Synthesis, Structural Characterization and Reactivity of Metal-Carboranyl and Metal-Dicarbollyl Complexes

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Abstract

Late transition metal (M = Co, Ni) complexes bearing linked Cp/Ind/$CpCH_2CH_2NMe_2$-carboranyl ligands were synthesized by treatment of the dilithium salts of the ligands with $MCl_2(PPh_3)_2$. The M-C(cage) bonds in these complexes were inert toward unsaturated molecules due to the steric hindrance of carboranyl cage. However, the ligand exchange reaction happened between metal complexes and isocyanide, or carbene or phosphines.

The carbon-linked Cp/Ind/C_5Me_4-dicarbollyl ligands were synthesized by deboration reaction of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$, $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ or $H_2C(C_5Me_4H)(C_2B_{10}H_{11})$ with piperidine in EtOH. Treatment of the trisodium salts of ligands with $MCl_4(THF)_2$ gave the mixed sandwich metal chloride complexes $[\{\eta^5:\eta^5\text{-}R^1{}_2C(R^2)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (R^1 = Me, R^2 = C_5H_4, C_9H_6; R^1 = H, R^2 = C_5Me_4; M = Zr, Hf). No neutral species were formed because of the more open coordination sphere and more electron deficiency of the metal centers than those of the corresponding unbridged ones. Neutral amide complexes $[\eta^5:\eta^5\text{-}Me_2C(R^2)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (R^2 = C_5Me_4, C_9H_6) were produced through amine elimination reaction of ligands with $Zr(NMe_2)_4$. Treatment of $[\{\eta^5:\eta^5\text{-}R^1{}_2C(R^2)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ with RLi (R = Cp, Bn, $TMSCH_2$)

afforded the corresponding ionic zirconium alkyl complexes. On the other hand, reaction of the zirconium chloride complexes with R^1NLi produced the neutral zirconium amide complexes due to the $p_\pi(N)$-$d_\pi(Zr)$ back-bonding interactions. These zirconocarborane chloride/amide complexes showed modest to good activity in ethylene polymerization after activation with MAO.

Neutral and stable sandwich metallacarborane alkyl/methyl complexes were synthesized by the reaction of 7-$(Me_2NH)(CH_2)_2$-7,8-$C_2B_9H_{11}$ with $(Cp^R)MMe_3$ (R = TMS_2, Me_5, M = Zr, Hf). The M-C(alkyl or methyl) bonds in these complexes were inert toward alkenes. However mono-insertion of alkynes was observed, and both steric and electronic factors affected the regioselectivity of insertion reaction. For terminal alkynes, either insertion reaction or acid-base reaction proceeded depending upon the substitutents. Insertion of nitriles, isocyanides, carbodiimides, ketones, and RNCS into the M-C bonds was also investigated. In some cases, the sequential insertion and B-H activation were observed.

摘 要

碳橋聯碳硼烷-環戊二烯基/茚基/胺取代的環戊二烯基配體的二鈉鹽跟後過渡金屬二氯化物（鎳，鈷）發生鹽消除反應生成相應的金屬絡合物。在這些碳硼烷金屬絡合物中，碳硼烷配體的位阻導致金屬-碳（碳硼烷上）鍵對於不飽和分子的插入反應是惰性的。但是金屬絡合物中的三苯基膦配體能被異腈，卡賓和其他的膦配體所取代。

碳橋聯碳硼烷-環戊二烯/茚/四甲基環戊二烯配體與過量的呱啶在回流的乙醇中反應形成脫硼配體。脫硼配體的三鈉鹽可以與 $MCl_4(THF)_2$ 反應生成相應的離子型的金屬氯化物。由於金屬原子的大配位空間和缺電子性，預期的中性金屬氯化物無法形成。中性的鋯胺化物可以通過脫硼配體與 $Zr(NMe_2)_4$ 的胺消除反應得到。金屬氯化物與烷基鋰反應也只能得到離子型的金屬烷基化合物。但是金屬氯化物跟胺鹽反應可以生成中性的金屬胺化物，因爲金屬-氮之間的反饋 π 鍵可以減弱金屬的 Lewis 酸性。在過量 MAO 存在條件下，這些金屬氯化物或胺化物可以催化乙烯聚合，活性中等到良好。

通過 $7\text{-}(Me_2NH)(CH_2)_2\text{-}7,8\text{-}C_2B_9H_{11}$ 和 $(Cp^R)MMe_3$ 的烷基消除反應合成了全夾心的第四族金屬碳硼烷烷基化合物。這些金屬烷基化合物中的金屬-碳鍵對烯烴是惰性的，但是炔烴可以發生單插入反應。根據炔烴上取代基的不同，插入反應的區域選擇性由位阻和電子效應來決定。對於不同的端基炔烴來說，可以得

到插入反應或者酸城反應的產物。腈，異腈，碳二亞胺，酮，硫代異腈酸酯等極性不飽和分子也可以與鋯烷基化合物反應，生成單插入或雙插入的產物。等量的甲醇可以與鋯烷基化合物發生酸城反應生產鋯烷氧基化合物。對於含有卡賓性質碳原子的極性不飽和有機分子如一氧化碳，異腈等，他們對金屬碳硼烷甲基化合物有不同於別的不飽和分子的反應性，插入反應之後碳硼烷的硼-氫鍵會被活化繼續進行插入反應。

Abbreviation

br	broad
br s	broad singlet (NMR)
^{n}BuLi	*n*-butyl lithium
^{t}Bu	*tert*-butyl
Bn	benzyl
Cp	cyclopentadienyl
Cp''	1,3-bis(trimethylsilyl)cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	doublet (NMR)
DCC	dicyclohexylcarbodiimide
dd	doublet of doublets (NMR)
DME	dimethoxyethane
DPC	diisopropylcarbodiimide
dppe	1,2-bis(diphenylphosphino)ethane
Et	ethyl
Et_2O	diethyl ether
Fig.	figure
h	hour
IR	infrared spectroscopy
Ln	lanthanide
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance spectroscopy

m	multiplet (NMR)
M	metal
Me	methyl
MeCN	acetonitrile
MS	mass spectrometry
$P(Cy)_3$	tricyclohexylphosphine
Ph	phenyl
Pr	propyl
^{i}Pr	*iso*-propyl
Py	pyridine
s	singlet (NMR)
t	triplet (NMR)
THF	tetrahydrofuran
TMS	trimethylsilyl
Ts	P-toluenesulfonyl
xs	excess

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Chapter 1

Introduction

Carboranes are a class of boron clusters in which one or more boron vertices are replaced by carbon atom(s). They have drawn great interests as inorganic ligands since 1960s. It is well established that *o*-carboranes can be readily converted to the monoanion *closo*-$C_2B_{10}H_{11}^-$ and dianion *closo*-$C_2B_{10}H_{10}^{2-}$ via stepwise deprotonation of the cage C-H protons,[1] the dicarbollide ion (*nido*-$C_2B_9H_{11}^{2-}$) by selective removal of one BH vertex,[2] the *nido*-$C_2B_{10}H_{12}^{2-}$ and *arachno*-$C_2B_{10}H_{12}^{4-}$ through reaction with group 1 metals.[3,4] Among them, the dicarbollide ion (*nido*-$C_2B_9H_{11}^{2-}$) is isoloble to the cyclopentadienyl anion but with one more negative charge. Group 4 metal complexes with dicarbollide ligands have been widely studied.

Cyclopentadienyl and carboranyl represent the two most important classes of organic and inorganic ligands in organometallic chemistry.[5-7] Bridged organic/inorganic hybrid cyclopentadienyl/carboranyl ligands have been synthesized and studied by our group[8] which possess not only the properties of both cyclopentadienyl and carboranyl moieties but also unique features of a bridged ligand such as stability, solubility and crystallizability. Their applications in group 3 and 4 metal complexes as well as Ru complexes have been studied.[9]

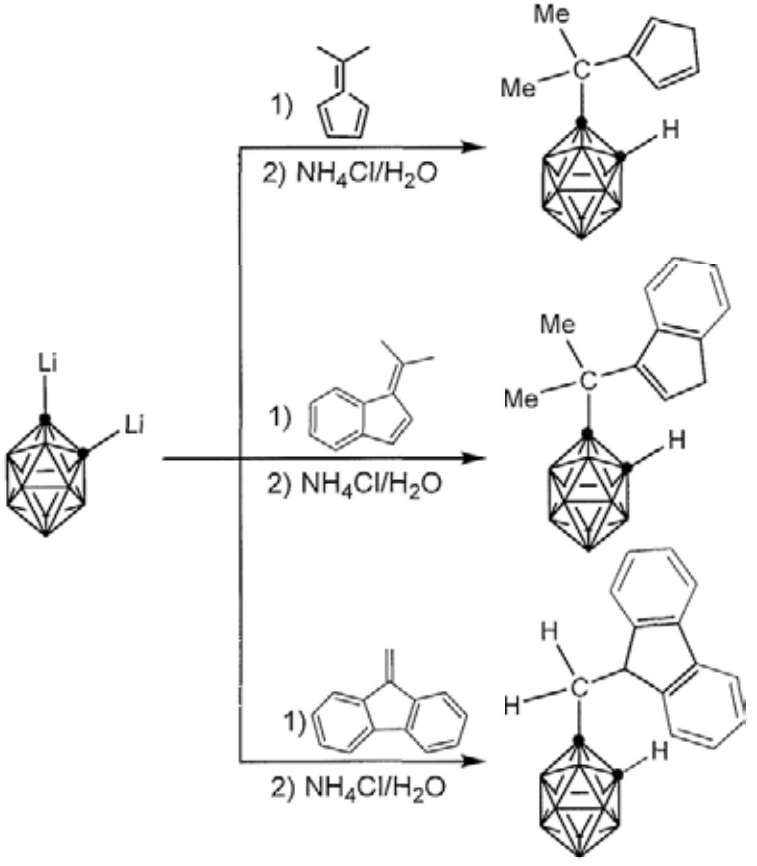
This chapter summarizes the development in these two fields.

1.1 Organometallic Complexes Bearing Carbon-Bridged Cyclopentadienyl /Indenyl-Carboranyl Systems

1.1.1 Group 4 Metal Complexes

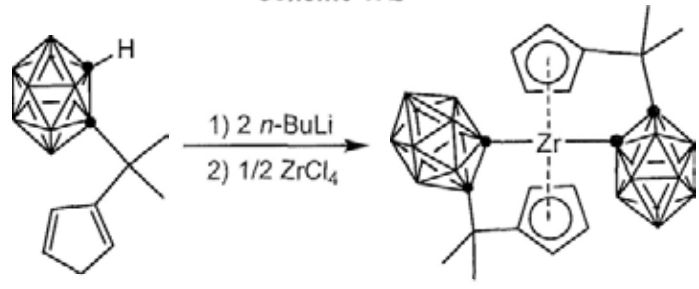
Carbon-bridged cyclopentadienyl-carboranyl ligands are synthesized by nucleophilic reaction of $Li_2C_2B_{10}H_{10}$ with fulvenes (Scheme 1.1). For the cyclopentadienyl/indenyl-carboranyl, dimethylfulvene/dimethylbenzofulvene are used.[8,9] But for more bulky fluorene, 6,6'-dimethyldibenzofulvene shows no reaction with $Li_2C_2B_{10}H_{10}$, dibenzofulvene is then chosen.[10]

Scheme 1.1



$Me_2C(C_5H_5)(C_2B_{10}H_{11})$ can be easily converted to the corresponding dilithium salt $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$, which reacted with $ZrCl_4$ in a 2:1 ratio in toluene to afford *rac*-$[\eta^5{:}\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]_2Zr$ (Scheme 1.2).[11]

Scheme 1. 2

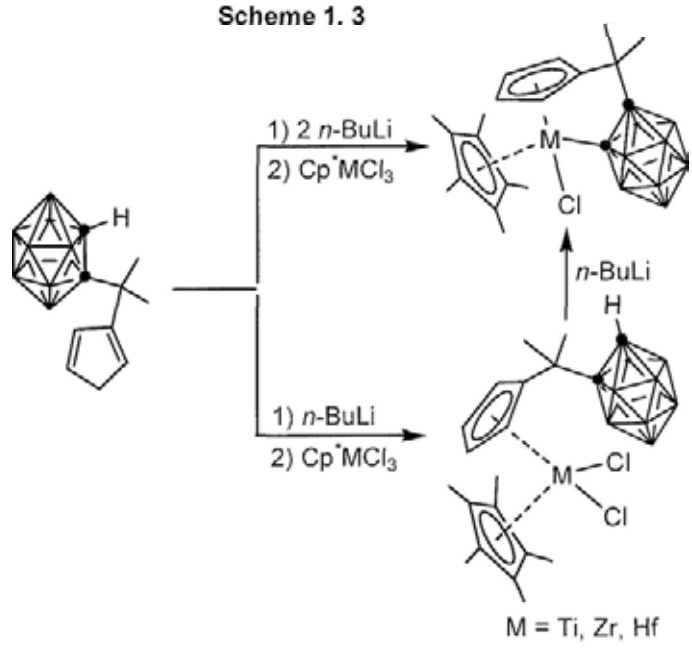


It is found that *rac*-$[\eta^5{:}\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]_2Zr$ can catalyze the formation of syndiotactic poly(methyl methacrylate) with a molecular weight distribution of 1.6 - 2.1. The characteristics worthy of mention for the catalyst *rac*-$[\eta^5{:}\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]_2Zr$ are its air and thermal stability and its neutral nature, which makes any additional use of alkylating reagent or cationic center generator unnecessary. The result indicates that the attachment of carborane cage leads to excellent thermal stability and unusual polymerization behavior of this complex.[11]

The catalytic behavior of the metallocene catalysts is very sensitive to the changes in ligands. Particularly, the steric and electronic environments around the metal centers are most important and can be controlled directly by the changes of the ligands. The effect of carborane cage as a substituent at Cp ring and as a σ-donor ligand in group 4 metallocene catalysts on ethylene polymerization has been explored. Thermally stable

complexes (η^5-C_5Me_5)[η^5-$Me_2C(C_5H_4)(RC_2B_{10}H_{10})$]$MCl_2$ (R = H and Me) and (η^5-C_5Me_5)[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]MCl have been prepared via salt metathesis reactions of Cp^*MCl_3 (M = Ti, Zr and Hf) with monolithium and dilithium salt of $Me_2C(C_5H_4)(C_2B_{10}H_{11})$, respectively (Scheme 1.3).[12]

Scheme 1. 3



The X-ray analyses study establishes their monomeric bent metallocene structural feature with carborane acting as a substituent or an ancillary ligand. The titanium and zircounium complexes produce high-density polyethylenes with the activity range of about 10^3-10^4 g PE/mol·atm·h in the presence of modified methylaluminoxane (MMAO) cocatalyst. The observed lower polymerization activities of the catalytic systems may be ascribed to the steric hindrance of the carborane cage coupled with possible involvement of the activation of a M-C(carborane) σ-bond.[12]

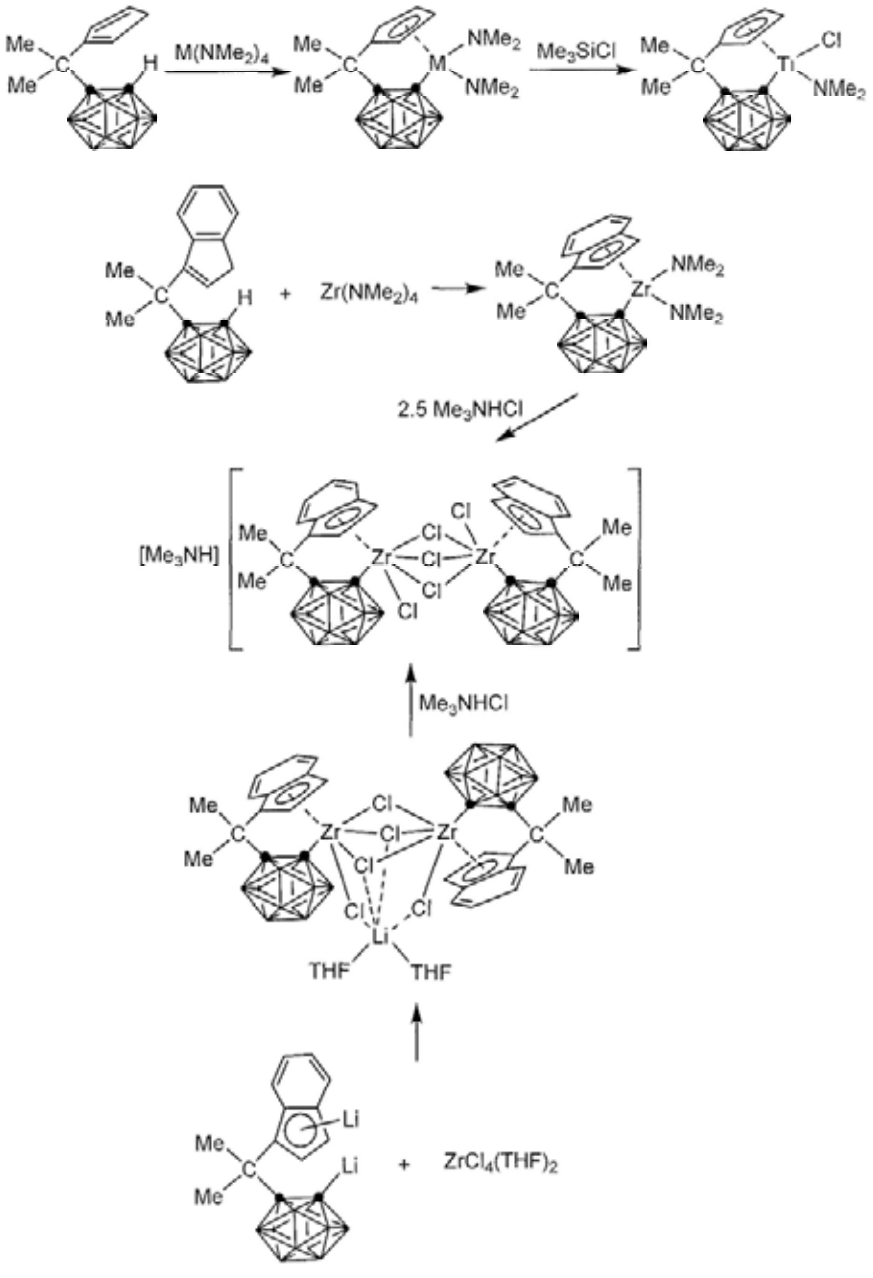
There are two general methods to prepare group 4 metallocenes: salt metathesis and amine elimination. The two acidic protons, cage CH and sp^3-CH of the five-membered ring in the linked compounds shown in Scheme 1.1 would allow the amine elimination to occur between the ligands and group 4 metal amides. In fact, treatment of $M(NR_2)_4$ (M = Ti, Zr, Hf; R = Me, Et) with 1 equiv of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ or $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ in toluene results in the formation of the corresponding constrained-geometry complexes $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NR_2)_2$ or $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2$, respectively (Scheme 1.4).[13]

Group 4 metal amides can be converted to the corresponding chloro derivatives by reaction with Me_3SiCl or Me_3NHCl. The products are dependent upon the ligands and central metal ions. For example, the reaction between the titanium amide $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ and excess Me_3SiCl affords the monoamide monochloride complex $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ (Scheme 1.4),[13] which offers a good method for the preparation of chiral metallocenes due to the simple workup and high yield. However, reaction of $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with excess Me_3NHCl produces the ionic zirconium chloride complex $[NMe_3H][\{[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]ZrCl\}_2\{\mu\text{-}Cl\}_3]$. The ionic chloro derivatives can also be prepared by salt metathesis reaction of MCl_4 with the corresponding dianionic salts, shown in Scheme 1.4.[13]

These constrained-geometry group 4 metal amides and chlorides can all catalyze the polymerization of ethylene with moderate to very high activities upon activation

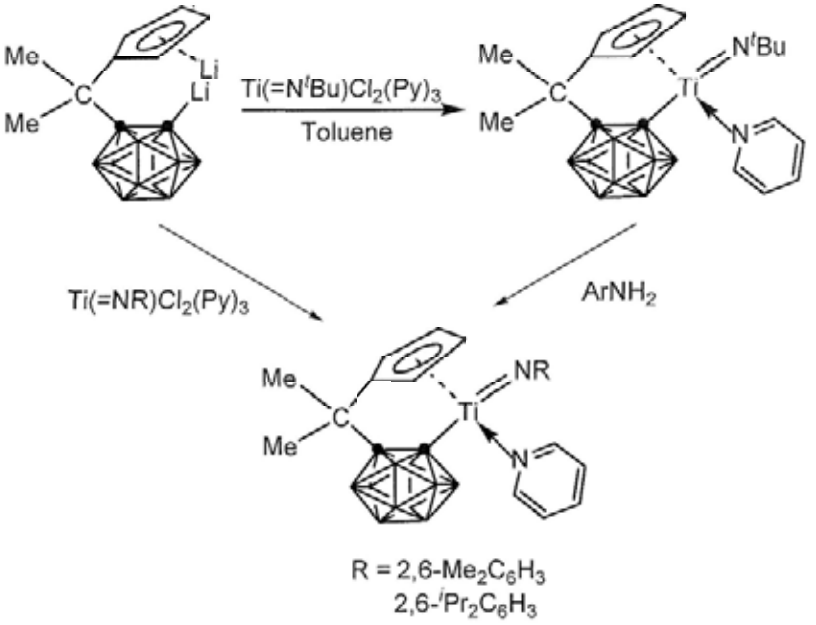
with MAO. Zirconocenes with Me_2C-linked indenyl-carboranyl ligands are 30 – 100 times more active than those with R_2C-linked cyclopentadienyl-amido ones, suggesting that carboranyl does play a role in enhancing the catalytic activity of metallocenes. The Zr-C(cage) bond remains intact in catalysis.[13]

Scheme 1.4



Group 4 metal imido complexes attract considerable interests for their applications in C-H activation, [2+2] cycloadditions, catalytic hydroamination of alkynes and NR group transfer reactions. Treatment of dilithium salt of the carbon-bridged ligand $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$ with 1 equiv of $Ti(=NR)Cl_2(Py)_3$ (R = ^{t}Bu, 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$) affords imido-titanium complexes $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=NR)(Py)$ (R = ^{t}Bu, 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$) (Scheme 1.5).[14] The aryl imido-titanium complexes have also been prepared by the imido exchange reaction of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=N^tBu)(Py)$ with $ArNH_2$ (Scheme 1.5).[14]

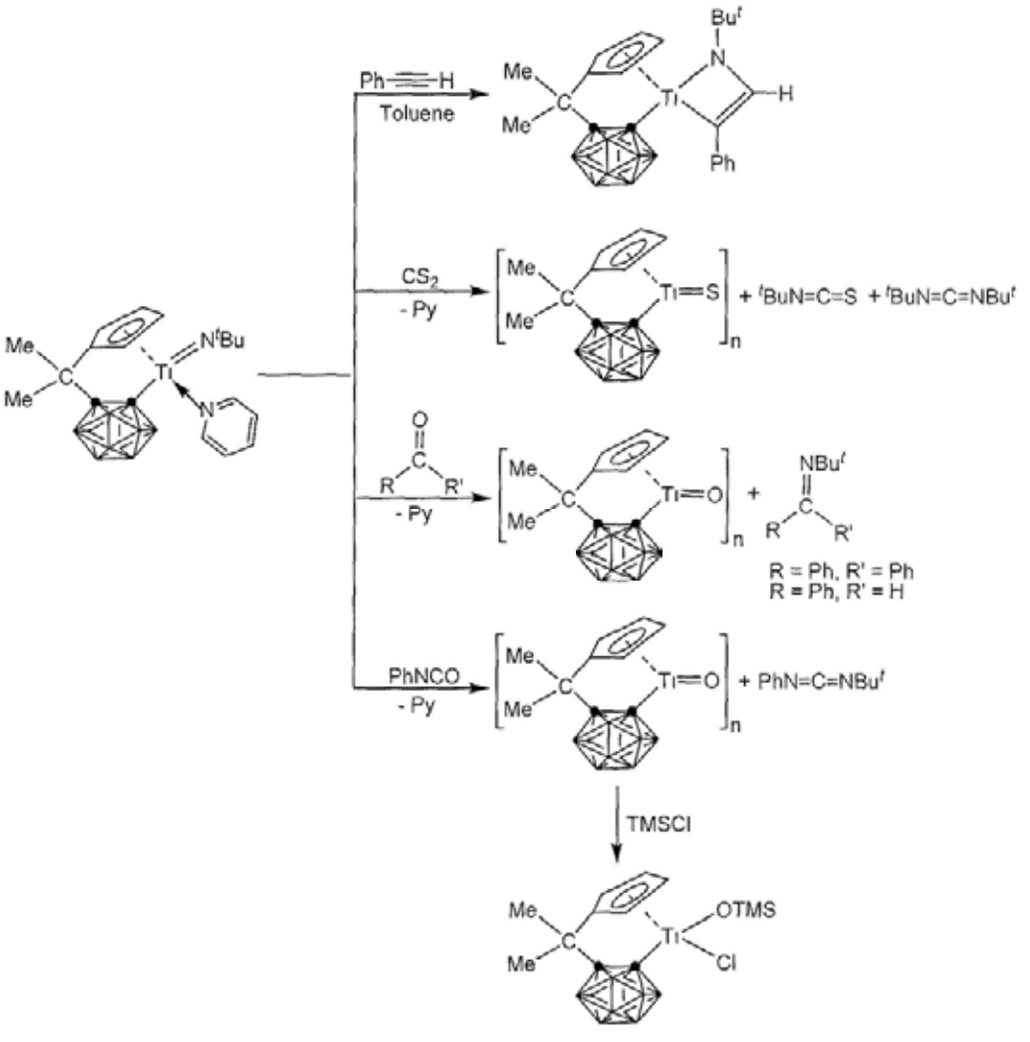
Scheme 1. 5



The titanium-imido complex $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=N^tBu)(Py)$ can undergo imido/oxo exchange reaction with $Ph_2C=O$, PhCHO or PhN=C=O to generate

the corresponding imine or carbodiimide and oxotitanium oligomer as a pale-yellow solid (Scheme 1.6).[14] Treatment of the oxotitanium oligomer with excess Me_3SiCl gives, after recrystallization from toluene/hexane, $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[OSi(CH_3)_3](Cl)$ (Scheme 1.6).[14] The imido exchange reactions are extended to other C=X (X = S, N) group. Reaction of titanium-imido complex with CS_2 shows the formation of $^tBuN{=}C{=}S$ and $^tBuN{=}C{=}N^tBu$. The latter is supposed to be formed by the reaction of titanium-imido with $^tBuN{=}C{=}S$. Reaction of the titanium-imido complex with phenylacetylene affords the [2+2] product which is thought to be the intermediate of hydroamination reaction catalyzed by titanium imido complex (Scheme 1.6).[14] The titanium imido complex can also catalyze the hydroamination reactions of phenylacetylene with amines with low to moderate regioselectivity.[14]

Scheme 1.6

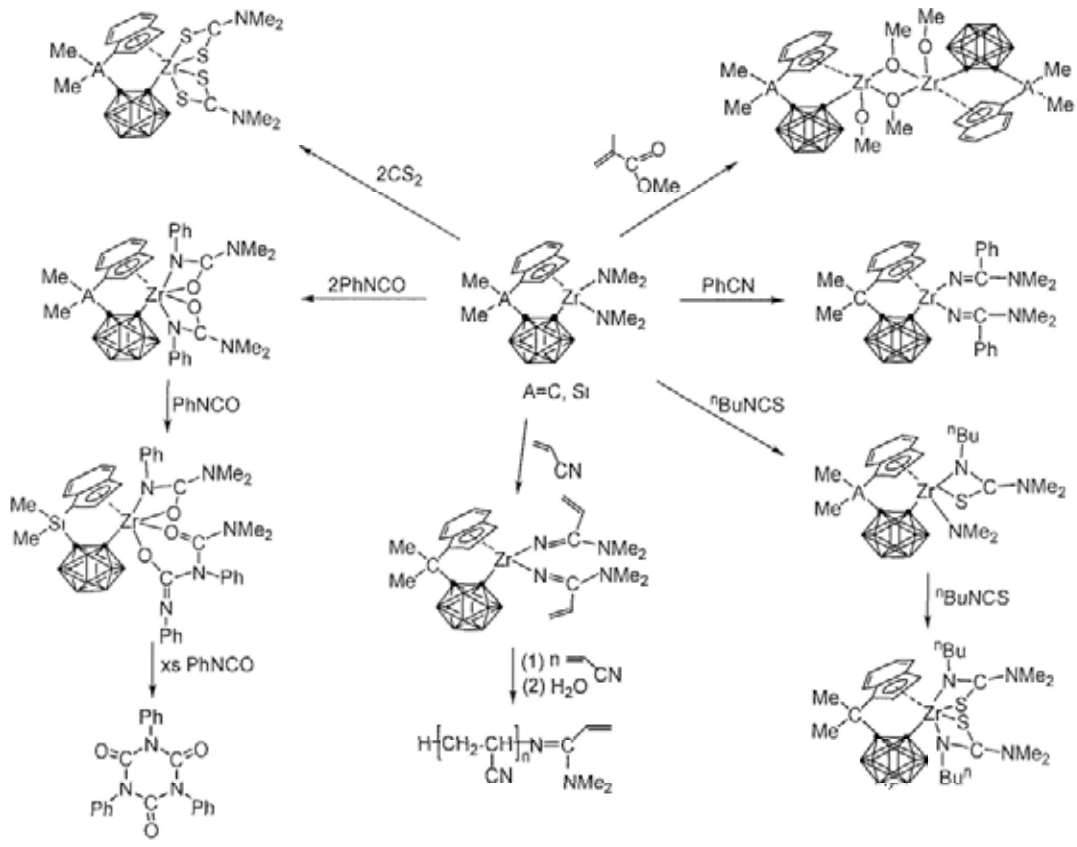


The group 4 metal amide complexes show a good reactivity towards unsaturated molecules. For example, the compounds $[\eta^5:\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (A = C, Si) can react with CS_2, PhCN, CH_2=CHCN, ^{n}BuNCS and PhNCO, respectively, to give the corresponding mono-, di-, and tri-insertion products, depending upon the substrates (Scheme 1.7).[15] The isolation and structural characterization of mono- and

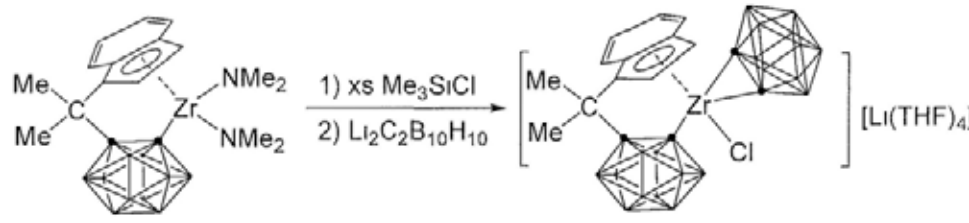
di-insertion products of $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr[NC(CHCH_2)(NMe_2)](NMe_2)$ and $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr[NC(CHCH_2)(NMe_2)]_2$ indicate that the Zr-N bonds are more reactive than the Zr-C(cage) bond. This result is also supported by the isolation and structural characterization of $[\{\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})\}Zr(\mu\text{-}OMe)(OMe)]_2$ from the reaction of $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with MMA. No poly(MMA) is detected (Scheme 1.7).[15] All these results indicate that these unsaturated substances insert exclusively into the Zr-N bonds, and the Zr-C(cage) bonds remain intact in all reactions. It is believed that the preference of Zr-N over Zr-C(cage) insertion is governed by steric factors.[15] Compounds $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ can initiate the polymerization of CH=CHCN to produce poly(acrylonitrile) and catalyze the trimerization of PhNCO. $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ can also react with methyl methacrylate to afford metal methoxide and $CH_2{=}C(Me)CONMe_2$ (Scheme 1.7), probably due to the high oxophilicity of the Zr atom.

1,2-Dehydro-*o*-carborane, a three-dimensional relative of benzyne, has attracted much attention recently due to its similar reactivity to that of benzyne. The first zirconocene-1,2-dehydro-*o*-carborane complex has been prepared and characterized. Treatment of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with excess Me_3SiCl, and then followed by reaction with 1 equiv of $Li_2C_2B_{10}H_{10}$ affords $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$ in 60% isolated yield (Scheme 1.8).[16]

Scheme 1.7



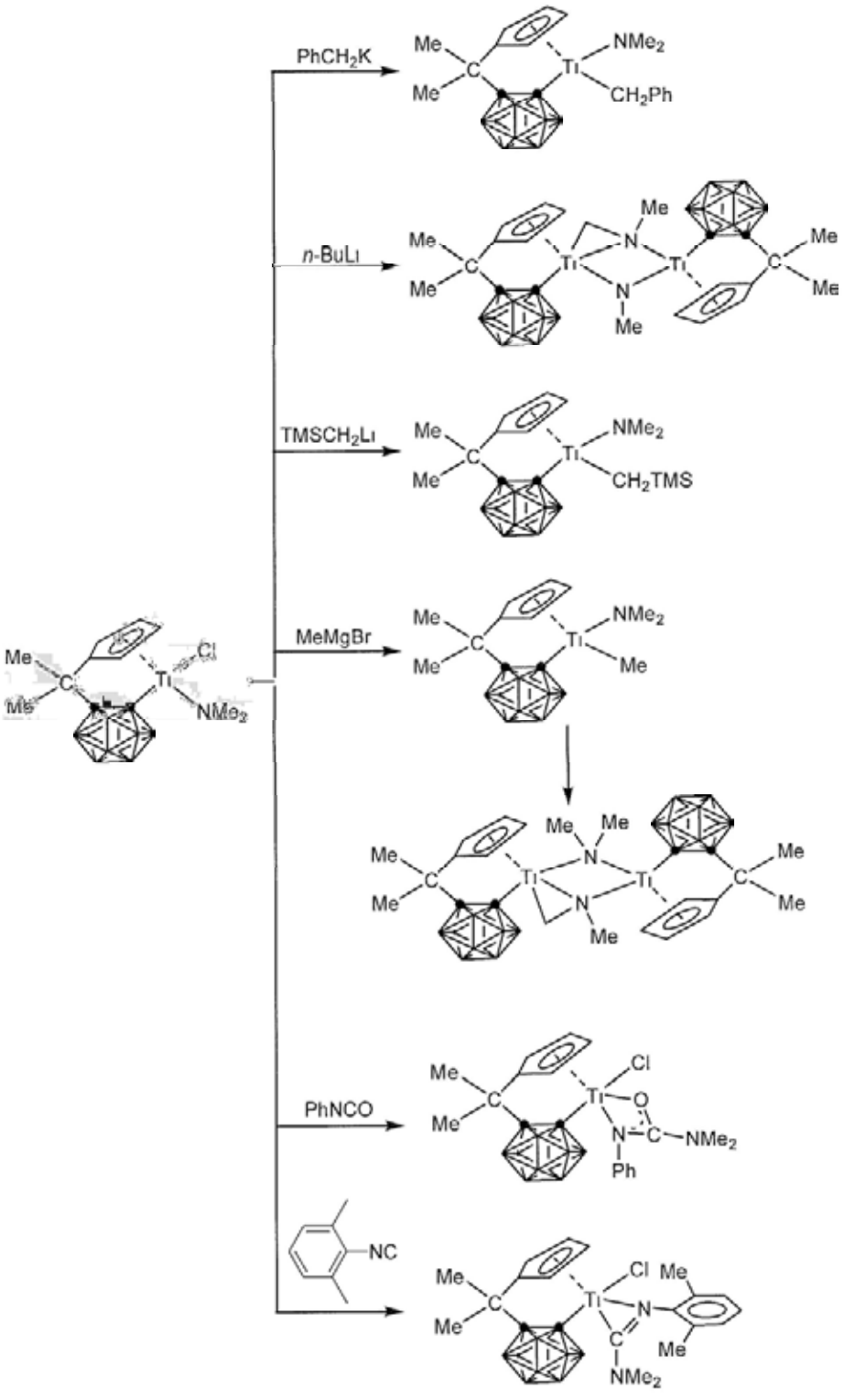
Scheme 1.8



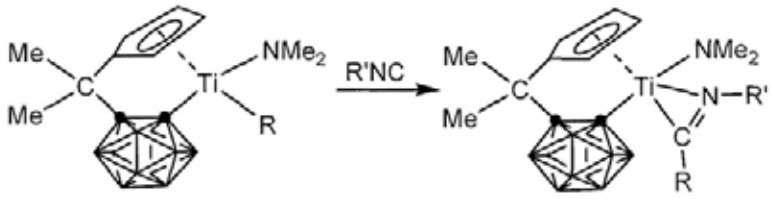
Molecular orbital calculations suggest that the bonding interactions between Zr and 1,2-dehydro-*o*-carborane are best described as a resonance hybrid of both the Zr-C σ and Zr-C π bonding forms, which exhibits a brand new bonding mode for carborane.

