, 2.00. Found: C, 62.91; H, 7.00; N, 2.05.

Preparation of {[η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr[$\mu$:$\eta^1$-$O(CH_2)_2OMe$]}$_2$•DME (63a•DME). To a toluene (20 mL) suspension of **47a** (200 mg, 0.47 mmol) was added dropwise a toluene (6 mL) solution of TMSCl (163 mg, 1.50 mmol) at -30 °C with stirring. The mixture was stirred at room temperature for 2 days. After filtration,

the clear pale yellow solution was evaporated to dryness under vacuum. The yellow residue was washed with *n*-hexane (10 mL X 3), and redissolved in DME (15 mL). After filtration, the resulting yellow solution was concentrated to about 8 mL, **63a•DME** was isolated as pale yellow crystals after this solution stood at room temperature for 5 days (44 mg, 21%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.44 (d, J = 2.8 Hz, 4H, C_5H_4), 6.40 (brs, 2H, C_5H_4), 6.35 (brs, 2H, C_5H_4), 4.60 (brs, 4H, OCH_2), 3.60 (brs, 4H, CH_3OCH_2), 3.33 (s, 6H, CH_3OCH_2), 1.67 (s, 3H, $C(CH_3)_2$), 1.57 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 120.7, 117.5, 108.3, 105.2 (C_5H_4), 73.9 (OCH_2), 73.2 (OCH_2), 57.6 (CH_3OCH_2), 49.2 (Cage *C*-H), 38.3 ($C(CH_3)_2$), 27.5, 26.8 ($C(CH_3)_2$), the other cage carbon was not observed. ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ 1.4 (2B), –3.4 (2B), –6.2 (4B), –8.1 (2B), –11.2 (4B), –13.7 (2B), –20.7 (2B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). Anal. Calcd. for $C_{26}H_{54}B_{18}O_4Zr_2$ (**63a**): C, 38.66; H, 6.74. Found: C, 38.30; H, 6.74.

Preparation of [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr[$\eta$:$\eta$:$\eta$:-NH(Me)$(CH_2)_2$N(Me)C(=S)N^{n}Bu] (64a). To a toluene suspension of **46a•$(C_2H_7N)_{0.5}$** (180 mg, 0.41 mmol) was added dropwise a toluene (5 mL) solution of ^{n}BuNCS (88 mg, 0.76 mmol) at -30 °C, the mixture was stirred at room temperature overnight. After filtration, the pale yellow solution was concentrated to about 10 mL. Complex **64a** was isolated as pale yellow crystals after this solution stood at room temperature for 4 days (127 mg, 58%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 6.87 (dd, J = 2.9, 5.6 Hz, 1H, C_5H_4), 6.40 (dd, J = 2.9, 5.4 Hz, 1H, C_5H_4), 6.27 (m, 1H, C_5H_4), 6.17 (m, 1H, C_5H_4), 6.02 (brs, N-*H*) 4.15 (m, 1H, NCH_2), 3.91 (m, 1H, NCH_2), 3.81 (m, 1H, NCH_2), 3.48 (m, 1H, NCH_2), 3.31 (m, 4H, NCH_3 + NCH_2), 3.16 (m, 1H, NCH_2), 3.02 (d, J = 5.7 Hz, 3H, $NHCH_3$), 2.89 (brs, 1H, Cage C-*H*), 2.10 (m, 1H, NCH_2CH_2), 1.92 (m, 1H, NCH_2CH_2), 1.55 (s, 3H, $C(CH_3)_2$), 1.39

(s, 3H, C(CH_3)$_2$), 1.32 (m, 2H, NCH$_2$CH$_2$CH_2), 0.86 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 186.4 (C=S), 119.8, 116.0, 106.0, 105.1 (C_5H_4), 54.7, 51.8, 49.1 (NCH_2), 43.4, 37.9 (NCH_3), 41.3 (C(CH$_3$)$_2$), 28.9, 27.7 (C(CH_3)$_2$), 25.7 (NCH$_2$$CH_2$), 20.6 (NCH$_2CH_2$$CH_2$), 13.5 ($CH_3$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (400 MHz, pyridine-d_5): δ 3.1 (1B), –3.3 (1B), –5.9 (2B), –8.7 (1B), –12.0 (3B), –17.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2523 (vs). Anal. Calcd. for $C_{19}H_{40}B_9N_3SZr$ (**64a**): C, 42.97; H, 7.59; N, 7.91. Found: C, 42.42; H, 7.75; N, 7.55.

Preparation of [η^5:η^5-Me$_2$C(C$_5$H$_4$)(C$_2$B$_9$H$_{10}$)]Zr[η:η:η-NH(Me)(CH$_2$)$_2$N(Me)C(=N^{i}Pr)N^{i}Pr]•(C$_7$H$_8$)$_{0.5}$ (65a•(C$_7$H$_8$)$_{0.5}$). To a toluene suspension of **46a•(C$_2$H$_7$N)$_{0.5}$** (200 mg, 0.45 mmol) was added dropwise a toluene solution of DIC (107 mg, 0.86 mmol) at -30 °C, the mixture was stirred at room temperature overnight. After filtration, the pale yellow solid was collected and redissolved in DME, the resulting pale yellow solution was concentrated to about 10 mL. Complex **65a•(C$_7$H$_8$)$_{0.5}$** was isolated as colorless crystals after this solution stood at room temperature for 5 days. Single crystal suitable for X-ray analyses was grown from a saturated toluene solution of **65a•(C$_7$H$_8$)$_{0.5}$** (153 mg, 58%) (Isomer A : Isomer B = 1.2:1). Isomer A: ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.72 (d, J = 2.2 Hz, 1H, C$_5$$H_4$), 6.34 (m, 1H, C$_5$$H_4$), 6.18 (d, J = 2.3 Hz, 1H, C$_5$$H_4$), 6.15 (d, J = 2.4 Hz, 1H, C$_5$$H_4$), 5.74 (m, 1H, N-$H$), 3.91 (m, 1H, NC$H_2$), 3.84 (m, 2H, C$H$(CH$_3$)$_2$), 3.59 (m, 1H, NC$H_2$), 3.40 (m, 1H, NC$H_2$), 3.30 (s, 3H, NC$H_3$), 3.16 (m 1H, NC$H_2$), 3.03 (d, J = 5.5 Hz, 3H, NHCH_3), 2.63 (brs, 1H, Cage C-H), 1.56 (s, 3H, C(CH_3)$_2$), 1.34 (s, 3H, C(CH_3)$_2$), 1.18 (m, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 148.8 (N-C=N), 129.3, 119.3, 115.3, 106.5, 105.2 (C_5H_4), 67.8 (Cage C), 53.5, 50.8 (NCH_2), 48.8 (Cage C-H), 46.8, 46.4 (CH(CH$_3$)$_2$), 42.9 (NCH_3), 41.3 (NHCH_3), 38.0 (C(CH$_3$)$_2$), 26.2, 25.5 (C(CH_3)$_2$), 20.1, 19.9, 18.9, 18.0 (CH(CH_3)$_2$). Isomer B:

^{1}H NMR (400 MHz, pyridine-d_5): δ 6.53 (brs, 1H, C_5H_4), 6.41 (d, J = 2.4 Hz, 1H, C_5H_4), 5.73 (d, J = 2.3 Hz, 2H, C_5H_4), 5.30 (m, 1H, N-*H*), 4.26 (m, 1H, C*H*$(CH_3)_2$), 3.84 (m, 2H, C*H*$(CH_3)_2$) + NCH_2), 3.47 (m, 1H, NCH_2), 3.35 (m, 1H, NCH_2), 3.30 (s, 3H, NCH_3), 3.06 (m, 1H, NCH_2), 3.30 (d, J = 5.5 Hz, 3H, NHCH_3), 2.84 (brs, 1H, Cage C-*H*), 1.74 (m, 9H, C(C$H_3)_2$ + CH(C$H_3)_2$), 1.57 (m, 6H, CH(C$H_3)_2$), 1.42 (s, 3H, C(C$H_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 147.1 (N-*C*=N), 129.5, 118.0, 112.3, 106.5, 105.2 (C_5H_4), 69.1 (Cage *C*), 54.0 (N*C*H_2), 53.6, 53.0 (*C*H$(CH_3)_2$), 50.5 (N*C*H_2), 48.8 (Cage *C*-H), 42.5 (N*C*H_3), 40.1 (NH*C*H_3), 37.7 (*C*$(CH_3)_2$), 29.1, 28.0, 27.1, 26.4 (CH(*C*$H_3)_2$), 26.0, 25.1 (C(*C*$H_3)_2$). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ 3.1 (1B), 1.3 (1B), –1.9 (2B), –4.8 (2B), –7.0 (2B), –9.8 (3B), –13.7 (5B), –19.6 (2B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). Anal. Calcd for $C_{22.75}H_{47}B_9N_4Zr$ (**65a** + 0.25Toluene): C, 48.35; H, 8.38; N, 9.91. Found: C, 48.08; H, 8.62; N, 9.42.