Organotitanium chloride complexes are usually useful precursors for the synthesis of organotitanium alkyl complexes. Treatment of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]TiCl($NMe_2$) with 1 equiv of alkylating reagents such as $PhCH_2K$, Me_3SiCH_2Li and CH_3MgBr results in the isolation of corresponding titanium alkyl complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti($CH_2Ph$)($NMe_2$), [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti($CH_2SiMe_3$)($NMe_2$) and [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti($CH_3$)($NMe_2$) in good yields (Scheme 1.9).[17] The titanium methyl complex is not very thermally stable, even at room temperature, which is converted to {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti}$_2$($\mu$-$NMe_2$)($\mu$:$\sigma$-$NMeCH_2$)·2THF as a dark blue solid. Treatment of titanium chloride complex directly with ^{n}BuLi affords {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti}$_2$($\mu$-NMe)($\mu$:$\sigma$-$NMeCH_2$)·2THF. Reaction of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]TiCl($NMe_2$) with PhNCO and RNC give the mono-insertion products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(Cl)[$\eta^2$-$OC(NMe_2)NPh$] and [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(Cl)[$\eta^2$-$C(NMe_2)$=$N(C_6H_3Me_2$-2,6)] (Scheme 1.9).[17] These results show that the unsaturated molecules insert exclusively into the Ti-N bond and the Ti-C(cage) bond remains intact because of the steric reasons. When treating [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]TiR($NMe_2$) (R = CH_2TMS, Me) with R'NC, mono-insertion products [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti($NMe_2$)[$\eta^2$-$C(CH_2SiMe_3)$=N(R')] (R' = 2,6-$Me_2C_6H_3$, ^{t}Bu) are produced (Scheme 1.10).[17] It is noted that the unsaturated molecules insert into the Ti-C bond rather than the Ti-N bond.

Scheme1.9

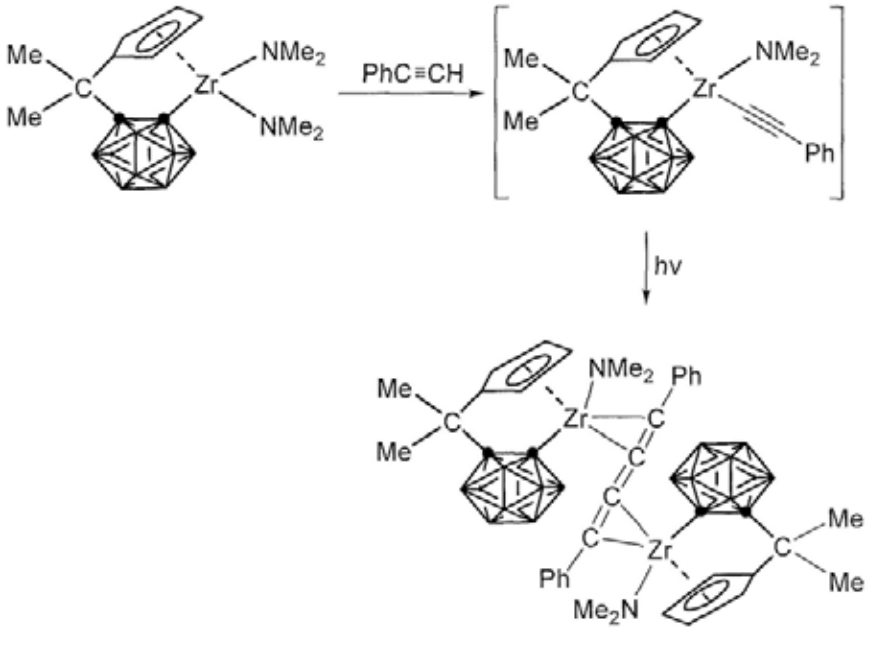


Scheme 1. 10



Treatment of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with 2 equiv of PhC≡CH affords, after recrystallization from THF/toluene, $\{[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)\}_2\{\eta^2:\eta^2\text{-}(PhC{=}C{=}C{=}CPh)\}$ (Scheme 1.11).[18] It is assumed that the acid-base reaction product zirconium alkynyl complex should be the intermediate and only one of the two NMe_2 groups is converted into PhCC unit, the other one remains intact even 2 equiv of PhCCH were used.

Scheme 1. 11



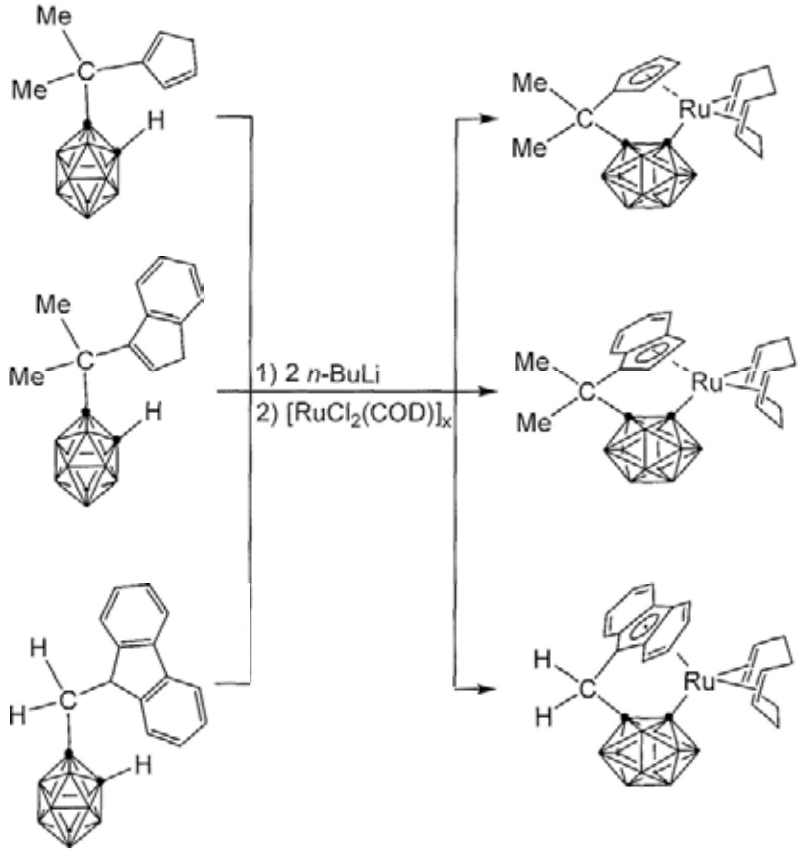
1.1.2 Organoruthenium Complexes

Carbon-carbon bond-forming reactions have attracted a great interest for their many applications in industrial and synthetic processes.[19] This type of conversion is catalyzed mainly by transition-metal complexes. Among them, ruthenium-catalyzed ring closing metathesis, and C-C bond-forming reactions are extensively developed in last two decades.[20] Ruthenium half-sandwich complexes of the type $(\eta^5\text{-}C_5R_5)RuXL_2$ are effective catalysts for C-C bond forming reactions[20f,21] such as coupling reactions of C≡C and C=C bonds to produce functional dienes,[20e,20g] head to head coupling of alkynes to form dienes and cyclobutenes[22,23] or the sequential coupling of alkynes generating aromatic compounds,[24] and double addition of carbene to alkynes and enynes to generate dienes and bicyclo[3.1.0]hexane derivatives.[25]

On the other hand, ruthenium half-sandwich complexes, in which a cyclopentadienyl ligand is tethered to a donor atom, are received much less attention.[26] The tethered donor atom in Cp-D chelating ligands can prevent rotation of Cp ring and allow the planar chirality to be exploited in an efficient discrimination, through a strong coordination to Ru atom, or can temporarily and reversibly coordinate to a Ru atom while stabilizing highly reactive, electronically and sterically unsaturated species,[27] to meet the requirements of various catalytic processes. A carbon-bridged cyclopentadienyl-carboranyl ligand[8,9,10] is expected to change the properties of the resulting Ru catalysts. Organoruthenium complexes incorporating linked cyclopentadienyl-carboranyl ligands are synthesized and studied in recent years.

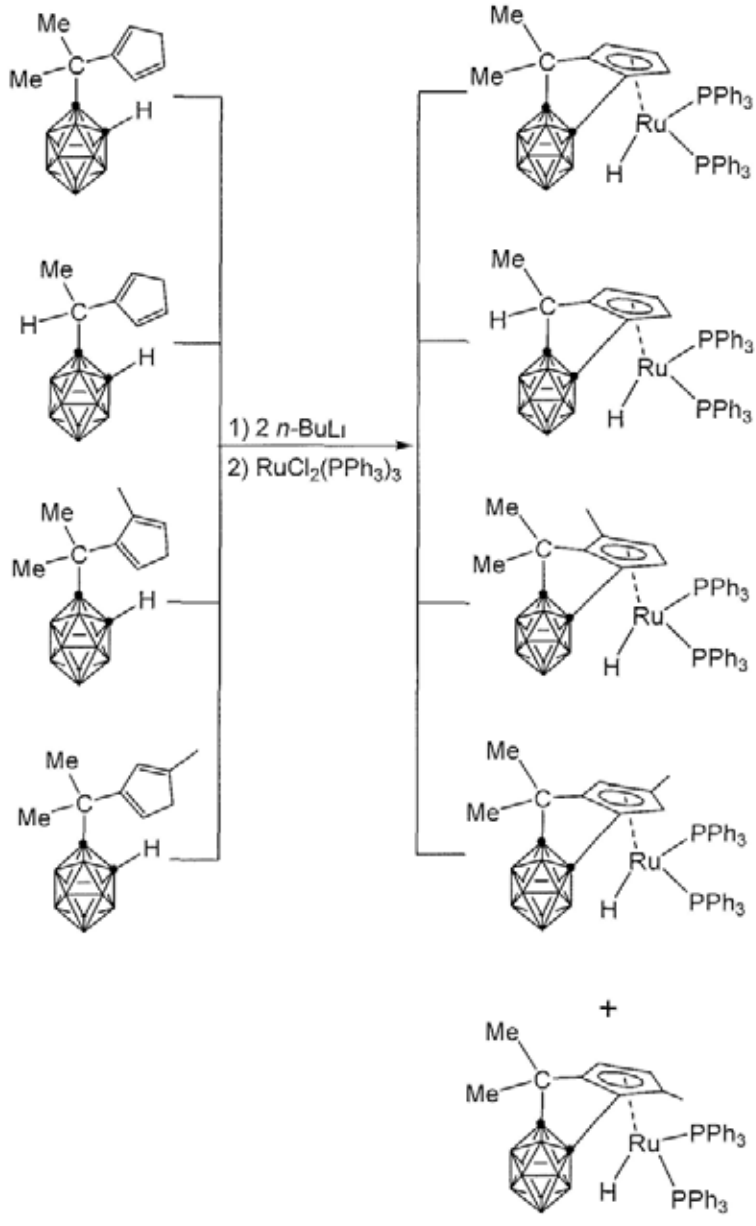
Just like the group 4 metal complexes, the ruthenium complexes $[R_2C(L)(C_2B_{10}H_{10})]Ru(COD)$ (R = CH_3, L = C_5H_4, C_9H_6; R = H, L = $C_{13}H_8$) can be prepared by the reaction of dilithium salts of the ligands $Li_2[R_2C(L)(C_2B_{10}H_{10})]$ with $[RuCl_2(COD)]_x$ in THF (Scheme 1.12).[10]

Scheme 1.12



Interestingly, when $RuCl_2(PPh_3)_3$ was treated with the dilithium salts of the bridged cyclopentadienyl-carboranyl ligands in THF, the Ru hydride complexes bearing doubly-linked cyclopentadienyl-carboranyl ligands are formed because of the steric hindrance of PPh_3 (Scheme 1.13).[28,29]

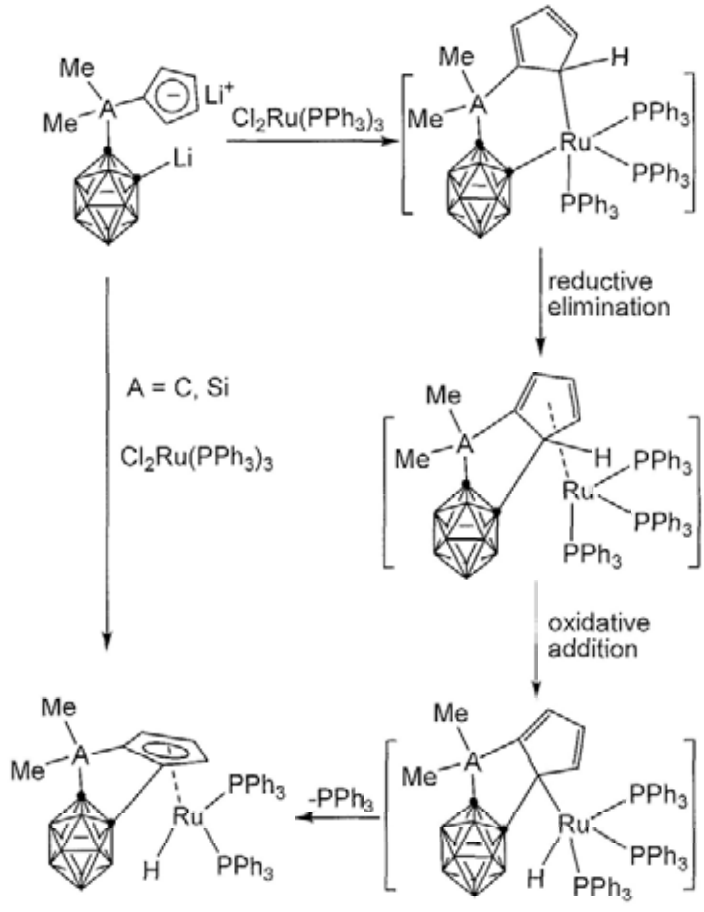
Scheme 1.13



A possible reaction pathway is proposed and shown in Scheme 1.14. Reaction of the dilithium salts of the ligands with $RuCl_2(PPh_3)_3$ gives the first intermediate $[\eta^1{:}\sigma\text{-}Me(R^1)A(C_5H_4)(C_2B_{10}H_{10})]Ru(PPh_3)_3$. Reductive elimination leads to the

formation of a new C(cage)-C(ring) bond and [η^4-Me(R^1)A(C_5H_4)($C_2B_{10}H_{10}$)]Ru(PPh_3)$_3$. Oxidative addition produces the species [η^1-Me(R^1)A(C_5H_3)($C_2B_{10}H_{10}$)]RuH(PPh_3)$_3$, followed by the dissociation of PPh_3 and haptotropic shift from η^1 to η^5 to yield the final product.[29]

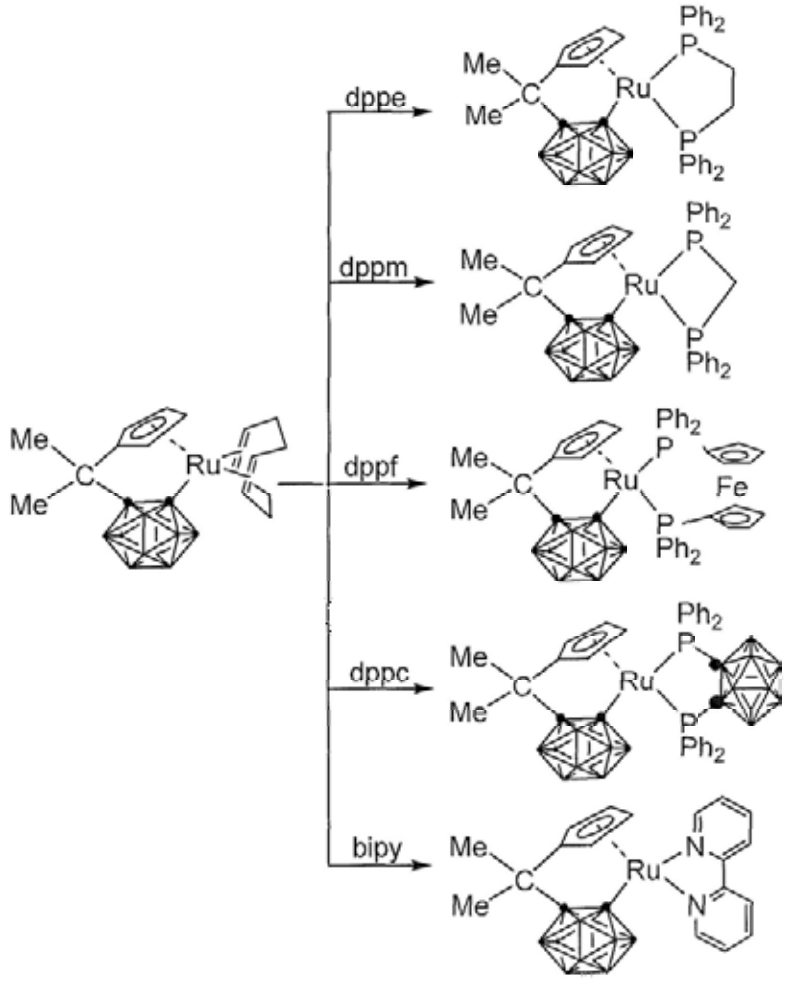
Scheme 1.14



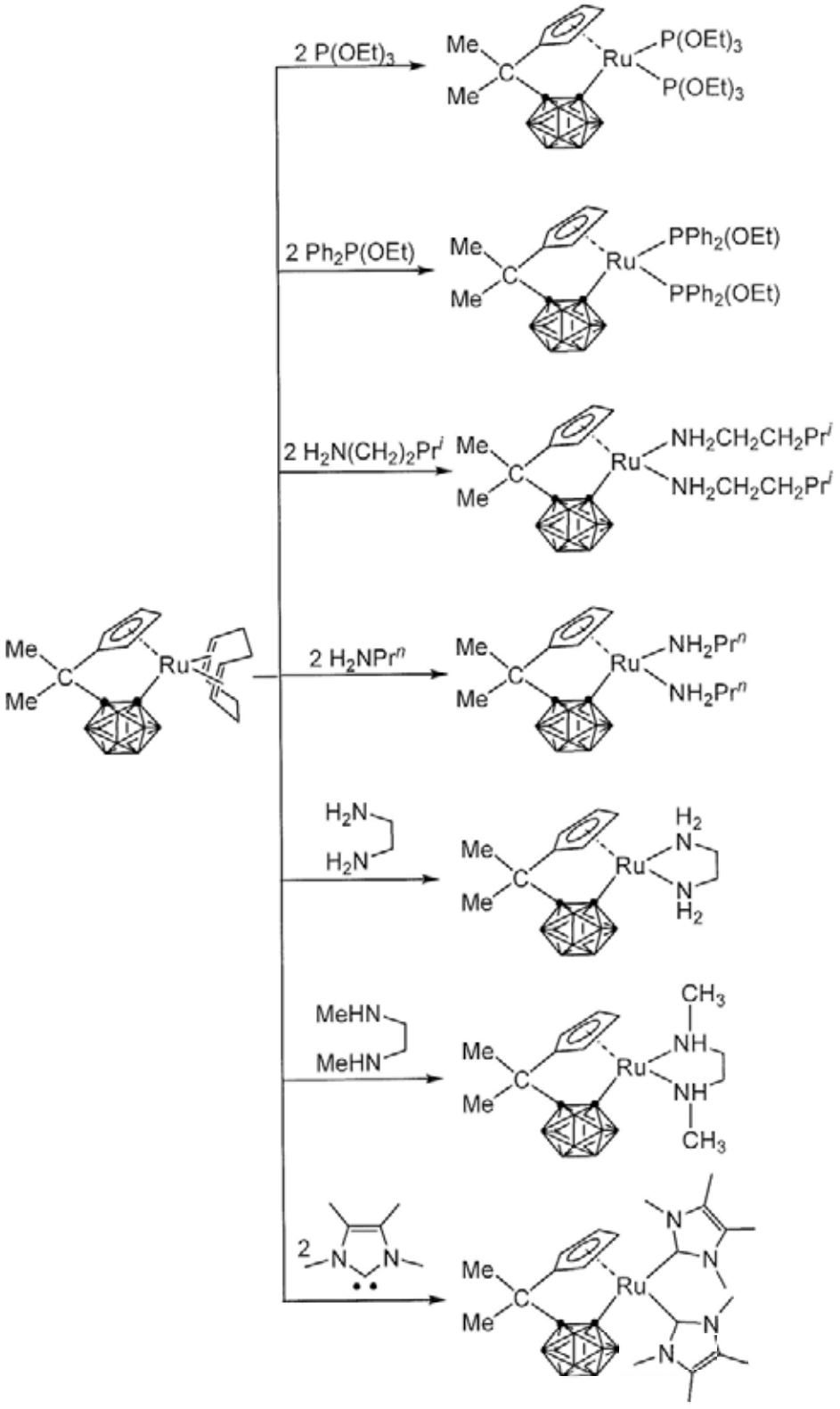
The labile COD ligand in LRuCl(COD) (L = Cp, C_9H_7) can usually be easily replaced by different tertiary phosphines.[30] It is noted that in the above ruthenium complexes, COD cannot be replaced by PR_3 (R = Ph, Cy) with large cone angles even in

refluxing THF solution because of the steric hindrance of phosphines. But it can be replaced by bidentate tertiary phosphines such as dppe (1,2-bis(diphenylphosphino)ethane), dppm (bis(diphenylphosphino)methane), dppc (1,2-$(Ph_2P)_2$-1,2-$C_2B_{10}H_{10}$), dppf (1,1'-bis(diphenylphosphino)ferrocene) and bidentate ligand 2,2′-bipyridine (bipy) (Scheme 1.15),[10] and Lewis bases such as amines, diamines, carbene, phosphates and small phosphines (Scheme 1.16).[31]

Scheme 1.15

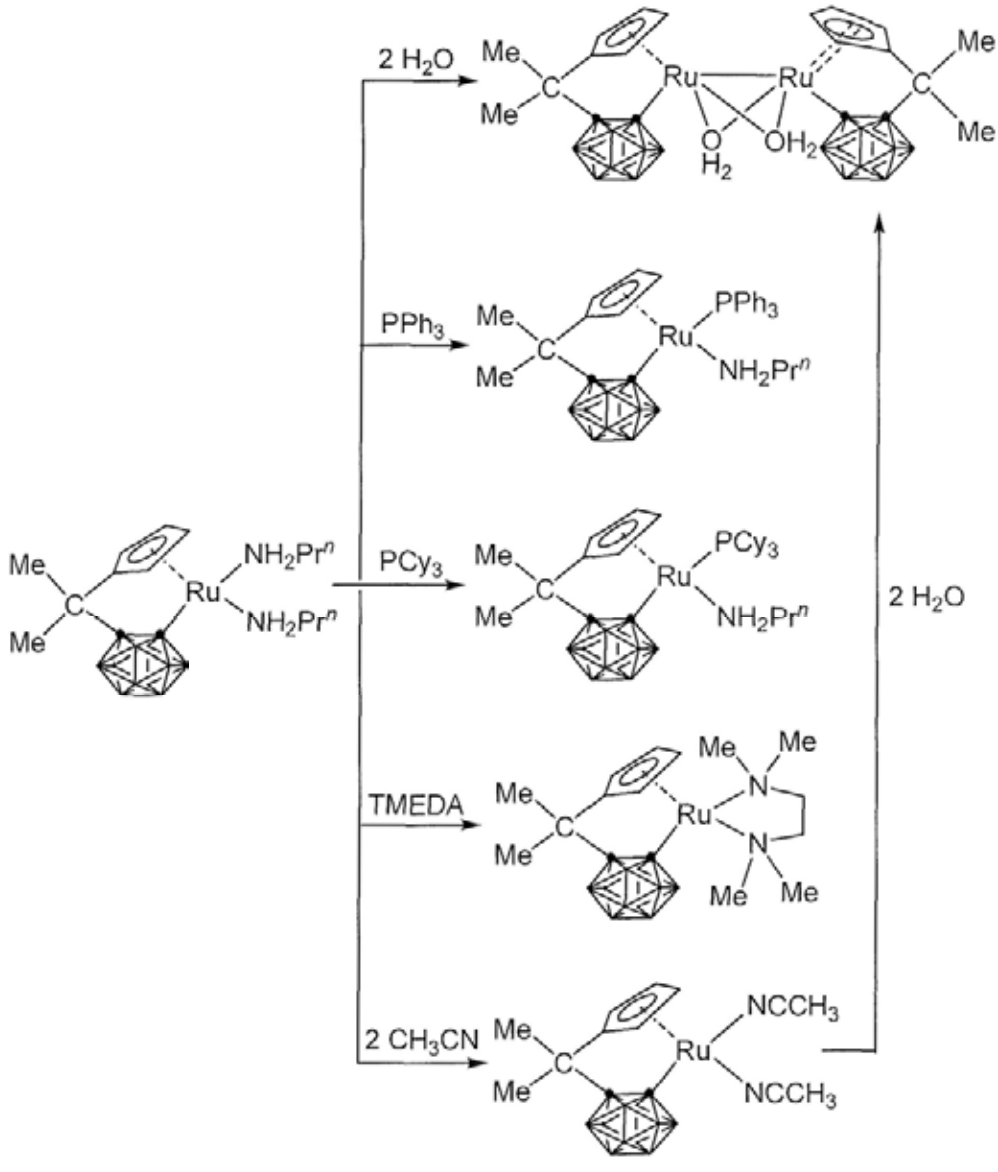


Scheme 1.16


2 P(OEt)3
2 Ph2P(OEt)
2 H2N(CH2)2Pri
2 H2NPrn
H2N
H2N
MeHN
MeHN
2
Me
C
Me
Ru
P(OEt)3
P(OEt)3
PPh2(OEt)
PPh2(OEt)
NH2CH2CH2Pri
NH2CH2CH2Pri
NH2Prn
NH2Prn
H2
N
N
H2
CH3
NH
NH
CH3
N
N
N
N

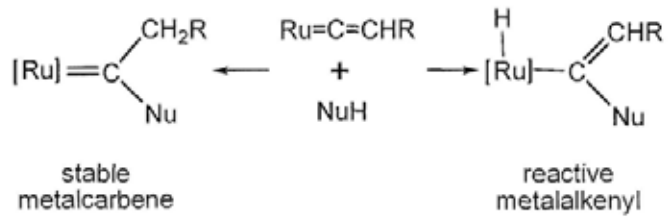
It is interesting to note that NH_2Pr^n ligand in $[R_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)_2$ complex can be easily replaced by nitriles, small phosphines, and TMEDA to give the corresponding coordination complexes, respectively (Scheme 1.17).[31]

Scheme 1.17

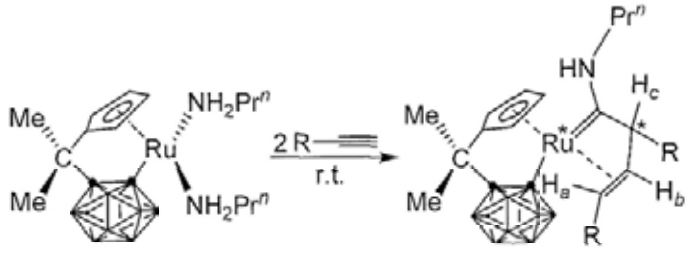


Ru-vinylidene complexes are important intermediates[32] in the catalytic reactions including dimerization of alkynes[33] and addition of nucleophiles to alkynes.[34] The reactivity of vinylidene metal complexes has been well studied in order to understand the reaction mechanism and to develop new catalytic reactions. It has been documented that Ru=C_α=CHR contain an electrophilic α-carbon atom which readily reacts with nucleophiles to form either stable metalcarbenes complexes or reactive metalalkenyls complexes (Scheme 1.18).[32h] These two types of metal complexes are very different in reactivity. Thus, the question arises as to what factor controls these nucleophilic reactions. Because of the inertness of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru$ moiety, during the reaction of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)_2$ with alkynes, stable Ru-vinylidene complexes can be formed, in which it was found that the electronic properties of the alkynes dominate the product of the reactions. Electron-rich alkynes favor the formation of Ru-carbene complexes whereas electron-deficient alkynes result in the formation of Ru-alkenyl intermediates (Scheme 1.19 and Scheme 1.20).[35] And also the solvents play a role in the reaction of Ru complex with phenylacetylene (Scheme 1.21).[35]

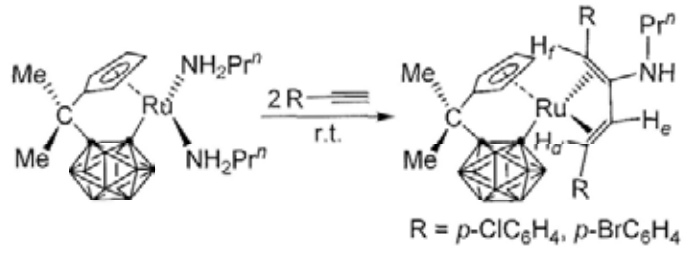
Scheme 1.18



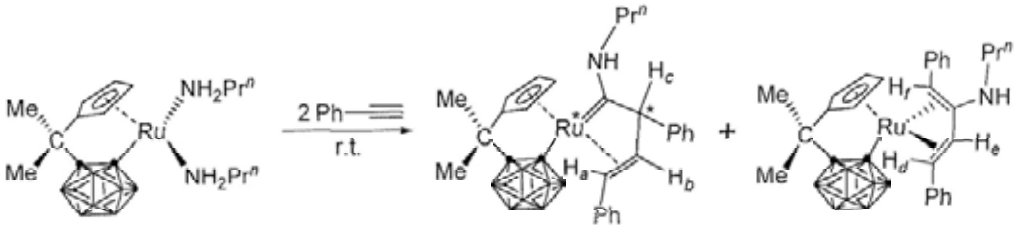
Scheme 1.19



Scheme 1. 20



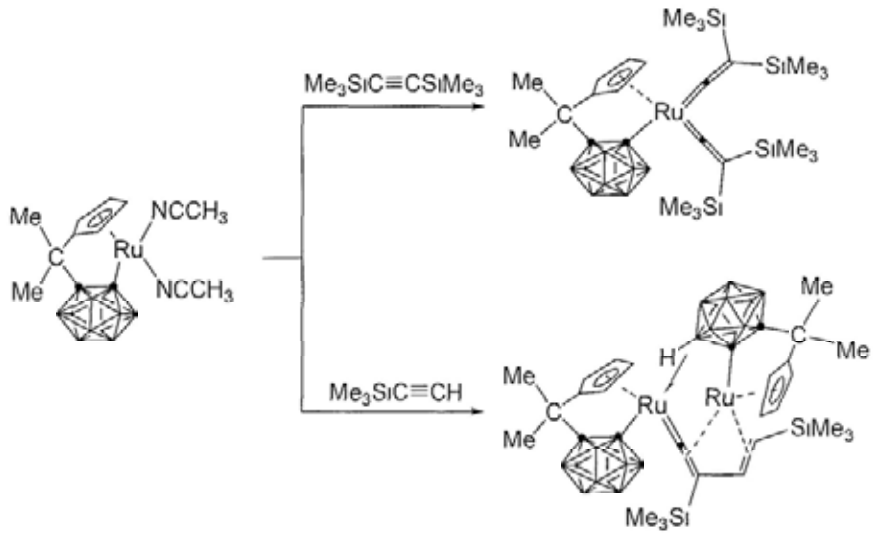
Scheme 1.21



solvent	a : b
CH_2Cl_2	76 : 24
toluene	32 : 68

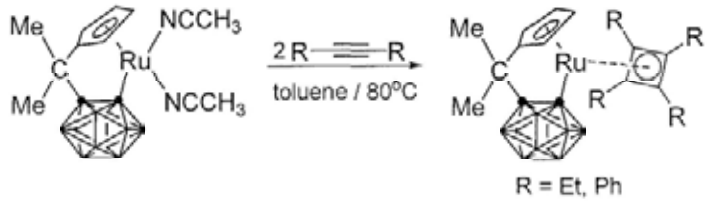
Unlike $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)_2$, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ reacts with TMS substituted alkynes, producing ruthenium bisvinylidene and vinylvinylidene complexes (Scheme 1.22).[36]

Scheme 1.22

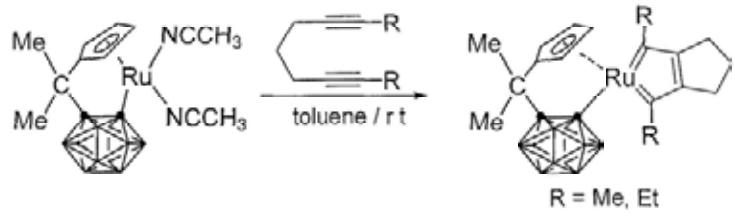


When $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ reacts with internal alkynes (3-hexyne and diphenylacetylene), ruthenium cyclobutadiene complexes are formed (Scheme 1.23). Treatment of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ with 2,7-nonadiyne or 3,8-undecadiyne affords ruthenacyclopentatriene complexes (Scheme 1.24).[36]

Scheme 1.23

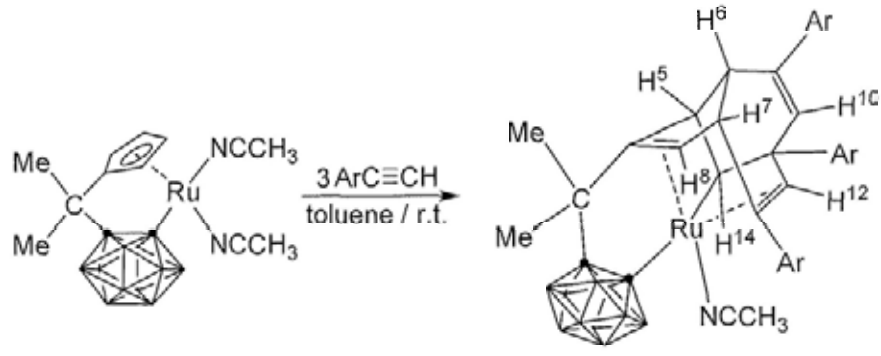


Scheme 1.24



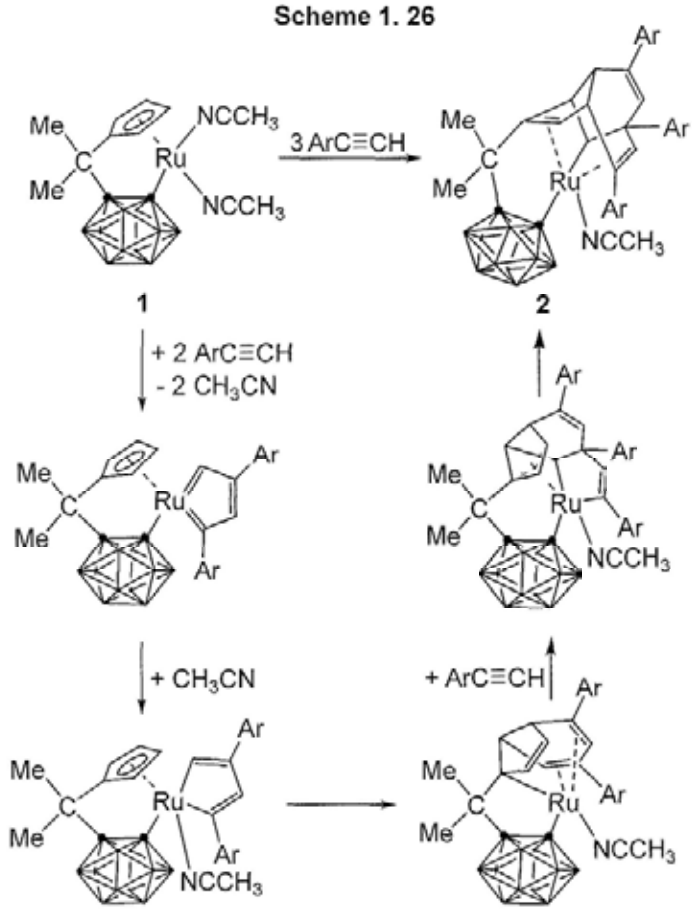
Reaction of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($NCCH_3$)$_2$ with 3 equiv of ArC≡CH in toluene at room temperature affords unexpected ruthenium complexes bearing a tricyclic moiety [η^4:σ-$Me_2C(C_{11}H_7Ar_3)(C_2B_{10}H_{10})$]Ru($NCCH_3$) (Ar = Ph, tolyl, 4-$ClC_6H_4$, and 4-$BrC_6H_4$) (Scheme 1.25).[37] The reaction mechanism was proposed (Scheme 1.26) and confirmed by DFT calculation.[37]

Scheme 1. 25



Ar = Ph, tolyl, 4-ClC_6H_4, 4-BrC_6H_4

Scheme 1. 26



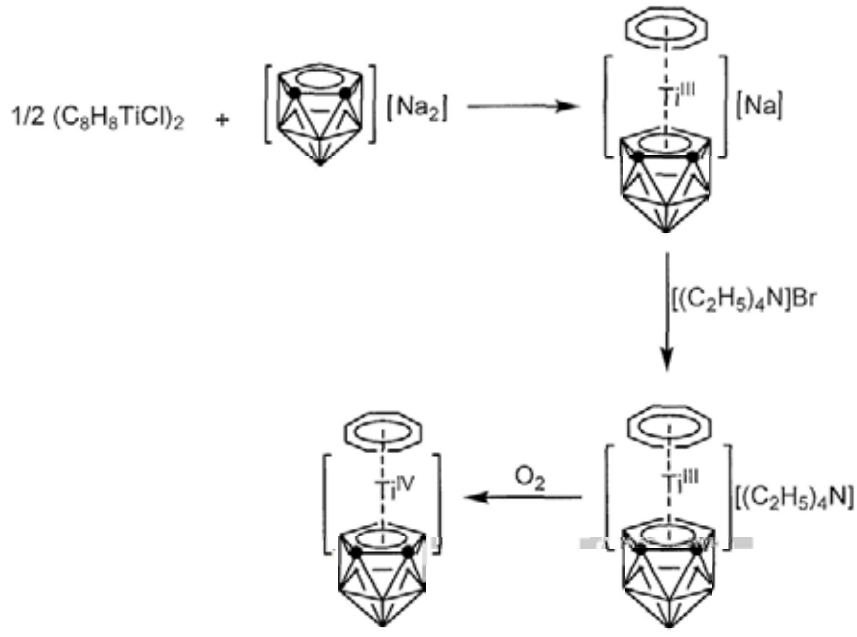
1.2 Group 4 Metal Complexes Bearing Dicarbollide Systems.