Preparation of [η^5:η^5-Me$_2$C(C$_5$H$_4$)(C$_2$B$_9$H$_{10}$)]Zr[η:η^2-NH(Me)(CH$_2$)$_2$N(Me)C=N^{n}Bu] (66a). This complex was prepared as colorless crystals from **47a** (211 mg, 0.49 mmol) and ^{n}BuNC (76 mg, 0.91 mmol) in toluene (20 mL) using a procedure identical with that reported for **64a**: yield 168 mg (68%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 6.57 (d, J = 2.5 Hz, C_5H_4), 6.45 (m, C_5H_4), 6.36 (m, C_5H_4), 6.29 (d, J = 2.5 Hz, C_5H_4), 6.24 (m, C_5H_4), 6.01 (d, J = 2.0 Hz, C_5H_4), 5.92 (m, C_5H_4), 5.87 (m, C_5H_4), 5,83 (m, C_5H_4), 5.78 (m, C_5H_4), 5.74 (m, C_5H_4), 5.68 (m, C_5H_4), 4.17 (m, NCH_2), 3.91 (t, J = 6.6 Hz, NCH_2), 3.83 (m, NCH_2), 3.74 (m, NCH_2), 3.38 (brs, Cage C-*H*), 3.18 (s, NCH_3), 3.16 (s, NCH_3), 3.12 (brs, Cage C-*H*), 3.09 (s, NCH_3), 3.07 (brs, Cage C-*H*), 2.90 (brs, Cage C-*H*), 2.70 (m, NCH_2), 2.56 (m, NCH_2), 2.40 (s, NCH_3), 2.38 (s, NCH_3), 2.37 (s, NCH_3), 2.35 (s, NCH_3), 2.10 (m, NCH$_2$CH_2), 1.97 (m, NCH$_2$CH_2), 1.80 (m, CH$_3$CH_2), 1.72 (m, NCH$_2$CH_2),

1.63 (m, CH_2CH_2), 1.56 (s, $C(CH_3)_2$), 1.51 (s, $C(CH_3)_2$), 1.50 (s, $C(CH_3)_2$), 1.46 (s, 3H, $C(CH_3)_2$), 1.44 (m, NCH_2CH_2 + CH_3CH_2 + $NCH_2CH_2CH_2N$), 1.35 (m, $NCH_2CH_2CH_2N$), 1.38 (s, $C(CH_3)_2$), 1.36 (s, $C(CH_3)_2$), 1.35 (m, $NCH_2CH_2CH_2N$), 1.34 (s, $C(CH_3)_2$), 1.28 (s, $C(CH_3)_2$), 1.25 (m, CH_3CH_2), 1.05 (m, $NCH_2CH_2CH_2N$), 0.91 (m, CH_3CH_2), 0.82 (t, J = 7.3 Hz, CH_3), 0.85 (t, J = 7.3 Hz, CH_3), 0.72 (t, J = 7.3 Hz, CH_3), 0.61 (t, J = 7.2 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 205.8, 201.1, 200.6, 200.0 (Zr-*C*=N), 130.5, 126.3, 125.6, 114.6, 114.2, 113.9, 113.7, 112.4, 106.2, 105.9, 105.7, 104.2, 103.9, 103.5, 103.0, 102.9, 101.4, 101.0, 100.9, 99.7 (C_5H_4), 70.7, 70.5, 70.4, 70.2 (Cage *C*), 57.5, 57.4, 57.2, 50.7, 50.5, 50.4, 49.8, 49.3, 49.2, 45.8, 44.0, 43.0 (NCH_2), 43.3, 42.9, 42.7, 42.5 (Cage *C*-H), 37.7, 37.6, 37.4 ($C(CH_3)_2$), 37.0, 37.0, 36.9, 36.7 (NCH_3), 33.7, 33.5, 31.0, 30.6 (NCH_2CH_2), 30.5, 29.4, 28.8, 28.6 (CH_3CH_2), 28.2, 27.9, 27.5, 27.4, 27.0, 26.9, 26.8, 26.3 ($C(CH_3)_2$), 20.7, 20.5, 19.8 ($NCH_2CH_2CH_2N$), 14.1, 13.6, 13.1 (CH_3). $^{11}B\{^1H\}$ NMR (400 MHz, pyridine-d_5): δ –1.0 (2B), –3.0 (1.5) , –6.8 (4B), –12.8 (7.5B), –20.0 (3B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). Anal. Calcd for $C_{20}H_{42}B_9N_3Zr$ (**66a**): C, 46.82; H, 8.25; N, 8.19. Found: C, 46.90; H, 8.17; N, 7.92.

Preparation of $\{[\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr\}_2\{Na_3(THF)_8\}$ (67). To a THF solution (30 mL) of **57a** (340 mg, 0.50 mmol) was added finely cut Na metal (115 mg, 5.00 mmol), and the mixture was stirred at room temperature for 7 days. The color of the solution was changed from yellow to brown. After removal of excess Na metal, the resulting brown solution was concentrated to about 20 mL under vacuum. *n*-Hexane (12 mL) vapor diffusion gave **67** as brown crystals over a period of 2 days at room temperature (168 mg, 52%). Several very broad, unresolved resonances were observed in NMR spectra. IR (KBr, cm^{-1}): ν_{BH} 2500, 2499, 2474 (vs). Anal. Calcd for $C_{30}H_{60}B_{18}Na_3O_{2.5}Zr_2$ (**67** – 5.5THF): C, 39.73; H, 6.67. Found: C, 39.55; H, 6.49.

Preparation of [{η^5:η^6-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Hf]$_2$[Li(THF)$_4$]$_2$ (68). To a THF solution (25 mL) of **57b** (230 mg, 0.30 mmol) was added finely cut Na metal (92 mg, 4.00 mmol), and the mixture was stirred at room temperature for 7 days. After removal of the precipitate (NaCl) and excess Na metal, the clear orange yellow solution was concentrated to about 15 mL under vacuum. *n*-Hexane (8 mL) vapor diffusion gave **68** as orange yellow crystals over a period of 5 days at room temperature (98 mg, 46%). ^{1}H NMR (400 MHz, d_8-THF): δ 6.25 (d, J = 2.4 Hz, 1H, C_5H_4), 6.04 (d, J = 2.1 Hz, 1H, C_5H_4), 5.50 (d, J = 2.4 Hz, 1H, C_5H_4), 5.26 (d, J = 2.4 Hz, 1H, C_5H_4), 3.62 (m, 16H, OCH_2CH_2), 1.78 (m, 16H, OCH_2CH_2), 0.95 (s, 3H, $C(CH_3)_2$), 0.87 (s, 3H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF): δ 120.0, 110.9, 110.7, 97.5, 94.6 (C_5H_4), 67.6 (OCH_2), 36.0 ($C(CH_3)_2$), 28.8 ($C(CH_3)_2$), 25.4 (OCH_2CH_2), 21.7 ($C(CH_3)_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (96 MHz, d_8-THF): δ 0.4 (1B), –8.8 (1B), –16.8 (2B), –18.8 (3B), –24.4 (1B), –43.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2504, 2460 (vs). Anal. Calcd for $C_{32}H_{64}B_{18}Hf_2Li_2O_3$ (**68** – 5THF): C, 36.18; H, 6.07. Found: C, 36.61; H, 6.47.

Preparation of [{η^5:η^6-$Me_2C(C_5H_4)(C_2B_9H_{10})$}Hf]$_2$[PPN]$_2$ (69). To a THF solution (20 mL) of **68** (142 mg, 0.10 mmol) was added [PPN]Cl (115 mg, 0.20 mmol) at -30 °C, and the mixture was stirred at room temperature overnight. After filtration, the clear yellow solution was concentrated to about 8 mL. *n*-Hexane (10 mL) vapor diffusion gave **69** as yellow crystals over a period of 3 days at room temperature (98 mg, 51%). ^{1}H NMR (400 MHz, d_5-pyridine): δ 7.64 (m, 18H, C_6H_5), 7.45 (m, 12H, C_6H_5), 7.16 (d, J = 2.3 Hz, 1H, C_5H_4), 6.68 (d, J = 2.1 Hz, 1H, C_5H_4), 5.95 (d, J = 2.3 Hz, 1H, C_5H_4), 5.86 (d, J = 2.4 Hz, 1H, C_5H_4), 2.31 (brs, 1H, Cage C-*H*), 1.48 (s, 3H, $C(CH_3)_2$), 1.36 (s, 3H, $C(CH_3)_2$). The ^{13}C NMR data were not obtained due to the poor solubility of **69**. ^{11}B{^{1}H} NMR (96 MHz, d_5-pyridine): δ –

0.9 (1B), –7.4 (1B), –15.4 (2B), –18.1 (3B), –23.7 (1B), –41.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2510, 2470 (vs). Anal. Calcd for $C_{92}H_{100}B_{18}Hf_2N_2P_4$ (**69**): C, 57.87; H, 5.28; N, 1.47. Found: C, 57.60; H, 5.74; N, 1.13. Note that **69** did not redissolve in THF after crystallizing out and it reacted slowly with pyridine. All NMR data must be recorded as soon as possible.

X-ray Structure Determination. Data were collected at 123 K for **51** and **69**, 143 K for **68**, and 298 K for other complexes on a Bruker SMART 1000 CCD diffractometer or Bruker AXS Kappa Apex II Duo diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[144] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[145] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Appendix II. CIF files are given in Appendix III in electronic format.

References

(1) (a) Shapiro, I.; Good, C. D.; Williams, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3837. (b) Shapiro, I.; Keilin, B.; Williams, R. E.; Good, C. D. *J. Am. Chem. Soc.* **1963**, *85*, 3167.

(2) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67; *Chem. Rev.*, **1992**, *92*, 177. (c) O'Neill, M. E.; Wade, K. in *Comprehensive Organometallic Chemistry*, Eds., Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Pergamon: N. Y., **1982**, Vol. 1, Chap. 1, p.1.

(3) (a) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A. Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862. (b) Sieckhaus, J. F.; Semenu, N. S.; Knowles, T. A.; Schroeder, H. *Inorg. Chem.* **1969**, *8*, 2452. (c) Schroeder, H. A. *Inorg. Macromol. Rev.* **1970**, *1*, 45.

(4) Hawthorne, M. F.; Wiesboeck, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

(5) (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Saccheo, S.; Gioia, G.; Grassi, A.; Bowen, D. E.; Jordan, R. F. *Mol. Cat. A* **1998**, *128*, 111. (c) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126.

(6) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818.

(7) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872.

(8) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

(9) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403.

(10) (a) Yoshida, M.; Crowther, D. J.; Jordan, R. F. *Organometallics* **1997**, *16*, 1349. (b) Yoshida, M.; Jordan, R. F. *Organometallics* **1997**, *16*, 4508.

(11) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993.

(12) Bei, X.; Young, V. G., Jr.; Jordan, R. F. *Organometallics* **2001**, *20*, 355.

(13) Bei, X.; Kreuder, C.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 1085.

(14) Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 3996.

(15) Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630.

(16) Kwong, W.-C.; Chan, H.-S.; Tang, Y.; Xie, Z. *Organometallics* **2004**, *23*, 4301.