Ligands are the essential part of coordination/organometallic complexes. They control the stability, solubility, chemical and physical properties of the resultant metal complexes. Cyclopentadienyl and dicarbollide represent the two most important classes of organic and inorganic π ligands in organometallic chemistry. The latter ($C_2B_9H_{11}^{2-}$) receives much interest in recent decades because it is isoloble with Cp^- and they have different negative charge. Many group 4 metallacarboranes have been synthesized and studied.

1.2.1 Group 4 Metal Complexes with $C_2B_9H_{11}^{2-}$ Ligand

Hawthorne reported some titanacarboranes bearing $C_2B_9H_{11}^{2-}$ ligands in 1976.[37] Reaction of $(C_8H_8TiCl)_2$ with $Na_2C_2B_9H_{11}$ affords Na[3-(η^8-C_8H_8)-3-Ti-1,2-$C_2B_9H_{11}$]. After removal of solvent and addition of $[(C_2H_5)_4N]Br$, $[(C_2H_5)_4N]$[3-(η^8-C_8H_8)-3-Ti-1,2-$C_2B_9H_{11}$] is isolated (Scheme 1.27).[37] This complex can be oxidized to 3-(η^8-C_8H_8)-3-Ti-1,2-$C_2B_9H_{11}$ (Scheme 1.27).[37] Similarly, $[(C_2H_5)_4N]$[2-(η^8-C_8H_8)-2-Ti-1,7-$C_2B_9H_{11}$] and 2-(η^8-C_8H_8)-2-Ti-1,7-$C_2B_9H_{11}$ are prepared from 1,7-$C_2B_9H_{12}^-$ and $(C_8H_8TiCl)_2$.[37]

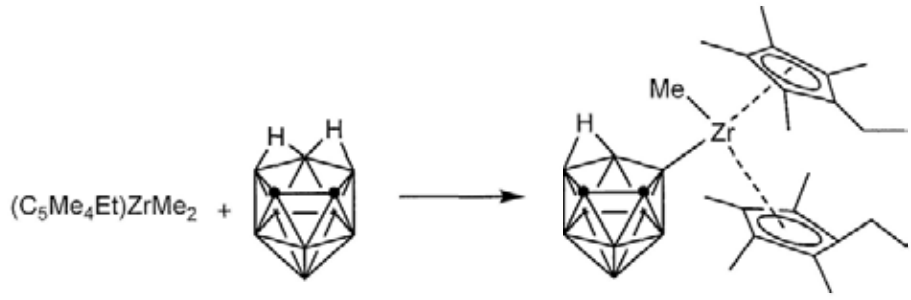
Scheme 1.27



Neutral carborane $C_2B_9H_{13}$ contains two acidic protons which is strong enough to cleave M-C bonds of electrophilic metals.[38,39,40] Treatment of $C_2B_9H_{13}$ with

$(C_5Me_5)_2ZrMe_2$ or $(C_5Me_4Et)_2ZrMe_2$ in pentane affords $(C_5Me_5)_2ZrMe(C_2B_9H_{12})$ or $(C_5Me_4Et)_2ZrMe(C_2B_9H_{12})$, respectively (Scheme 1.28).[38]

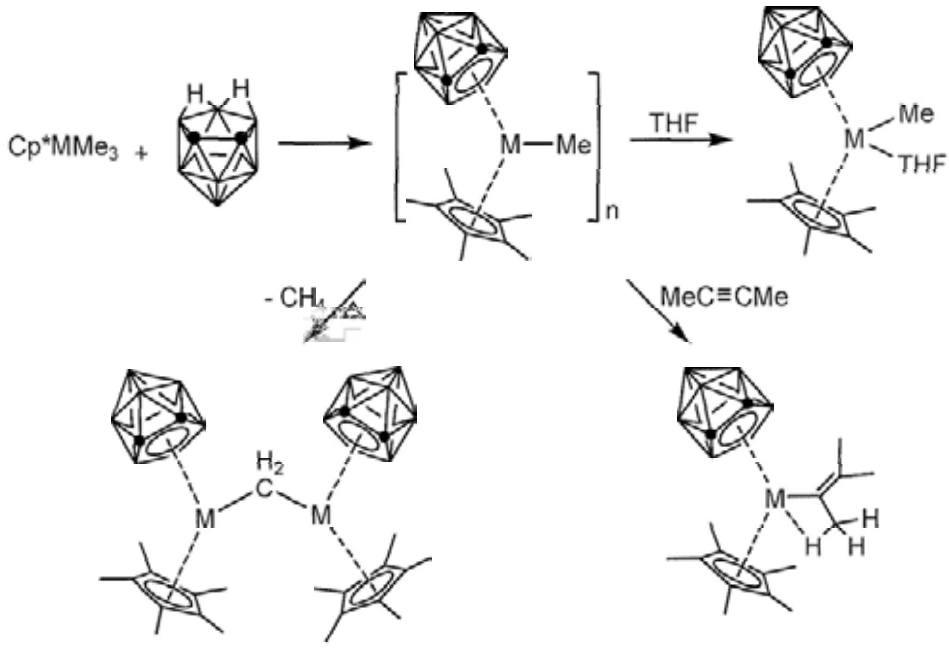
Scheme 1.28



In 1991, Jordan and coworkers performed an equimolar reaction of $C_2B_9H_{13}$ with $Cp^*M(Me)_3$ in aromatic solvent yielding $[(Cp^*)(C_2B_9H_{11})M(Me)]_n$ (M = Zr, Hf).[40] The methyl complexes $Cp^*_2(C_2B_9H_{11})_2M_2Me_2$ react with 2-butyne via single insertion to yield the monomeric alkenyl complexes $Cp^*(C_2B_9H_{11})M[C(Me)=CMe_2]$ (M = Zr, Hf).[40] These monomeric alkenyl complexes do not undergo further insertion reaction with 2-butyne, and $Cp^*(C_2B_9H_{11})M[C(Me)=CMe_2]$ does not coordinate THF. Complexes $Cp^*_2(C_2B_9H_{11})_2M_2Me_2$ form THF adducts $Cp^*(C_2B_9H_{11})M(Me)(THF)$ (M = Zr, Hf) which do not undergo exchange with free THF on the NMR time scale at 23°C (Scheme 1.29).[40] Complexes $Cp^*_2(C_2B_9H_{11})_2M_2Me_2$ (M = Zr, Hf) are moderately active ethylene polymerization catalysts.[40] They can also catalyze the oligomerization of propylene to 2-methylpentene and 2,4-dimethylheptene as major products. Isobutene is detected as a minor product by GC. This product distribution is characteristic of an insertion/β-H elimination process.

Thermolysis of $Cp^*_2(C_2B_9H_{11})_2Zr_2Me_2$ at 45°C in toluene-d_8 quantitatively yields the methylidene-bridged complex $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$ and methane. $Cp^*_2(C_2B_9H_{11})_2Hf_2Me_2$ undergoes a slower methane elimination reaction at 75°C to yield $[(Cp^*)(C_2B_9H_{11})Hf]_2(\mu\text{-}CH_2)$ (Scheme 1.29).[40]

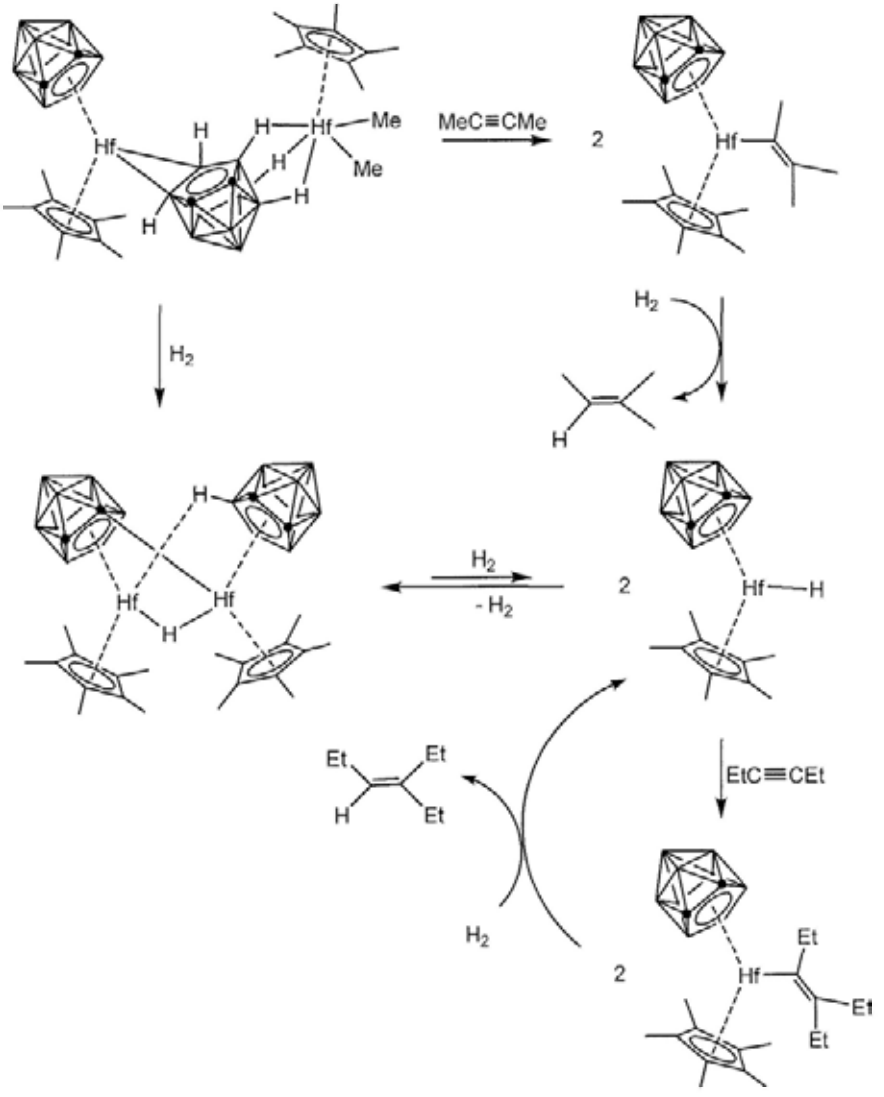
Scheme 1.29



In 1995, Jordan and his coworkers found that $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfMe$ has an unusual bridging $C_2B_9H_{11}^{2-}$ bonding mode and forms a dinuclear metallacarborane $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^2\text{:}\eta^5\text{-}C_2B_9H_{11})Hf(\eta^5\text{-}C_5Me_5)Me_2$.[41] Reaction of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^2\text{:}\eta^5\text{-}C_2B_9H_{11})Hf(\eta^5\text{-}C_5Me_5)Me_2$ with H_2 affords the novel hafnium carboranyl hydride complex $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_2B_9H_{11})Hf(\eta^5\text{-}C_5Me_5)(H)$, in which the two metal centers are linked by a C-metalated $\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_2B_9H_{11}$ ligand and Hf-H-Hf and B-H-Hf

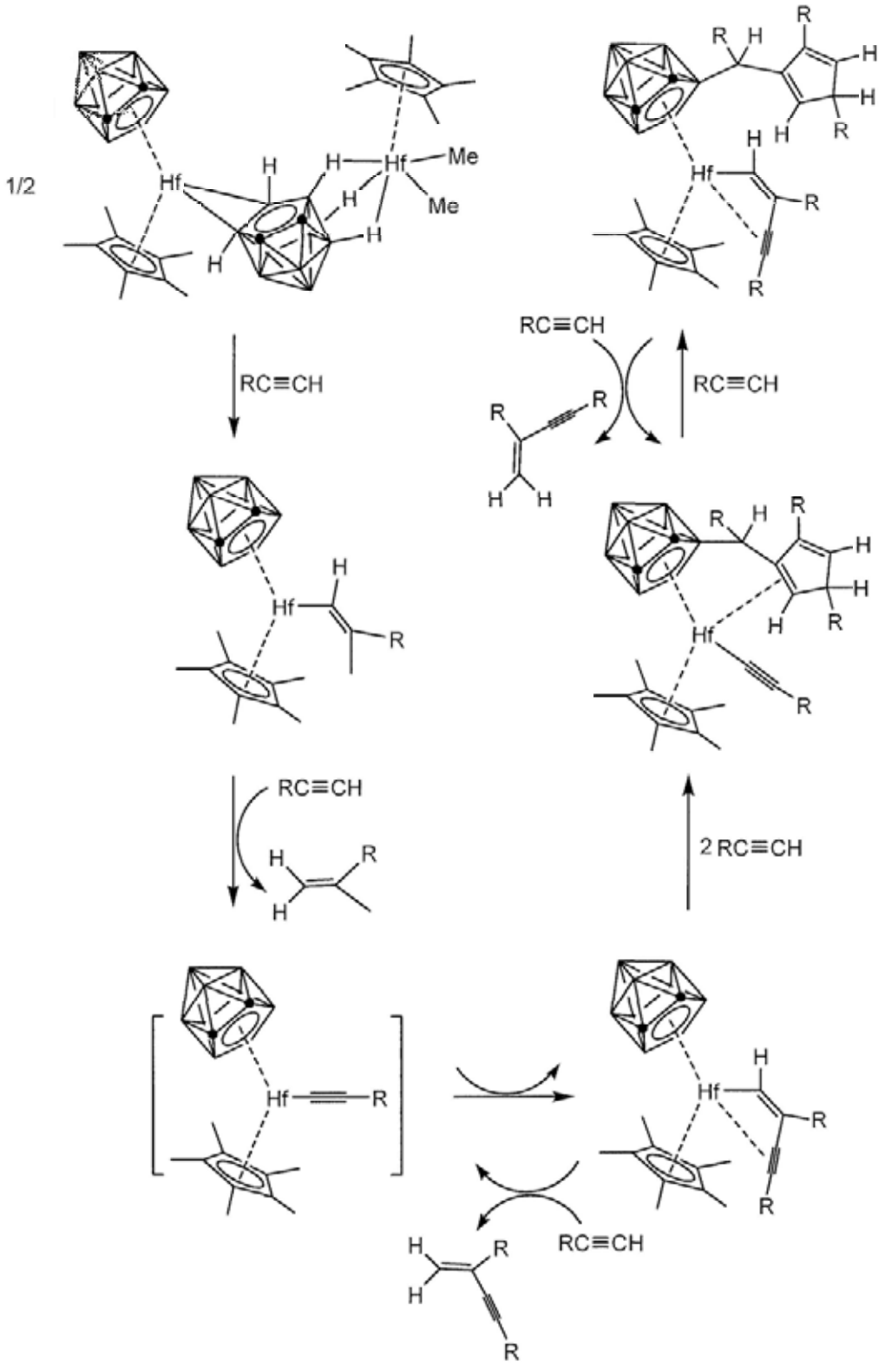
bridges. Complex $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_2B_9H_{11})Hf(\eta^5\text{-}C_5Me_5)(H)$ can catalyze the hydrogenation of internal alkynes to *cis*-alkenes. It is proposed that the active species in this reaction is the mononuclear hydride $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(H)$, which is formed by hydrogenolysis of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_2B_9H_{11})Hf(\eta^5\text{-}C_5Me_5)(H)$ and undergoes rapid alkyne or alkene insertion and Hf-C hydrogenolysis steps (Scheme 1.30).[42]

Scheme 1.30

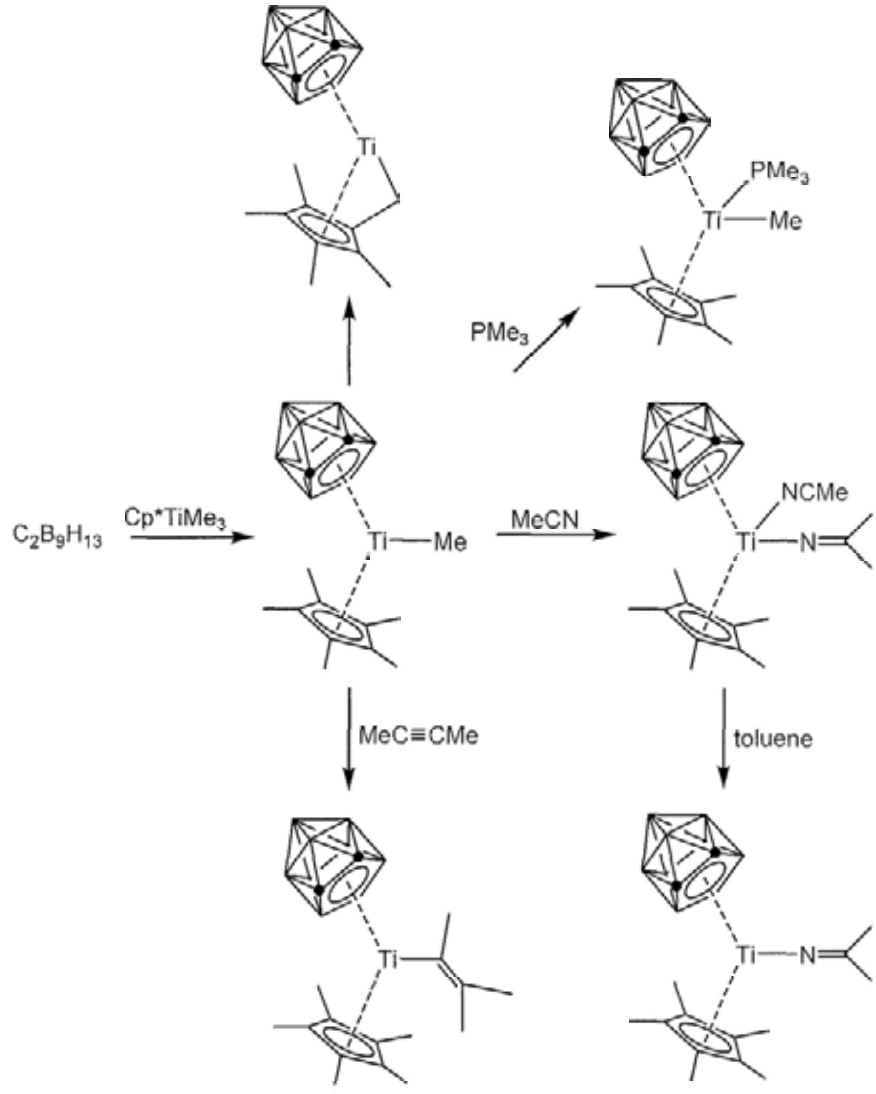


Reaction of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^2\text{:}\eta^5\text{-}C_2B_9H_{11})Hf(\eta^5\text{-}C_5Me_5)Me_2$ with alkyne to afford the alkenyl complex $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC(H)=CRMe$.[43] This species is not observed but is directly analogous to $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC(Me)=CMe_2$. It undergoes rapid σ-bond metathesis with alkyne to afford the unobserved alkynyl species $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC\equiv CR$ and $CH_2=CRMe$. $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC\equiv CR$ then undergoes rapid alkyne insertion to form $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC(H)=C(R)C\equiv CR$. Actually, $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC(H)=C(R)C\equiv CR$ can react with alkyne in two ways.[43] Simple σ-bond metathesis of it and alkyne results in the release of dimer 2,4-disubstituted 1-buten-3-yne, regeneration of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC\equiv CR$, and formation of one catalytic dimerization cycle. Alternatively, $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})HfC(H)=C(R)C\equiv CR$ can react with 2 equiv of alkyne by a more complex mechanism to afford $(\eta^5\text{-}C_5Me_5)[\eta^5\text{-}7\text{-}CH(R)(3,5\text{-}R_2\text{-}2\text{-}C_5H_3)\text{-}1,2\text{-}C_2B_9H_{10}]HfC\equiv CR$. This complex catalyzes the dimerization of alkyne by a second insertion/σ-bond metathesis cycle involving the unobserved alkenyl intermediate $(\eta^5\text{-}C_5Me_5)[\eta^5\text{-}7\text{-}CH(R)(3,5\text{-}R_2\text{-}2\text{-}C_5H_3)\text{-}1,2\text{-}C_2B_9H_{10}]HfC(H)=C(R)C\equiv CR$ (Scheme 1.31).[43]

Scheme 1. 31



Scheme 1.32



Jordan and his coworkers extended their studies to titanium dicarbollide species (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)TiR.[44] As shown in Scheme 1.32, treatment of $C_2B_9H_{13}$ with 1 equiv of $(C_5Me_5)TiMe_3$ affords a neutral complex (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)TiMe which is unstable and decomposes at 23°C to the fulvene complex (η^6-$C_5Me_4CH_2$)(η^5-$C_2B_9H_{11}$)Ti, and forms labile adduct with PMe_3. The structures of

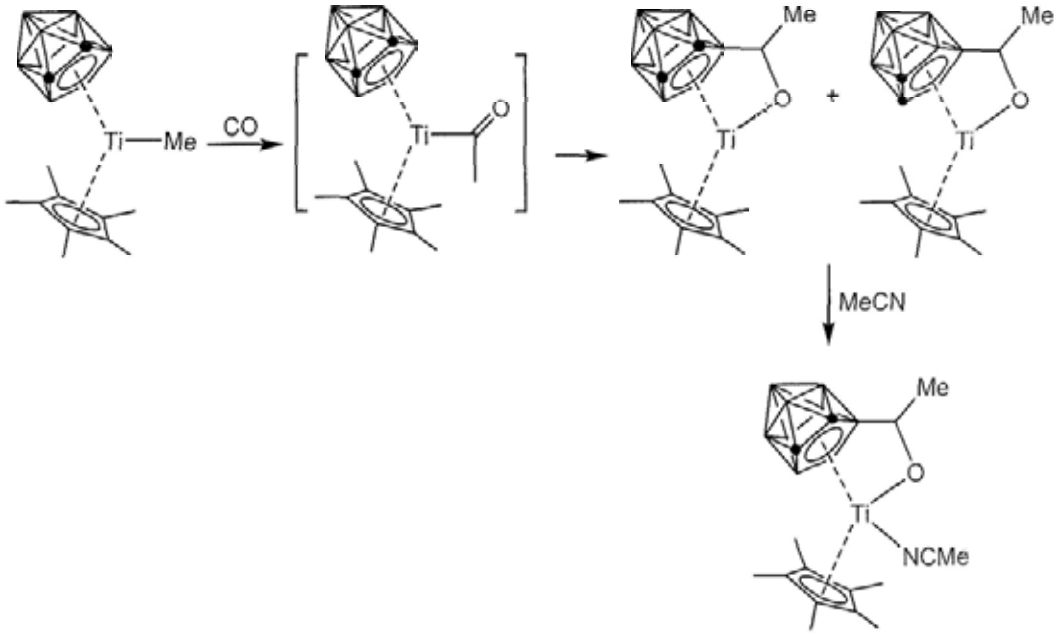
(η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)TiMe and (η^6-$C_5Me_4CH_2$)(η^5-$C_2B_9H_{11}$)Ti were recently characterized.[45] (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)TiMe inserts MeCN to form (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)Ti(N=CMe)(MeCN), which loses MeCN upon recrystallization from toluene to afford (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)Ti(N=CMe). (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)TiMe inserts 2-butyne, yielding (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)Ti(CMe=CMe_2).

Reaction of (η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)TiMe with CO (0.5-1atm) in toluene (-78 to 23°C) affords a mixture of two products, (η^5-C_5Me_5)(η^5:η^1-8-CHMeO-$C_2B_9H_{10}$)Ti and (η^5-C_5Me_5)(η^5:η^1-4-CHMeO-$C_2B_9H_{10}$)Ti (Scheme 1.33).[46] These two complexes both contain a linked carborane-alkoxide ligand but differ in the site of attachment of the -CHMeO- linker to the carborane cage. Complexes (η^5-C_5Me_5)(η^5:η^1-8-CHMeO-$C_2B_9H_{10}$)Ti and (η^5-C_5Me_5)(η^5:η^1-4-CHMeO-$C_2B_9H_{10}$)Ti do not interconvert under the reaction conditions. Treatment of a mixture of (η^5-C_5Me_5)(η^5:η^1-8-CHMeO-$C_2B_9H_{10}$)Ti and (η^5-C_5Me_5)(η^5:η^1-4-CHMeO-$C_2B_9H_{10}$)Ti with excess MeCN followed by recrystallization of the crude product from MeCN affords the acetonitrile adduct (η^5-C_5Me_5)(η^5:η^1-4-CHMeO-$C_2B_9H_{10}$)Ti(MeCN) (Scheme 1.33).[46]

The amine elimination between $C_2B_9H_{13}$ and M(NR_4) (M = Ti, Zr) affords the half-sandwich complexes (η^5-$C_2B_9H_{11}$)M(NR_2)$_2$(NHR_2) (R = Me, Et). Reaction of (η^5-$C_2B_9H_{11}$)Zr(NEt_2)$_2$($NHEt_2$) with 2 equiv of NH_2Et_2Cl, affords (η^5-$C_2B_9H_{11}$)$ZrCl_2$($NHEt_2$)$_2$ (Scheme 1.34).[47] Later, Jordan and his coworkers found that

$(\eta^5\text{-}C_2B_9H_{11})M(NEt_2)_2(NHEt_2)$ shows a high activity in ethylene polymerization in the presence of cocatalyst MAO.[48]

Scheme 1.33



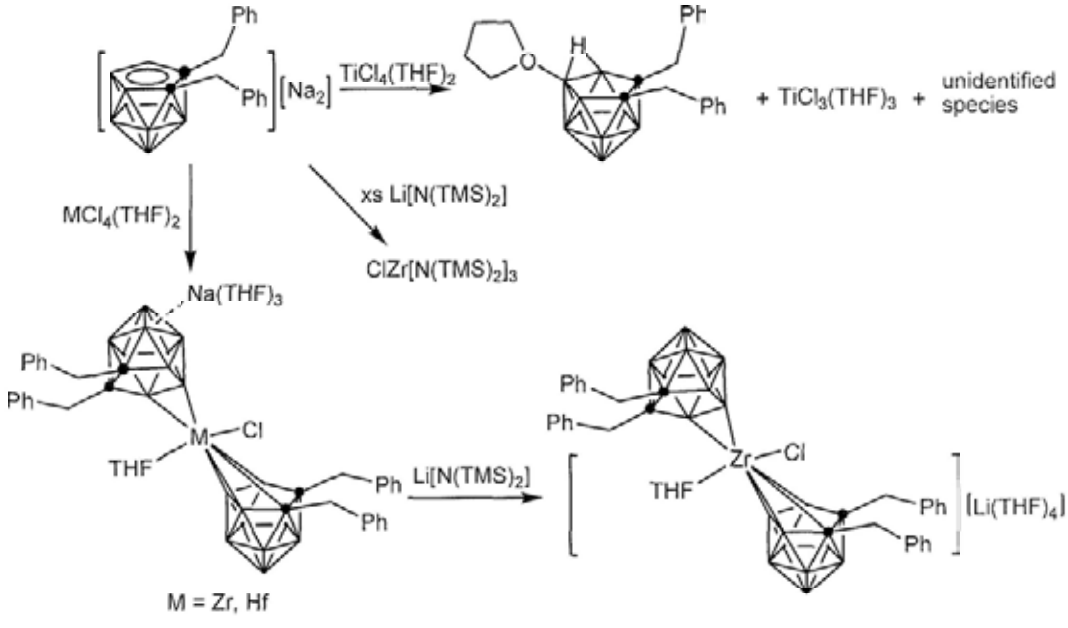
Scheme 1.34

M = Ti, Zr
R = Me, Et

Substituents on the carborane cage carbons affect not only bonding interactions between the group 4 metal ion and the C_2B_9 ligand but also the reactivity pattern of the

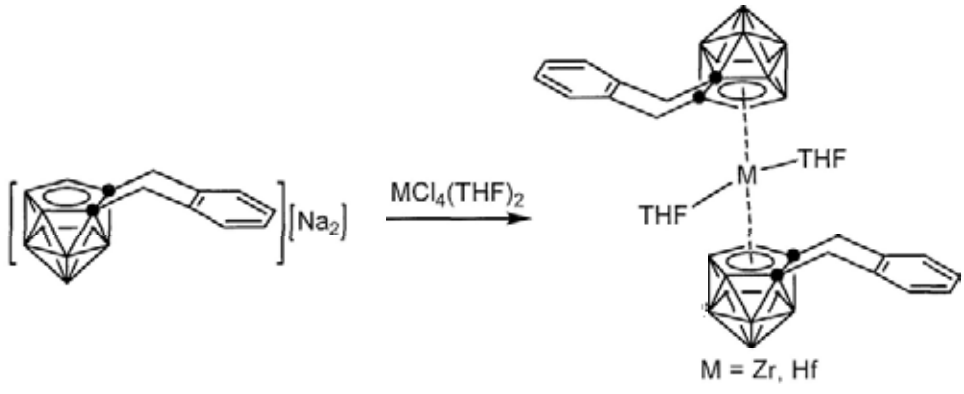
resulting metal complexes. Treatment of $MCl_4(THF)_2$ with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ in THF affords the bis(carboranyl) complexes $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2MCl(THF)\}\{Na(THF)_3\}$ (M = Zr, Hf) (Scheme 1.35).[49] Reaction of $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ with 1 equiv of $LiN(TMS)_2$ results in the replacement of a Na^+ by Li^+, giving the ionic complex $[\eta^3:\eta^2\text{-}\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)][Li(THF)_4]$. $ClZr[N(TMS)_2]_3$ is isolated from the reaction of $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ with excess $LiN(TMS)_2$ (Scheme 1.35).[49] Under the same reaction conditions, interaction of $TiCl_4(THF)_2$ with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ leads to the isolation of a small amount of $TiCl_3(THF)_3$ and B-substituted zwitterionic compound $(C_6H_5CH_2)_2C_2B_9H_9(THF)$ (Scheme 1.35).[49]

Scheme 1.35



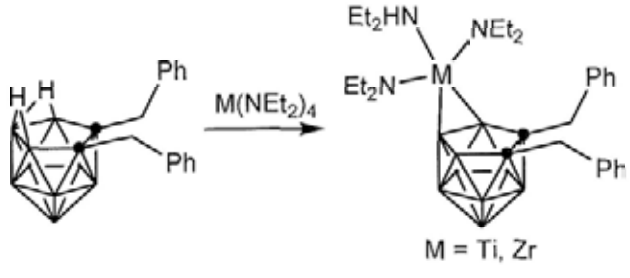
Treatment of $MCl_4(THF)_2$ with 1 equiv of less bulky yet rigid $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_x$ affords a bent-metallocene type of complex, $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]_2M(THF)_2$ (M = Zr, Hf) (Scheme 1.36).[49]

Scheme 1.36



An equimolar reaction between $M(NEt_2)_4$ and $(C_6H_5CH_2)_2C_2B_9H_{11}$ affords the half-sandwich complexes $[\eta^2\text{-}(C_6H_5CH_2)_2C_2B_9H_9]M(NEt_2)_2(NHEt_2)$ (M = Ti, Zr) (Scheme 1.37).[49] It is believed that the additional $N(p_\pi)\rightarrow M(d_\pi)$ interactions stabilize this type of complex.

Scheme 1.37

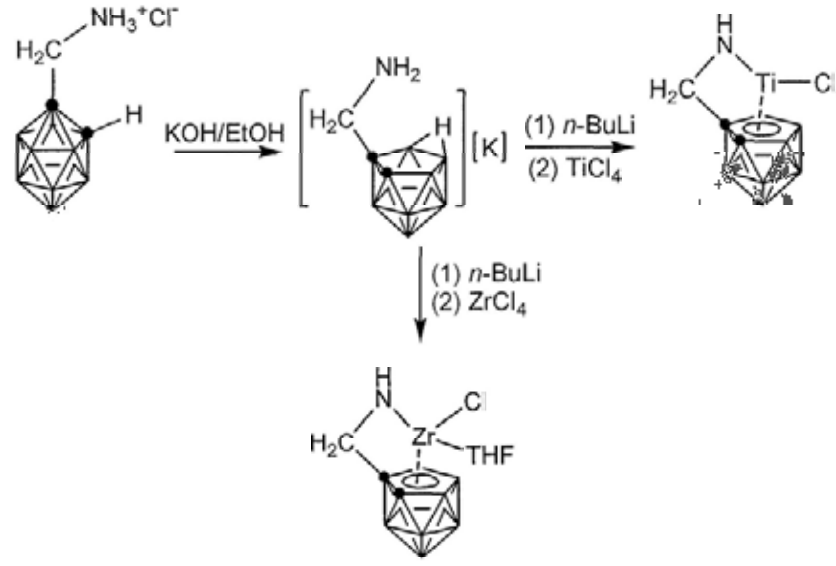


1.2.2 Group 4 Metal Complexes Bearing Dicarbollide Ligands with Appended Hetero-Atoms.

Constrained-geometry catalysts bearing cyclopentadienyl ligands tethered to a heteroatom have received great interest. Similarly group 4 metal complexes with isoloble dicarbollyl-amido ligands have also drawn much attention.