(17) Kim, D.-H.; Won, J. H.; Kim, S.-J.; Ko, J.; Kim, S. H.; Cho, S.; Kang, S. O. *Organometallics* **2001**, *20*, 4298.

(18) Zhu, Y.; Vyakaranam, K.; Maguire, J. A.; Quintana, W.; Teixidor, F.; Viñas, C.; Hosmane, N. S. *Inorg. Chem. Commun.* **2001**, *4*, 486.

(19) Lee, Y.-J.; Lee, J.-D.; Ko, J.; Kim, S.-H.; Kang, S. O. *Chem. Commun.* **2003**, 1364.

(20) Lee, Y.-J.; Lee, J.-D.; Jeong, H.-J.; Son, K.-C.; Ko, J.; Cheong, M.; Kang, S. O.

Organometallics **2005**, *24*, 3008.

(21) Cheung, M.-S.; Chan, H.-S.; Xie, Z *Organometallics* **2005**, *24*, 5217.

(22) Zhu, Y.; Sia. S. L. P.; Kooli, F.; Carpenter, K.; Kemp, R. A. *J. Organomet. Chem.* **2005**, *690*, 6284.

(23) Zhu, Y.; Zhong, Y.; Carpenter, K.; Maguire, J. A.; Hosmane, N. S. *J. Organomet. Chem.* **2005**, *690*, 2802.

(24) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2007**, *26*, 2694.

(25) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2006**, *25*, 5515.

(26) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 1157.

(27) Shen, H.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2007**, *129*, 12934.

(28) Wang, Y.; Liu, D.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 2825.

(29) Liu, D.; Wang, Y.; Chan, H.-S.; Tang, Y.; Xie, Z. *Organometallics* **2008**, *27*, 5295.

(30) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 1136.

(31) Gao, M.; Tang, Y.; Xie, M.; Qian, C.; Xie, Z. *Organometallics* **2006**, *25*, 2578.

(32) Wang, H.; Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 3964.

(33) Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259.

(34) Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2003**, *22*, 4522.

(35) Wang, H.; Wang, Y.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 5110.

(36) Wang, J.; Zheng, C.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **2003**, *22*, 4839.

(37) Hong, E.; Kim, Y.; Do, Y. *Organometallics* **1998**, *17*, 2933.

(38) Wang, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 3772.

(39) Shin, C. H.; Han, Y.; Lee, M. H.; Do. Y *J. Organomet. Chem.* **2009**, *694*, 1623.

(40) Wang, H. Li, H.-W.; Huang, X.; Lin, Z.; Xie, Z. *Angew. Chem. Int. Ed.* **2003**, *42*, 4347.

(41) Deng, L.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2005**, *127*, 13774.

(42) Ren, S.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2009**, *131*, 3862.

(43) Ren, S.; Chan, H.-S.; Xie, Z. *Organometallics* **2009**, *28*, 4106.

(44) Ren, S.; Deng, L.; Chan, H.-S.; Xie, Z. *Organometallics* **2009**, *28*, 5749.

(45) (a) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 3836. (b) Zi, G.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2001**, 1110. (c) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 5415. (d) Xie, Z. *Pure Appl. Chem.* **2003**, *75*, 1335.

(46) Wang, Y.; Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 3311.

(47) Wang, J.; Zhu, Y.; Li, S.; Zheng, C.; Maguire, J. A.; Hosmane, N. S. *J. Organomet. Chem.* **2003**, *680*, 173.

(48) Cheung. M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 3037.

(49) Kwong, W.-C.; Chan, H.-S.; Tang, Y.; Xie, Z. *Organometallics* **2004**, *23*, 3098.

(50) Cheung, M.-S.; Chan, H.-S.; Bi, S.; Lin, Z.; Xie, Z. *Organometallics* **2005**, *24*, 4333.

(51) Wang, H.; Chan, H.-S.; Okuda, J.; Xie, Z. *Organometallics* **2005**, *24*, 3118.

(52) Wang, H.; Wang, H; Chan, H.-S.; Xie, Z. *Inorg. Chem.* **2006**, *45*, 5675.

(53) Xie, Z *Acc. Chem. Res.* **2003**, *36*, 1.

(54) Han, Y; Hong, E.; Kim, Y.; Lee, M. H.; Kim, J.; Hwang, J.-W.; Do, Y. *J. Organomet. Chem.* **2003**, *679*, 48.

(55) (a) Chandra, G.; Lappert, M. F. *J. Am. Chem. A* **1968**, 1940. (b) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (c) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. (d) Carpenetti, D. W.; Kloppenburg, L; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572. (e) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Organometallics*, **1999**, *19*, 2573. (f) Broder, C. K.; Goeta, A. E.; Howard, J. A. K.; Hughes, A. K.; Johnson, A. L.; Malget, J. M.; Wade, K. *J. Chem. Soc., Dalton Trans.* **2000**, 3526. (g) Lee, C. H.; La, Y.-H.; Park, J. W. *Organometallics* **2000**, *19*, 344. (h) Amor, F.; Sánchez-Nieves, J.; Royo, P.; Jacobsen, H.; Blacque, O.; Berke, H.; Lanfranchi, M.; Pellinghelli, M. A.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **2002**, 2810. (i) Lee, Y.-J.; Lee, J.-D.; Ko, J.; Kim, S.-H.; Kang, S. O. *Chem. Commun.* **2003**, 1364. (j) Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 4207. (k) Ward, B. D.; Orde, G.; Clot, E.; Cowley, A. R.; Grade, L. H.; Mountford, P. *Organometallics* **2005**, *24*, 2368. (l) Guiducci, A. E.; Boyd, C.L.; Mountford, P. *Organometallics* **2006**, *25*, 1167. (m) Zhang, J.; Cai, R.; Chen. Z.; Zhou, X. *Inorg. Chem.* **2007**, *46*, 321. (n) Cámpora, J.; Matas, T.; Palma, P.; Álvarez, E.; Graiff, C.; Tiripicchio, A. *Organometallics* **2007**, *26*, 3840. (o) Cuenca, T. in *Comprehensive Organometallic Chemistry III*, Eds., Crabtree, R. H.; Mingoes, D. M. P. Elsevier: Oxford, **2007**, Vol. 4, Chap. 4.05, p.723. (p) Chan, E. Y.-X.; Rodriguez-Delgado, A. in *Comprehensive Organometallic*

Chemistry III, Eds., Crabtree, R. H.; Mingoes, D. M. P. Elsevier: Oxford, **2007**, Vol. 4, Chap. 4.08, p.759.

(56) (a) Benetollo, F.; Carta, G.; Cavinato, G.; Crociani, L.; Paolucci, G.; Rossetto, G.; Veronese, F.; Zanella, P. *Organometallics* **2003**, *22*, 3985. (b) Martins, A. M.; Ascenso, J. R.; de Azevedo, C. G.; Dias, A. R.; Duarte, M. T.; da Silva, J. F.; Veiros, L. F.; Rodrigues, S. S. *Organometallics* **2003**, *22*, 4218.

(57) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952.

(58) (a) Ramos, C.; Royo, P.; Lanfranchi, M.; Pellinghelli, M. A.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **2005**, 3962. (b) Bernskoetter, W. H.; Olmos, A. V.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 1021. (c) Bernskoetter, W. H.; Olmos, A. V.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10696. (d) Wang, C.; Luo, H.-K.; van Meurs, M.; Stubbs, L. P.; Wong, P.-K. *Organometallics* **2008**, *27*, 2908.

(59) (a) Cano, J.; Sudupe, M.; Royo, P.; Mosquera, M. E. G. *Organometallics* **2005**, *24*, 2424. (b) Scott, M. J.; Lippard, S. J. *Organometallics* **1997**, *16*, 5857.

(60) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225.

(61) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193.

(62) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(63) Dufree, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(64) (a) Pizzano, A.; Sánchez, L.; Altmann, M.; Monge, A.; Ruiz, C.; Carmona, E. *J. Am. Chem. Soc.* **1995**, *117*, 1759. (b) Chen, L.; Nie, W.-L.; Paradies, J.; Kehr,

G.; Fröhlich, R.; Wedeking, K.; Erker, G. *Organometallics* **2006**, *25*, 5333. (c) Waterman, R.; Tilley, T. D. *Inorg. Chem.* **2006**, *45*, 9625. (d) Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J. *Organometallics* **2008**, *27*, 3254. (e) Roering, A. J.; Davidson, J. J.; MacMillan, S. N.; Tanski, J. M.; Waterman, R. *Dalton Trans.* **2008**, 4488.

(65) (a) Novak, B. M.; Deming, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 9101. (b) Tanase, T.; Ohizuni, T.; Kobayashi, K.; Yamamoto, Y. *Organometallics* **1996**, *15*, 3404.

(66) (a) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068. (b) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 830. (c) Greidanus-Strom, G.; Carter, C. A. G. Stryker, J. M. *Organometallics* **2002**, *21*, 1011. (d) Bach, M. A.; Beweries, T.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 4592. (e) Cano, J.; Sudupe, M.; Royo, P. *J. Organomet. Chem.* **2007**, *692*, 4448. (f) Suzuki, N.; Hashizume, D.; Yoshida, H.; Tezuka, M.; Ida, K.; Nagashima, S.; Chihara, T. *J. Am. Chem. Soc.* **2009**, *131*, 2050.

(67) Bashall, A.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Pugh, S. M.; Radojevic, S.; Schubart, M.; Scowen, I. J.; Trösch, D. J. M. *Organometallics* **2000**, *19*, 4784.

(68) (a) Berg, F. J.; Peterson, J. L. *Organometallics* **1993**, *12*, 3890. (b) Owen, G. R.;

Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2002**, *21*, 4799. (c) Beweries, T.; Burlakov, V. V.; Peitz, S.; Bach, M. A.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 6827.

(69) (a) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Chem. Soc.* **1997**, *119*, 9709. (b) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C. *Organometallics* **1997**, *16*, 5457. (c) Wu, Z.; Diminnie. J. B.; Xue, Z. *Organometallics* **1999**, *18*, 1002.