Hosmane and his coworkers reported that the 1:1 molar ratio reaction of the potassium/dilithium triple salt of the [*nido*-7-$NHCH_2$-7,8-$C_2B_9H_{10}$]$^{3-}$ with anhydrous MCl_4 in THF affords half-sandwich metallacarboranes, [η^5:η^1-$C_2B_9H_{10}$-CH_2NH]$MCl(THF)_n$ (M = Zr, n = 1; Ti, n = 0) (Scheme 1.38).[50]

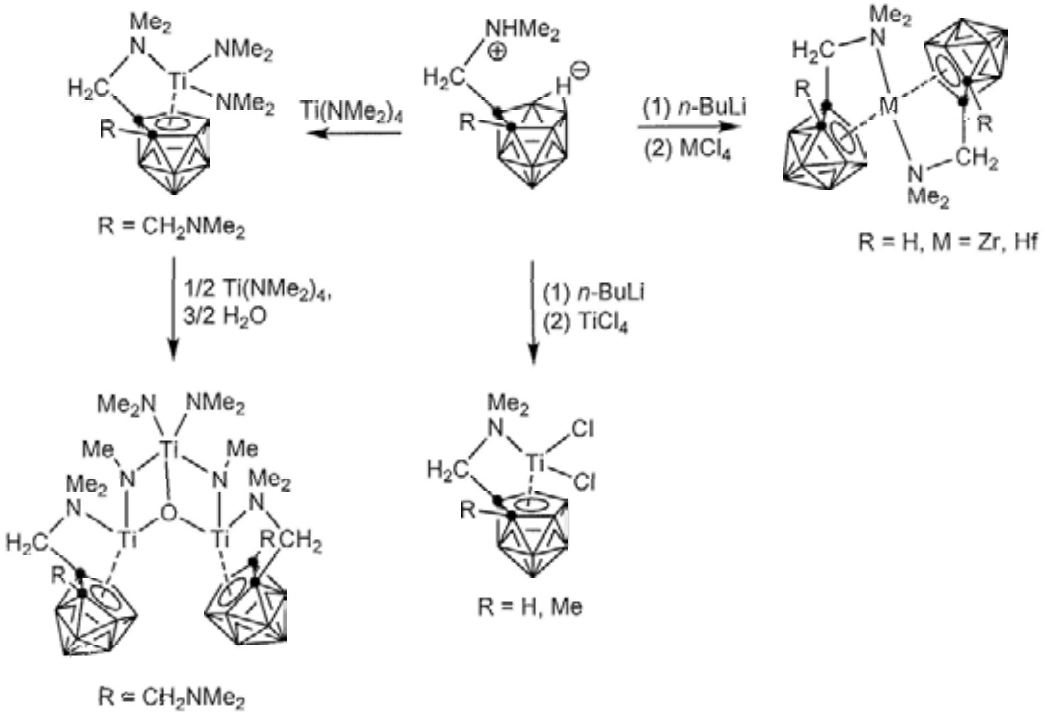
Scheme 1.38



Kang and his coworkers reported that treatment of [*nido*-7-NMe_2CH_2-7,8-$C_2B_9H_{11}$]$^-$ with 1 equiv of *n*-BuLi and subsequent reaction with $TiCl_4$ in toluene affords the

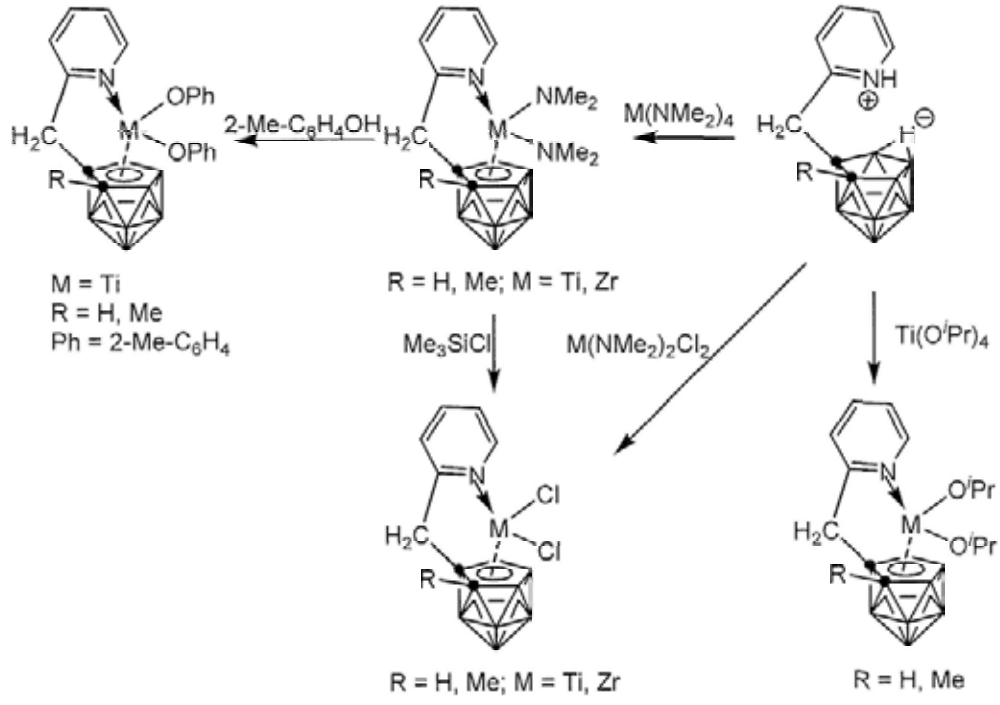
half-sandwich metallacarborane $[\eta^5:\eta^1\text{-}C_2B_9H_{10}\text{-}CH_2NMe_2]TiCl_2$, which shows a moderate activity in ethylene polymerization in the presence of MMAO (Scheme 1.39).[51] Treatment of $[nido\text{-}7\text{-}NMe_2CH_2\text{-}7,8\text{-}C_2B_9H_{11}]^-$ with 1 equiv of *n*-BuLi and subsequent reaction with 1 equiv of MCl_4 in toluene affords full-sandwich metallacarboranes, $[\eta^5:\eta^1\text{-}C_2B_9H_{10}\text{-}CH_2NMe_2]_2M$ (M = Zr, Hf) (Scheme 1.39).[51] Interaction of zwitterionic complex *nido*-7-$NHMe_2CH_2$-8-NMe_2CH_2-7,8-$C_2B_9H_{11}$ with $Ti(NMe_2)_4$ in toluene affords a half-sandwich metallacarborane $\{\eta^5:\eta^1\text{-}(NMe_2CH_2)C_2B_9H_9CH_2NMe_2\}Ti(NMe_2)_2$ (Scheme 1.39).[51] Complex $\{\eta^5:\eta^1\text{-}(NMe_2CH_2)C_2B_9H_9CH_2NMe_2\}Ti(NMe_2)_2$ reacts with 0.5 equiv of $Ti(NMe_2)_4$ and 1.5 equiv of H_2O in toluene to form a novel trimetallic complex $[\eta^5:\eta^1\text{-}\{(NMe_2CH_2)C_2B_9H_9CH_2NMe_2\}Ti(NMe)]_2\text{-}\mu^3\text{-}O\text{-}Ti(NMe_2)_2$ (Scheme 1.39).[51]

Scheme 1. 39



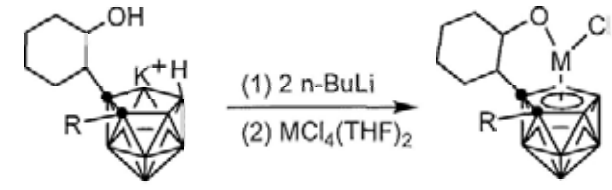
Picolyl substituted dicarbollyl ligand was also reported by Kang and coworkers. The homologous series of picolyldicarbolly group 4 metal complexes ($Dcab^{Py}$)ML_2 (L = Cl, M = Ti, Zr, L = NMe_2, M = Ti, Zr) are prepared by reaction of 1:1 mixture of picolyldicarbollyl and $M(NMe_2)_2Cl_2$ or $M(NMe_2)_4$ in toluene at room temperature (Scheme 1.40).[52] Treatment of picolyldicarbollyl group 4 metal amides with 3.3 equiv of TMSCl in CH_2Cl_2 affords the desired dichloride derivatives, ($Dcab^{Py}$)MCl_2 (Scheme 1.40).[52] The titanium oxide complexes ($Dcab^{Py}$)$Ti(OR)_2$ (R = ^{i}Pr, Ph) can be produced by either the interaction of $Dcab^{Py}H$ with $Ti(O^iPr)_4$ in 1:1 molar ratio or ($Dcab^{Py}$)$Ti(NMe_2)_2$ with PhOH (Ph = 2-Me-C_6H_4) in 1:2 molar ratio (Scheme 1.40).[52] Both ($Dcab^{Py}$)MCl_2 and ($Dcab^{Py}$)$Ti(OR)_2$ complexes exhibit low activity in ethylene polymerization when activated with excess $[Ph_3C][B(C_6F_5)_4]$.[52]

Scheme 1. 40



Cyclohexyloxo-substituted dicarbollyl compounds were synthesized by Hosmane and coworkers. Deprotonation of the ligands by 2 equiv of *n*-BuLi in THF, followed by reaction with anhydrous $MCl_4(THF)_2$, produces $(\sigma:\eta^5\text{-}O(CH_2)_6\text{-}(R)C_2B_9H_9)MCl$ (R = Me, Merrifield's peptide resin, M = Zr, Ti) (Scheme 1.41).[53] The zirconium complexes are moderately active catalysts for olefin polymerization affording polymers with narrow molecular mass distributions in the presence of cocatalyst MMAO-7.[53]

Scheme 1. 41



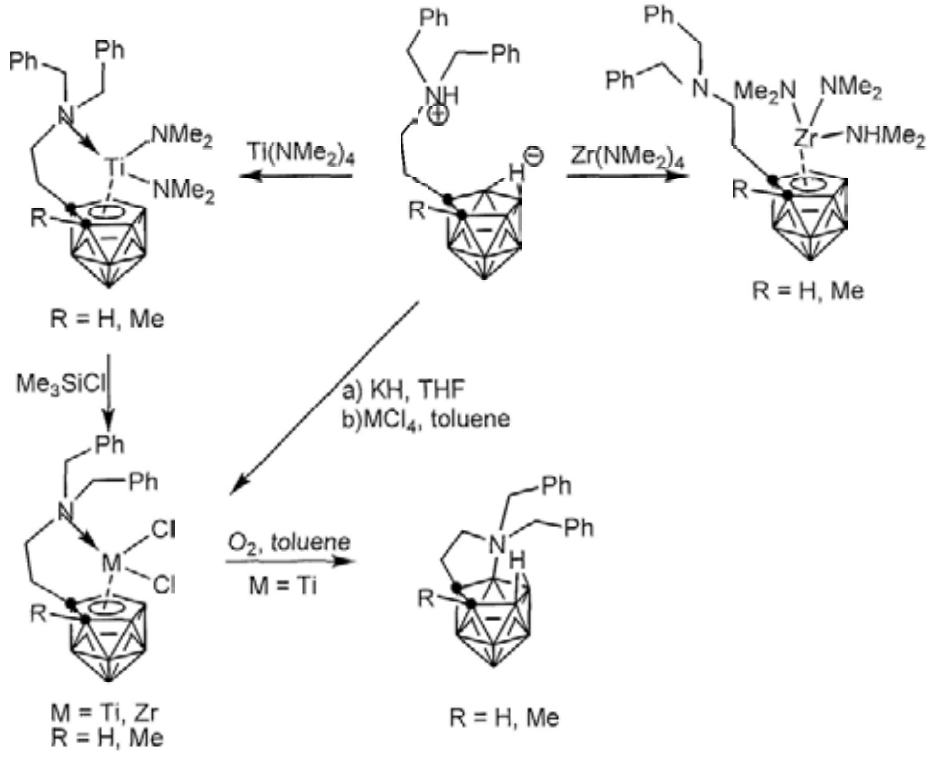
R = Me, poly(Merrifield's peptide resin)

R = Me, M = Zr, Ti
R = poly, M = Zr

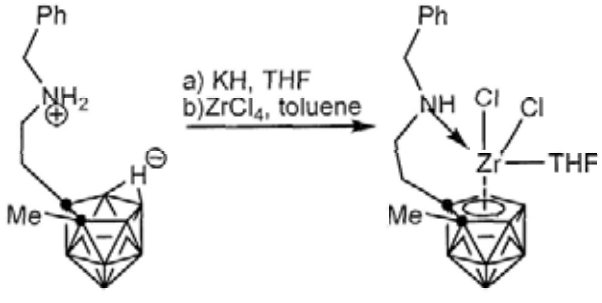
Reaction of the potassium salt of $7\text{-}HNBz_2(CH_2)_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}$ with $MCl_4(THF)_2$ gives metal dichloride complexes $[\eta^1:\eta^5\text{-}NBz_2(CH_2)_2(R)C_2B_9H_{10}]MCl_2$ (M = Ti, Zr, R = H, Me) (Scheme 1.42).[54] The reaction of the dicarbollyl ligands directly with $Ti(NMe_2)_4$ in toluene affords $[\eta^1:\eta^5\text{-}NBz_2(CH_2)_2(R)C_2B_9H_{10}]Ti(NMe_2)_2$ (R = Me, H), which readily reacts with Me_3SiCl to yield the corresponding titanium dichloride complex (Scheme 1.42).[54] In contrast, the reaction of the ligands with $Zr(NMe_2)_4$ produces the untethered half-metallocene complexes $[\eta^5\text{-}NBz_2(CH_2)_2(R)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$ (R = Me, H) (Scheme 1.42).[54] The titanium(IV) CGC (constrained-geometry catalyst) complexes

$[\eta^1:\eta^5\text{-NBz}_2(CH_2)_2(R)C_2B_9H_{10}]Ti(NMe_2)_2$ (R = Me, H) exhibit unusual B,N-cyclization when reacted with O_2, leading to the production of exocyclic dicarbollides (Scheme 1.42).[54] Treatment of potassium salt of less bulky dicarbollide $7\text{-}H_2NBz(CH_2)_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}$ with $ZrCl_4(THF)_2$ gives $[\eta^1:\eta^5\text{-NHBz}(CH_2)_2(Me)C_2B_9H_{10}]ZrCl_2(THF)$ (Scheme 1.43).[54]

Scheme 1. 42

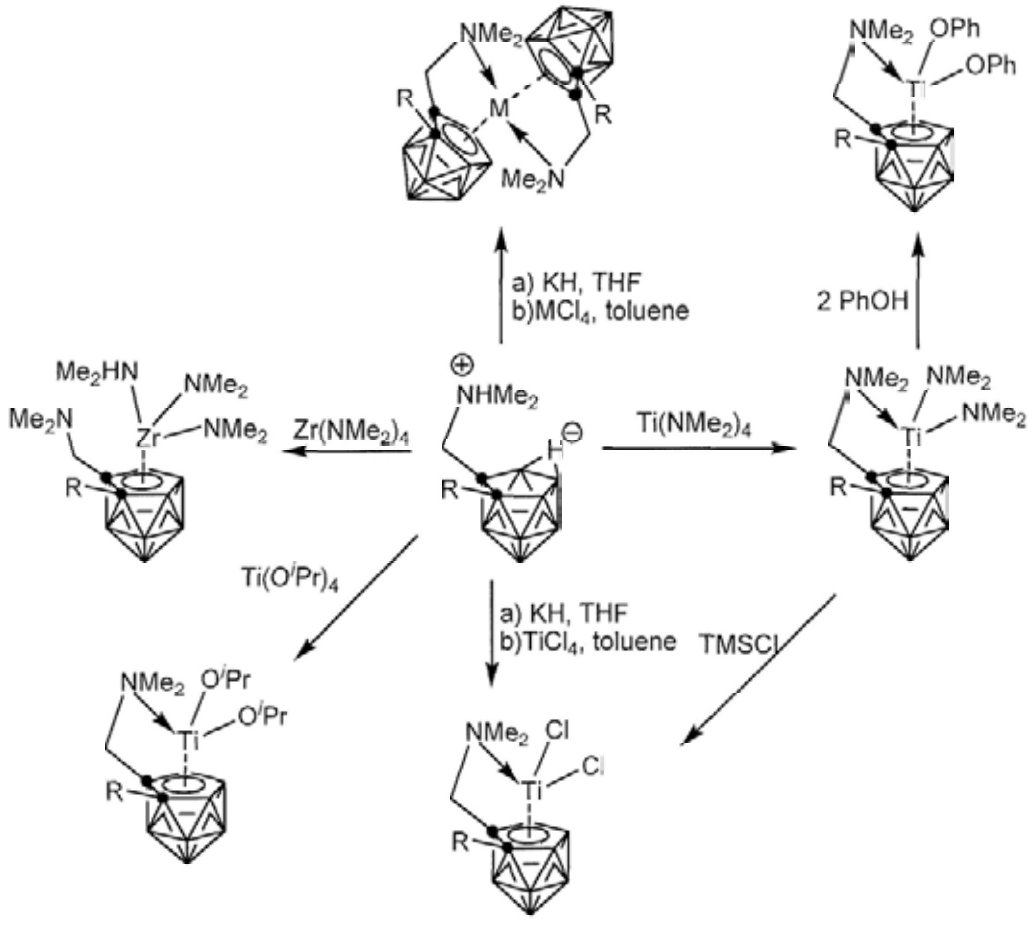


Scheme 1. 43



A series of constrained geometry group 4 metal complexes containing the (N,N'-dimethylaminomethyl)dicarbollyl ligand 7-$NHMe_2(CH_2)$-8-R-7,8-$C_2B_9H_{10}$ were also reported by Kang and coworkers. Reaction of the potassium salt of the dicarbollyl ligands with $TiCl_4$ in 1:1 molar ratio produces [η^1:η^5-$NMe_2(CH_2)(R)C_2B_9H_{10}$]$TiCl_2$ (R = H, Me) (Scheme 1.44).[55] Treatment of the potassium salt of 7-$NHMe_2(CH_2)$-8-H-7,8-$C_2B_9H_{10}$ with MCl_4 in 2:1 molar ratio affords the bis-chelated complexes [η^1:η^5-$NMe_2(CH_2)C_2B_9H_{11}$]$_2$M (M = Ti, Zr, Hf) (Scheme 1.44). The reaction of ligands with $Ti(NMe_2)_4$ in toluene give [η^1:η^5-$NMe_2(CH_2)(R)C_2B_9H_{10}$]$Ti(NMe_2)_2$ (R = H, Me), which readily reacted with Me_3SiCl to yield the corresponding dichloride complexes [η^1:η^5-$NMe_2(CH_2)(R)C_2B_9H_{10}$]$TiCl_2$. However, the reaction of dicarbollyl ligands with $Zr(NMe_2)_4$ in toluene affords [η^1:η^5-$NMe_2(CH_2)(R)C_2B_9H_{10}$]$Zr(NMe_2)_2(NHMe_2)$ (R= H, Me) (Scheme 1.44). New types of titanium alkoxides, [η^1:η^5-$NMe_2(CH_2)C_2B_9H_{11}$]$Ti(O^iPr)_2$, are synthesized from the reaction of the dicarbollyl ligand with $Ti(O^iPr)_4$. Sterically less-demanding phenols such as C_6H_5OH and 2-MeC_6H_4OH can replace the coordinated amido ligands in [η^1:η^5-$NMe_2(CH_2)C_2B_9H_{11}$]$Ti(NMe_2)_2$ to yield the aryloxy-stabilized CGC complexes [η^1:η^5-$NMe_2(CH_2)C_2B_9H_{11}$]$Ti(OPh)_2$ (Ph = C_6H_5, 2-MeC_6H_4) (Scheme 1.44).[55] The titanium chloride and alkoxide complexes show very low catalytic activities in ethylene polymerization in the presence of excess $[Ph_3C][B(C_6F_5)_4]$ comparing with Dow-CGC-type catalyst.

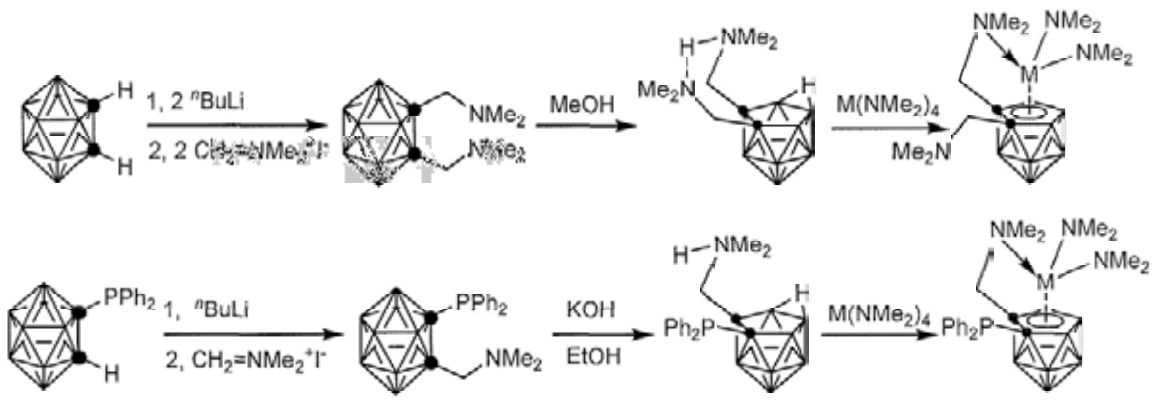
Scheme 1. 44



Two homo- or hetero-donor tethered ligands of type 7,8-$(Me_2NCH_2)(\mu$-H$)(Me_2NCH_2)$-7,8-$C_2B_9H_{10}$ ($Dcab^{NN}H$) and 7-PPh_2-8-Me_2NHCH_2-7,8-$C_2B_9H_{10}$ ($Dcab^{PN}H$) were prepared using the standard deboration methods from 1,2-$(Me_2NCH_2)_2$-1,2-$C_2B_{10}H_{10}$ and 1-PPh_2-2-Me_2NCH_2-1,2-$C_2B_{10}H_{10}$, respectively (Scheme 1.45).[55] Subsequent reaction of $Dcab^{NN}H$ with $M(NMe_2)_4$ (M = Ti, Zr) produced single nitrogen donors involving π,σ-dicarbollides of the type $[\eta^5$-$C_2B_9H_9(CH_2NMe_2)(\eta^1$-$NMe_2CH_2)]M(NMe_2)_2$.

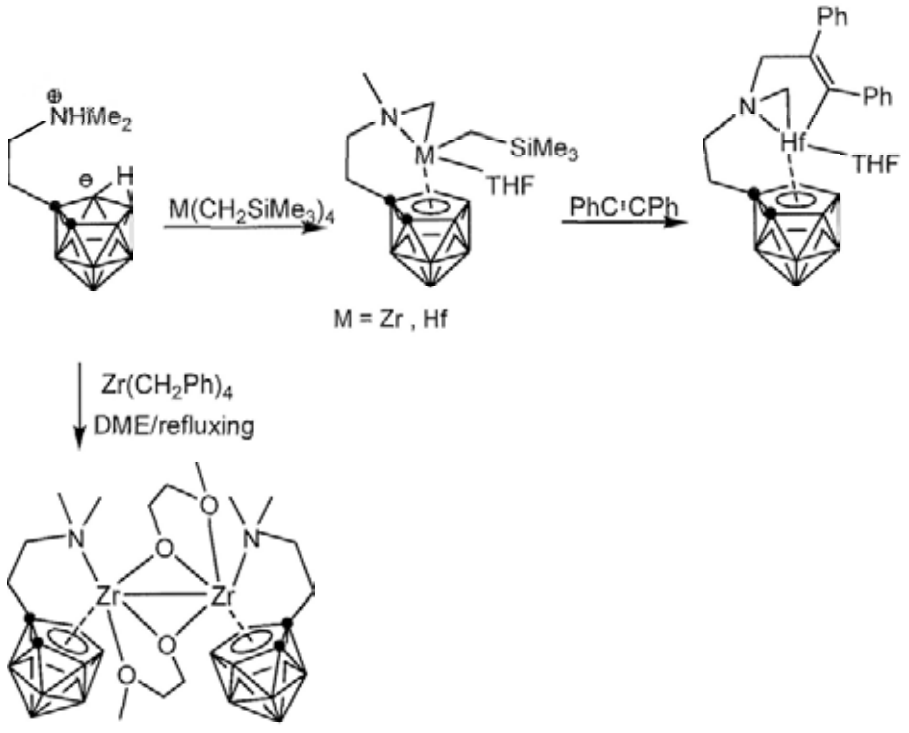
Structurally similar nitrogen donor stablized π,σ-dicarbollides of the type $[\eta^5\text{-}C_2B_9H_9(PPh_2)](\eta^1\text{-}NMe_2CH_2)M(NMe_2)_2$ were produced from the reaction of $Dcab^{PN}H$ with $M(NMe_2)_4$ (M = Ti, Zr).

Scheme 1.45



Treatment of 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ with $M(CH_2SiMe_3)_4$ in toluene gives the C-H activation products $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]M(CH_2SiMe_3)(THF)$ (M = Zr, Hf) (Scheme 1.46).[56] Insertion of diphenylacetylene into the Hf alkyl complex and subsequent elimination of $SiMe_4$ affords a metallacyclic complex, $[\sigma{:}\sigma{:}\eta^1{:}\eta^5\text{-}\{(CH_2)[(CH_2)PhC{=}CPh]N(CH_2CH_2)C_2B_9H_{10}\}]Hf(THF)$ (Scheme 1.46).[56] Reaction of $Zr(CH_2Ph)_4$ with 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ in DME generates a C-H/C-O activation product, $[\{\eta^1{:}\sigma{:}\eta^5\text{-}[MeN(CH_2)CH_2CH_2]C_2B_9H_{10}\}Zr(\mu{:}\eta^1\text{-}OCH_2CH_2OCH_3)]_2$ (Scheme 1.46).[56]

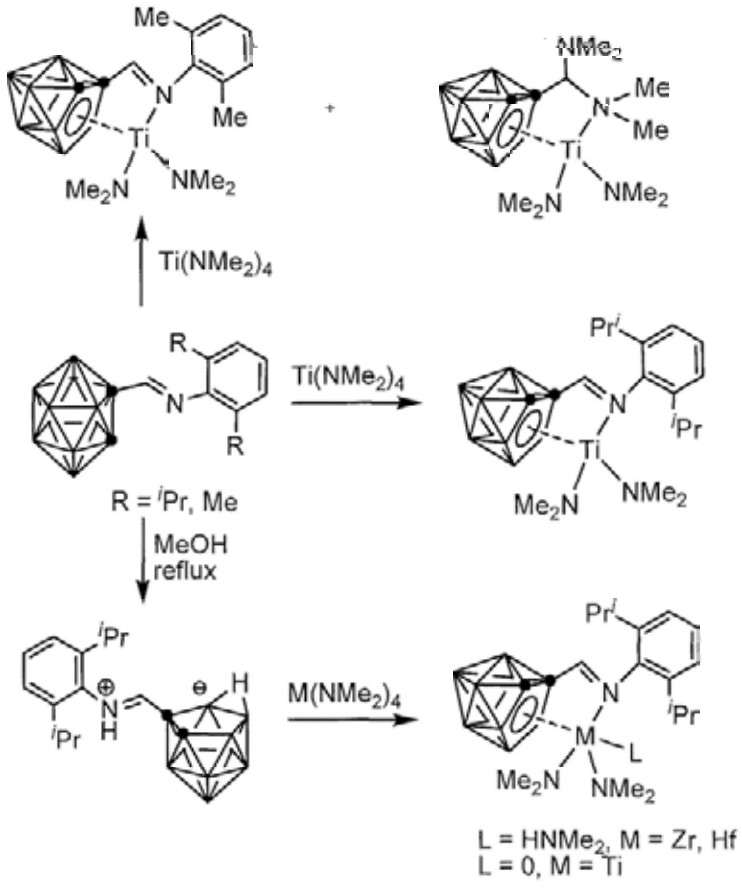
Scheme 1. 46



Treatment of imido-carborane ligand 1-(CH=NC$_6$H$_3$^{i}Pr$_2$-2,6)-1,2-C$_2$B$_{10}$H$_{11}$ with Ti(NMe$_2$)$_4$ in hot toluene affords a constrained-geometry titanium amide complex, [η^1:η^5-(^{i}Pr$_2$C$_6$H$_3$N=CH)C$_2$B$_9$H$_{10}$]Ti(NMe$_2$)$_2$ (Scheme 1.47), in which, deboration is observed.[57] Under the same conditions, interaction of 1-(CH=NC$_6$H$_3$Me$_2$-2,6)-1,2-C$_2$B$_{10}$H$_{11}$ with Ti(NMe$_2$)$_4$ produces a mixture of [η^1:η^5-(Me$_2$C$_6$H$_3$N=CH)C$_2$B$_9$H$_{10}$]Ti(NMe$_2$)$_2$ and [η^1:η^5-(Me$_2$N)CH(NMe$_2$)C$_2$B$_9$H$_{10}$]Ti(NMe$_2$)$_2$ (Scheme 1.47).[57] Reaction of the corresponding imido-dicarbollyl ligand 7-(CH=NHC$_6$H$_3$^{i}Pr$_2$-2,6)-7,8-C$_2$B$_9$H$_{11}$ with M(NMe$_2$)$_4$ afforded [η^1:η^5-(^{i}Pr$_2$C$_6$H$_3$N=CH)C$_2$B$_9$H$_{10}$]Ti(NMe$_2$)$_2$ and [η^1:η^5-(^{i}Pr$_2$C$_6$H$_3$N=CH)C$_2$B$_9$H$_{10}$]M(NMe$_2$)$_2$(NHMe$_2$) (M = Zr, Hf) (Scheme 1.47).[57] The

Group 4 metal amide complexes show low activities for ethylene polymerization in the presence of cocatalyst MMAO.

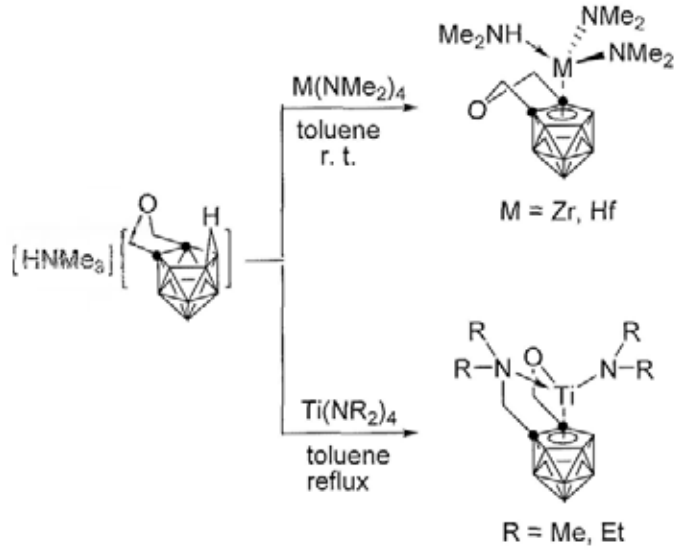
Scheme 1. 47



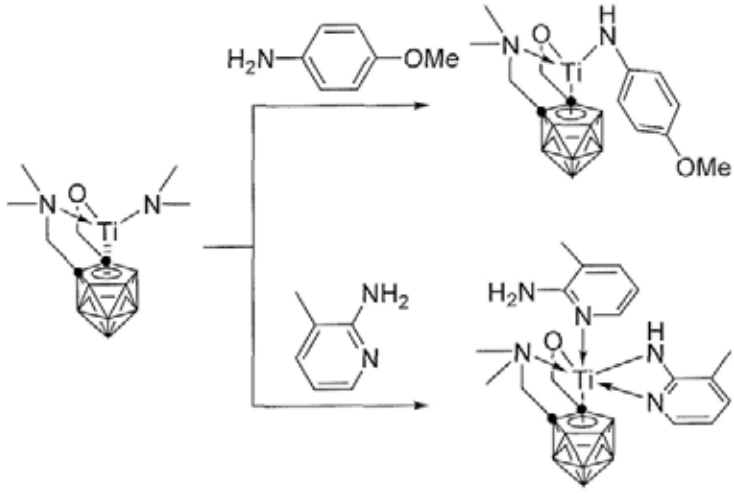
A new oxo-dicarbollyl ligand $[Me_3NH][7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]$ was prepared by our group which reacted with $M(NR_2)_4$ to afford different half-sandwich group 4 metal carborane amide complexes (Scheme 1.48).[58] The half-sandwich titanacarborane amide can undergo amine exchange reaction (Scheme 1.49) and insertion reaction with different unsaturated molecules (Scheme 1.50).[58] It also shows good catalytic activity

toward guanylation of amines (Scheme 1.51)[59] and transamination of guanidines (Scheme 1.52)[60].

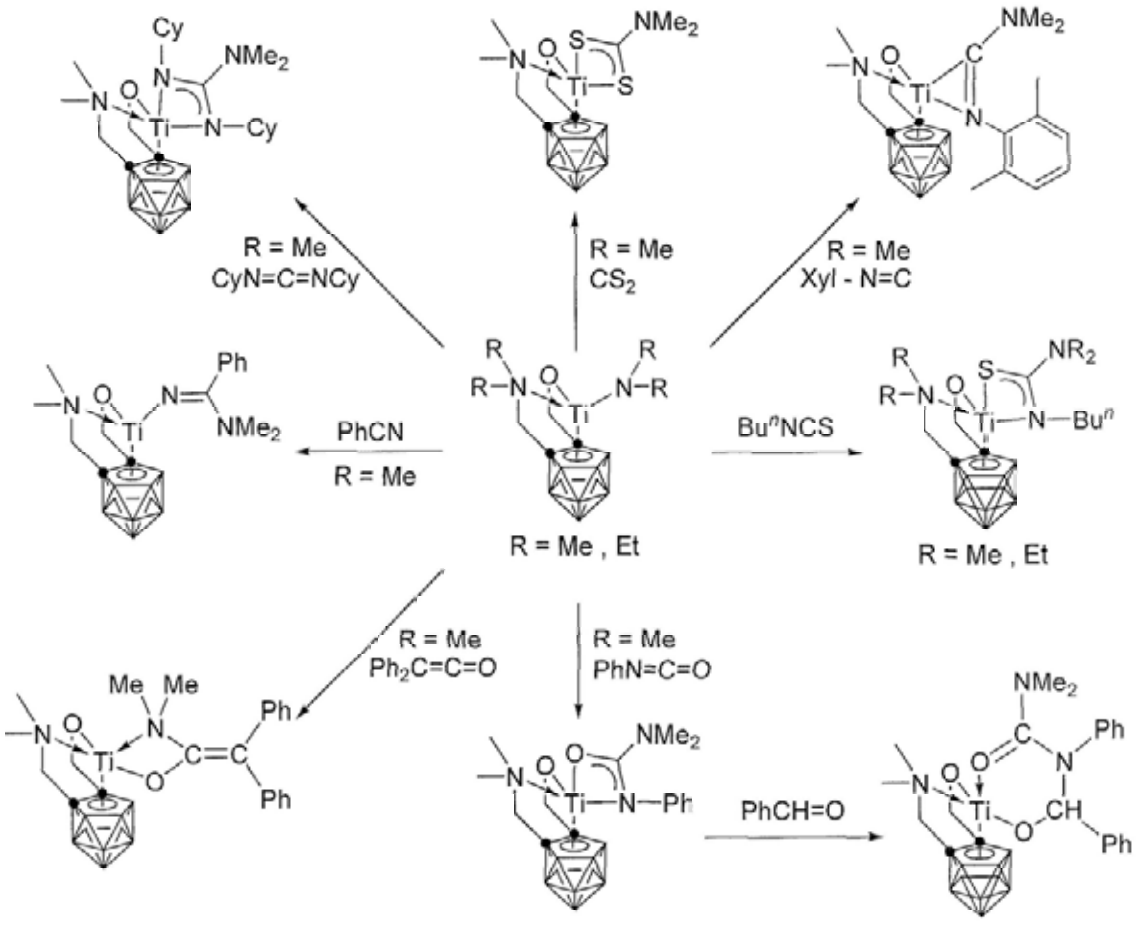
Scheme 1.48



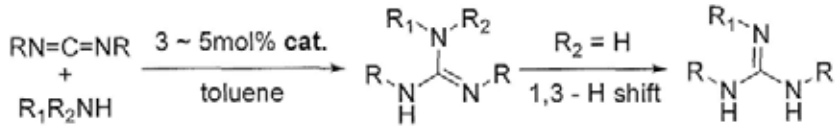
Scheme 1.49



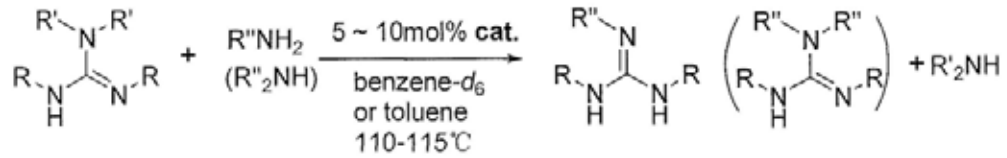
Scheme 1.50



Scheme 1.51



Scheme 1.52



1.3 Objectives of this research

The objectives of this research are (1) to synthesize late transition metal complexes with $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ ligands and study their chemical properties, (2) to explore the chemistry of group 4 metal complexes with carbon-bridged cyclopentadienyl/indenyl/tetramethylcyclopentadienyl-dicarbollyl ligands, and (3) to explore the chemistry of group 4 metallocene alkyl complexes with cyclopentadienyl-functionalized dicarbollyl ligands. In the following chapters of this thesis, we would like to describe the details of our research on the subjects mentioned above.

Chapter 2

Synthesis, Structural Characterization and Reactivity of Late Transition Metal (Co, Ni) Complexes Bearing Linked Cyclopentadienyl-Carboranyl Ligands

2.1 Introduction

A series of hybrid organic-inorganic linked cyclopentadienyl/indenyl-carboranyl ligands were reported in the past years.[8,9,11] They are finding a wide range of applications in rare earth and early transition metal chemistry.[12-18] It is found that the metal-carbon(cage) bonds in these complexes are inert in ethylene polymerization and insertion reactions of unsaturated molecules due probably to the presence of sterically bulky carboranyl unit.[17] Ruthenium complexes with these bridging ligands were also synthesized and studied.[10,28,29,31,35,36] The Ru-C(cage) bond is generally inactive in $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(L_2)$ (L = COD, NHR_2, CH_3CN). They are starting materials for the preparation of Ru-carbene, Ru-alkenyl and Ru-vinylidene complexes bearing $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ ligand.[35] It is noted that $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(CH_3CN)_2$ can activate the incorporated C_5H_4 when treated with ArC≡CH to form the unexpected tricyclic compounds.[36]

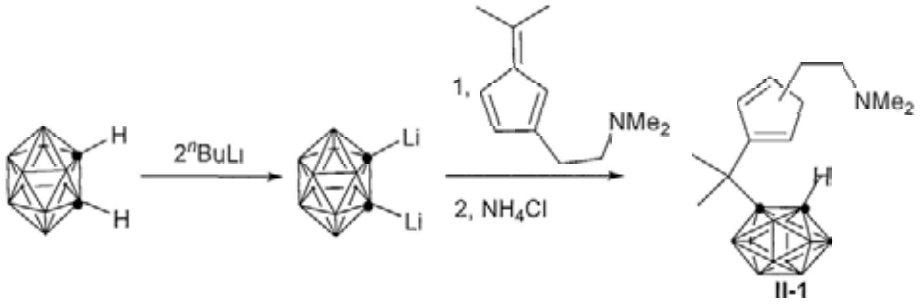
Late transition metal (Ni, Co) complexes show the common features with the Ru complexes such as [2+2+2] trimerization of alkynes and C-C coupling reactions.[61] On the other hand, Ni, Co complexes can catalyze the ethylene polymerization via

coordination-insertion mechanism, whereas the ring-opening polymerization is observed in the Ru case.[62] In this chapter, we report the synthesis and the reactivities of late transition metal (Co, Ni) complexes with carbon bridged Cp/indenyl-carboranyl ligands.

2.2 Ligand Synthesis.

Late transition metal half-sandwich complexes, in which a cyclopentadienyl ligand is tethered to a donor atom, receive much attention.[63a] The tethered donor atom in Cp-D chelating ligands can prevent rotation of Cp ring or can temporarily and reversibly coordinated to the metal atoms to stabilize highly reactive, electronically and sterically unsaturated species.[63b] The Si-bridged $Me_2Si(XCH_2CH_2C_9H_6)(C_2B_{10}H_{11})$ (X = OMe, NMe_2) ligands were developed earlier in our laboratory,[63c,d] in which the donor O, N atoms can coordinate to the lanthanide metal centers during the formation of organolanthanide complexes. We attempted to prepare carbon-bridged $Me_2C(Me_2NCH_2CH_2C_5H_4)(C_2B_{10}H_{11})$ using the known procedures. Treatment of $Li_2C_2B_{10}H_{10}$ with dimethyl(dimethylaminoethyl)fulvene afforded, after hydrolysis with a saturated NH_4Cl solution, $Me_2C(Me_2NCH_2CH_2C_5H_4)(C_2B_{10}H_{11})$ (**II-1**) in 83% isolated yield (Scheme 2.1). Compound **II-1** is isolated as an oil that is an isomeric mixture with the substituted group $Me_2NCH_2CH_2$-bound to either sp^2 or sp^3 carbons of the Cp ring. The composition of **II-1** was confirmed by various spectroscopic techniques and mass spectrometry. The ^{11}B NMR spectrum showed a 2:2:2:4 pattern which is typical for monosubstituted carboranes.

Scheme 2.1



2.3 Synthesis of Late Transition Metal Complexes.

Treatment of the dilithium salts of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ [8,11,13,14,17,18,28,102] with 1 equiv of $MCl_2(PPh_3)_2$ (M = Co, Ni) in THF at room temperature afforded, after recrystallization from Et_2O, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**II-2a**), Ni (**II-2b**)) in ~ 90% isolated yields (Scheme 2.2). Complex **II-2a** is paramagnetic which showed no useful NMR spectra. The ^{1}H NMR spectrum of **II-2b** exhibited multiplets at 7.62 – 7.01 ppm corresponding to the protons of phenyl ring, two singlets at 5.96 and 3.70 ppm assignable to cyclopentadienyl protons, and one singlet at 1.39 ppm attributable to the Me_2C-linkage. The ^{13}C NMR spectrum was consistent with the above result. The ^{11}B NMR spectrum showed a pattern of 2:3:5. The ^{31}P NMR spectrum showed one singlet at 47.3 ppm. The compositions of complexes **II-2a** and **II-2b** were further confirmed by elemental analyses. The structures of both complexes were revealed by single-crystal X-ray diffraction study. The X-ray analyses showed that the

late transition metal Co and Ni atoms are η^5-coordinated to the cyclopentadienyl ligand, σ-bound to one cage carbon atom and coordinated to the P atom of triphenylphosphine in a trigonal planar geometry (Figures 2.1 and 2.2). The average M-C_{ring} bond distances of 2.085(3)/2.145(6) Å (M = Co (**II-2a**)/Ni (**II-2b**)) are comparable to each other and that of 2.087(2) Å in [WCoAu(μ_3-CC_6H_4Me-4)(CO)$_2$(η^5-C_5Me_5)(η^6-$C_2B_{10}H_{10}Me_2$)],[64] 2.126(4) Å in [Ni(η^5-C_5H_5)(PPh_3)C≡CCH(OEt)$_2$],[65] 2.102(6) Å in [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO],[65] 2.106(3) Å in [Ni(η^5-C_5H_5)(PPh_3)C≡CCH=C(CN)$_2$],[65] 2.128(6) Å in Ni(η^5-C_5H_5)(PPh_3)C{C_6H_4C(CN)$_2$}C{C(CN)$_2$}C_6H_5,[66] 2.129(9) Å in {(PPh_3)$_2$Ni[μ-(η^5-C_5H_4)CMe_2(η^5-C_5H_4)]Ni(PPh_3)$_2$}{PF_6}$_2$,[67] 2.119(9)/2.116(9) Å in [(CN^tBu)(PPh_3)Ni{μ-(η^5-C_5H_4)CMe_2(η^5-C_5H_4)}Ni(PPh_3)(CN^tBu)][PF_6]$_2$[67] and 2.137(2) Å in Cp*Ni(PPh_3)(CH_2CO^tBu).[68] The M-C_{cage} bond distances of 1.989(3)/1.975(5) Å (M = Co (**II-2a**)/Ni (**II-2b**)) compare to each other and those of 2.002(9)/2.002(9)/1.998(9)/2.013(9) Å in [Ni{($C_2B_{10}H_{10}$)$_2$}$_2$]Li_2,[69] 2.00(2)/1.91(2) Å in (PPh_3)$_2$Ni($C_2B_{10}H_{10}$),[70] 1.972(5)/1.973(5) Å in [η:σ-(2-$C_5H_4NCH_2C_2B_{10}H_{10}$)]$_2$Ni,[71] but are a little shorter than those of 2.070(12)/2.051(12) Å in [Co{($C_2B_{10}H_{10}$)2}$_2$]Li_2.[69] The M-P bond distances of 2.209(1)/2.210(1) Å are comparable to each other and those of 2.29(1)/2.20(1) Å in (PPh_3)$_2$Ni($C_2B_{10}H_{10}$),[70] 2.172(3)/2.175(3) Å in [(CN^tBu)(PPh_3)Ni{μ-(η^5-C_5H_4)CMe_2(η^5-C_5H_4)}Ni(PPh_3)(CN^tBu)][PF_6]$_2$,[67] 2.211(2)/2.214(2) Å in {(PPh_3)$_2$Ni[μ-(η^5-C_5H_4)CMe_2(η^5-C_5H_4)]Ni(PPh_3)$_2$}{PF_6}$_2$,[72] 2.182(2) Å in Ni(η^5-C_5H_5)(PPh_3)C{C_6H_4C(CN)$_2$}C{C(CN)$_2$}C_6H_5,[66] but are longer than that of 2.134(1) Å in Cp*Ni(PPh_3)(CH_2CO^tBu),[68] 2.138(1) Å in

[Ni(η^5-C_5H_5)(PPh_3)C≡CCH($OEt)_2$],[65] 2.142(1) Å in [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO],[65] 2.145(1) Å in [Ni(η^5-C_5H_5)(PPh_3)C≡CCH=C($CN)_2$],[65] 2.146(1) Å in (η^5-C_9H_6)Co(CO)(PPh_3),[73] and 2.145(1) Å in Ni(η^5-C_5H_5)(PPh_3)(SC_6H_4N=CHC_6H_4Br).[74]

Treatment of the dilithium salts of $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ with 1 equiv of $MCl_2(PPh_3)_2$ (M = Co, Ni) in THF at room temperature afforded, after recrystallization from Et_2O, [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]M($PPh_3$) (M = Co (**II-3a**), Ni (**II-3b**)) in ~ 70% isolated yields (Scheme 2.2). The structures of both complexes are confirmed by various spectroscopic techniques, elemental analyses and single-crystal X-ray analyses. Complex **II-3a** is paramagnetic, and no valuable NMR spectra were observed. For complex **II-3b**, both ^{1}H and ^{13}C NMR spectra showed the existence of the bridging ligand and coordinated PPh_3 ligand. The ^{11}B NMR spectrum of **II-3b** showed a pattern of 2:3:5 which was similar to the cyclopentadienyl analogue **II-2b**. The ^{31}P NMR spectrum showed one singlet at 33.8 ppm. Single-crystal X-ray analyses revealed that the metal centers in both complexes are η^5-coordinated to the indenyl ligand, σ-bound to one cage carbon atom and coordinated to the P atom of triphenylphosphine in a trigonal planar geometry (Figures 2.3 and 2.4). The average M-C_{ring} bond distances of 2.149(5)/2.169(3) Å (M = Co (**II-3a**)/Ni (**II-3b**)) are similar to each other and comparable to that of 2.154(9) Å in (η^5-C_9H_6)(C_3H_7)($PMe_3)_2$CoI,[75] 2.169(2) Å in [(η^5-1-Me-C_9H_6)Ni(PMe_3)(PPh_3)]$^+$,[76] 2.182(3) Å in [(η^5-1-TMS-C_9H_5)NiCl(PPh_3),[77] 2.186(2) Å in [(η^5-1,3-$(TMS)_2$-C_9H_4)NiCl(PPh_3),[77] 2.173(2) Å in

[(η^5-1-H_2C=CH$(CH_2)_2$-C_9H_4)NiCl(PPh_3),[78] and 2.176(7) Å in [(η^5-1-H_2C=CHCH_2SiMe_2-C_9H_4)NiCl(PPh_3).[78] The M-C_{cage} bond distances of 2.008(5)/1.950(3) Å (M = Co (**II-3a**)/Ni (**II-3b**)) are comparable to each other, and similar to that of 1.989(3) Å in **II-2a** and 1.975(5) Å in **II-2b**. The M-P bond distances of 2.247(1) Å in **II-3a** is a little longer than that of 2.194(1) Å in **II-3b**, but both are comparable to that of 2.209(1)/2.210(1) Å in **II-2a/II-2b**.

Treatment of the dilithium salt of $[Me_2C(Me_2NCH_2CH_2C_5H_3)(C_2B_{10}H_{10})]^{2-}$ (**II-1**) with 1 equiv of $NiCl_2(PPh_3)_2$ in THF afforded, after recrystallization from Et_2O, [η^5:σ-$Me_2C(Me_2NCH_2CH_2C_5H_4)(C_2B_{10}H_{10})$]Ni($PPh_3$) (**II-4**) in 69% isolated yields (Scheme 2.2). Amino groups on Cp ring are usually labile ligands, which can coordinate to or dissociate from the metal centers at different situations to change the catalytic ability of the organometallic complexes.[63b] However in complex **II-4**, because of the stronger coordination ability of PPh_3, the amino group on Cp ring was pushed away from the Ni center and there was no coordination between the N atom and Ni center, which was confirmed by the ^1H, ^{31}P NMR data and single-crystal X-ray diffraction study. Except for the resonances corresponding to the protons of bridging ligand, multiplets at 7.69 and 7.02 ppm assignable to the protons on phenyl group of PPh_3 were observed in the ^1H NMR spectrum. According to 18-electron rule, if PPh_3 ligand is coordinated to the Ni atom, N atom will not coordinate to the Ni atom at the same time. The ^{11}B NMR spectrum showed the same pattern of 2:3:5 as that of **II-2b** and **II-3b**. The ^{31}P NMR spectrum showed one singlet at 36.5 ppm. Single-crystal X-ray analyses revealed that

the Ni atom is η^5-coordinated to the cyclopentadienyl ligand, σ-bound to one cage carbon atom and coordinated to P atom of the triphenylphosphine in a trigonal planar geometry (Figure 2.5). The average Ni-C_{ring} bond distance of 2.131(3) Å is similar to that of 2.145(6) Å in **II-2b**, 2.103(7) Å in (η^5:η^1-$C_5H_4CH_2CH_2NMe_2$)NiI,[81] 2.106(7) Å in (η^5-μ-$C_5H_4CH_2CH_2NMe_2$)(PMe_3)Ni-InI_2,[80] 2.114(7) Å in (η^5:η^1-$C_5H_4CH_2CH_2NMe_2$)Ni($C_{12}H_8N$),[79] 2.106(4) Å in (η^5:η^1-$C_5H_4CH_2CH_2NMe_2$)Ni($NC_8H_4Me_2$-2,9),[79] 2.112(7) Å in [(η^5:η^1-$C_5H_4CH_2CH_2NMe_2$)Ni(PPh_3)][PF_6],[81] 2.098(9) Å in [(η^5-$C_5H_4CH_2CH_2NMe_2$)Ni(dmpe)][PF_6],[81] and 2.111(8) Å in (η^5:η^1-$C_5H_4CH_2CH_2NMe_2$)Ni($C_6H_3Me_2$-2,6).[81] The Ni-C_{cage} and Ni-P bond distances of 1.960(2) Å and 2.188(1) Å are comparable to those of 1.975(5) Å and 2.210(1) Å in **II-2b**.

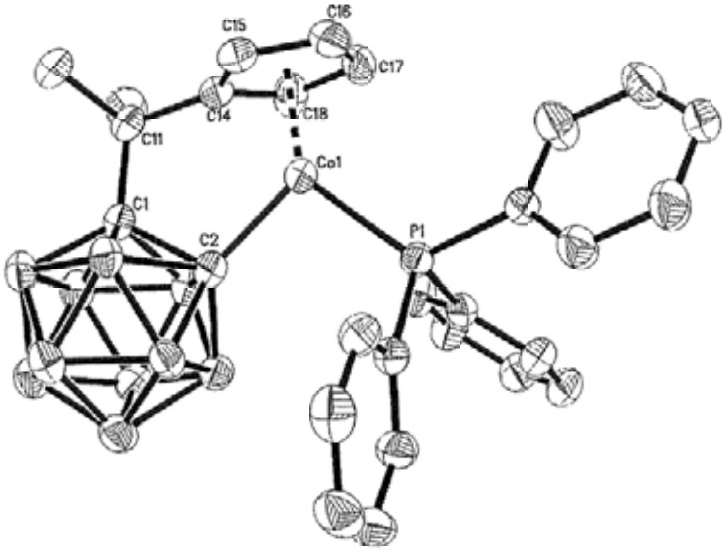
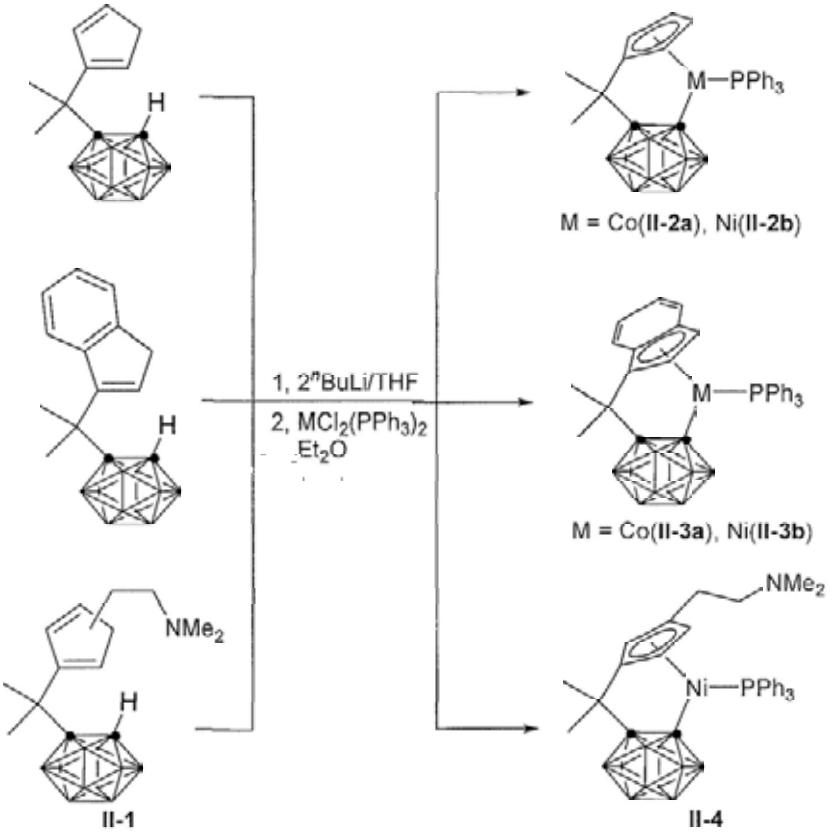


Figure 2.1. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co($PPh_3$) (**II-2a**).

Scheme 2.2



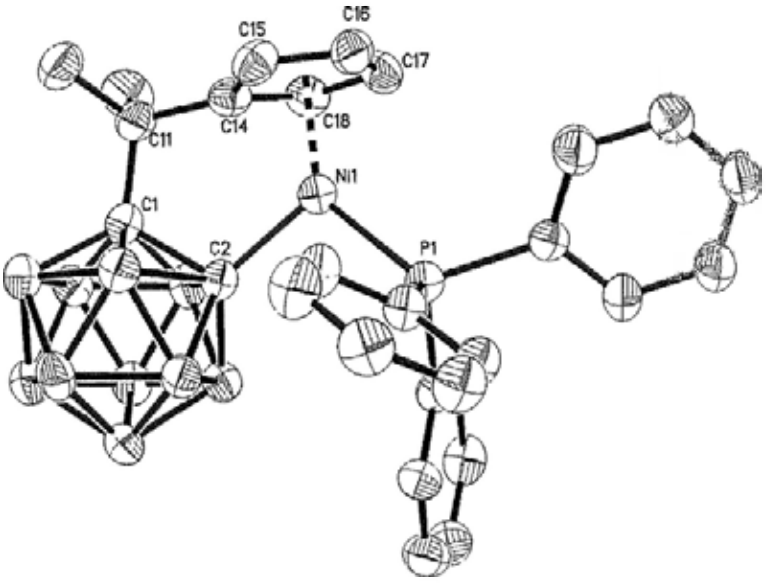


Figure 2.2. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**II-2b**).

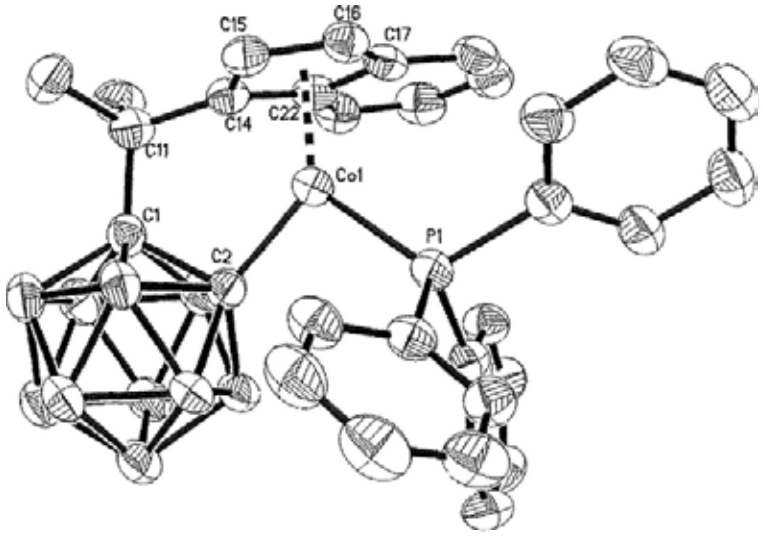


Figure 2.3. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Co(PPh_3)$ (**II-3a**).

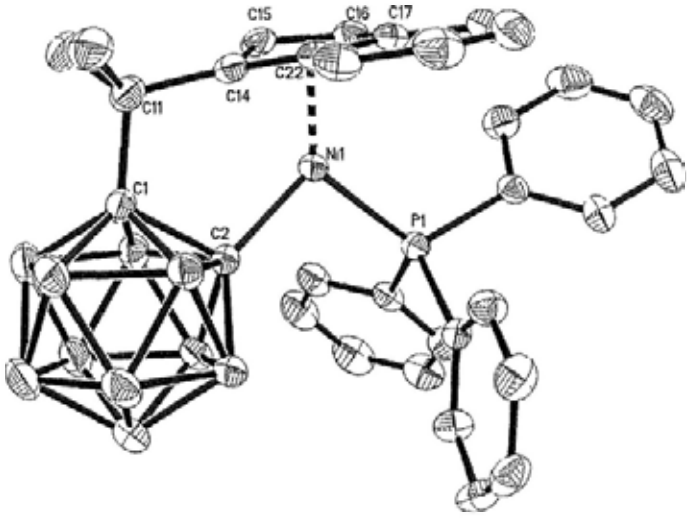


Figure 2.4. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**II-3b**).

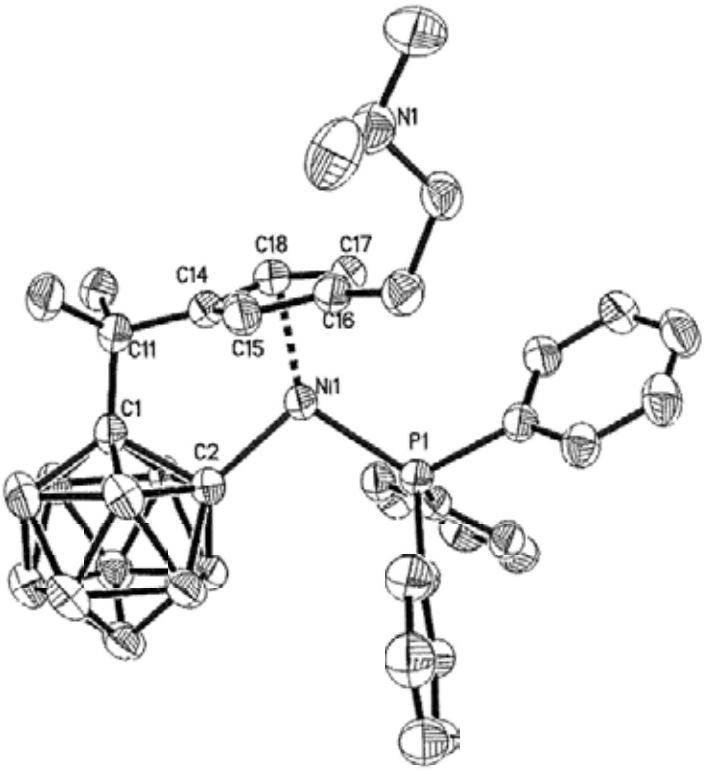


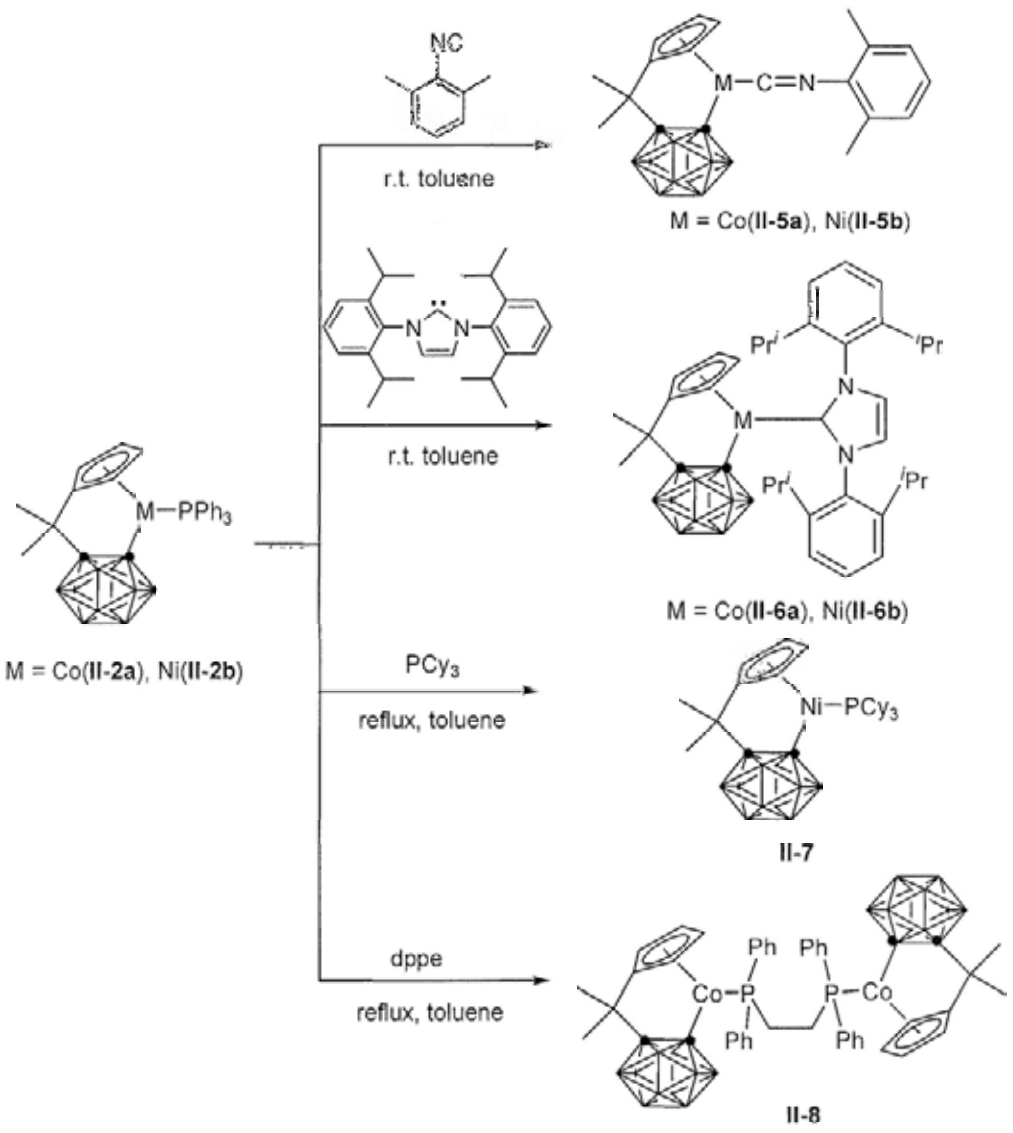
Figure 2.5. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(Me_2NCH_2CH_2C_5H_3)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**II-4**).

2.4 Reactivity of the Late Transition Metal Complexes.

Organometallic complexes of late transition metals are effective catalysts for Suzuki coupling reaction,[82] Heck reaction,[83] ethylene polymerization,[84] alkynes trimerization,[85] ethylene dimerization or oligomerization,[86] etc. We studied the reactivity of the late transition metal complexes aforementioned. Complex **II-2a** or **II-2b** did not react with alkynes or nitriles as evidenced by ^1H NMR. The M-C_{cage} bonds are inert for the insertion reactions probably due to the steric hindrance of the icosahedral carborane

cage. There was no any reaction between **II-2a** or **II-2b** with H_2, no metal hydride complexes or B-H activation products were formed.

Scheme 2.3



Treatment of **II-2a** or **II-2b** with 1 equiv of 2,6-dimethylphenylisocyanide (XyNC) at room temperature in toluene afforded, after recrystallization from Et_2O, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(CNC_6H_3Me_2\text{-}2,6)$ (M = Co (**II-5a**), Ni (**II-5b**)) in

59-77% isolated yields (Scheme 2.3). Substitution of PPh_3 by isocyanide proceeded. Complex **II-5b** showed a very good NMR spectrum. Except for the resonances corresponding to protons of bridging ligand, signals in the range 6.66 - 6.51 ppm assignable to the protons on aromatic ring and one singlet at 2.11 ppm attributable to the protons of methyl group on phenyl ring were observed in the ^{1}H NMR spectrum. The characteristic resonance of N=*C* at 162.8 ppm was observed in the ^{13}C NMR spectrum. The ^{11}B NMR spectrum showed a 1:2:3:4 pattern. No signals were observed in the ^{31}P NMR spectrum. Both structures were confirmed by single-crystal X-ray analyses (Figures 2.6 and 2.7). The average M-C_{ring} bond distances of 2.074(3)/2.099(4) Å (M = Co (**II-5a**)/Ni (**II-5b**)) are similar to each other and comparable to that of 2.085(3)/2.145(6) Å in **II-2a/II-2b**. The M-C_{cage} bond distances of 1.922(3)/1.898(3) Å (M = Co (**II-5a**)/Ni (**II-5b**)) are close to each other but shorter than that of 1.989(3)/1.975(5) Å in **II-2a/II-2b**. The M-C bond distances of 1.838(3)/1.790(3) Å (M = Co (**II-5a**)/Ni (**II-5b**)) are comparable to each other and close to that of 1.787(3) Å in Ni(triphos)($CNC_6H_3Me_2$-2,6),[87] 1.820(4) Å in Ni{$S_2P(O)(OEt)$}($CNC_6H_3Me_2$-2,6)(PCy_3),[88] 1.821(7)/1.831(7) Å in Ni{$S_2P(O)(OEt)$}($CNC_6H_3Me_2$-2,6)$_2$,[88] 1.867(2) Å in $Ni_2(\mu$-$CNC_6H_5)(dppm)_2Cl_2$,[89] 1.847(6)/1.843(6)/1.857(6) Å in $[Ni_2(\mu$-$CNC_6H_3Me_2$-2,6)($CNC_6H_3Me_2$-2,6)$_2$(dppm)$_2$][PF_6]$_2$,[89] and 1.789(9)/1.789(8) Å in $[Ni(\mu$-$^tBu_2As)$(p-tol-NC)$_2$]$_2$.[90]

Treatment of **II-2a** or **II-2b** with 1 equiv of N-heterocyclic carbene (NHC) in toluene at room temperature afforded, after recrystallization from Et_2O, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[C(2,6\text{-}{}^iPr_2C_6H_3\text{-}NCH)_2]$ (M = Co (**II-6a**), Ni (**II-6b**)) in 51-60% isolated yields (Scheme 2.3). The composition of **II-6b** was confirmed by various spectroscopic techniques and elemental analyses. The characteristic resonance at 163.1 ppm corresponding to the NHC carbene carbon was observed in the ^{13}C NMR spectrum. A 2:3:5 pattern was observed in the ^{11}B NMR spectrum. The solid-state structures of both complexes were also confirmed by single-crystal X-ray analyses (Figures 2.8 and 2.9). The average $M\text{-}C_{ring}/M\text{-}C_{cage}$ bond distances of 2.143(3)/2.152(4) Å in **II-6a** are comparable to those of 2.085(3)/2.145(6) Å in **II-2a.** The average $M\text{-}C_{ring}/M\text{-}C_{cage}$ bond distances of 2.003(3)/1.945(3) Å in **II-6b** are close to those of 1.989(3)/1.975(5) Å in **II-2b**. The Co-C bond distance of 2.011(2) Å in **II-6a** is comparable to that of 2.043(2)/2.019(2) Å in $[(TIMEN^{xyl})Co][BPh_4]_2$ (TIMEN = tris[2-(3-arylimidazol-2-ylidene)ethyl]amine, xyl = 2,6-dimethylphenyl).[91] The Ni-C bond distance of 1.934(2) Å in **II-6b** is longer than that of 1.861(4) Å in $[3,5\text{-}{}^tBu\text{-}2\text{-}(O)C_6H_2CH{=}NC_6H_3{}^iPr\text{-}2,6]Ni(C\{BnNCHCHN{}^iPr\})Ph$,[92] 1.875(3) Å in $[3,5\text{-}{}^tBu\text{-}2\text{-}(O)C_6H_2CH{=}NC_6H_3{}^iPr\text{-}2,6]Ni(C\{{}^iPrNCHCN{}^iPr\})Ph$,[92] 1.882(4) Å in $\{Cp[(\eta^2{:}\eta^1\text{-}CH_2{=}CHCH_2NCHCHNMe)C]Ni\}\{BF_4\}$,[93] 1.883(6) Å in $[\{Ni[C(N{}^tBuCH)_2][O(Me_2SiOSiMe_2)\text{-}\mu\text{-}O]\}_2]$,[94] 1.865(2) Å in $\{[(MeNCH)_2C]NiCl(PPh_3)_2\}\{BF_4\}$,[95] 1.863(1) Å in $\{[(Me_2N)_2C]NiCl(PPh_3)_2\}\{BF_4\}$,[95] 1.886(3) Å in $(C_9H_7)[({}^iPrNCH)_2C]NiCl$,[96] 1.888(4) Å in $(C_9H_7)[({}^iPrNCH)_2C]NiBr$,[96] but

is comparable to that of 1.908(4) Å in [(BnNCHCHNBn)C]NiI_2,[93] 1.914(7)/1.876(7) Å in [$(C_{10}H_7CH_2NCHCHNCH_2CH_2PPh_2)C]_2NiCl_2$,[97] 1.971(4)/1.985(4) Å in [$(BnNCHCHNCH_2CH_2PPh_2)C]_2NiCl_2$,[97] 1.898(4) Å in [$(p\text{-}FC_6H_4CH_2NCHCHNCH_2CH_2PPh_2)C]_2NiCl_2$,[97] 1.901(3) Å in [$(m\text{-}MeOC_6H_4CH_2NCHCHNCH_2CH_2PPh_2)C]_2NiCl_2$[97] and 1.932(4)/1.920(5) Å in [2,6-$\{(MeNCHCHN)_2\}_2C_5H_3N$]NiBr.[98]

Treatment of **II-2b** with 1 equiv of PCy_3 in refluxing toluene afforded, after recrystallization from Et_2O, [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PCy_3$) (**II-7**) in 57% isolated yield (Scheme 2.3). The substitution of PPh_3 by PCy_3 was confirmed by the ^1H NMR, ^{31}P NMR spectroscopic techniques and single-crystal X-ray analyses. Except for the resonances assignable to the protons on the bridging ligand, multiplets in the region 2.11-1.07 ppm corresponding to the protons of cyclohexyl group were observed in the ^1H NMR spectrum. The ^{31}P NMR spectrum showed a singlet at 44.4 ppm. Single-crystal X-ray analyses revealed that the Ni atom is η^5-coordinated to the cyclopentadienyl ligand, σ-bound to one cage carbon atom and coordinated to the P atom of the tricyclohexylphosphine in a trigonal planar geometry (Figure 2.10). The average Ni-C_{ring} and Ni-C_{cage} bond distances of 2.140(5) Å and 1.949(5) Å are comparable to those of 2.145(6) Å and 1.975(5) Å in **II-2b**. The Ni-P bond distance of 2.226(1) Å is similar to that of 2.210(1) Å in **II-2b**.

Treatment of **II-2a** with 0.5 equiv of bidentate phosphine ligand (dppe) in refluxing toluene afforded, after recrystallization from Et_2O,

{[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co}$_2$(dppe) (**II-8**) in 62% isolated yield (Scheme 2.3). According to 18-electron rule, except for the bridging ligand, the Co atom can only coordinate to one P atom of the bidentate ligand to give a dimeric complex. The composition of **II-8** was confirmed by elemental analyses. The solid-state structure of **II-8** was also confirmed by single-crystal X-ray diffraction study (Figure 2.11). Two [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co moieties are connected by a $Ph_2PCH_2CH_2PPh_2$ linkage. The average Co-C_{ring}/Co-C_{cage}/Co-P bond distances of 2.084(4)/1.951(3)/2.216(1) Å compare to those of 2.085(3)/1.989(3)/2.207(1) Å in **II-2a**.

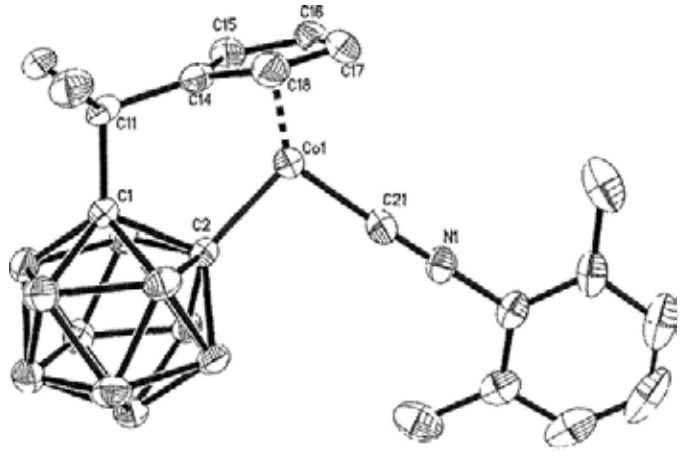


Figure 2.6. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co($CNC_6H_3Me_2$-2,6) (**II-5a**).

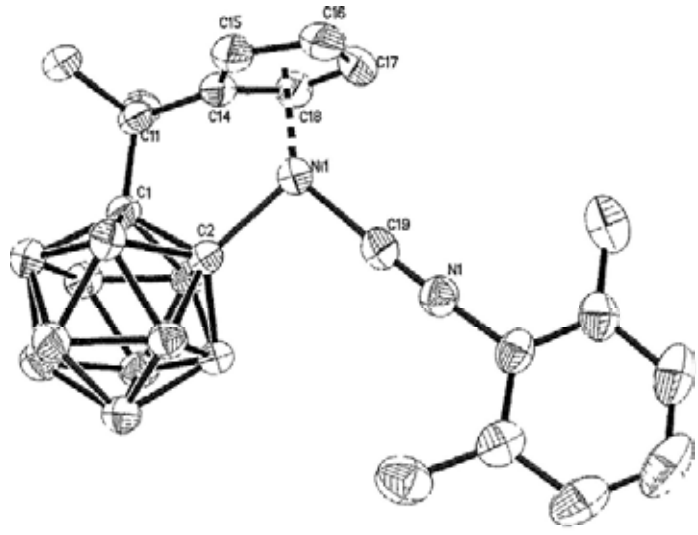


Figure 2.7. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(CNC_6H_3Me_2\text{-}2,6)$ (**II-5b**).