(70) (a) Boyer, J. H.; Beverung, W. *J. Chem. Soc., Chem. Commun.* **1969**, 1377. (b) Obata, N.; Takizawa, T. *Tetrahedron Lett.* **1969**, 3403. (c) Green, J. A.; Singer, L. A. *Tetrahedron Lett.* **1969**, 5093. (d) Ciganek, E. *J. Org. Chem.* **1970**, *35*, 862. (e) Krow, G. R. *Angew. Chem., Int. Ed.* **1971**, *10*, 435.

(71) (a) Lee, K.-W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622. (b) Neuman, R. C., Jr.; Sylwester, A. P. *J. Org. Chem.* **1983**, *48*, 2285. (c) Alajarín, M.; Vidal, A.; Tovar, F. *Lett. Org. Chem.* **2004**, *1*, 340.

(72) (a) Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 4069. (b) Bell, A.; Lippard, S. J.; Roberts, M.; Walton, R. A. *Organometallics* **1983**, *2*, 1562. (c) Scott. M. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 3411.

(73) Goerdeler, J.; Lindner, C.; Zander, F. *Chem. Ber.* **1981**, *114*, 536.

(74) (a) Bertuleit, A.; Fitze, C.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 2891. (b) Pflug, J.; Bertuleit, A.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **1999**, *18*, 3818. (c) Weng, W.; Guo, C.; Moura, C.; Yang, L.;

Foxman, B. M.; Ozerov, O. V. *Organometallics* **2005**, *24*, 3487. (d)

(75) Itami, K.; Terakawa, K.; Yoshida, J.-i.; Kajimoto, O. *J. Am. Chem. Soc.* **2003**, *125*, 6058.

(76) (a) van Klink, G. P. M.; de Boer, H. J. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Spek, A. L. *Organometallics* **2002**, *21*, 2119. (b) Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499. (c) Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257. (d) Zhang, L.; Fung, C. W.; Chan, K. S. *Organometallics* **2006**, *25*, 5381. (e) Wang, C.; Luo, Q.; Sun, H.; Guo, X.; Xi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 3094. (f) Xi, Z. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1021. (g) Yu, N.; Wang, C.; Zhao, F.; Liu, L. Zhang, W.-X.; Xi, Z. *Chem. Eur. J.* **2008**, *14*, 5670. (h) Tobisu, M.; Onoe, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 7506.

(77) Bailey, P. H.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91.

(78) Selected examples: (a) Tin, M. K. T.; Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Dalton Trans.* **1999**, 2947. (b) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808. (c) Holland, A. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 9010. (d) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 2839. (e) Ong, T.-G.; Yap, G. P. A.; Richeson, D. R. *J. Am. Chem.. Soc.* **2003**, *125*, 8100. (f) Zhang, Y.; Sita, L. R. *Chem. Commun.* **2003**, 2358. (g) Oakley, S. H.; Coles, M. P.; Hitchcock, P. B. *Inorg. Chem.* **2004**, *43*, 7564. (h) Carmalt, C. J.; Newport, A. C.; O'Neil, S. A.; Parkin, I. P.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2005**, *44*, 615. (i)

Harney, M. B.; Zhang, Y.; Sita, L. R. *Angew. Chem. Int. Ed.* **2006**, *45*, 2400. (j) Jones, C; Junk, P. C.; Platts, J. A.; Stasch, A. *J. Am. Chem. Soc.* **2006**, *128*, 2206.

(79) Selected examples: (a) Aelits, S. L.; Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1998**, *17*, 3265. (b) Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1998**, *17*, 4387. (c) Lu, Z.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2001**, *20*, 706. (d) Feil, F.; Harder, S. *Eur. J. Inorg. Chem.* **2005**, 4438. (e) Wilder, C. B.; Reitfort, L. L.; Abboud, K. A.; McElwee-White, L. *Inorg. Chem.* **2006**, *45*, 263. (f) Milanov, A.; Bhakta, R.; Baunemann, A.; Becker, H.-W.; Thomas, R.; Ehrhart, P.; Winter, M.; Devi, A. *Inorg. Chem.* **2006**, *45*, 11008.

(80) Selected examples: (a) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 2809. (b) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2003**, *22*, 387. (c) Bazinet, P.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2003**, *42*, 6225.

(81) Selected examples: (a) Coles, M. P.; Hitchcock, P. B. *Eur. J. Inorg. Chem.* **2004**, 2662. (b) Kenny, A. P.; Yap, G. P. A.; Richeson, D. S.; Barry, S. T. *Inorg. Chem.* **2005**, *44*, 2926. (c) Rische, D.; Baunemann, A.; Winter, M.; Fischer, R. A. *Inorg. Chem.* **2006**, *45*, 269.

(82) El-Kadri, O. M.; Heeg, M. J.; Winter, C. H. *Dalton Trans.* **2006**, 4506.

(83) Shen, H.; Chan, H.-S.; Xie, Z. *J. Am Chem. Soc.* **2007**, *129*, 12934.

(84) Tunge, J. A.; Czerwinski, C. J.; Gately, D. A.; Norton, J. R. *Organometallics*

2001, *20*, 254.

(85) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2001**, *20*, 1792.

(86) (a) Birdwhistell, K. R.; Lanza, J.; Pasos, J. *J. Organomet. Chem.* **1999**, *584*, 200. (b) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, *19*, 4795. (c) Royo, P.; Sánchez-Nieves, J. *J. Organomet. Chem.* **2000**, *597*, 61. (d) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *Chem. Commun.* **2003**, 2612. (e) Montilla, F.; Pastor, A.; Galindo, A. *J. Organomet. Chem.* **2004**, *689*, 993. (f) Shen, H.; Xie, Z. *Organometallics* **2008**, *27*, 2685.

(87) (a) Coyle, J. P.; Monillas, W. H.; Yap, G. P. A.; Barry, S. T. *Inorg. Chem.* **2008**, *47*, 683. (b) Ziffle, L. C.; Kennedy, A. P.; Barry, S. T.; Müller, J. *Polyhedron* **2008**, *27*, 1832. (c) Xu, K.; Milanov, A. P.; Winter, M,; Barreca, D.; Gasparotto, A.; Becker, H.-W.; Devi, A *Eur. J. Inorg. Chem.* **2010**, 1679.

(88) (a) Williams, G. D.; Lieszkovszky, M.-C.; Mirkin, C. A.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 2228. (b) Campion, B. K.; Falk, J.; Tilley, D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. (c) Dupont, J.; Pfetter, M.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 899. (d) Mirkin, C. A.; Lu, K.-L.; Snead, T. E.; Young, B. A.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 3800. (e) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *Inorg. Chem.* **1992**, *31*, 63.

(89) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Hofmann, P.; Stauffert, P.; Frede, M.; Tatsumi, K. *Chem. Ber.* **1989**, *122*, 1559.

(90) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29.

(91) (a) Chamberlain, R. L.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390.

(92) (a) Bellachioma, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84. (b) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665. (c) de Lange, P. P. M.; de Boer, R. P.; van Wijnkoop, M.; Ernsting, J. M.; Frühauf, H.-W.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L.; Goubitz, K. *Organometallics* **1993**, *12*, 440. (d) Cámpora, J.; Gutiérrez, E.; Monge, A.; Poveda, M. L.; Ruiz, C.; Carmona, E. *Organometallics* **1993**, *12*, 4025. (e) Kuniyasu, H.; Sugoh, K.; Su, M. S.; Kurosawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4669. (f) Bianchini, C.; Masi, D.; Romerosa, A.; Zanobini, F.; Peruzzini, M. *Oragnometallics* **1999**, *18*, 2376. (g) Seino, H.; Arita, C.; Nonokawa, D.; Nakamura, G.; Harada, Y.; Mizobe, Y.; Hidai, M. *Organometallics* **1999**, *18*, 4165. (h) Alcalde. M. I.; Gómez-Sal, M. P.; Royo, P. *Organometallics* **2001**, *20*, 4623. (i) Taw, F. L.; Mueller, A. H.; Bergman, R. G.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 9808. (j) Tobisu, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2006**, *128*, 8152. (k) Tsuchiya, K.; Konda, H.; Nagashima, H. *Organometallics* **2007**, *26*, 1044.

(93) Smith, H. D., Jr.; Obenland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013.

(94) Jin, G.-X. *Coord. Chem. Rev.* **2004**, *248*, 587.

(95) (a) Kim, D. H.; Ko, J.; Park, K.; Cho, S.; Kang, S. O. *Organometallics* **1999**, *18*, 2738. (b) Won, J.-H.; Kim, D.-H.; Kim, B. Y.; Kim, S.-J.; Lee, C.; Cho, S.;

Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 1443.

(96) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem. Int. Ed.* **1999**, *38*, 3689.

(97) (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **1999**, 873. (b) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *587*, *252*.

(98) Herberhold, M.; Yan, H.; Milius, W. *J. Organomet. Chem.* **2000**, *598*, 142.

(99) Herberhold, M.; Yan, H.; Milius, W. *Chem. Eur. J.* **2000**, *6*, 3026. (b) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2002**, *8*, 388.

(100) (a) McKinney, J. D.; Chen, H.; Hamor, T. A.; Paxton, K.; Jones, C. J. *J. Chem. Chem. Soc., Dalton Trans.* **1998**, 2163. (b) Base, K.; Grinstaff, M. W. *Inorg. Chem.* **1998**, *37*, 1432.

(101) Yu, X. Y.; Jin, G.-X.; Weng, L. H. *Chin. J. Chem.* **2002**, *20*, 1256.

(102) Liu, S.; Han, Y.-F.; Jin, G.-X. *Chem. Soc. Rev.* **2007**, *36*, 1543.

(103) Cai, S. Y.; Hou, X.; Weng, L.-H.; Jin, G.-X. *J. Organomet. Chem.* **2005**, *690*, 910.

(104) Bae, J.-Y.; Park, Y.-I.; Lo, J.; Park, K.-I.; Cho, S.-I.; Kang, S. O. *Inorg. Chim. Acta.* **1999**, *289*, 141.