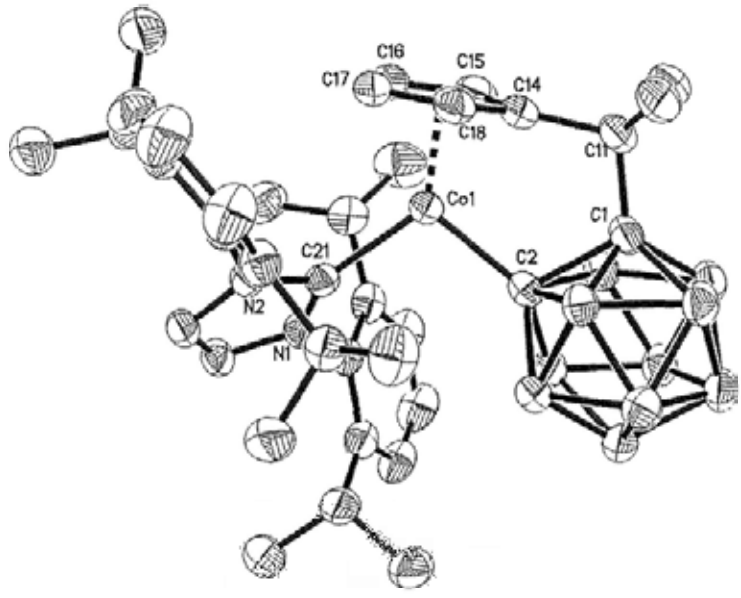


Figure 2.8. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co[C(2,6\text{-}{}^{i}Pr_2C_6H_3\text{-}NCH)_2]$ (**II-6a**).

Table 2.1. Selected Bond Lengths (Å) and Angles (deg) for **II-2a** — **II-8**

	$M\text{-}C_{cage}$	av. $M\text{-}C_{ring}$	M-Cent [a]	M-X	Cent-M-C_{cage}	$C_{ring}\text{-}C_{bridge}\text{-}B_{cage}$
II-2a	1.989(3)	2.085(3)	1.706	2.209(1) (X = P)	122.6	113.9(2)
II-2b	1.975(5)	2.145(6)	1.765	2.210(1) (X = P)	122.0	114.1(4)
II-3a	2.008(5)	2.149(5)	1.763	2.247(1) (X = P)	123.3	114.7(3)
II-3b	1.950(3)	2.169(3)	1.800	2.194(1) (X = P)	122.4	114.3(2)
II-4	1.960(2)	2.131(3)	1.752	2.188(1) (X = P)	122.0	114.4(2)
II-5a	1.922(3)	2.074(3)	1.689	1.838(3) (X = C)	124.0	114.1(2)
II-5b	1.898(3)	2.099(4)	1.722	1.790(3) (X = C)	123.4	114.0(2)
II-6a	2.003(3)	2.143(3)	1.762	2.011(2) (X = C)	121.0	114.3(2)
II-6b	1.945(3)	2.152(4)	1.786	1.934(2) (X = C)	120.5	114.2(2)
II-7	1.949(5)	2.140(5)	1.770	2.226(1) (X = P)	121.4	114.1(4)
II-8	1.951(3)	2.084(4)	1.697	2.216(1) (X = P)	123.4	114.3(2)

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

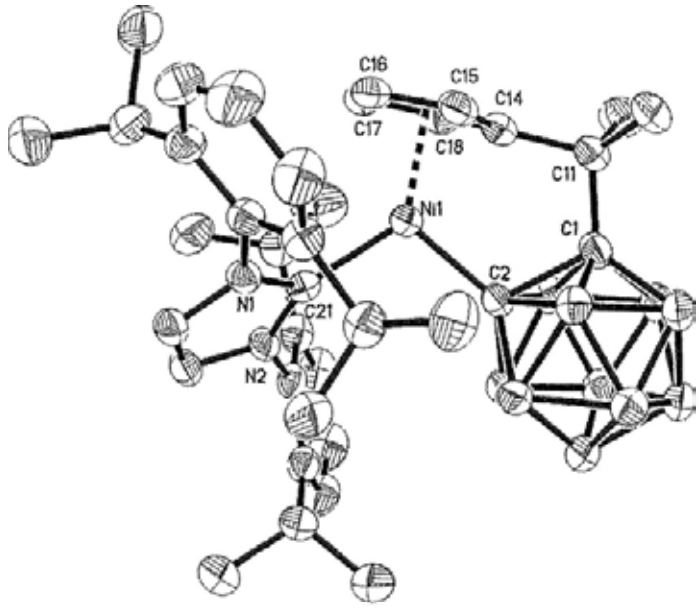


Figure 2.9. Molecular structure of

$[\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni[C(2,6\text{-}^iPr_2C_6H_3\text{-}NCH)_2]$ (**II-6b**).

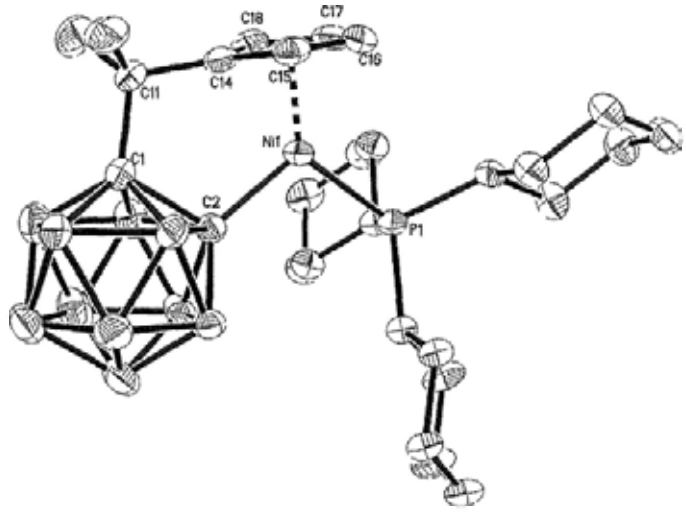


Figure 2.10. Molecular structure of $[\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(PCy_3)$ (**II-7**).

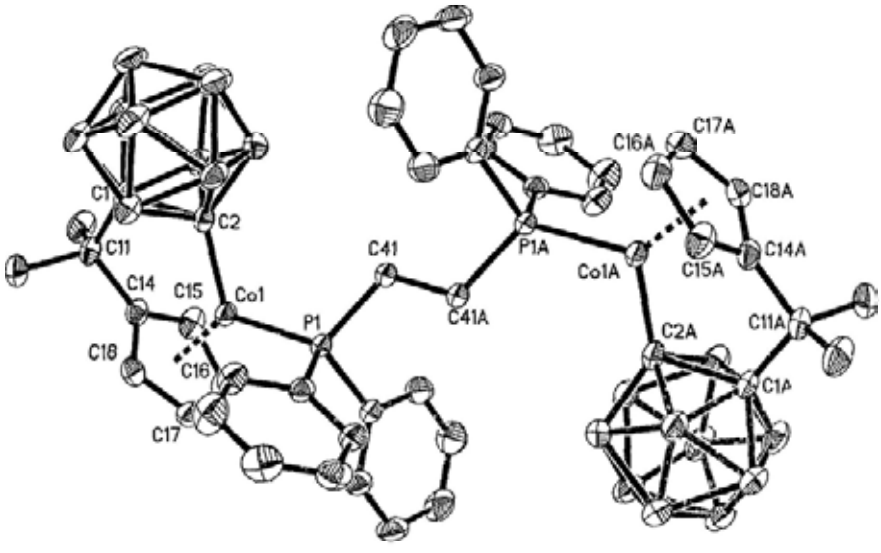


Figure 2.11. Unique molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co\}_2(dppe)$ (**II-8**).

2.5 Summary

Treatment of dilithium salts of carbon-bridged Cp/indenyl/$CpCH_2CH_2NMe_2$-carboranyl ligands with $MCl_2(PPh_3)_2$ afforded the late transition metal complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**II-2a**), Ni (**II-2b**)), $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**II-3a**), Ni (**II-3b**)), and $[\eta^5{:}\sigma\text{-}Me_2C(Me_2NCH_2CH_2C_5H_3)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**II-4**) in good yields. In complex **II-4**, the amino substitution group on Cp does not coordinate to the metal center.

The M-C_{cage} bonds in these late transition metal complexes (**II-2a**, **II-2b**, **II-3a**, **II-3b** and **II-4**) were inert for the insertion reaction of unsaturated molecules because of the steric hindrance of carboranyl ligand. When treating the late transition metal complexes $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(PPh_3)$ with 2,6-dimethylphenylisocyanide (XyNC) and N-heterocyclic carbene (NHC), ligand substitution products

$[\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(2,6\text{-}Me_2\text{-}C_6H_3NC)$ (M = Co (**II-5a**), Ni (**II-5b**)), and $[\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[1,3\text{-}(2,6\text{-}^iPr_2(C_6H_3))_2\text{-}C_3N_2H_2]$ (M = Co (**II-6a**), Ni (**II-6b**)) rather than the insertion products were formed. Ligand substitution reaction can also proceed between $[\eta^5$:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(PPh_3)$ and PCy_3 or dppe.

Chapter 3

Synthesis, Structural Characterization, and Reactivity of Group 4 Metallacarboranes Containing $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ Ligand

3.1 Introduction

Fourteen electron, d^0 bent metallocene alkyl complexes of general type $(C_5R_5)_2M(R)^{n+}$ (M = lanthanide, n = 0; M = group 4 metals, n = 1) have received great interests as they exhibit a rich insertion, olefin polymerization, and C-H bond activation chemistry, which is highly sensitive to the structural and electronic properties of $(C_5R_5)_2M$ fragment.[99,100] The Jordan group reported that the replacement of a uninegative $C_5R_5^-$ ligand of cationic group 4 metal alkyls $(C_5R_5)_2M(R)^+$ by the isolobal, dinegative dicarbollide ligand ($C_2B_9H_{11}^{2-}$) leads to the formation of a class of neutral mixed sandwich complexes $(C_5R_5)(C_2B_9H_{11})M(R)$, showing a variety of ligand exchange, insertion and ligand C-H activations characteristics of electrophilic metal alkyls.[40-46] In view of the differences in chemical and physical properties between $(C_5H_5)_2MCl_2$ and $[Me_2C(C_5H_4)_2]MCl_2$ complexes,[101] we wondered whether a Me_2C-linkage could be introduced to $(C_5R_5)(C_2B_9H_{11})M(R)$ system to link the organic π - ligand $C_5R_5^-$ and inorganic π - ligand $C_2B_9H_{11}^{2-}$, thus alternating the geometry of the resulting mixed sandwich complexes so as to change their properties.

It is well-documented that $C_2B_9H_{11}^{2-}$ can be conveniently prepared from deboration of *o*-$C_2B_{10}H_{12}$.[2a,2c] However, the selective deboration of

$Me_2C(C_5H_5)(C_2B_{10}H_{11})$[8,11,13,14,17,18,28,102] using typical reagents such as MeOH/KOH, MeOH/Na_2CO_3 and MeOH/CsF was unsuccessful. Only $C_2B_9H_{12}^-$ was generated via the cleavage of the C_{cage}-C_{bridge} bond. Such a result may be ascribed to the electron-withdrawing nature of the carboranyl unit, enhancing the electrophilicity of the bridging carbon atom in the ligand which is easily attacked by nucleophiles, resulting in the cleavage of the C_{cage}-C_{bridge} bond. We found, after many attempts, that piperidine/EtOH reagent can selectively remove one BH vertex from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ and leave the C_{cage}-C_{bridge} bond intact. This chapter reports the synthesis and structural characterization of the new ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ and its group 4 metal complexes.

3.2 Synthesis and Characterization of Ligand

Treatment of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ with a large excess amount of piperidine in refluxing ethanol for two days gave, after the addition of Me_3NHCl, the selective deboration product $[Me_3NH][Me_2C(C_5H_5)(C_2B_9H_{11})]$ (**III-1**) in 80% isolated yield (Scheme 3.1). The reaction was closely monitored by ^{11}B NMR. It is noteworthy that piperidine/EtOH is the best reagent for this reaction after examining many primary, secondary and tertiary amines in MeOH or EtOH.[103]

The composition of **III-1** was fully characterized by various spectroscopic techniques and elemental analyses. Its ^{11}B NMR showed a 2:2:1:1:1:1:1 pattern, which differs significantly from that of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$. Both ^1H and ^{13}C NMR data suggested that **III-1** is a mixture of isomers in which the bridging carbon atom bonds to either sp^3 or sp^2-C of the cyclopentadienyl ring.

Compound **III-1** was easily converted to its sodium salt $[\{[(\mu\text{-}\eta^5):\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Na(THF)\}\{Na(THF)_3\}\{Na(THF)_2\}]_2$ (**III-2**) by reacting with an excess amount of NaH in refluxing THF solution (Scheme 3.1). The ^1H NMR spectrum showed two multiplets at 6.58 and 6.37 ppm attributable to the cyclopentadienyl ring protons, two singlets at 1.90 and 1.65 ppm corresponding to the Me_2C-linkage and two multiplets of THF molecules. The ^{13}C NMR data were consistent with the above result. Its ^{11}B NMR exhibited a 6:2:1 pattern. Thus, this deprotonation was closely monitored by ^{11}B NMR. The molecular structure of **III-2** was further confirmed by single-crystal X-ray analyses.

There are two crystallographically independent molecules in the unit cell. One of them is shown in Figure 3.1. It is a centrosymmetric dimer with the inversion center at the mid-point of the Na(1)…Na(1A) connectivity. The Na(2) atom is η^5-bound to both cyclopentadienyl ring and dicarbollyl ligand and coordinated to one THF molecule to form the structural motif. Two of such a unit are linked to each other via several B-H Na(1)/B-H Na(1A) interactions leading to the formation of a dimeric structure. The average Na(2)/Na(3)-C_{ring} distances of 2.744(1)/2.766(1) Å compare to that of 2.705(4)/2.775(4) Å in $[\{(\mu\text{-}\eta^5):\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$,[104] and 2.736(9) Å in $[(THF)_3Na(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_5)(\eta^2\text{-}PhNHNPh)Sm]_2(\mu\text{-}\eta^2:\eta^3\text{-}N_2Ph_2)_2$.[105] The average Na(2)-cage atom distance of 2.894(1) Å is much longer than that of 2.743(18) Å in $\{Na_2(THF)_4[2,4\text{-}(SiMe_3)_2C_2B_4H_4]\}_2$.[106] The average Na(1)···B distance of 3.006(1) Å is comparable to those of 2.977(9)/3.029(9)/3.015(9) Å in $[\{[\eta^5:\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$,[105c] 3.010(4)/3.019(4) Å in $[\{(\mu\text{-}\eta^5):\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$,[104] 3.012(6) Å in

$[\eta^5\text{-}(Me_3Si)_2C_2B_4H_5]Na(THF)$,[107] and 2.953(6) Å in $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$.[49] The Cent($C_5$)-Na(2)-Cent($C_2B_3$) angle is 104.1°.

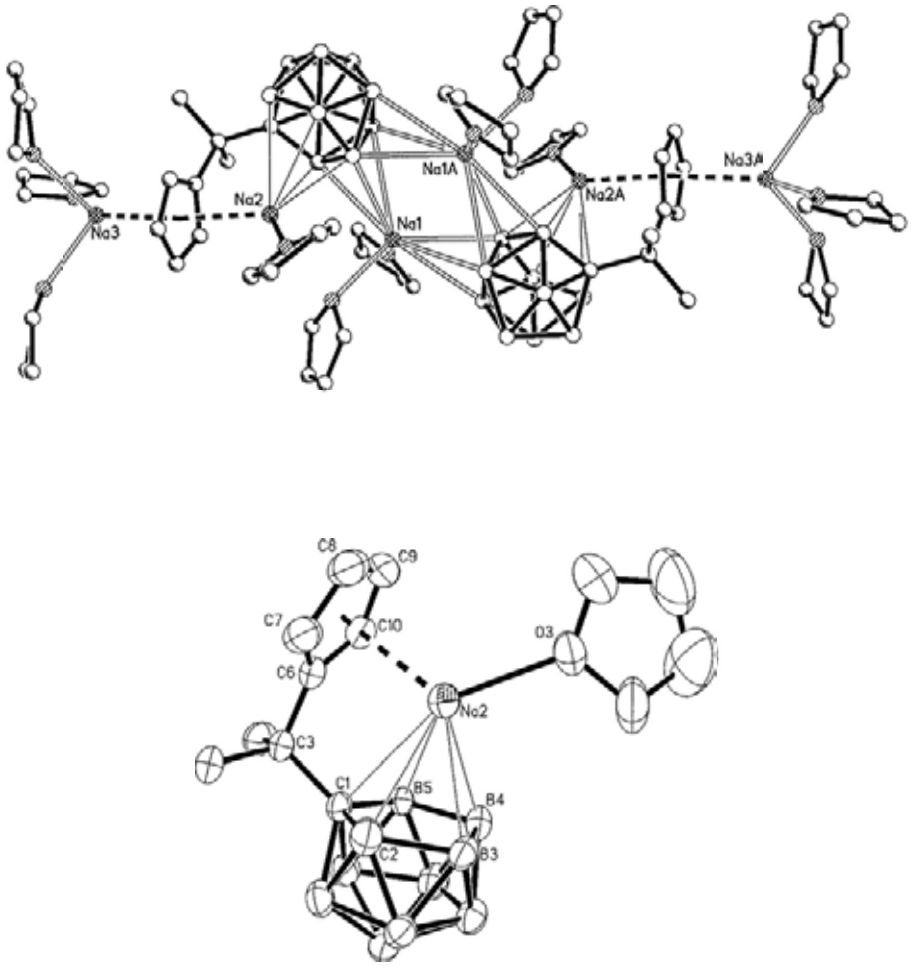
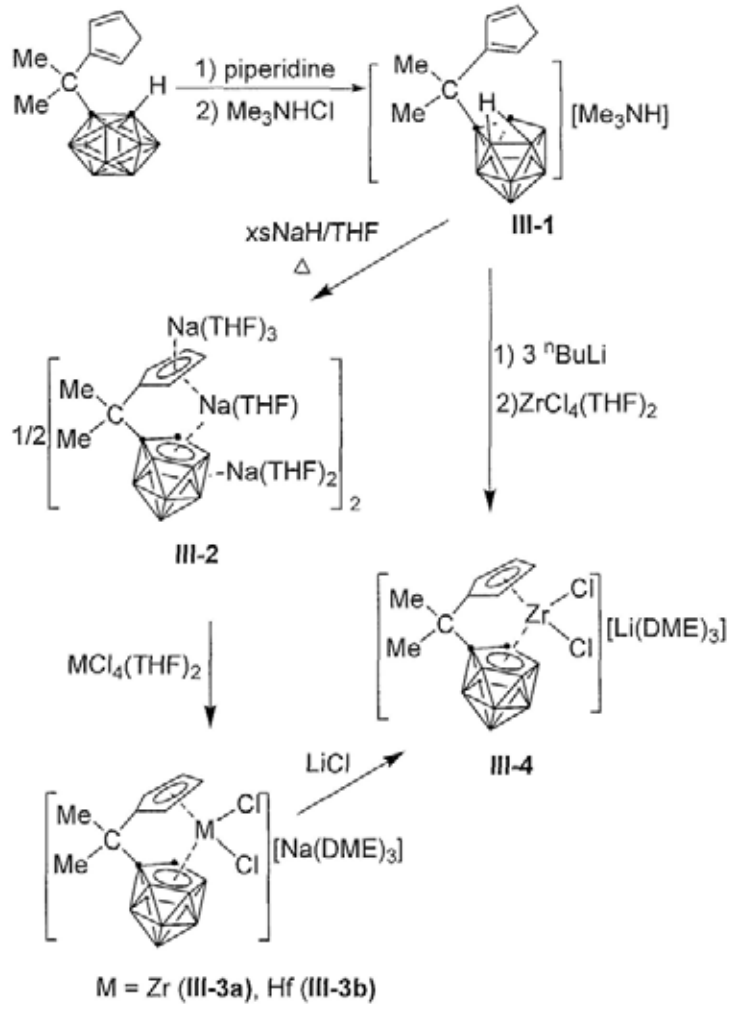


Figure 3.1. Top: molecular structure of

$[\{[(\mu\text{-}\eta^5):\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Na(THF)\}\{Na(THF)_3\}\{Na(THF)_2\}]_2$ (**III-2**)

Bottom: closer view of the coordination around the Na(2)

Scheme 3.1



3.3 Synthesis and Reactivity of Group 4 Metal Complexes

Reaction of **III-2** with 1 equiv of $MCl_4(THF)_2$ in THF at room temperature afforded, after recrystallization from a DME solution, the mixed sandwich complexes $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr (**III-3a**), Hf (**III-3b**)) in ~ 70% isolated yields (Scheme 3.1). The yields were much lower using one-port synthesis from **III-1**. The ^1H and ^{13}C NMR spectra of **III-3a** and **III-3b** were very similar. Their ^{11}B NMR spectra were different: **III-3a** showed a 1:1:3:3:1 pattern whereas **III-3b**

exhibited a 1:1:2:1:2:1:1 one. Single-crystal X-ray analyses revealed that **III-3a** has an ionic structure, consisting of well-separated, alternating layers of discrete tetrahedral anions $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2]^-$ and octahedral cations $[Na(DME)_3]^+$. In the anion, the Zr atom is η^5-bound to both cyclopentadienyl ring and dicarbollyl, and σ-bound to two terminal chlorine atoms in a distorted-tetrahedral geometry (Figure 3.2). The Zr-Cent(C_5 ring) distance of 2.188 Å (Table 4.1) is shorter than that of 2.196 Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$ and 2.234 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$.[40] The average Zr-cage atom distance of 2.528(4) Å is comparable to that of 2.523(5) Å in $[\eta^1:\eta^5\text{-}(Me_2NCH_2)C_2B_9H_{10}]_2Zr$,[55] 2.538(5) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$,[52] 2.499 Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$,[40] 2.535/2.533 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[40] 2.568(4) Å in $[\eta^1:\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[54] 2.601(5) Å in $[\eta^1:\eta^5\text{-}(^iPr_2C_6H_3N=CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] and 2.544(6) Å in $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$.[56] The average Zr-Cl distance of 2.447(1) Å is similar to that of 2.414(1) Å in $[\eta^1:\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[54] 2.395(2)/2.388(1) Å in $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{M(THF)_x\}$ (M = Na, x = 3; M = Li, x = 4)[49] and 2.403(2) Å in $[[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]]$.[16] The Cent($C_5$)-Zr-Cent($C_2B_3$) angle of 120.5° is significantly smaller than that of 141.3° in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$[40] and 134.9° in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$[40] due to the presence of a short Me_2C linkage, but it is larger than that of 116.7° observed in $[Me_2C(C_5H_4)_2]ZrCl_2$.[108] These data suggest that the open coordination sphere of the Zr atom in **III-3a** is much larger than that of the corresponding unbridged ones. This is

probably why the chloride ion can approach the electrophilic Zr center to form the complex anion.

The cation in **III-3a** is exchangeable. Reaction of **III-3a** with 1 equiv of LiCl at room temperature produced, after recrystallization from DME, [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][$Li(DME)_3$] (**III-4**) in 24% isolated yield (Scheme 3.1). This complex was also prepared in 41% isolated yield from the reaction of $[Me_2C(C_5H_4)(C_2B_9H_{10})]Li_3(THF)_x$ with 1 equiv of $ZrCl_4(THF)_2$ at room temperature. Its spectroscopic data were very similar to those of **III-3a**. X-ray analyses revealed that **III-4** and **III-3a** are isostructural. The structure parameters of both **III-4** and **III-3a** are listed in Table 3.1.

In general, Cp_2ZrCl_2 is an excellent precursor for the preparation of organozirconium alkyls and amides.[109] The chloro group in **III-3a** can also be replaced by other groups. Treatment of **III-3a** with 1 equiv of C_5H_5Na in THF at room temperature afforded, after recrystallization from DME, {[η^5:η^2-$Me_2C(C_5H_4)(C_2B_9H_{10})$]$Zr(\eta^5$-$C_5H_5)(\mu$-Cl){$Na(DME)_2$ (**III-5a**) in 47% isolated yield (Scheme 3.2). It is noted that **III-5a** is stable even in refluxing DME, and no elimination of NaCl was observed, suggesting a very strong bonding interaction between the Zr center and Cl atom. In addition to the resonances of the bridged ligand, the ^1H NMR spectrum showed a singlet at 6.39 ppm attributable to the Cp protons and two singlets at 3.48 and 3.25 ppm corresponding to DME protons. A pattern of 1:1:1:1:1:2:1:1 was observed in its ^{11}B NMR spectrum. An X-ray diffraction study revealed that the Zr atom in **III-5a** adopts a distorted-tetrahedral geometry by two η^5-cyclopentadienyl rings, one η^2-dicarbollyl ligand and one doubly bridging chlorine

atom (Figure 3.3). The two average Zr-C (C_5 ring) distances (2.534(3) and 2.518(3) Å) are similar. These measured values are also close to that of 2.531(3) Å in **III-3a**. The average Zr-B distance of 2.545(3) Å is longer than that of 2.485(6) Å in $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$.[49] The Zr-Cl distance of 2.547(1) Å is much longer than that of 2.447(1) Å in **III-3a**, 2.394(2) Å in $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$,[49] 2.461(1) Å in $\{[\eta^5\text{-}(Me_3Si)_2C_2B_4H_4]_2ZrCl(THF)\}\{Li(THF)_2\}$[110] and 2.469(2) Å in $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_9H_{10})Li(OEt_2)_2$.[111] This result clearly indicates that the coordination mode of the dicarbollyl is changed from η^5 in **III-3a** to η^2 in **III-5a** probably due to the steric reasons. It is unexpected that the second chloro still bonds to the Zr atom in **III-5a**, suggesting the high Lewis acidity of the metal center.

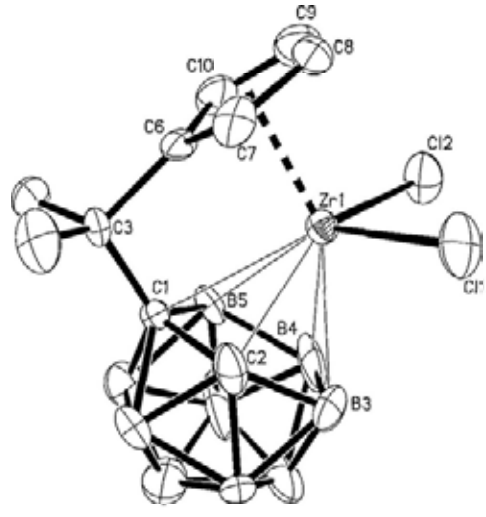
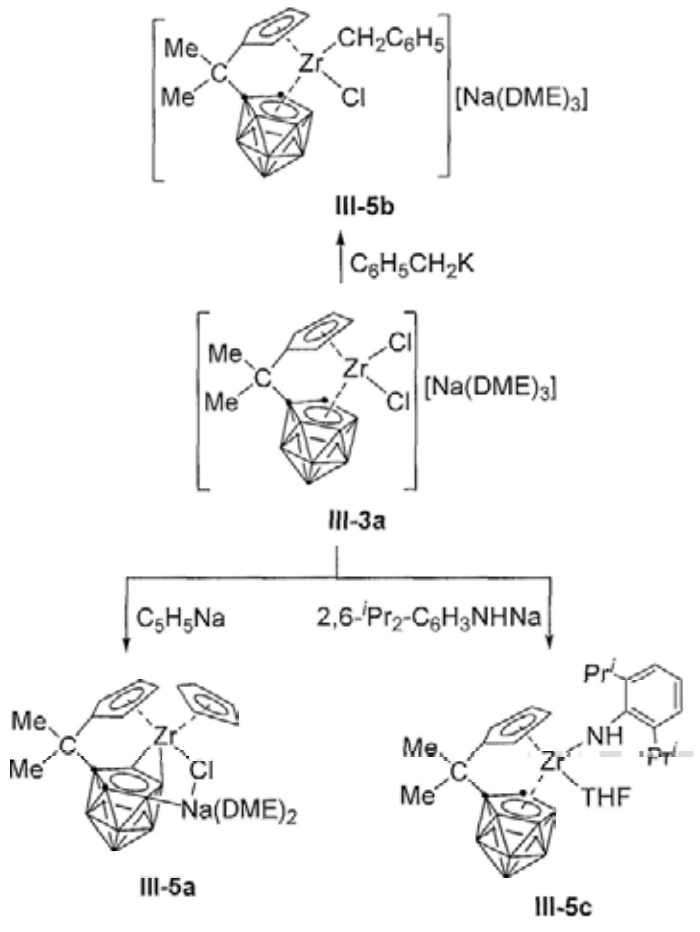


Figure 3.2 Molecular structure of the anion in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$ (**III-3a**)

Scheme 3.2



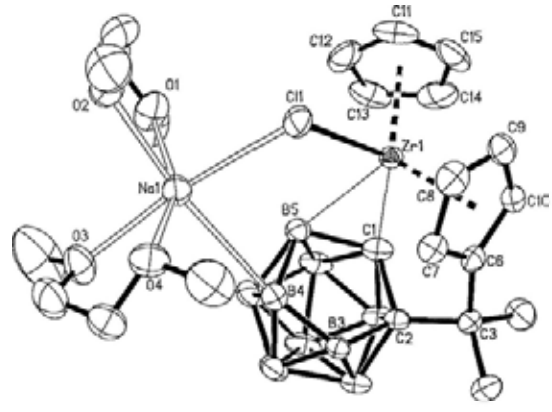


Figure 3.3 Molecular structure of

$\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_4)(\mu\text{-}Cl)\{Na(DME)_2\}$ (**III-5a**)

Table 3.1. Selected Bond Lengths (Å) and Angles (deg) for III-2 – III-5c

	III-2[b]	III-3a[b]	III-4	III-5a	III-5b	III-5c
av. M-C_{ring}	2.755(1)	2.531(3)	2.526(6)	2.534(3)	2.523(1)	2.516(3)
				2.518(3)		
av. M-cage atom	2.899(1)	2.528(4)	2.558(7)	2.545(3)	2.573(1)	2.585(3)
av. Zr-Cl		2.458(1)	2.596(2)	2.547(1)	2.466(1)	
Zr-N						2.055(2)
Zr-C					2.316(1)	
M-Cent(C_5)[a]	2.513	2.219	2.225	2.234	2.221	2.214
M-Cent(C_2B_3)[a]	2.540	2.090	2.112		2.132	2.148
Cent(C_5)-M-Cent(C_2B_3)	104.1	120.3	119.3		119.5	119.2
C_{ring}-C_{bridge}-C_{cage}	108.7(1)	102.2(1)	103.0(4)	103.4(2)	103.3(1)	103.3(2)

[a] Cent(C_5), Cent(C_2B_9): the centroid of the cyclopentadienyl ring and the C_2B_3 bonding face, respectively. [b] Average values of the two cystallographically independent molecules in the unit cell.

Reaction of **III-3a** with 1 equiv of KCH_2Ph in THF at room temperature produced, after recrystallization from DME, $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ (**III-5b**) in 36% isolated yield (Scheme 3.2). In addition to the peaks derived from the bridged ligand, three multiplets in the range 7.48-6.92 ppm corresponding to the aromatic protons of the benzyl group, one broad resonance at 2.60 ppm attributable to the CH_2 protons of the benzyl and two singlets of DME molecule were observed in the ^1H NMR spectrum. Its ^{11}B NMR spectrum showed a 1:1:1:2:1:1:1 pattern. The ionic nature of **III-5b** was confirmed by single-crystal X-ray diffraction study. The geometry of the anion $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)]^-$ is similar to that found in **III-3a** with one Cl atom being replaced by a benzyl group (Figure 3.4). The average Zr-C(C_5 ring)/Zr-Cl distances (2.523(1)/2.466(1) Å) and the Cent(C_5)-Zr-Cent(C_2B_3) angle (119.3°) are similar to the corresponding values (2.531(3)/2.447(1) Å and 120.3°) observed in **III-3a**, whereas the average Zr-cage atom distance of 2.573(1) Å in **III-5b** is longer than that of 2.528(4) Å in **III-3a**. The Zr-C σ bond distance of 2.316(1) Å is much longer than that of 2.233(6) Å in $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$,[56] 2.209(6) Å in $[\{\eta^1:\sigma:\eta^5\text{-}[MeN(CH_2)CH_2CH_2]C_2B_9H_{10}]\}Zr(\mu:\eta^1\text{-}OCH_2CH_2OCH_3)]_2$,[56] 2.198(4) Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$,[40] and 2.187(6)/2.176(7) Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[40] but is comparable to that of 2.294(4) Å in $[\eta^1:\sigma\text{-}^tBuC_6H_3(PPh_2)O]Zr(CH_2Ph)_2$,[112] and 2.308(5) Å in $[Bu^n(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]Zr(CH_2Ph)_2$.[113]

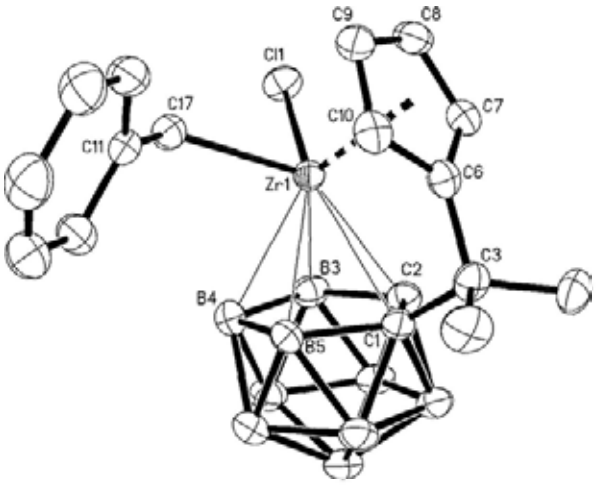


Figure 3.4 Molecular structure of the anion in

$[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ (**III-5b**)

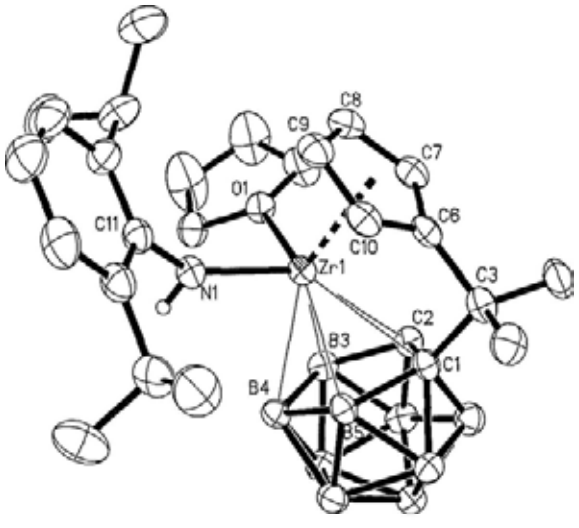


Figure 3.5 Molecular structure of

$[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$ (**III-5c**)

The aforementioned results showed that the chloro group always bonds to the Zr atom to stabilize the electron deficient metal species, preventing the formation of neutral metal complexes. We then turned our attention to amido groups, since the additional lone-pair can form p_π-d_π backbonding with d^0 metal center, facilitating the elimination of NaCl. Treatment of **III-3a** with 1 equiv of $NaNHC_6H_3Pr^i_2$ in THF at room temperature gave, after recrystallization from toluene, a neutral species $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$ (**III-5c**) in 62% isolated yield (Scheme 3.2). Complex **III-5c** was fully characterized by various spectroscopic techniques and elemental analyses. Single-crystal X-ray analyses revealed that **III-5c** is a neutral species and showed one toluene of solvation. The Zr atom is η^5-bound to both cyclopentadienyl and dicarbollyl ligands, σ-bound to the amido nitrogen atom and coordinated to one THF molecule in a distorted-tetrahedral geometry (Figure 3.5). The average Zr-C(C_5 ring) distance of 2.516(3) Å is comparable to that of 2.531(3) Å in **III-3a**, but the average Zr-cage atom distance of 2.585(3) Å is longer than that of 2.528(4) Å in **III-3a**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 119.2° is very close to that of 120.3° in **III-3a**. The Zr-N bond distance of 2.055(2) Å is similar to that of 2.036(4)/2.043(4) Å in $[\eta^1:\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] 2.029(4)/2.020(4) Å in $[\eta^5\text{-}(C_2B_9H_{10})(CH_2)_2NBz_2)]Zr(NMe_2)_2(NHMe_2)$,[54] and 2.015(3)/2.018(3) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$.[52] The relatively shorter Zr-N bond distance and a large Zr-N-C angle of 143.8(1)° imply the presence of $p_\pi(N)$-$d_\pi(Zr)$ interactions, which reduces the Lewis acidity of the metal center. Such electronic effects plus steric effects imposed by two ^{i}Pr groups lead to the formation of a neutral metal complex.