(105) (a) Howard, W. A.; Parkin, G. *Organometalics* **1993**, *12*, 2363. (b) d'Arbeloff-Wilson, S. E.; Hitchcock, P. B.; Nixon, J. F.; Kawaguchi, H.; Tatsumi, K. *J. Organomet. Chem.* **2003**, *672*, 1. (c) Hernandz-Grual, M. A. F.;

Pérez-Torrente, J. J.; Ciriano, M. A.; Lahoz, F. J.; Oro, L. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 2769.

(106) (a) Tamm, M.; Kunst, A.; Bannenberg, T.; Herdtweck, E.; Schmid, R. *Organometallics* **2005**, *24*, 3163. (b) Berno, P.; Floriani, C.; Chiesi,-Villa, A.; Rizzoli, C. *J. Chem. Soc. Dalton Trans.* **1991**, 3085. (c) Brackemeyer, T.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 531.

(107) (a) Doub, L.; Richardson, L. M.; Herbst, D. R.; Black, M. L.; Stevenson, O. L.; Bambas, L. L.; Youmans, G. P.; Youmas, A. S. *J. Am. Chem. Soc.* **1958**, *80*, 2205. (b) Mazzocchi, P. H.; Rao, M. P. *J. Agr. Food. Chem.* **1972**, *20*, 957.

(108) Krepps, M. K.; Parkin, S.; Atwood, D. A. *Cryst. Growth Des.* **2001**, *1*, 291.

(109) (a) Duan, Z.; Xuan, X.; Li, T.; Yang, C.; Wu, Y. *Tetrahedron Lett.* **2006**, *47* 5433. (b) Mukherjee, C.; Misra, A. K. *Lett. Org. Chem.* **2007**, *4*, 54. (c) Smitha, G.; Reddy, Ch., S. *Catal. Commun.* **2007**, *8*, 434. (d) Reddy, B. M.; Patil, M. K.; Reddy, B. T. *Catal. Lett.* **2008**, *126*, 413. (e) You, L.; Feng, S.; An, R.; Wang, X.; Bai, D. *Tetrahedron Lett.* **2008**, *49*, 5147.

(110) Spivak, C. E.; Waters, J. A.; Aronstam, R. S. *Mol. Pharmacol.* **1988**, *36*, 177.

(111) (a) Bullock, W. H.; Kluender, H. C. E.; Collibee, W. L.; Dally, R.; Rodriguez, M. E.; Wang, M. WO-2002020526, 2002. (b) Zhu, B.-Y.; Su, T.; Li, W.; Goldman, E. A.; Zhang, P.; Jia, Z. J.; Scarborough, R. M. WO-2002026734, 2002. (c) Maguire, M. P.; Dai, M.; Vos, T. J.; WO-2002062766, 2002. (d) John, V.; Maillard, M.; Jagodzinska, B.; Beck, J. P.; Gailunas, A.; Fang, L.; Sealy, J.; Tenbrink, R.; Freskos, J.; Mickelson, J.; Samala, L.; Hom, R. WO-2003040096,

2003. (e) Taveras, A. G.; Chao, J.; Biju, P. J.; Yu, Y.; Fine, J. S.; Hipkin, W.; Aki, C. J.; Merritt, J. R.; Li, G.; Baldwin, J. J.; Lai, G.; Wu, M.; Hecker, E. A. WO-2004033440, 2003.

(112) Wang, J.; Xu, F.; Cai, T.; Shen, Q. *Org. Lett.* **2008**, *10*, 445.

(113) Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. *J. Org. Chem.* **1987**, *52*, 1017.

(114) For recent reviews, see: (a) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081. (b) Grimes, R. N. *Coord. Chem. Rev.* **2000**, *200-202*, 773. (c) Xie, Z. *Coord. Chem. Rev.* **2002**, *231*, 23. (d) Deng, L.; Xie, Z. *Organometallics* **2007**, *26*, 1832. (e) Chizhevsky, I. T. *Coord. Chem. Rev.* **2007**, *251*, 1590. (f) Hosmane, N. S.; Maguire, J. A. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. 3, pp. 175.

(115) Selected examples: (a) Belmont, J. A.; Soto, J.; King, III, R. E.; Donaldson, A. J.; Hewes, J. D.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1989**, *111*, 7475. (b) Kang, H. C.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2327. (c) Teixidor, F.; Núñez, R.; Flores, M. A.; Demonceau, A.; Viñas, C. *J. Organomet. Chem.* **2000**, *614-615*, 48. (d) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, 11830. (e) Teixidor, F.; Cirera, M. R.; Viñas, C.; Kivekäs, R.;

Sillanpää, R.; Demonceau, A. *J. Organomet. Chem.* **2003**, *680*, 89.

(116) Selected examples: (a) Masalles, C.; Borrós, S.; Viñas, C.; Teixidor, F. *Adv. Mater.* **2000**, *12*, 1199. (b) Kazheva, O. N.; Alexandrov, G. G.; Kravchenko, A. V.; Starodub, V. A.; Sivaev, I. B.; Lobanova, I. A.; Bregadze, V. I.; Buravov, L. I.; Dyachenko, O. A. *J. Organomet. Chem.* **2007**, *692*, 5033. (c) Kazheva, O.; Alexandrov, G.; Kravchenko, A.; Starodub, V.; Lobanova, I.; Sivaev, I.; Bregadze, V.; Buravov, L.; Dyachenko, O. *Solid State Sci.* **2008**, *10*, 1734. (d) Dymon, J.; Wibby, R.; Kleingardner, J.; Tanski, J. M.; Guzei, I. A.; Holbrey, J. D.; Larsen, A. S. *Dalton Trans.* **2008**, 2999. (e) Farràs, P.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Viñas, C.; Grüner, B.; Cisarova, I. *Inorg. Chem.* **2008**, 47, 9497. (f) Crespo, O.; Gimeno, M. C.; Laguna, A. *J. Organomet. Chem.* **2009**, *694*, 1588.

(117) Selected examples: (a) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, *99*, 3421. (b) Valliant, J. F.; Guenther, K. J.; King, A. S.; Morel, P.; Schaffer, P.; Sogbein, O. O.; Stephenson, K. A. *Coord. Chem. Rev.* **2002**, *232*, 173. (c) Zhu, Y.; Peng, A. T.; Carpenter, K.; Maguire, J. A.; Hosmane, N. S.; Takagaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 9875. (d) Armstrong, A. F.; Valliant, J. F. *Dalton Trans.* **2007**, 4240.

(118) Selected examples: (a) Viñas, C.; Gomez, S.; Bertran, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H. *Chem. Commun.* **1998**, 191. (b) Viñas, C.; Gomez, S.; Bertran, J.; Barron, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H.; Kivekäs, R.; Sillanpää, R. *J. Organomet. Chem.* **1999**, *581*, 188. (c) Grüner, B.; Kvíčalová,

M.; Plešek, J.; Šícha, V.; Císařová, I.; Lučaníková, M.; Selucký, P. *J. Organomet. Chem.* **2009**, *694*, 1678.

(119) Selected examples: (a) Park, J.-S.; Kim, D.-H.; Kim, S.-J.; Ko, J.; Kim, S. H.; Cho, S.; Lee, C.-H.; Kang, S. O. *Organometallics* **2001**, *20*, 4483. (b) Park, J.-S.; Kim, D.-H.; Ko, J.; Kim, S. H.; Cho, S.; Lee, C.-H.; Kang, S. O. *Organometallics* **2001**, *20*, 4632. (c) Fox, M. A.; Goeta, A. E.; Hughes, A. K.; Johnson, A. L. *Dalton Trans.* **2002**, 2132. (d) Viñas, C.; Laromaine, A.; Teixidor, F.; Horáková, H.; Langauf, A.; Vespalec, R.; Mata, I.; Molins, E. *Dalton Trans.* **2007**, 3369.

(120) Selected examples: (a) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812. (b) Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K.; Colquhoun, H. M. *Polyhedron* **1996**, *15*, 565. (c) Fox, M. A.; MacBride, J. A. H.; Wade, K. *Polyhedron* **1997**, *16*, 2499. (d) Fox, M. A.; Wade, K. *Polyhedron* **1997**, *16*, 2517. (e) Fox, M. A.; Wade, K. *J. Organomet. Chem.* **1999**, *573*, 279. (f) Yoo, J.; Hwang, J.-W.; Do, Y. *Inorg. Chem.* **2001**, *40*, 568. (g) Wei, X.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **2006**, *25*, 609.

(121) Selected examples: (a) Teixidor, F.; Viñas, C.; Benakki, R.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 1719. (b) Teixidor, F.; Gómez, S.; Lamrani, M.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Organometallics* **1997**, *16*, 1278. (c) Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Hughes, A. K.; Malget, J. M. J. *Dalton Trans.* **2001**, 1820. (f) Laromaine, A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Benakki, R.; Grüner, B.; Viñas, C. *Dalton Trans.*

2005, 1785.

(122) Adams, J. J.; Del Negro, A. S.; Arulsamy, N.; Sullivan, B. P. *Inorg. Chem.* **2008**, *47*, 1871.

(123) (a) Diamond, G. M.; Jordan, R. F.; Peterson, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024. (b) Diamond, G. M.; Jordan, R. F. *Organometallics* **1996**, *15*, 4030.

(124) Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.

(125) Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Han, W.-S.; Cheong, M.; Ko, J.; Kang, S. O. *J. Organomet. Chem.* **2007**, *692*, 5403.

(126) Sun, Y.; Chan, H.-S.; Dixneuf, P. H.; Xie, Z. *Organometallics* **2004**, *23*, 5864.

(127) Teixidor, F.; Viñas, C.; Abad, M. M.; Kivekäs, R.; Sillanpää, R. *J. Organomet. Chem.* **1996**, *509*, 139.

(128) Selected examples: (a) Chamberlin, R. M.; Scott, B. L.; Melo, M. M.; Abney, K. D. *Inorg. Chem.* **1997**, *36*, 809. (b) Núñez, R.; Tutusaus, O.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Chem. Eur. J.* **2005**, *11*, 5637. (c) Herber, R. H.; Kudinov, A. R.; Zanello, P.; Nowik, I.; Perekalin, D. S.; Meshcheryakov, V. I.; Lyssenko, K. A.; Corsini, M.; Fedi, S. *Eur. J. Inorg. Chem.* **2006**, 1786. (d) Hawthorne, M. F.; Ramachandran, B. M.; Kennedy, R. D.; Knobler, C. B. *Pure Appl. Chem.* **2006**, *78*, 1299.