3.4 Polymerization Activities of Group 4 Metal Complexes

Complexes **III-3a**, **III-3b** and **III-5b** underwent preliminary testing for catalytic activity, using methylalumoxane (MAO) as cocatalyst in toluene at room temperature (1 atm of ethylene). The results were compiled in Table 3.2. All three complexes were very active catalysts for polymerization of ethylene in the presence of MAO under the reaction conditions specified in Table 3.2. However, the catalytic activity of **III-3a** dropped from 4.51 x 10^6 to 1.62 x 10^3 g/mol·atm·h as the Al/Zr molar ratio was decreased from 1500 to 750. When this ratio was 200, only trace amount of polymer was observed. Complex **III-5b** was inactive in the absence of MAO. These results may indicate that a large excess amount of MAO is necessary to abstract the chloro ligand from the metal complexes due to the very strong interactions between the electron-deficient metal center and Lewis base Cl^- as previously discussed. The active species was suggested to be the neutral metal complex $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]M(R)$.

Table 3.2. Ethylene Polymerization Results[a]

catalyst	activity (10^6 g/mol·atm·h)	$M_w/10^3$	M_w/M_n[b]	T_m (°C)[c]
III-3a (Zr)	4.51	48.6	6.87	131.3
III-3b(Hf)	1.38	26.6	4.38	130.1
III-5b (Zr)	4.32	50.2	6.35	131.0

[a] Condtions: toluene (50 mL), 1 atm of ethylene, T = 25 °C, catalyst (3.0 μmol), MAO (4.5 mmol), Al/M = 1500, reaction time = 30 min. [b] Measured by GPC (using polystyrene standards in 1, 2, 4-trichlorobenzene at 150 °C). [c] Measured by DSC (heating rate: 10 °C / min).

3.5 Summary

A new inorganic/organic hybrid π ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ was prepared via a selective deboration of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ with piperidine in ethanol. Treatment of its sodium salt with $MCl_4(THF)_2$ gave the ionic mixed sandwich complexes $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr (**III-3a**), Hf (**III-3b**)). No neutral species were formed probably due to the presence of a short Me_2C linkage increasing the open coordination sphere of the Zr atom comparing with the unbridged ones which made the chloride ion can approach the electrophilic Zr center to form the complex anion. Complex **III-3a** reacted with C_5H_5Na, KCH_2Ph or $NaNH(C_6H_3\text{-}2,6\text{-}Pr^i_2)$ to afford $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_2\}$ (**III-5a**), $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ (**III-5b**) and $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$ (**III-5c**), respectively. Both **III-5a** and **III-5b** were stable, and no NaCl elimination was observed upon heating the toluene solution. The presence of $p_\pi(N)\text{-}d_\pi(Zr)$ interactions make the formation of neutral **III-5c** possible.

Complex **III-3a**, **III-3b** and **III-5b** showed a very high activity in ethylene polymerization after activation with a large amount of MAO. The active species were suggested to be neutral group 4 metal methyl complexes $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]MCH_3$.

Chapter 4

Synthesis, Structure, and Reactivity of Group 4 Metallacarboranes Bearing the Ligand $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$

4.1 Introduction

Fourteen electron, bent metallocene alkyl complexes $(C_5R_5)_2Ln(R^1)$,[100] $(C_5R_5)_2M(R^1)^+$,[99,101] and $(C_5R_5)(C_2B_9H_{11})M(R^1)$[40-46] (Ln = lanthanides, M = group 4 metals) share common features of ligand exchange, insertion, olefin polymerization, and C-H bond activation. These characteristics of electrophilic metal alkyls are highly sensitive to the structural and electronic properties of the $(C_5R_5)_2M$ fragment.[40-46,99-101] Therefore, an extensive work on the modification of cyclopentadienyl ligand has been done in order to control the properties of metallocenes. In sharp contrast, modifications of the dicarbollyl ligand in $(C_5R_5)(C_2B_9H_{11})M(R^1)$ are much less explored,[40-46] although many examples of group 4 metallacarboranes bearing tethered Lewis base functionalities have been documented.[50,51a,b,53-58,114] We have reported a linked *ansa*-ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ in last chapter.[115] It can largely increase the "bite angle"[101c] of the resulting group 4 metallocenes in comparison with the corresponding unbridged ones.[115] On the other hand, the high electrophilicity of the metal center plus a more open coordination sphere make the synthesis of neutral metal alkyls very difficult. To overcome this problem, we extended our work to indenyl systems in the hope that the sterically demanding yet planar indenyl ring and the known diverse bonding modes

(η^5-η^3-η^1) between the central metal and five-membered ring of indenyl ligand could facilitate the formation of neutral metal alkyls.[116] In this chapter, we report a new Me_2C-linked indenyl-dicarbollyl ligand $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ and its group 4 metal chloride, amide, oxide and alkyl complexes. Similarities and differences between $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ and $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ in coordination chemistry are also discussed.

4.2 Synthesis and Characterization of Ligand.

Treatment of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$[9,10,13,15] with a large excess amount of piperidine in refluxing ethanol for two days gave, after addition of Me_3NHCl, a selective deboration product $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**IV-1**) in 91% isolated yield (Scheme 4.1). The reaction was closely monitored by ^{11}B NMR spectra. It was noted that piperidine/EtOH is the best reagent for this reaction after screening many other reagents such as MOH/MeOH (M = Na, K),[117] the fluoride ion,[118] and various amines,[103] which led to either a mixture of products or the cleavage of the C_{bridge}-C_{cage} bond.

The composition of **IV-1** was fully characterized by various spectroscopic techniques and elemental analyses. Its ^{11}B NMR spectrum showed a 2:2:1:1:1:1:1 pattern, which differs significantly from that of its parent compound $Me_2C(C_9H_7)(C_2B_{10}H_{11})$. Both ^1H and ^{13}C NMR data showed that the bridging carbon atom in **IV-1** is bonded only to the sp^2-carbon of the indenyl unit, which is confirmed by single-crystal X-ray analyses (Figure 4.1). The C(24)-C(25)/C(24)-C(32)/C(25)-C(30)/C(30)-C(31)/C(31)-C(32) distances of

1.481(4)/1.330(4)/1.394(4)/1.498(5)/1.494(4) Å and the planar geometry of C(24) atom clearly indicate the sp^2 hybridization of C(24).

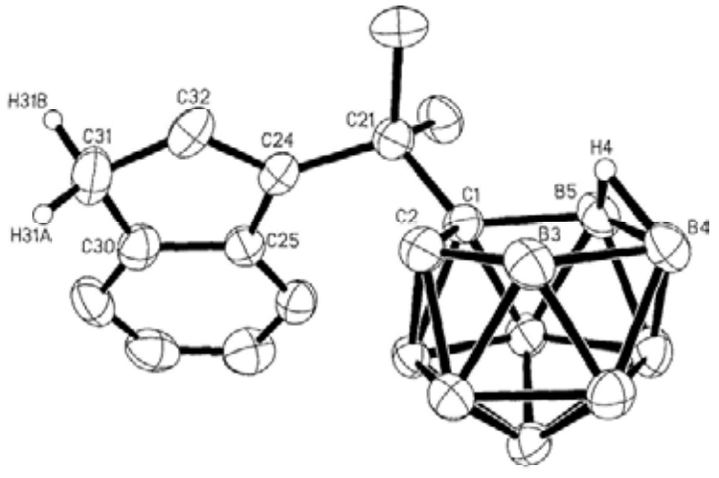


Figure 4.1. Molecular structure of the anion in $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**IV-1**)

4.3 Synthesis and Reactivity of Group 4 Metal Complexes

Compound **IV-1** contains three types of acidic protons, namely the B-H-B, the sp^3-CH_2 of the indenyl group and the NH, which may be deprotonated by metal amides.[99d,119] Treatment of **IV-1** with 1 equiv of $Zr(NMe_2)_4$ in DME (1,2-dimethoxyethane) at room temperature overnight afforded a neutral metal amide complex *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NMe_2)(NHMe_2)$ (**IV-2**) in 54% isolated yield (Scheme 4.1). Only *trans* isomer was isolated, in which the six-membered ring of indenyl is *trans* to the unbridged cage carbon atom (Chart 4.1).[120] This complex has a very low solubility in toluene and benzene, decomposes in $CDCl_3$ and CD_2Cl_2, and reacts slowly with THF. Its ^1H and ^{13}C NMR spectra in pyridine-d_5 showed, in addition

to the ligand protons, a free dimethylamine and a dimethylamido group. The amine is dissociated in pyridine-d_5, resulting in the observation of only one set of NMR data. The ^{11}B NMR spectrum exhibited a 1:2:3:2:1 pattern due to coincidence of resonances.

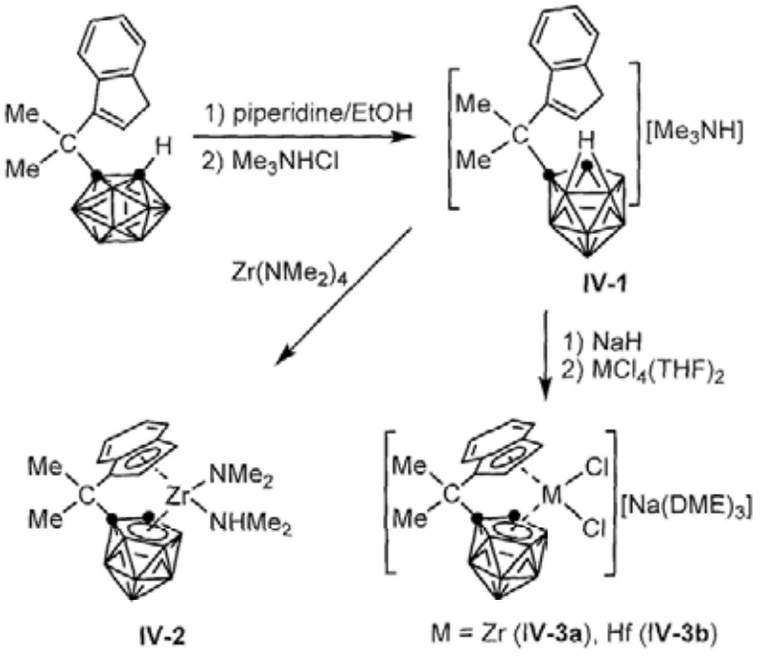
Chart 4.1

cis-isomer *trans*-isomer

Single-crystal X-ray analyses confirm the formation of *trans* isomer of **IV-2**. The Zr atom is η^5-bound to both the five-membered ring of indenyl group and dicarbollyl ligand, σ-bound to one NMe_2 moiety, and coordinated to one $NHMe_2$ molecule in a distorted-tetrahedral geometry (Figure 4.2). The average Zr-C(C_5 ring) distance of 2.599(3) Å compares to that of 2.610(2) Å in *rac*-$[Me_2Si(C_9H_6)_2]Zr(NMe_2)_2$,[121] 2.515(4)/2.514(4) Å in *meso*-$[Me_2C(C_9H_6)_2]ZrCl_2$,[122] 2.513(3) Å in *rac*-$[Me_2C(C_9H_6)_2]ZrCl_2$,[122] 2.521(8) Å in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$,[13] and 2.541(5) Å in $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$.[13] The average Zr-cage atom distance of 2.597(3) Å is similar to that of 2.601(5) Å in $[\eta^1{:}\eta^5\text{-}(^tPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[56] and 2.585(3) Å in $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3{}^iPr_2)(THF)$,[115] but is longer than that of 2.469(8) Å in $[\sigma{:}\eta^5\text{-}(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(DME)$,[119a] 2.523(5) Å in $[\eta^1{:}\eta^5\text{-}(Me_2NCH_2)C_2B_9H_{10}]_2Zr$,[55] 2.538(5) Å in $[\eta^1{:}\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$,[52] 2.499 Å in

$(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$,[40] 2.535/2.533 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[40] 2.568(4) Å in $[\eta^1:\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[54] and 2.544(6) Å in $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$.[56] The Zr-N(1) distance of 2.057(2) Å is very similar to that of 2.078(2) Å in *rac*-$[Me_2Si(C_9H_6)_2]Zr(NMe_2)_2$,[131] 2.016(8) Å in $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$,[13] 2.036(4)/2.043(4) Å in $[\eta^1:\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[56] 2.029(4)/2.020(4) Å in $[\eta^5\text{-}(C_2B_9H_{10})(CH_2)_2NBz_2)]Zr(NMe_2)_2(NHMe_2)$,[54] and 2.015(3)/2.018(3) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$.[52] The Cent($C_5$ ring)-Zr-Cent(C_2B_3) angle of 115.9° is smaller than that of 119.2° in $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3{}^iPr_2)(THF)$,[115] and is significantly smaller than that of 122.9° in *rac*-$[Me_2Si(C_9H_6)_2]Zr(NMe_2)_2$,[121] and 134.9° in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$.[40] These data suggest that the open coordination sphere around the Zr atom in **IV-2** is larger than that observed in the corresponding cyclopentadienyl analogue, and is significantly larger than that found in the unbridged ones.

Scheme 4.1



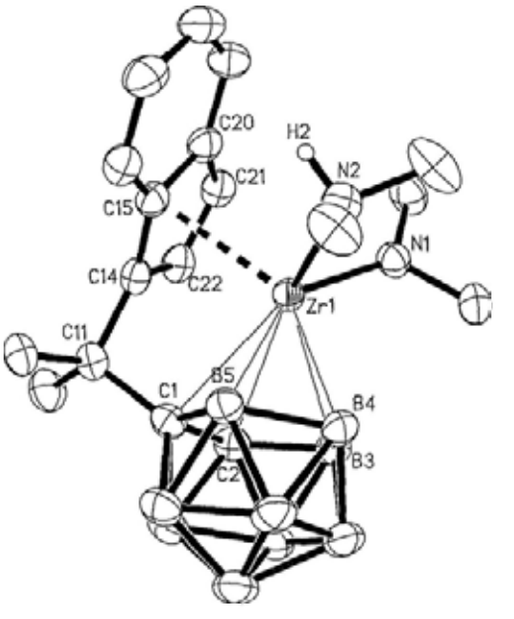


Figure 4.2. Molecular structure of

trans-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NMe_2)(NHMe_2)$ (**IV-2**)

The above amine elimination method serves a convenient way to prepare neutral metal amide complexes. We then attempted the alkane elimination for the synthesis of neutral metal alkyls. Unfortunately, reaction of **IV-2** with 1 equiv of $Zr(CH_2Ph)_4$ or $Zr(CH_2SiMe_3)_4$ was complicated under various reaction conditions as indicated by ^1H NMR spectra, and no pure product was isolated from the above reactions. Since organo-transition-metal halides are useful precursors for a variety of organometallics, their syntheses are, therefore, explored.

Treatment of **IV-1** with excess NaH in refluxing THF gave presumably the trianionic salt $[Me_2C(C_9H_6)(C_2B_9H_{10})]Na_3(THF)_x$, followed by reaction with $MCl_4(THF)_2$ to afford, after recrystallization from DME, the mixed sandwich complexes *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$MCl_2$][$Na(DME)_3$] (M = Zr (**IV-3a**), Hf (**IV-3b**)) as the single isomer[120] in ~ 60% isolated yields (Scheme 4.1). Their ^1H NMR spectra showed multiplets in the range 7.96 — 6.66 ppm attributable to the indenyl protons, two singlets at 1.85 and 1.74 ppm corresponding to the Me_2C-linkage and two singlets at 3.48 and 3.25 ppm assignable to the DME molecules. The ^{13}C NMR data were consistent with the above results. Their ^{11}B NMR spectra exhibited a 1:1:3:3:1 pattern. The compositions of both **IV-3a** and **IV-3b** were confirmed by elemental analyses.

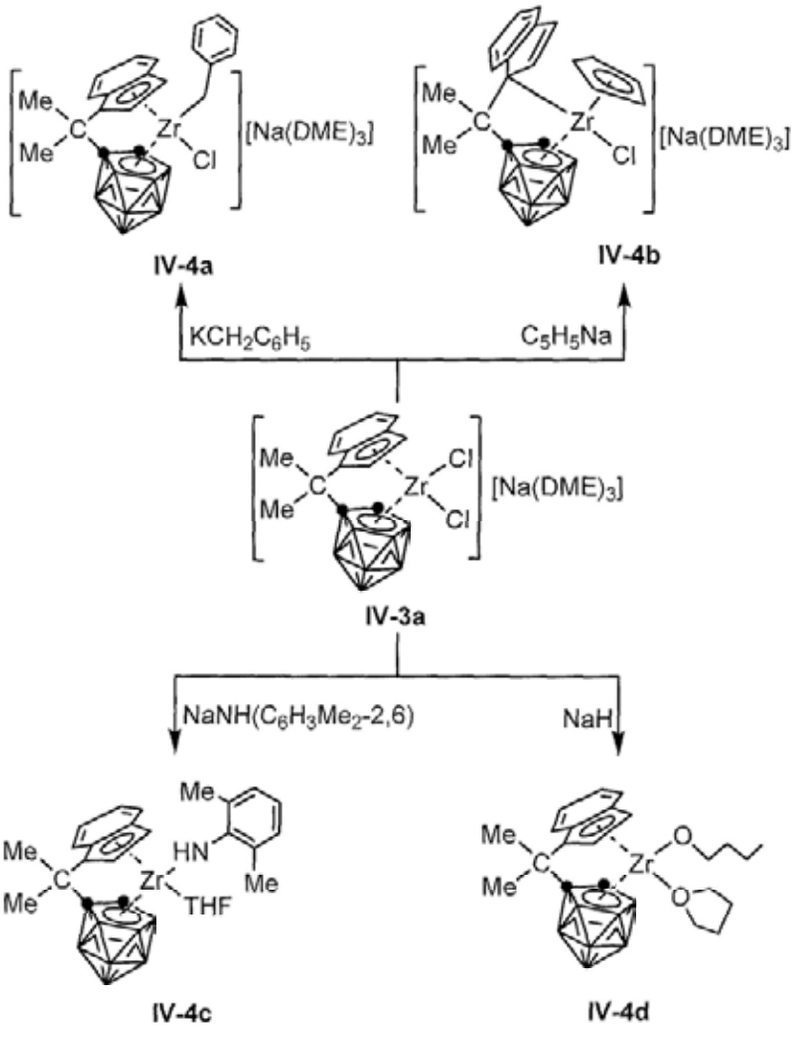
Reaction of **IV-3a** with 1 equiv of KCH_2Ph in THF at room temperature produced, after recrystallization from DME, *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl(CH_2C_6H_5)$][$Na(DME)_3$] (**IV-4a**) in 29% isolated yield (Scheme 4.2). In addition to the peaks derived from the bridging ligand, one broad resonance at 2.60 ppm attributable to the CH_2 protons of the benzyl group[123] and two singlets at 3.48 and 3.25 ppm corresponding to DME molecule were observed

in the ^{1}H NMR spectrum. Its ^{11}B NMR spectrum showed a 1:1:1:1:2:1:1:1 pattern. Single-crystal X-ray diffraction study confirms that **IV-4a** is a *trans* isomer and is ionic in nature. The Zr atom is η^5-bound to both five-membered ring of the indenyl group and dicarbollyl unit, σ-bound to one benzyl and one chlorine atom in a distorted-tetrahedral geometry (Figure 4.3). The average Zr-C(C_5 ring) and Zr-cage atom distances of 2.619(6) and 2.591(7) Å are similar to the corresponding values of 2.599(3) and 2.597(3) Å observed in **IV-2**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 117.3° is very comparable to that of 115.9° in **IV-2** and 119.3° in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$.[115] The Zr-Cl distance of 2.442(2) Å is very close to that of 2.466(1) Å in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$,[115] 2.421(1)/2.413(1) Å in *meso*-$[Me_2C(C_9H_6)_2]ZrCl_2$,[132] 2.417(1) Å in *rac*-$[Me_2C(C_9H_6)_2]ZrCl_2$,[122] and 2.403(2) Å in $[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$.[16] The Zr-C σ bond distance of 2.312(6) Å is comparable to that of 2.316(1) Å in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$,[115] 2.301(1) Å in $[\eta^5\text{-}C_9H_5\text{-}1,3\text{-}(SiMe_3)_2]_2Zr(OCH_2CH_2CH_2CH_2)$,[124] 2.256(3) Å in $[\eta^5\text{-}C_9H_6\text{-}2\text{-}(5\text{-}Me\text{-}C_4H_3O)]_2Zr(CH_2CMe_3)_2$,[125] 2.298(2)/2.289(2) Å in $(\eta^5\text{-}4,7\text{-}F_2C_9H_6)_2Zr(CH_2C_6H_5)_2$,[123c] and 2.269(2)/2.242(2) Å in $[meso\text{-}CH_2CH_2\text{-}(4,7\text{-}Me_2\text{-}C_9H_4)_2]ZrMe_2$.[126]

Treatment of **IV-3a** with 1 equiv of C_5H_5Na in THF at room temperature afforded, after recrystallization from DME, *trans*-$\{[\eta^1:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]ZrCl(\eta^5\text{-}C_5H_5)\}\{Na(DME)_3\}$ (**IV-4b**) in 53% isolated yield (Scheme 4.2). It was noted that **IV-4b** is stable even in refluxing DME,

and no elimination of NaCl was observed.[49,127] Addition of chloride abstracting reagents such as $AgClO_4$ and $AgBPh_4$ led to inseparable mixture of products as indicated by ^1H NMR spectra. An X-ray diffraction study revealed that the Zr atom in **IV-4b** adopts a distorted-tetrahedral geometry by η^5-bound to both cyclopentadienyl ring and dicarbollyl ligand, and η^1-bound to the indenyl group and chlorine atom, respectively (Figure 4.4). The average Zr-cage atom distance of 2.536(8) Å is shorter than that of 2.597(3) Å in **IV-2** and 2.591(7) Å in **IV-4a**, but is longer than that of 2.469(8) Å in $[\sigma:\eta^5\text{-}(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(DME)$.[119a] The average Zr-C(Cp ring) distance of 2.507(7) Å is similar to that of 2.534(3)/2.518(3) Å in $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_3\}$.[115] The Zr-C($\eta^1$) σ bond distance of 2.420(6) Å is comparable to that of 2.477(6) Å in $[\sigma:\eta^5\text{-}(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(DME)$,[119a] but is much shorter than that of 2.603(8) Å in $(Ph_2C_9H_6P{=}NPh)Zr(CH_2C_6H_5)_3$.[128] The Zr-Cl distance of 2.511(2) Å is longer than that of 2.442(2) Å in **IV-4a**, but is slightly shorter than that of 2.547(1) Å in $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_3\}$.[115]

Scheme 4.2



The aforementioned results show that the chloro group always bonds to the Zr atom to stabilize the electron-deficient metal species, preventing the formation of neutral metal alkyls.[40-46] On the other hand, the isolation of **IV-2** suggests that the $p_{\pi}(N)$-$d_{\pi}(Zr)$ interaction can lower Lewis acidity of the Zr center, resulting in the formation of neutral metal amides. This is supported by the following experiments. Treatment of **IV-3a** with 1 equiv of $NaNHC_6H_3Me_2$ in THF at room temperature gave, after recrystallization from

toluene, a neutral species *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($NHC_6H_3Me_2$)(THF) (**IV-4c**) in 54% isolated yield (Scheme 4.2). Complex **IV-4c** was fully characterized by various spectroscopic techniques and elemental analyses. Its structure is confirmed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both indenyl and dicarbollyl ligands, σ-bound to the amido nitrogen atom and coordinated to one THF molecule in a distorted-tetrahedral geometry (Figure 4.5). The average Zr-C(C_5 ring)/Zr-cage atom distances of 2.577(6)/2.583(6) Å is similar to those of 2.599(3)/2.597(3) Å in **IV-2**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 119.4° is larger than that of 115.9° in **IV-2,** but is very similar to that of 119.2° in [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr($NHC_6H_3Pr^i_2$)(THF)[115] probably due to the steric reasons. The Zr-N σ bond distance of 2.035(4) Å is close to that of 2.055(2) Å in [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr($NHC_6H_3Pr^i_2$)(THF),[115] and 2.057(2) Å in **IV-2**. The relatively large Zr-N-C angle of 150.1(3)° implies the presence of p_π(N)-d_π(Zr) interactions.

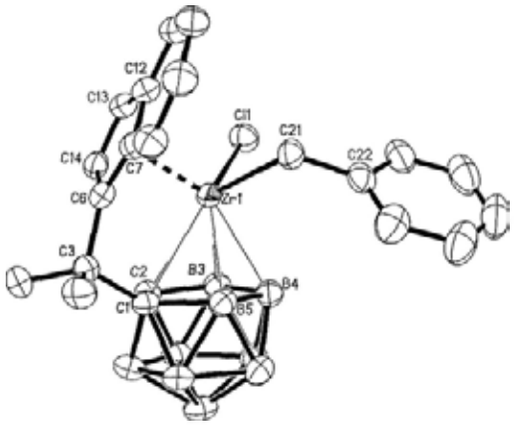


Figure 4.3. Molecular structure of the anion in

trans-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl(CH_2C_6H_5)$][$Na(DME)_3$] (**IV-4a**)

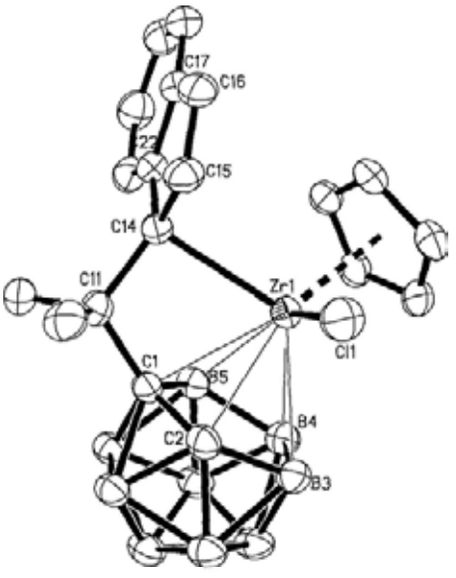


Figure 4.4. Molecular structure of the anion in

trans-[{η^1:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl(\eta^5$-$C_5H_5)$][$Na(DME)_3$] (**IV-4b**)

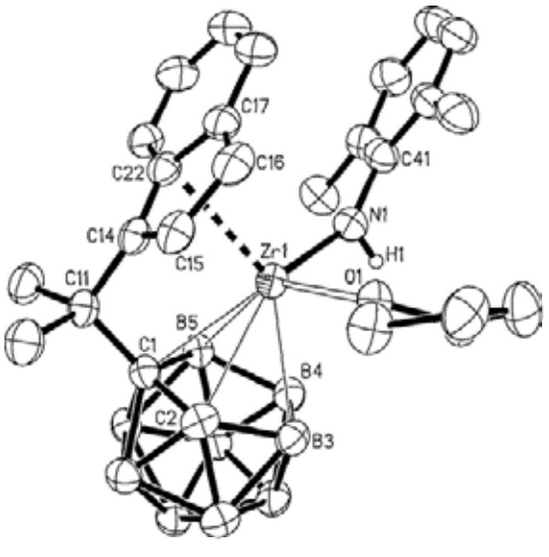


Figure 4.5. Molecular structure of

trans-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NHC_6H_3Me_2$-2,6)(THF) (**IV-4c**)

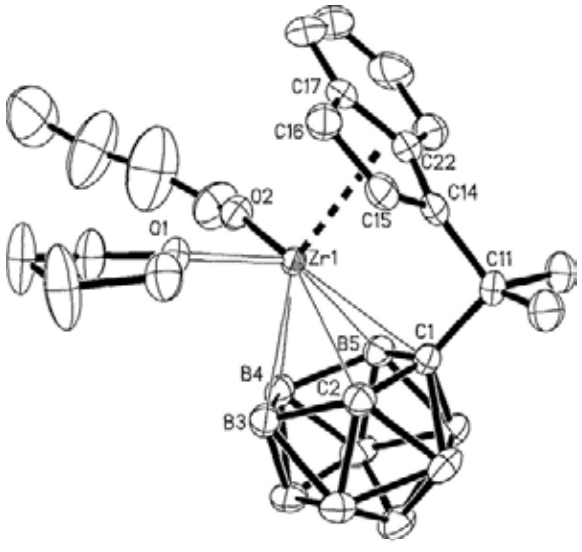


Figure 4.6. Molecular structure of

trans-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($OCH_2CH_2CH_2CH_3$)(THF) (**IV-4d**)

Table 4.1. Selected Bond Lengths (Å) and Angles (deg) for IV-2, and IV-4a — IV-4d

	IV-2	IV-4a	IV-4b	IV-4c	IV-4d
Zr-C(C_5 ring)	2.468(3)	2.480(5)	2.452(6)	2.431(4)	2.422(6)
	2.515(3)	2.491(5)	2.490(7)	2.482(5)	2.517(6)
	2.599(3)	2.640(6)	2.517(7)	2.595(5)	2.558(6)
	2.677(3)	2.692(5)	2.537(7)	2.630(6)	2.671(7)
	2.738(3)	2.792(6)	2.541(7)	2.747(6)	2.734(6)
av. Zr-C_{ring}	2.599(3)	2.619(6)	2.507(7)	2.577(6)	2.580(7)
av. Zr-cage atom	2.597(3)	2.591(7)	2.536(8)	2.583(6)	2.554(8)
av. Zr-Cl		2.442(2)	2.511(2)		
Zr-N	2.057(2)			2.035(4)	
Zr-O					1.930(5)
Zr-C		2.312(6)	2.420(6)		
Zr-Cent(C_5) [a]	2.300	2.327	2.213	2.275	2.282
Zr-Cent(C_2B_3) [a]	2.164	2.154	2.090	2.147	2.105
Cent(C_5)-Zr-Cent(C_2B_3)	115.9	117.3		119.4	120.6
C_{ring}-C_{bridge}-C_{cage}	103.1(2)	103.8(4)	108.0(5)	104.4(4)	103.8(5)

[a] Cent(C_5), Cent(C_2B_3): the centroids of the five-membered rings of the indenyl and the C_2B_3 bonding face, respectively.

Another example of neutral metal complexes is the metal alkoxide, *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($OCH_2CH_2CH_2CH_3$)(THF) (**IV-4d**). It was isolated in 33% yield from the reaction of **IV-3a** with excess NaH in refluxing THF (Scheme 4.2). Single-crystal X-ray analyses confirm that **IV-4d** is a *trans* isomer and show half benzene of solvation in the crystal lattice. The Zr atom is η^5-bound to both indenyl and dicarbollyl ligands, σ-bound to the oxygen atom of the alkoxy group and coordinated to one THF molecule in a distorted-tetrahedral geometry (Figure 4.6). The average Zr-C(C_5 ring) distance of 2.580(7) Å is similar to that of 2.599(7) Å in **IV-2** and 2.577(6) Å in **IV-4c**. The average Zr-cage atom distance of 2.554(8) Å can be compared to that of 2.597(3) Å in **IV-2**, 2.583(6) Å in **IV-4c**, and 2.552(6) Å in [{η^1:σ:η^5-[$MeN(CH_2)CH_2CH_2$]$C_2B_9H_{10}$}Zr(μ:η^1-$OCH_2CH_2OCH_3$)]$_2$.[56] The Zr-O σ bond distance of 1.930(5) Å compares to that of 2.167(3) Å in [{η^1:σ:η^5-[$MeN(CH_2)CH_2CH_2$]$C_2B_9H_{10}$}Zr(μ:η^1-$OCH_2CH_2OCH_3$)]$_2$,[56] 1.897(3) Å in [*rac*-η^5:η^5-CH_2CH_2-1,2-$(C_9H_6)_2$Zr($OCMe_2CH_2CH_2CH{=}CH_2$)][$MeB(C_6F_5)_3$],[129] 2.015(2) Å in [4,6-^{t}Bu$_2$-2-(η^5-C_9H_6)-C_6H_2O]$_2$Zr,[130] 1.979(3)/2.022(3) Å in [*meso*-CH_2CH_2-(4,7-Me_2-C_9H_4)$_2$]Zr(OC_6F_5)$_2$,[126] and 1.918(1) Å in [η^5-C_9H_5-1,3-$(SiMe_3)_2$]$_2$Zr($OCH_2CH_2CH_2CH_2$).[124] The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 120.6° in **IV-4d** is larger than that of 115.9° in **IV-2**, but is close to that of 119.4° in **IV-4c**. The C-O-Zr angle of 156.4(6)° is significantly larger than that of 142.4° in [η^5-C_9H_5-1,3-$(SiMe_3)_2$]$_2$Zr($OCH_2CH_2CH_2CH_2$),[124] and is comparable to that of 152.2(3)° in [*meso*-CH_2CH_2-(4,7-Me_2-C_9H_4)$_2$]Zr(OC_6F_5)$_2$,[126] and 159.7(3)° in [*rac*-η^5:η^5-CH_2CH_2-1,2-$(C_9H_6)_2$Zr($OCMe_2CH_2CH_2CH{=}CH_2$)][$MeB(C_6F_5)_3$],[129] suggestive of the presence of p_π(O)-d_π(Zr) interactions. It is assumed that the formation

of **IV-4d** may involve the organozirconium hydride intermediate,[131] followed by nucleophilic ring-opening of THF.[132]

4.4 Polymerization Activities of Group 4 Metal Complexes.

Complexes **IV-2**, **IV-3a** and **IV-4a** underwent preliminary testing for catalytic activity, using methylalumoxane (MAO) as cocatalyst in toluene at room temperature (1 atm of ethylene). The results were compiled in Table 4.2. All three complexes were active catalysts for polymerization of ethylene in the presence of MAO under the reaction conditions specified in Table 4.2. Their activities were higher than that of 7.2 x 10^4 g/mol·atm·h for $[(Cp^*)(C_2B_9H_{11})ZrMe]_n$,[40] but lower than 1.38 ~ 4.51 x 10^6 g/mol·atm·h observed in the corresponding cyclopentadienyl analogues $[Me_2C(C_5H_4)(C_2B_9H_{10})]ZrX_2$.[115] It was noted that the catalytic activity dropped from 6.82 x 10^5 to 1.21 x 10^3 g/mol·atm·h for **IV-3a** if the Al/Zr molar ratio was decreased from 1500 to 750. When this ratio was 200, only trace amount of polymer was observed. These results may indicate that a large excess amount of MAO is necessary to abstract the chloro ligand from the metal complexes due to the strong interactions between the electron-deficient metal center and Lewis base Cl^- as previously discussed. The active species might be suggested to be the neutral metal alkyl $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(Me)$ in view of the properties of $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})]M(Me)$.[40]

Table 4.2. Ethylene Polymerization Results[a]

catalyst	activity (10^5 g/mol·atm·h)	$M_w/10^3$	M_w/M_n[b]	T_m (°C)[c]
IV-2	1.53	52.2	4.3	133.5
IV-3a	6.82	38.5	3.5	133.2
IV-4a	2.31	41.1	3.9	132.0

[a] Condtions: toluene (50 mL), 1 atm of ethylene, T = 25 °C, catalyst (3.0 μmol), MAO (4.5 mmol), Al/Zr = 1500, reaction time = 30 min. [b] Measured by GPC (using polystyrene standards in 1, 2, 4-trichlorobenzene at 150 °C). [c] Measured by DSC (heating rate: 10 °C / min).

4.5 Summary

The new inorganic/organic hybrid ligand $[NMe_3H][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**IV-1**) was prepared via a selective deboration of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ with piperidine in ethanol. The Me_2C-bridged indenyl-dicarbollyl ligand $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ shows features similar to those observed in the corresponding cyclopentadienyl analogue $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$. Reaction of the ligand **IV-1** with $Zr(NMe_2)_4$ provided the neutral group 4 metal amide complex *trans*-$[\eta^5:\eta^5$-$Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (**IV-2**) through amine elimination reaction in the presence of the p_π-d_π interactions between the central metal ion and the N atom of σ-ligand. While treatment of the trianionic salt of the ligand **IV-1** with $MCl_4(THF)_2$ gave the ionic mixed sandwich complexes *trans*-$[\{\eta^5:\eta^5$-$Me_2C(C_9H_6)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr (**IV-3a**), Hf (**IV-3b**)) due to the high electron deficiency of the central metal atoms and more open

coordination face around the metal atoms. Complex **IV-3a** reacted with KCH_2Ph, C_5H_5Na, or $NaNH(C_6H_3\text{-}2,6\text{-}Me_2)$ to afford *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl(CH_2C_6H_5)$][$Na(DME)_3$] (**IV-4a**), *trans*-{[η^1:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$ZrCl(\eta^5\text{-}C_5H_5)$}{$Na(DME)_3$} (**IV-4b**), or *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NHC_6H_3Me_2)(THF)$ (**IV-4c**), respectively. Both **IV-4a** and **IV-4b** were thermally stable, and no NaCl elimination was observed upon heating their DME solutions. Complex **IV-3a** also reacted with excess NaH in THF to generate the ring opening product, *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(OCH_2CH_2CH_2CH_3)(THF)$ (**IV-4d**) probably through the formation of Zr-H intermediate, following by nucleophilic ring-opening of THF.