(129) Hawthorne, M. F.; Zink, J. I.; Skelton, J. M.; Bayer, M. J.; Liu, C.; Livshits, E.; Baer, R.; Neuhauser, D. *Science* **2004**, *303*, 1849.

(130) (a) Dustin, D. F.; Evans, W. J.; Hawthorne, M. F. *J. Chem. Soc., Chem.*

Commun. **1973**, 805. (b) Evans, W. J.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 869. (c) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1978**, *17*, 1498. (d) Lopez, M. E.; Edie, M. J.; Ellis, D.; Horneber, A.; Macgregor, S. A.; Rosair, G. M.; Welch, A. J. *Chem. Commun.* **2007**, 2243. (e) Deng, L.; Xie, Z. *Coord. Chem. Rev.* **2007**, *251*, 2452.

(131) Kudinov, A. R.; Perekalin, D. S.; Rynin, S. S.; Lyssenko, K. A.; Grintselev-Knyazev, G. V.; Petrovskii, P. V. *Angew. Chem. Int. Ed.* **2002**, *41*, 4112.

(132) (a) Xie, Z.; Yan, C.; Yang, Q.; Mak, T. C. W. *Angew. Chem. Int. Ed.* **1999**, *38*, 1761. (b) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W. H.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2000**, *122*, 5758. (c) Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 4468.

(133) Baker, R. J.; Jones, C.; Murphy, D. M. *Chem. Commun.* **2005**, 1339.

(134) The B-H···M interactions in metallacarboranes usually lead to significantly reduced J_{BH} values, see: (a) Brew, S. A.; Stone, F. G. A. *Adv. Organomet. Chem.* **1993**, *35*, 135. (b) Hodson, B. E.; McGrath, T. D.; Stone, F. G. A. *Organometallics* **2005**, *24*, 3386. (c) Franken, A.; McGrath, T. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **2006**, *128*, 16169. (d) McGrath, T. D.; Du, S.; Hodson, B. E.; Lu, X. L.; Stone, F. G. A. *Organometallics* **2006**, *25*, 4444. (e) McGrath, T. D.; Du, S.; Hodson, B. E.; Stone, F. G. A. *Organometallics* **2006**, *25*, 4452.

(135) The B-H···M interactions in metallacarboranes usually lead to splitting of ν_{BH} stretching bands, see: (a) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.;

Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107,* 5955. (b) Shelly, K.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 3117. (c) Gupta, G. P.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022. (d) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111* , 6643. (e) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897.

(136) Bazhenova, T. A.; kulikov, A. V.; Shestakov, A. F.; Shilov, A. E.; Yu. Antipin, M.; Lyssenko, K. A.; Struchkov, Yu. T.; Makhaev. V. D. *J. Am. Chem. Soc.* **1995**, *117*, 12176.

(137) The cage carbons are more electronegative and less connected than the cage borons in the cluster, resulting in high electron density, see: ref. 132b

(138) Low valent metal complexes often have elongated bond distances.

(139) (a) Williams, R. E. In *Electron Deficient Boron and Carbon Cluster*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp. 11. (b) Holub, J.; Wille, A. E.; Štíbr, B.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1994**, *33*, 4920.

(140) (a) Attfield, M. J.; Howard, J. A. K.; Jelfs, A. N. de M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.*, **1986**, 918. (b) Attfield, M. J.; Howard, J. A. K.; Jelfs, A. N. de M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans*, **1987**, 2219. (c) Carr, N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics*, **1992**, *11*, 3697.

(141) Kennedy, J. D. *Inorg. Chem.*, **1986**, *25*, 111.

(142) Vogel, A.; Priermeier, T.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *527*, 297.

(143) Voskoboynikov, A. Z.; Yu. Agarkov, A.; Chernyskev, E. A.; Beletskaya, I. P.; Churakov, A. V.; Kuz'mina, L. G. *J. Organomet. Chem.* **1997**, *530*, 75.

(144) Sheldrick, G. M. SADABS: Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen: Germany, 1996.

(145) Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.

Appendix I. Publications Based on the Research Findings

1. Mei-Mei Sit, Hoi-Shan Chan and Zuowei Xie. "Synthesis, Structure, and Reactivity of Group 4 Metallacycles Incorporating a Me_2C-Linked Cyclopentadienyl-Carboranyl Ligand" *Dalton Trans.* **2008**, 1454-1464.
2. Mei-Mei Sit, Hoi-Shan Chan and Zuowei Xie. "Metallacarboranes Incorporating an *arachno*-η^6-C_2B_9 Ligand" *Organometallics* **2009**, *28*, 5998–6002.

Appendix II. Crystal Data and Summary of Data Collection and Refinement

	2c	**3c**	**4a**•0.5C_6H_6	**4c**•0.5C_6H_6
formula	$C_{14}H_{30}B_{10}N_2Ti$	$C_{15}H_{32}B_{10}N_2Ti$	$C_{35}H_{51}B_{10}N_4Zr$	$C_{35}H_{51}B_{10}N_4Ti$
crystal size (mm)	0.50 x 0.50 x 0.40	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20
fw	382.40	396.43	727.12	683.80
crystal system	trigonal	trigonal	monoclinic	monoclinic
space group	*R*3*m*	*R*3*m*	$P2_1/n$	$P2_1/n$
a, Å	25.806(4)	26.045(1)	10.472(1)	10.500(2)
b, Å	25.806(4)	26.045(1)	17.389(2)	17.092(3)
c, Å	9.888(2)	9.844(1)	21.659(3)	21.352(4)
α, deg	90	90	90	90
β, deg	90	90	98.68(3)	98.56(3)
γ, deg	120	120	90	90
V, Å^3	5702.7(16)	5782.8(7)	3898.8(9)	3789.5(13)
Z	9	9	4	4
D_{calcd}, Mg/m^3	1.002	1.025	1.239	1.199
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50	56.0	56.6	50
μ, mm^{-1}	0.339	0.336	0.313	0.257
F(000)	1800	1872	1516	1444
no. of obsd reflns	1271	2843	9663	6681
no. of params refnd	133	139	451	451
goodness of fit	0.956	0.973	1.014	0.968
R1	0.054	0.043	0.049	0.071
*w*R2	0.131	0.105	0.119	0.174

	5a	**6a**	**7a**	**8a**•0.75THF
formula	$C_{56}H_{80}B_{20}N_8O_4Zr_2$	$C_{36}H_{72}B_{20}N_8Zr_2$	$C_{36}H_{80}B_{20}N_8Si_2Zr_2$	$C_{61}H_{90}B_{20}N_8O_{0.75}Zr_2$
crystal size (mm)	0.50 x 0.30 x 0.10	0.40 x 0.30 x 0.20	0.30 x 0.20 x 0.20	0.40 x 0.20 x 0.20
fw	1327.92	1015.66	1079.90	1346.05
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*-1	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, Å	10.896(2)	14.933(2)	15.741(2)	19.677(2)
b, Å	17.104(2)	9.927(1)	10.721(1)	24.137(3)
c, Å	20.437(3)	17.170(2)	16.257(2)	34.482(4)
α, deg	73.67(1)	90	90	90
β, deg	80.77(1)	93.55(1)	101.21(1)	98.69(1)
γ, deg	74.87(1)	90	90	90
V, Å^3	3512.7(8)	2540.3(4)	2691.0(5)	16189(3)
Z	2	2	2	8
D_{calcd}, Mg/m^3	1.255	1.328	1.333	1.105
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.0	56.0	50.0
μ, mm^{-1}	0.345	0.448	0.469	0.297
F(000)	1368	1048	1120	5584
no. of obsd reflns	12298	4479	6500	28466
no. of params refnd	811	310	307	1721
goodness of fit	0.841	1.045	1.003	0.817
R1	0.062	0.054	0.048	0.086
*w*R2	0.126	0.136	0.117	0.211

	9a'•Tol	**9b'•Tol**	**10a**	**10a'•0.5Tol**
formula	$C_{35}H_{62}B_{10}N_4Zr$	$C_{35}H_{62}B_{10}HfN_4$	$C_{20}H_{41}B_{10}N_3SZr$	$C_{27.5}H_{45}B_{10}N_3SZr$
crystal size (mm)	0.50 x 0.40 x 0.30	0.50 x 0.50 x 0.40	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
fw	738.21	825.48	554.94	649.04
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	*P*-1	$P2_1/n$
a, Å	10.615(1)	10.599(2)	8.610(1)	15.250(3)
b, Å	14.165(2)	14.168(3)	10.569(1)	18.002(4)
c, Å	15.427(2)	15.416(3)	16.517(1)	24.805(5)
α, deg	95.59(1)	95.78(1)	93.01(1)	90
β, deg	107.61(2)	107.81(1)	90.23(1)	97.74(1)
γ, deg	110.98(2)	110.77(1)	104.52(1)	90
V, Å^3	2008.4(5)	2003.0(8)	1452.7(3)	6748(2)
Z	2	2	2	8
D_{calcd}, Mg/m^3	1.221	1.369	1.269	1.278
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.0	56.1	50.0
μ, mm^{-1}	0.304	2.635	0.466	0.412
F(000)	780	844	576	2696
no. of obsd reflns	7022	7001	6886	11878
no. of params refnd	460	460	316	766
goodness of fit	1.070	1.051	1.030	1.029
R1	0.040	0.034	0.037	0.048
*w*R2	0.109	0.088	0.097	0.112

	10b	**11a**	**12a**	**12b**
formula	$C_{20}H_{41}B_{10}HfN_3S$	$C_{48}H_{53}B_{10}N_5O_3Zr$	$C_{33}H_{50}B_{10}N_4Zr$	$C_{33}H_{50}B_{10}HfN_4$
crystal size (mm)	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
fw	642.21	947.27	702.09	789.36
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	*P*-1	*Pccn*	$P2_1/n$	$P2_1/n$
a, Å	9.079(1)	38.951(7)	10.696(2)	10.696(2)
b, Å	10.475(2)	13.815(3)	17.369(3)	17.355(3)
c, Å	15.955(2)	24.485(5)	21.358(2)	21.308(4)
α, deg	90.07(1)	90	90	90
β, deg	93.33(1)	90	96.45(1)	96.40(1)
γ, deg	107.83(1)	90	90	90
V, Å^3	1441.7(4)	13175(4)	3942.7(10)	3930.8(11)
Z	2	8	4	4
D_{calcd}, Mg/m^3	1.479	0.955	1.183	1.334
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.0	50.0	50.0
μ, mm^{-1}	3.706	0.201	0.307	2.682
F(000)	640	3920	1464	1592
no. of obsd reflns	5019	11620	6939	6917
no. of params refnd	316	605	433	433
goodness of fit	1.043	0.924	1.070	1.009
R1	0.034	0.068	0.036	0.033
*w*R2	0.087	0.166	0.093	0.078

	13a	**13b**	**14a**	**14b**
formula	$C_{35}H_{68}B_{10}N_6Zr$	$C_{35}H_{68}B_{10}HfN_4$	$C_{43}H_{80}B_{10}N_{10}O_4Zr$	$C_{43}H_{79}B_{10}HfN_{10}O_4$
crystal size (mm)	0.30 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.20
fw	772.27	859.54	1000.49	1086.75
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	P-1	P-1
a, Å	12.433(2)	12.415(2)	10.898(1)	10.863(5)
b, Å	19.980(4)	19.922(4)	11.398(1)	11.303(5)
c, Å	17.695(3)	17.670(3)	23.590(1)	23.568(10)
α, deg	90	90	77.86(1)	78.02(1)
β, deg	99.93(1)	100.01(1)	81.09(1)	81.03(1)
γ, deg	90	90	71.17(1)	71.33(1)
V, Å^3	4329.8(14)	4303.8(14)	2699.5(2)	2669(2)
Z	4	4	2	2
D_{calcd}, Mg/m^3	1.185	1.327	1.231	1.352
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.0	50.0	50.0
μ, mm^{-1}	0.286	2.456	0.252	2.003
F(000)	1640	1768	1060	1122
no. of obsd reflns	7604	7579	9359	9301
no. of params refnd	469	469	613	613
goodness of fit	1.073	0.993	1.015	1.070
R1	0.075	0.037	0.056	0.051
wR2	0.219	0.092	0.144	0.128

	15b•0.5DME	**16a**	**16b**	**17a**•0.5Tol
formula	$C_{48}H_{64}B_{10}HfN_5O$	$C_{35}H_{76}B_{10}N_6Si_4Zr$	$C_{35}H_{76}B_{10}HfN_6Si_4$	$C_{43.5}H_{55}B_{10}N_6Zr$
crystal size (mm)	0.40 x 0.30 x 0.20	0.50 X 0.30 X 0.20	0.40 x 0.20 x 0.20	0.40 x 0.30 x 0.20
fw	1013.63	892.70	979.97	861.26
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	P-1	P-1	P-1
a, Å	17.61(3)	11.197(1)	11.249(3)	12.376(2)
b, Å	15.73(3)	12.585(1)	12.616(3)	12.708(2)
c, Å	19.75(4)	20.310(1)	20.499(5)	16.534(2)
α, deg	90	95.86(1)	75.93(1)	75.33(1)
β, deg	108.69(4)	103.79(1)	86.60(1)	87.34(1)
γ, deg	90	91.58(1)	88.32(1)	62.87(1)
V, Å^3	5183(16)	2761.0(2)	2816.6(12)	2231.3(5)
Z	4	2	2	2
D_{calcd}, Mg/m^3	1.299	1.074	1.155	1.282
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.0	50.0	50.0
μ, mm^{-1}	2.052	0.315	1.965	0.286
F(000)	2068	948	1012	896
no. of obsd reflns	9101	9712	9815	7827
no. of params refnd	613	505	505	550
goodness of fit	1.078	1.105	1.086	1.030
R1	0.042	0.036	0.069	0.058
wR2	0.105	0.097	0.189	0.139

	18a	**18b•2Tol**	**19a•Tol**	**20a**
formula	$C_{42}H_{64}B_{10}N_6Zr$	$C_{98}H_{144}B_{20}Hf_2N_{12}$	$C_{51}H_{76}B_{10}N_6Zr$	$C_{28}H_{53}B_{10}N_5Zr$
crystal size (mm)	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20
fw	852.31	2063.34	972.50	659.07
crystal system	triclinic	triclinic	triclinic	orthorhombic
space group	*P*-1	*P*-1	*P*-1	$P2_12_12_1$
a, Å	10.514(1)	13.274(2)	10.885(2)	14.118(2)
b, Å	13.151(2)	14.791(3)	13.484(2)	14.882(2)
c, Å	18.462(3)	16.488(3)	19.065(3)	16.513(2)
α, deg	101.38(3)	105.39(1)	103.62(1)	90
β, deg	91.41(2)	100.35(1)	91.84(1)	90
γ, deg	90.64(2)	92.11(1)	96.14(1)	90
V, Å^3	2501.4(6)	3058.0(10)	2699.2(7)	3469.4(8)
Z	2	1	2	4
D_{calcd}, Mg/m^3	1.132	1.120	1.197	1.262
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	56.1	50.0	56.1	56.1
μ, mm^{-1}	0.254	1.739	0.244	0.345
F(000)	896	1060	1028	1384
no. of obsd reflns	11856	10688	12864	8400
no. of params refnd	532	595	613	397
goodness of fit	1.179	0.974	0.966	1.015
R1	0.051	0.050	0.070	0.036
*w*R2	0.184	0.107	0.146	0.082

	21a	**21b**	**23a**	**24a**•0.5THF
formula	$C_{34}H_{59}B_{10}N_5Zr$	$C_{34}H_{59}B_{10}HfN_5$	$C_{34}H_{63}B_{10}N_5Si_2Zr$	$C_{34}H_{54}B_{10}N_4O_{0.50}Zr$
crystal size (mm)	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30
fw	737.18	824.45	797.39	726.13
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	P-1	$P2_1/n$
a, Å	10.921(2)	10.945(1)	13.106(1)	10.852(2)
b, Å	17.085(3)	17.087(1)	19.078(1)	17.389(4)
c, Å	21.524(4)	21.504(1)	19.418(1)	21.045(4)
α, deg	90	90	98.94(1)	90
β, deg	95.42(1)	95.51(1)	101.46(1)	94.17(1)
γ, deg	90	90	105.39(1)	90
V, Å^3	3998.1(11)	4002.8(3)	4475.1(5)	3960.5(14)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.225	1.368	1.184	1.218
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.0	50.0	56.0
μ, mm^{-1}	0.306	2.637	0.329	0.309
F(000)	1552	1680	1680	1520
no. of obsd reflns	7034	7019	15720	9543
no. of params refnd	469	478	937	460
goodness of fit	1.018	1.104	1.072	1.024
R1	0.061	0.026	0.050	0.058
wR2	0.146	0.063	0.116	0.145

	25a	**25b**	**25b'**	**26a**
formula	$C_{31}H_{46}B_{10}N_4SZr$	$C_{31}H_{46}B_{10}HfN_4S$	$C_{29}H_{50}B_{10}HfN_4S$	$C_{29}H_{42}B_{10}N_4ZrS$
crystal size (mm)	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
fw	706.10	793.37	773.38	678.05
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	*P*-1	*P*-1	$P2_1/c$	*P*-1
a, Å	11.841(1)	11.840(2)	11.798(1)	11.797(2)
b, Å	12.159(1)	12.134(2)	19.512(2)	12.024(2)
c, Å	12.976(1)	12.965(2)	16.128(2)	14.111(2)
α, deg	93.23(1)	93.23(1)	90	95.54(1)
β, deg	99.79(1)	99.72(1)	106.18(1)	91.74(1)
γ, deg	103.23(1)	103.25(1)	90	109.97(1)
V, Å^3	1783.3(2)	1778.2(6)	3565.6(7)	1868.5(5)
Z	2	2	4	2
D_{calcd}, Mg/m^3	1.315	1.482	1.441	1.205
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.5	50.0	50.5	50.0
μ, mm^{-1}	0.396	3.021	3.011	0.375
F(000)	732	796	1560	700
no. of obsd reflns	6418	6227	6468	6536
no. of params refnd	424	424	406	406
goodness of fit	0.955	1.055	1.130	1.094
R1	0.025	0.042	0.034	0.044
*w*R2	0.071	0.106	0.080	0.124

	28b	**30'**	**31•0.5Tol**	**32**
formula	$C_{33}H_{50}B_{10}HfN_4$	$C_{14}H_{37}B_{20}NS_2Zr$	$C_{33.50}H_{52}B_{20}N_2S_2Zr$	$C_{30}H_{54}B_{20}N_4O_2S_2Zr$
crystal size (mm)	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30
fw	789.36	590.99	854.31	874.31
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	21.262(4)	12.906(1)	15.517(2)	21.281(3)
b, Å	16.347(3)	9.080(1)	16.642(2)	12.701(2)
c, Å	21.019(3)	26.430(1)	17.666(2)	17.917(3)
α, deg	90	90	90	90
β, deg	90.15(1)	103.68(1)	96.31(1)	106.85(1)
γ, deg	90	90	90	90
V, Å^3	7305(2)	3009.3(3)	4534.1(10)	4634.5(11)
Z	8	4	4	4
D_{calcd}, Mg/m^3	1.435	1.304	1.252	1.253
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.5	50.0	50.0
μ, mm^{-1}	2.886	0.514	0.364	0.361
F(000)	3184	1200	1756	1800
no. of obsd reflns	12875	5448	7951	8154
no. of params refnd	865	343	541	532
goodness of fit	1.043	1.028	1.033	1.117
R1	0.045	0.043	0.045	0.049
wR2	0.090	0.088	0.109	0.122

	33	**34•Tol**	**35**	**37•3THF**
formula	$C_{19}H_{46}B_{20}N_2S_3Zr$	$C_{25}H_{53}B_{20}NOS_2Zr$	$C_{30}H_{54}B_{20}N_4S_2Zr$	$C_{33}H_{69}B_{20}NO_6S_2Zr$
crystal size (mm)	0.50 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30 mm
fw	706.18	755.22	842.31	947.43
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/m$	$P2_1/c$
a, Å	11.006(1)	13.455(6)	22.405(2)	13.666(1)
b, Å	20.210(2)	18.181(7)	15.095(2)	21.732(1)
c, Å	16.778(2)	16.373(7)	14.776(2)	19.034(1)
α, deg	90	90	90	90
β, deg	100.50(1)	97.42(1)	90.47(1)	101.50(1)
γ, deg	90	90	90	90
V, Å^3	3669.3(7)	3972(3)	4997.3(9)	5539.4(3)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.278	1.263	1.120	1.136
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	50.0	50.0	50.5
μ, mm^{-1}	0.489	0.407	0.330	0.311
F(000)	1448	1560	1736	1976
no. of obsd reflns	6457	6988	4568	10038
no. of params refnd	415	479	277	568
goodness of fit	1.081	1.076	1.120	1.083
R1	0.054	0.036	0.071	0.047
wR2	0.134	0.096	0.241	0.134

	42a•Tol	**44a**	**45a**	**46a**•0.5HNMe$_2$
formula	$C_{21}H_{41}B_9N_2Zr$	$C_{20}H_{32}B_{10}N_2Zr$	$C_{30}H_{64}B_9N_7Zr_2$	$C_{15}H_{34.5}B_9N_{2.5}Zr$
crystal size (mm)	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.30 x 0.20 x 0.10
fw	510.07	499.80	802.61	438.46
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$	$P2_1/c$	$P2_1/n$
a, Å	10.822(2)	11.736(2)	11.418(2)	10.477(1)
b, Å	20.100(4)	13.795(2)	14.843(3)	12.404(1)
c, Å	13.273(3)	16.259(3)	25.088(4)	18.533(2)
α, deg	90	90	90	90
β, deg	111.32(1)	104.20(1)	97.48(1)	100.85(1)
γ, deg	90	90	90	90
V, Å^3	2689.6(9)	2551.9(7)	4215.7(12)	2365.6(4)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.260	1.301	1.265	1.231
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	56.1	50.0	50.0	50.0
μ, mm^{-1}	0.422	0.443	0.524	0.469
F(000)	1064	1024	1672	908
no. of obsd reflns	6481	8629	7438	4162
no. of params refnd	298	595	433	253
goodness of fit	1.006	1.029	1.085	1.012
R1	0.053	0.074	0.043	0.075
wR2	0.140	0.179	0.117	0.228

	48a	**50a**	**51**	**52a**•0.5Tol
formula	$C_{30}H_{64}B_{18}Li_2N_4Zr_2$	$C_{19}H_{35}B_9N_2Zr$	$C_{52}H_{52}B_9NP_2$	$C_{21.5}H_{32}B_{10}N_2Zr$
crystal size (mm)	0.30 x 0.20 x 0.20	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.40
fw	871.75	480.00	850.18	517.81
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*C*2/*c*	$P2_1/n$	$P2_1$	*Pbcn*
a, Å	29.602(4)	16.032(3)	10.903(1)	22.528(3)
b, Å	15.398(2)	8.815(2)	19.217(1)	16.036(2)
c, Å	20.410(2)	17.216(3)	13.492(1)	13.935(2)
α, deg	90	90	90	90
β, deg	109.55(1)	105.82(1)	111.10(1)	90
γ, deg	90	90	90	90
V, Å^3	8766.7(18)	2341.0(7)	2637.2(3)	5034.2(12)
Z	8	4	2	8
D_{calcd}, Mg/m^3	1.321	1.362	1.071	1.366
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	50.0	56.1	50.0	56.1
μ, mm^{-1}	0.504	0.480	0.116	0.452
F(000)	3584	992	892	2120
no. of obsd reflns	7727	5664	9183	6095
no. of params refnd	505	284	577	328
goodness of fit	1.041	1.030	1.047	1.030
R1	0.069	0.049	0.043	0.041
*w*R2	0.168	0.110	0.111	0.108

	53a	**54a**	**55a•C_6H_6**	**56b**
formula	$C_{16}H_{31}B_9N_2Zr$	$C_{24}H_{45}B_9N_2Zr$	$C_{22}H_{51}B_{19}N_2S_2Zr$	$C_{26}H_{62}B_9HfLiN_2O_6$
crystal size (mm)	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30
fw	439.94	550.13	704.38	781.50
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$Cmca$
a, Å	12.931(1)	9.972(1)	12.787(4)	20.288(5)
b, Å	9.163(1)	20.416(1)	16.241(6)	28.026(8)
c, Å	17.983(2)	14.774(1)	19.157(7)	13.812(4)
α, deg	90	90	90	90
β, deg	101.98(2)	103.67(1)	108.35(1)	90
γ, deg	90	90	90	90
V, Å^3	2084.2(4)	2922.5(2)	3776(2)	7853(4)
Z	4	4	4	8
D_{calcd}, Mg/m^3	1.402	1.250	1.239	1.322
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	56.1	55.6	50.5	50.0
μ, mm^{-1}	0.532	0.393	0.422	2.693
F(000)	904	1152	1456	3200
no. of obsd reflns	5023	6863	6829	3579
no. of params refnd	257	325	415	394
goodness of fit	1.048	1.005	1.090	1.095
R1	0.028	0.039	0.037	0.037
wR2	0.073	0.091	0.100	0.095

	58a	**59a**•0.5Tol	**60a**•THF	**61a**
formula	$C_{34}H_{68}B_9ClLiNO_6Zr$	$C_{29.5}H_{50}B_9NOZr$	$C_{57}H_{73}B_9N_2O_3Zr$	$C_{15}H_{35}B_9Cl_2N_2Zr$
crystal size (mm)	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
fw	817.79	623.21	1022.68	502.86
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P2_1/n$	$P\text{-}1$
a, Å	9.591(2)	34.123(7)	19.274(4)	7.188(1)
b, Å	28.294(5)	12.159(2)	12.531(2)	9.965(2)
c, Å	16.780(3)	23.190(5)	26.162(5)	17.241(3)
α, deg	90	90	90	81.70(1)
β, deg	92.05(1)	129.65(1)	100.32(1)	78.01(1)
γ, deg	90	90	90	84.88(1)
V, Å^3	4550.5(14)	7409(2)	6216.3(19)	1193.1(3)
Z	4	8	4	2
D_{calcd}, Mg/m^3	1.194	1.117	1.093	1.400
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	56.0	56.1	56.1	50.0
μ, mm^{-1}	0.339	0.319	0.217	0.690
F(000)	1728	2616	2152	516
no. of obsd reflns	10942	8905	15005	4182
no. of params refnd	478	406	694	262
goodness of fit	0.985	0.888	0.936	1.067
R1	0.051	0.073	0.0910	0.043
wR2	0.131	0.197	0.0246	0.114

	62a•DME	**63a**•DME	**64a**	**65a**•0.5 Tol
formula	$C_{43}H_{64}B_{10}N_2O_2Zr$	$C_{30}H_{64}B_{18}O_6Zr_2$	$C_{19}H_{40}B_9N_3SZr$	$C_{24.5}H_{49}B_9N_4Zr$
crystal size (mm)	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.20 x 0.20
fw	840.28	897.83	531.11	588.19
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	P-1	$P2_1/n$
a, Å	18.409(1)	15.531(3)	10.005(2)	11.339(2)
b, Å	17.749(1)	14.877(3)	11.432(2)	9.917(2)
c, Å	29.490(2)	9.319(2)	12.192(2)	28.483(5)
α, deg	90	90	80.50(1)	90
β, deg	106.68(1)	99.30(1)	69.17(1)	93.62(1)
γ, deg	90	90	83.49(1)	90
V, Å^3	9230.4(11)	2125.0(7)	1283.1(4)	3196.5(9)
Z	8	2	2	4
D_{calcd}, Mg/m^3	1.209	1.403	1.375	1.222
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	55.9	50.0	56.1	56.1
μ, mm^{-1}	0.275	0.531	0.524	0.365
F(000)	3536	924	552	1236
no. of obsd reflns	21956	3738	6080	7674
no. of params refnd	1061	253	302	361
goodness of fit	1.001	1.069	1.048	1.009
R1	0.058	0.045	0.058	0.045
wR2	0.152	0.111	0.141	0.114

	66a	**67**	**68**	**69**
formula	$C_{20}H_{42}B_9N_3Zr$	$C_{52}H_{104}B_{18}Na_3O_8Zr_2$	$C_{52}H_{104}B_{18}Hf_2Li_2O_8$	$C_{92}H_{100}B_{18}Hf_2N_2P_4$
crystal size (mm)	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
fw	513.08	1303.34	1422.80	1909.18
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2/n$	$P2/n$	$Pca2_1$
a, Å	17.224(5)	15.209(1)	27.091(2)	17.065(1)
b, Å	9.737(3)	10.971(1)	10.844(1)	17.988(1)
c, Å	16.537(5)	22.585(1)	27.203(2)	28.017(1)
α, deg	90	90	90	90
β, deg	112.19(1)	92.82(1)	119.48(1)	90
γ, deg	90	90	90	90
V, Å^3	2567.9(12)	3764.0(2)	6957.4(9)	8600.5(6)
Z	4	2	8	4
D_{calcd}, Mg/m^3	1.327	1.150	1.358	1.474
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	56.1	50.0	50.0	56.5
μ, mm^{-1}	0.443	0.336	3.027	2.536
F(000)	1072	1366	2880	3840
no. of obsd reflns	6189	6607	11092	20988
no. of params refnd	302	411	739	1059
goodness of fit	1.035	0.950	1.053	1.005
R1	0.045	0.069	0.067	0.036
wR2	0.109	0.183	0.194	0.068