Complexes **IV-2**, **IV-3a** and **IV-4a** are active catalysts for ethylene polymerization after activation with a large excess amount of MAO, but their activities are lower than the corresponding cyclopentadienyl analogues.

Chapter 5

Synthesis, Structural Characterization, and Reactivity of Group 4 Metallacarboranes Bearing $[H_2C(C_5Me_4)(C_2B_9H_{10})]^{3-}$ Ligand

5.1 Introduction

Fourteen-electron metallocene alkyl complexes $[(C_5R_5)_2Ln(R')]$[100] and $[(C_5R_5)_2M(R')^+]$[99] (Ln = lanthanides, M = group 4 metals) have attracted a lot of interests because of their wide applications in ligand exchange, insertion reaction, olefin polymerization, and C-H bond activation.[40-47,99,100] It is reported that the reactivity characteristics of metal alkyl complexes highly depend on the structures of $(C_5R_5)_2M$ fragments. Therefore, modification of the cyclopentadienyl ligand has been extensively studied, and a series of metallocenes were synthesized and showed various properties.[99,100] In contrast, the carboranyl ligand supported group 4 metal complexes $[(C_5R_5)(C_2B_9H_{11})M(R')]$ are much less explored.[40-47] It is anticipated that the incorporation of such an inorganic dicarbollyl ligand would result in new metal/charge combinations. We have recently reported *ansa*-ligands $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ and $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$. These ligands largely increase the "bite angle"[99h] of the resultant group 4 metallocenes,[115,133] compared with the corresponding unbridged ones.[40-47] Unfortunately, the relatively small size of $C_5H_5^-$ and the diverse bonding modes of the indenyl ligand disfavor the formation of neutral metal alkyls. It is

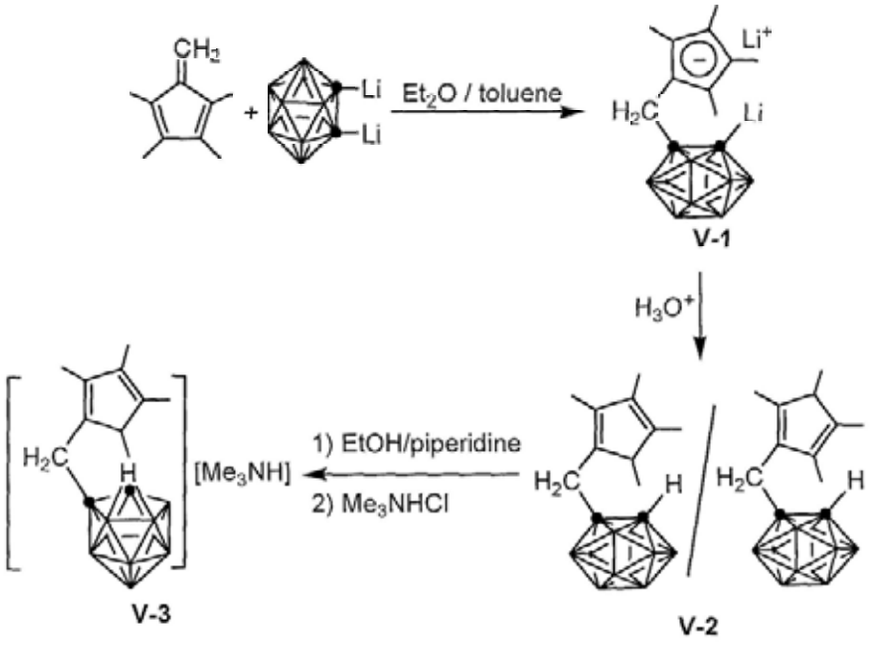
anticipated that the incorporation of a bulkier C_5Me_5 unit in the aforementioned *ansa*-ligand systems would make the preparation of group 4 metal alkyl complexes possible. Herein, we report the synthesis and characterization of a new H_2C-linked tetramethylcyclopentadienyl-dicarbollyl ligand $[H_2C(C_5Me_4)(C_2B_9H_{10})]^{3-}$ and its group 4 metal chloride/amide/oxide/alkyl complexes. Their catalytic properties in ethylene polymerization are also discussed.

5.2 Synthesis and Characterization of Ligand.

It has been reported that treatment of $Li_2C_2B_{10}H_{10}$ with dimethylfulvene or dimethylbenzofulvene afforded, after hydrolysis with a saturated NH_4Cl solution, compounds $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ or $Me_2C(C_9H_7)(C_2B_{10}H_{11})$.[8-11,13-15,17,18,28,29,102] On the other hand, $Li_2C_2B_{10}H_{10}$ reacted with dibenzofulvene to give $H_2C(C_{13}H_9)(C_2B_{10}H_{11})$ after hydrolysis, whereas no reaction was observed between $Li_2C_2B_{10}H_{10}$ and dimethyldibenzofulvene, which implies that bulkier electrophiles would disfavor the reaction.[10] Therefore, 1,2,3,4-tetramethylfulvene was considered as the appropriate electrophile for the preparation of the target molecule. Treatment of $Li_2C_2B_{10}H_{10}$ with a slightly excess amount of 1,2,3,4-tetramethylfulvene in toluene/ether solution produced the expected dilithium salt $[H_2C(C_5Me_4)(C_2B_{10}H_{10})][Li_2(Et_2O)_2]$ (**V-1**) as a white solid in 91% isolated yield (Scheme 5.1). Its composition was confirmed by various spectroscopic data and elemental analyses. The ^1H NMR spectrum displayed a singlet at 3.91 ppm attributable to the bridging CH_2, two singlets at 2.47 and 2.25 ppm assignable to the methyl groups on the Cp ring, and the resonances of the two coordinated Et_2O protons. The ^{13}C NMR spectrum was consistent with the ^1H NMR data. The ^{11}B NMR spectrum exhibited a 1:4:2:2:1 pattern.

Hydrolysis of the dilithium salt **V-1** with a saturated aqueous NH_4Cl solution afforded a neutral compound $H_2C(C_5Me_4H)(C_2B_{10}H_{11})$ (**V-2**) in 97% isolated yield (Scheme 5.1). Both ^1H and ^{13}C NMR spectra indicated that **V-2** is a mixture of isomers (the bridging carbon atom bonds to either the sp^2- or sp^3-carbon on the Cp ring). This phenomenon was also observed in other cyclopentadienyl derivatives.[29,115] The ^{11}B NMR spectrum showed a 1:1:2:2:2:2 pattern which is totally different from that of **V-1**. Thus, this reaction could be monitored by the ^{11}B NMR spectrum.

Scheme 5.1



Treatment of $H_2C(C_5Me_4H)(C_2B_{10}H_{11})$ (**V-2**) with a large excess amount of piperidine in refluxing ethanol for two days gave, after addition of Me_3NHCl, a selective deboration product $[Me_3NH][H_2C(C_5Me_4H)(C_2B_9H_{11})]$ (**V-3**) in 79% isolated yield (Scheme 5.1). The reaction was closely monitored by ^{11}B NMR spectrum. It was noted that a series of reagents were examined for this deboration reaction, such as MOH (M =

Na, K),[117] the fluoride ion,[118] and various amines.[103] Piperidine was found to be the best one. Other reagents led to either a mixture of products or the cleavage of the C_{bridge}–C_{cage} bond. The ^{11}B NMR spectrum of **V-3** showed a 1:1:1:1:1:1:1:1:1 pattern that is characteristic for an unsymmetric C_2B_9 unit. Both ^1H and ^{13}C NMR data suggested that the bridging carbon atom is bonded to either the sp^2- or sp^3-carbon on the five-membered ring.[29,115]

5.3 Synthesis and Reactivity of Group 4 Metal Complexes.

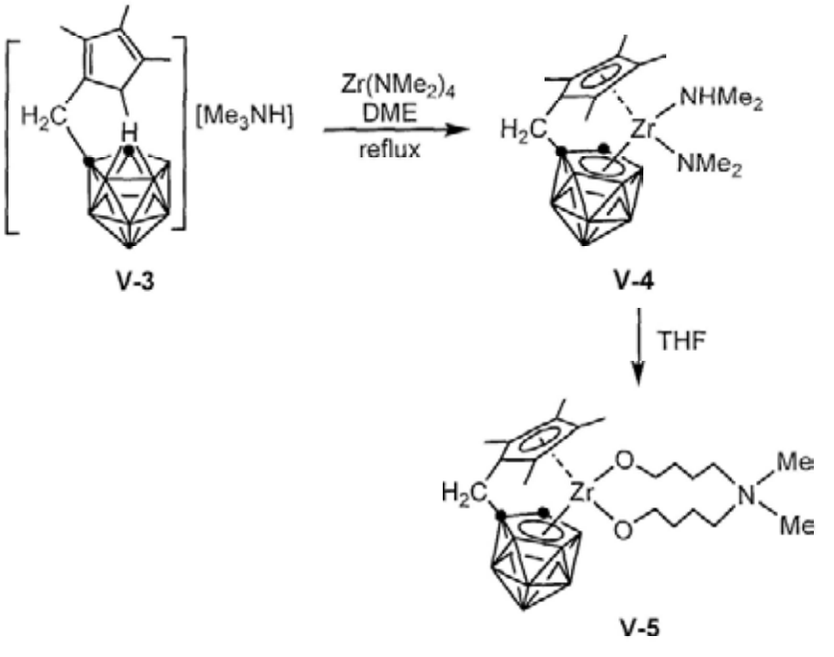
Amine elimination serves as a powerful method for the preparation of metal amides.[2i,57,119] Compound **V-3** contains three acidic protons (the B–H–B, the sp^3-CH on the five-membered ring, and the NH) which may be deprotonated by metal amides. Treatment of **V-3** with 1 equiv of $Zr(NMe_2)_4$ in DME (1,2-dimethoxyethane) at room temperature afforded, after recrystallization from DME, a neutral metal amide complex $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (**V-4**) in 53% isolated yield (Scheme 5.2). The ^1H NMR spectrum showed two characteristic doublets at 3.39 and 3.19 ppm with the coupling constant of 14.1 Hz assignable to the bridging CH_2, four singlets at 2.21, 2.01, 1.98, and 1.96 ppm attributable to four methyl protons, and two singlets at 3.22 and 2.32 ppm corresponding to the dimethylamido and the coordinated dimethylamine groups. The ^{13}C NMR spectrum was consistent with the ^1H NMR one. The ^{11}B NMR spectrum exhibited a 1:1:1:2:1:2:1 pattern.

A single-crystal X-ray diffraction study revealed that the Zr center in **V-4** adopts a distorted-tetrahedral geometry by one η^5-tetramethylcyclopentadienyl ring, one η^5-dicarbollyl ligand, and two nitrogen atoms (Figure 5.1). As shown in Table 5.1, the Zr–Cent(C_5 ring) distance of 2.288 Å is barely longer than that of 2.196 Å in

$(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$,[40] 2.234 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[40] 2.214 Å in $Cp^*(2,4\text{-}^tBu_2\text{-}6\text{-}(OCH_2CH_2N{=}CH)\text{-}C_6H_2O)ZrCl_2$,[134] 2.217 Å in $Cp^*(2,4\text{-}^tBu_2\text{-}6\text{-}(OCH_2C(Me)_2N{=}CH)\text{-}C_6H_2O)ZrCl_2$,[134] 2.231 Å in $Cp^*(2,4\text{-}^tBu_2\text{-}6\text{-}(OCH_2CH_2N{=}CH)\text{-}C_6H_2O)ZrMe_2$,[134] 2.231 Å in $(Cp^*)[Me_2C(C_5H_4)(C_2B_{10}H_{11})]ZrCl_2$,[12] 2.226 Å in $(Cp^*)[Me_2C(C_5H_4)(MeC_2B_{10}H_{10})]ZrCl_2$,[12] 2.233 Å in $(Cp^*)[Me_2C(C_5H_4)(C_2B_{10}H_{10})]ZrCl$,[12] 2.213 Å in $[Me_2C(C_5Me_4)_2]ZrCl_2$,[108] 2.230 Å in $[Si(Me)H(C_5Me_4)_2]ZrCl_2$,[135] and 2.229 Å in $[(CH_2{=}CHCH_2)(H)Si(C_5Me_4)_2]ZrCl_2$.[136] The average Zr−cage atom distance of 2.596(5) Å is very close to that of 2.597(3) Å in $[\eta^5{:}\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$,[133] 2.601(5) Å in $[\eta^1{:}\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] and 2.585(3) Å in $[\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3{}^iPr_2)(THF)$,[115] but is longer than that of 2.469(8) Å in $[\sigma{:}\eta^5\text{-}(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(DME)$,[2i] 2.523(5) Å in $[\eta^1{:}\eta^5\text{-}(Me_2NCH_2)C_2B_9H_{10}]_2Zr$,[55] 2.538(5) Å in $[\eta^1{:}\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$,[52] 2.499 Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$,[40] 2.535/2.533 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[40] 2.568(4) Å in $[\eta^1{:}\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[55] and 2.544(6) Å in $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$.[56] The Zr−N(1) distance of 2.132(4) Å is very comparable to that of 2.057(2) Å in $[\eta^5{:}\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$,[133] 2.111(9) Å in $Cp^*(2,4\text{-}^tBu_2\text{-}6\text{-}(OCH_2CH(^tBu)N{=}CH)\text{-}C_6H_2O)Zr(NMe_2)_2$,[134] 2.036(4)/2.043(4) Å in $[\eta^1{:}\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] 2.029(4)/2.020(4) Å in $[\eta^5\text{-}(C_2B_9H_{10})(CH_2)_2NBz_2)]Zr(NMe_2)_2(NHMe_2)$,[55] and 2.015(3)/2.018(3) Å in $[\eta^1{:}\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$.[52] The Cent($C_5$ ring)-Zr-Cent(C_2B_3) angle of

119.2° is similar to that of 119.2° in $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3{}^iPr_2)(THF)$,[115] and is a little larger than that of 115.9° in $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$,[133] 116.7° in $[Me_2C(C_5Me_4)_2]ZrCl_2$,[108] and 115.9° in $[Me_2C(C_5H_4)_2]ZrMe_2$,[138] but is significantly smaller than those observed in the non-bridged metallacarboranes such as that of 141.3° in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$[40] and 134.9° in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$.[40]

Scheme 5.2



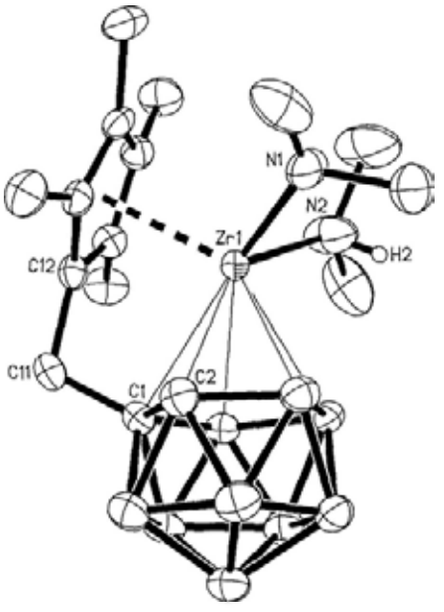


Figure 5.1. Molecular structure of

$[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (**V-4**)

Recrystallization of **V-4** from a hot THF solution resulted in the isolation of a zweritterionic complex $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_2)_2N(CH_3)_2\cdot THF$ (**V-5**·THF) in 48% isolated yield (Scheme 5.2). Although the Zr-N bond is known to be active toward a wide range of polar unsaturated molecules and amine exchange reactions,[2i,13,15,18,57,119,139] it is very rare for the Zr-NMe_2 moiety to initiate the ring-opening of THF molecules. This could be ascribed to the high Lewis acidity of the Zr center in **V-4**, which activates the C-O bond of the coordinated THF molecule. The possible pathway may involve the replacement of the coordinated Me_2NH by a THF, followed by an intramolecular nucleophilic attack of the NMe_2 group to give the first

ring-opening intermediate $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr[OCH_2CH_2CH_2CH_2\text{-}N(CH_3)_2]$. Coordination of the second THF molecule followed by another intramolecular nucleophilic attack by the lone-pair on the N atom affords the final product **V-5**.

The ^1H and ^{13}C NMR spectra all supported the formation of **V-5**. The ^{11}B NMR spectrum showed a 1:1:4:2:1 pattern. Its molecular structure was further confirmed by single-crystal X-ray analyses. The Zr atom is η^5-bound to the five-membered rings of both tetramethylcyclopentadienyl and dicarbollyl, and σ-bound to two oxygen atoms in a distorted-tetrahedral geometry (Figure 5.2). The average Zr-C(C_5 ring) distance of 2.608(6) Å (Table 5.1) is comparable to that of 2.585(4) Å in **V-4**, and 2.580(7) Å in $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_3)(THF)$.[133] The average Zr-cage atom distance of 2.633(6) Å is slightly longer than that of 2.596(5) Å in **V-4**, and 2.554(8) Å in $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_3)(THF)$.[133] The average Zr-O distance of 1.965(4) Å is close to that of 1.930(5) Å in $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_3)(THF)$,[133] 2.167(3) Å in $[\{\eta^1:\sigma:\eta^5\text{-}[MeN(CH_2)CH_2CH_2]C_2B_9H_{10}\}Zr(\mu:\eta^1\text{-}OCH_2CH_2OCH_3)]_2$,[56] 1.897(3) Å in $[rac\text{-}\eta^5:\eta^5\text{-}CH_2CH_2\text{-}1,2\text{-}(C_9H_6)_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)][MeB(C_6F_5)_3]$,[129] 2.015(2) Å in $[4,6\text{-}^tBu_2\text{-}2\text{-}(\eta^5\text{-}C_9H_6)\text{-}C_6H_2O]_2Zr$,[130] 1.979(3)/2.022(3) Å in $[meso\text{-}CH_2CH_2\text{-}(4,7\text{-}Me_2\text{-}C_9H_4)_2]Zr(OC_6F_5)_2$,[126] and 1.918(1) Å in $[\eta^5\text{-}C_9H_5\text{-}1,3\text{-}(SiMe_3)_2]_2Zr(OCH_2CH_2CH_2CH_2)$.[124]

Table 5.1. Selected Bond Lengths (Å) and Angles (deg) for V-4 – V-7b

	V-4	V-5[b]	V-6a	V-6c	V-7a[b]	V-7b
Zr-C(C_5 ring)	2.435(4)	2.505(5)	2.415(6)	2.419(2)	2.434(1)	2.437(7)
	2.521(4)	2.560(5)	2.492(6)	2.502(3)	2.518(1)	2.494(6)
	2.559(4)	2.571(5)	2.504(6)	2.509(3)	2.544(1)	2.510(7)
	2.695(4)	2.686(6)	2.660(6)	2.658(3)	2.669(1)	2.646(7)
	2.714(4)	2.698(6)	2.667(6)	2.666(3)	2.678(1)	2.677(8)
av. Zr-C_{ring}	2.585(4)	2.608(6)	2.548(6)	2.550(3)	2.568(1)	2.553(8)
av. Zr-cage atom	2.596(5)	2.633(6)	2.533(7)	2.568(3)	2.609(1)	2.540(8)
av. Zr-Cl			2.479(2)	2.450(1)		
Zr-N	2.132(4)					2.393(6)
av. Zr-O		1.966(4)				
Zr-C					2.265(1)	2.272(7)
Zr-Cent(C_5)[a]	2.288	2.311	2.244	2.252	2.270	2.255
Zr-Cent(C_2B_3)[a]	2.168	2.202	2.091	2.131	2.185	2.105
Cent(C_5)-Zr-Cent(C_2B_3)	119.2	118.5	122.8	121.5	120.7	120.2
C_{ring}-C_{bridge}-C_{cage}	106.5(3)	107.7(4)	106.5(5)	106.2(2)	107.0(1)	105.4(6)

[a] Cent(C_5), Cent(C_2B_3): the centroid of the five-membered ring of the tetramethylcyclopentadienyl and the C_2B_3 bonding face, respectively. [b] Average values of the two crystallographically independent molecules in the unit cell.

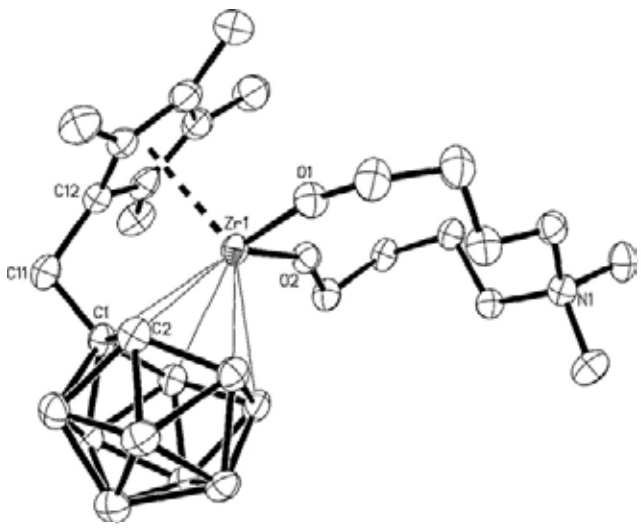


Figure 5.2. Molecular structure of

$[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_2)_2N(CH_3)_2$ (**V-5**)

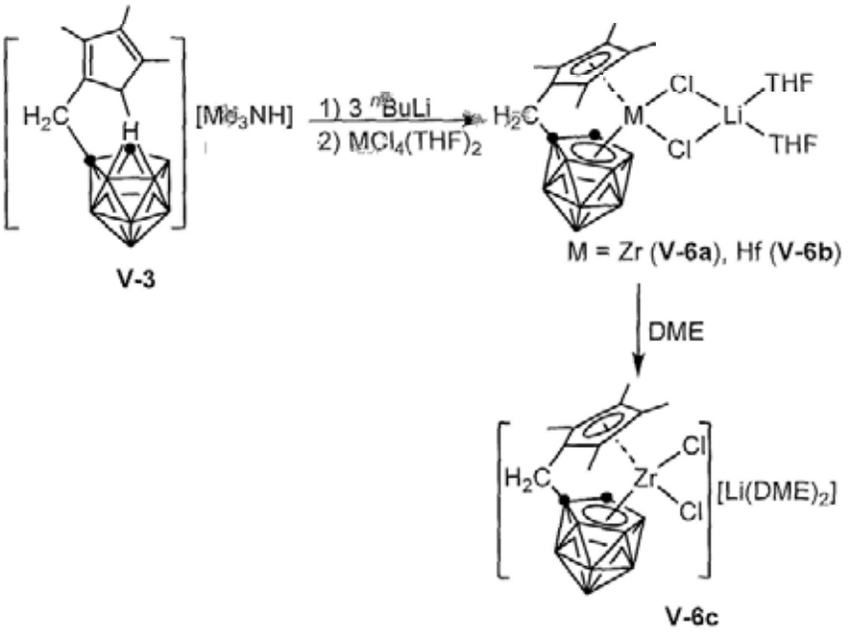
Stimulated by the successful preparation of neutral group 4 metal amide complex **V-4** via amine elimination reaction, we attempted the alkane elimination of **V-3** with $Zr(CH_2Ph)_4$ and $Zr(CH_2SiMe_3)_4$ in the hope to synthesize the target neutral metal alkyls. Unfortunately, the reaction of **V-3** with 1 equiv of $Zr(CH_2Ph)_4$ or $Zr(CH_2SiMe_3)_4$ was complicated under various reaction conditions examined, as indicated by ^1H and ^{11}B NMR spectra, and no pure product was isolated. We then tried an alternative route using salt metathesis method for the synthesis of the alkyl complexes.

Treatment of **V-3** with 3 equiv of ^{n}BuLi in THF, which presumably generated the trianionic salt $[H_2C(C_5Me_4)(C_2B_9H_{10})]Li_3(THF)_x$, followed by the reaction with 1 equiv of $MCl_4(THF)_2$ afforded the expected group 4 metallocene chloride complexes $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]M(\mu\text{-}Cl)_2Li(THF)_2$ (M = Zr (**V-6a**), Hf (**V-6b**)) in 42% –

53% isolated yields (Scheme 5.3). Recrystallization of **V-6a** from DME produced the corresponding ionic complex $[\eta^5{:}\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(\mu\text{-}Cl)_2Li(DME)_2$ (**V-6c**) in 45% isolated yield (Scheme 5.3). Their ^{1}H NMR spectra showed two doublets at 3.46 and 3.12 ppm (in **V-6a**) with J = 14.7 Hz, 3.28 and 3.12 ppm (in **V-6b**) with J = 14.7 Hz, 3.43 and 3.06 ppm (in **V-6c**) with J = 14.4 Hz attributable to the bridging CH_2, four singlets in the region 2.18 − 1.42 ppm corresponding to the four methyl groups on tetramethylcyclopentadienyl rings, two multiplets assignable to the THF (in **V-6a** and **V-6b**) or two singlets at 3.09 and 2.98 ppm corresponding to DME (in **V-6c**), and a singlet at around 2.48 ppm for the cage C*H* proton. Their ^{13}C NMR data were consistent with the above results. The ^{11}B NMR spectra exhibited a 1:1:2:2:1:1:1 pattern for both **V-6a** and **V-6c**, and a 1:1:1:1:2:1:1:1 pattern for **V-6b**. Single-crystal X-ray diffraction studies confirmed the molecular structure of **V-6a**. The Zr atom adopts a distorted-tetrahedral geometry by one η^5-tetramethylcyclopentadienyl ring, one η^5-dicarbollyl unit, and two doubly bridging chlorine atoms (Figure 5.3). The solid-state structure of **V-6c** derived from X-ray analyses consists of well-separated, alternating layers of discrete tetrahedral anions $[\{\eta^5{:}\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})\}ZrCl_2]^-$ and tetrahedral cations $[Li(DME)_2]^+$. The coordination environment of the Zr atom in the anion is very similar to that observed in **V-6a** (Figure 5.4). The Zr−Cent(C_5 ring) distance of 2.244 Å (Table 1) in **V-6a** is very close to that of 2.252 Å in **V-6c**, but is longer than that of 2.188 Å in $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$,[115] 2.196 Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me){=}CMe_2]$[40] and 2.234 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$.[40] The average Zr-cage atom distance of 2.533(7) Å in **V-6a** is comparable to that of 2.568(3) Å in **V-6c**, 2.528(4) Å in $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$,[115] 2.523(5) Å in

$[\eta^1{:}\eta^5\text{-}(Me_2NCH_2)C_2B_9H_{10}]_2Zr$,[55] 2.538(5) Å in $[\eta^1{:}\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$,[52] 2.499 Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$,[40] 2.535/2.533 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[40] 2.568(4) Å in $[\eta^1{:}\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[56] 2.601(5) Å in $[\eta^1{:}\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] and 2.544(6) Å in $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$.[137] As expected, the average Zr–Cl (bridging) distance of 2.479(2) Å in **V-6a** is a bit longer than those of terminal Zr-Cl ones, for example, 2.450 (1) Å in **V-6c**, 2.447(1) Å in $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$,[115] 2.414(1) Å in $[\eta^1{:}\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[56] 2.395(2)/2.388(1) Å in $\{\eta^4{:}\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{M(THF)_x\}$ (M = Na, x = 3; M = Li, x = 4),[49] 2.403(2) Å in $[[\{\eta^5{:}\sigma\text{:-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]]$,[16] and 2.419(3) Å in $[(CH_2{=}CHCH_2)(H)Si(C_5Me_4)_2]ZrCl_2$.[136] The Cent($C_5$)-Zr-Cent($C_2B_3$) angle of 122.8° in **V-6a** is close to that of 121.5° in **V-6c**, and 120.5° in $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$,[115] but is significantly smaller than that of 141.3° in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$,[40] and 134.9° in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$[40] owing to the presence of the short CH_2 linkage between the two π-ligands.

Scheme 5.3



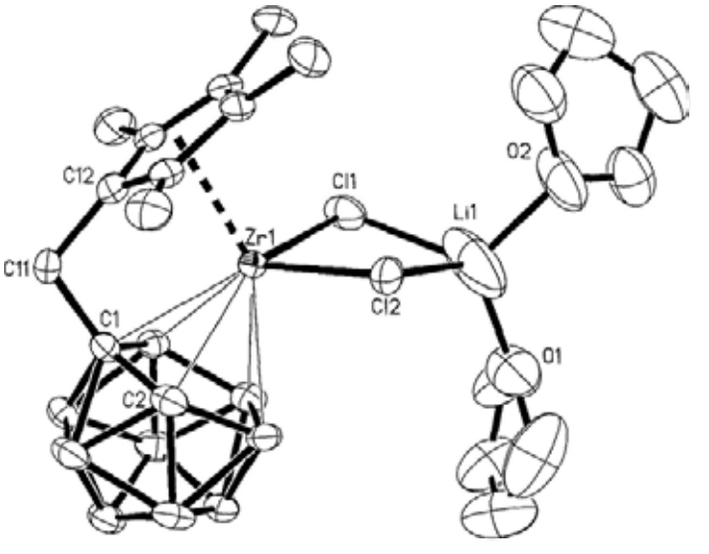


Figure 5.3. Molecular structure of

$[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]M(\mu\text{-}Cl)_2Li(THF)_2$(**V-6a**)

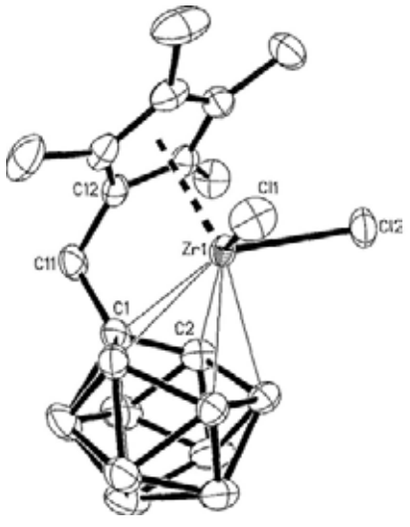


Figure 5.4. Molecular structure of the anion in

$[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(\mu\text{-}Cl)_2Li(DME)_2$ (**V-6c**)

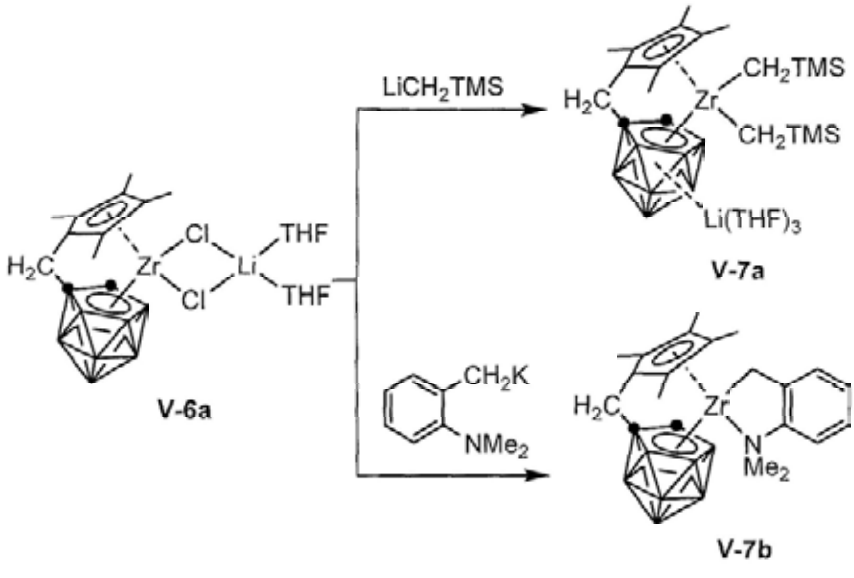
The salt metathesis reaction is a well established method for the preparation of metal amides or metal alkyls. Our previous work showed that reaction of $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$ (**III-3a**) or $[\{\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$ (**IV-3a**) with KCH_2Ph or C_5H_5Na led to the isolation of ionic adducts containing a Zr-Cl-Na unit.[115,133] Due to the high Lewis acidity of the metal center, NaCl could not be removed from the *ate*-complexes even at refluxing condition. Therefore, a bulkier alkylating reagent $LiCH_2TMS$ (TMS = $SiMe_3$) was chosen in the current work.

Treatment of $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(\mu\text{-}Cl)_2Li(THF)_2$ (**V-6a**) with 1 equiv of $LiCH_2TMS$ in THF at room temperature afforded a double alkylation product $\{[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(CH_2TMS)_2\}\{Li(THF)_3\}$ (**V-7a**) in 36% isolated yield

(Scheme 5.4). It is still an ionic adduct. Unfortunately, no pure product was isolated if $LiCH(TMS)_2$ was employed as the alkylating agent.

The ^1H NMR spectrum of **V-7a** exhibited, in addition to the solvent resonances, two doublets at 2.95 and 2.63 ppm with $J = 14.7$ Hz for the bridging CH_2, four singlets at the region 2.14 - 1.69 ppm attributable to CH_3 on the five-membered ring, four doublets at 0.81 - 0.57 ppm with $J = 11.0$ Hz corresponding to the methylene protons of $CH_2Si(CH_3)_3$, and two singlets at 0.38 and 0.36 ppm assignable to the methyl groups of $CH_2Si(CH_3)_3$. Its ^{13}C NMR data were consistent with the above results. The ^{11}B NMR spectrum showed a 1:1:2:2:1:1:1 pattern.

Scheme 5.4



The molecular structure of **V-7a** was confirmed by a single-crystal X-ray diffraction study. The coordination geometry of the Zr atom is similar to that in **V-6a** but two CH_2TMS groups replacing those of Cl atoms (Figure 5.5). The values of the average Zr–C(C_5 ring), Zr–cage atom distances and Cent(C_5)-Zr-Cent(C_2B_3) angle (2.568(1) Å/

2.609(1) Å/120.7°) are comparable to those of 2.548(6) Å/2.533(7) Å/122.8° observed in **V-6a**, and 2.550(3) Å/2.568(3) Å/121.5° in **V-6c**. The average Zr–C(alkyl) distance of 2.265(1) Å is close to that of 2.256(3) Å in $[\eta^5\text{-}C_9H_6\text{-}2\text{-}(5\text{-}Me\text{-}C_4H_3O)]_2Zr(CH_2CMe_3)_2$,[140] 2.233(6) Å in $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$,[56] 2.269(2)/2.307(2) Å in $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr(CH_2SiMe_3)_2$,[141] and 2.270 Å in $[Me_2Si(\eta^5\text{-}C_9H_6)_2]Zr(Me)(CH_2SiMe_3)$,[142] but is a little shorter than that of 2.312(6) Å in *trans*-$[\{\eta^5{:}\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$,[133] and 2.316(1) Å in $[\{\eta^5{:}\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$.[115]

In order to prepare the neutral metal alkyl complex, the alkylating agent bearing a donor functionality $KCH_2(NMe_2)\text{-}o\text{-}C_6H_4$ was selected in the hope that the intramolecular coordination of the donor atom would prevent the formation of the *ate*-complex. Treatment of **V-6a** with 1 equiv of $KCH_2(NMe_2)\text{-}o\text{-}C_6H_4$ in THF at room temperature gave, after recrystallization from THF, a neutral complex $[\eta^5{:}\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr[\sigma{:}\sigma\text{-}CH_2(NMe_2)\text{-}o\text{-}C_6H_4]\cdot THF$ (**V-7b**·THF) in 57% isolated yield (Scheme 5.4). Its ^1H NMR spectrum showed two multiplets at 7.26 and 7.02 ppm attributable to the aromatic protons, two doublets of the bridging CH_2 unit at 3.52 and 3.43 ppm with J = 14.4 Hz, one singlet at 2.57 ppm assignable to Zr-CH_2, one singlet at 2.54 ppm corresponding to the coordinated NMe_2, and four singlets of Me_4C_5 protons at the region 2.29 - 1.59 ppm. The ^{13}C NMR data were consistent with the above results. The ^{11}B NMR spectrum displayed a 1:1:2:2:1:1:1 pattern.

The solid-state structure of **V-7b** was confirmed by single-crystal X-ray analyses, revealing that the Zr atom is η^5-bound to two five-membered rings of the tetramethylcyclopentadienyl and dicarbollyl, σ-bound to CH_2, and coordinated to the N

atom in a distorted-tetrahedral geometry (Figure 5.6). The average Zr-C(C_5 ring), Zr-cage atom distances and Cent(C_5)-Zr-Cent(C_2B_3) angle of 2.553(8) Å/2.540(8) Å/120.2° are comparable to those (2.548(6) Å, 2.533(7) Å and 122.8°) in **V-6a**. The Zr-C σ bond distance of 2.272(7) Å is close to that of 2.265(1) Å in **V-7a**, but is a little shorter than that of 2.312(6) Å in *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl(CH_2C_6H_5)$][$Na(DME)_3$],[133] and 2.316(1) Å in [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl(CH_2C_6H_5)$][$Na(DME)_3$].[115]

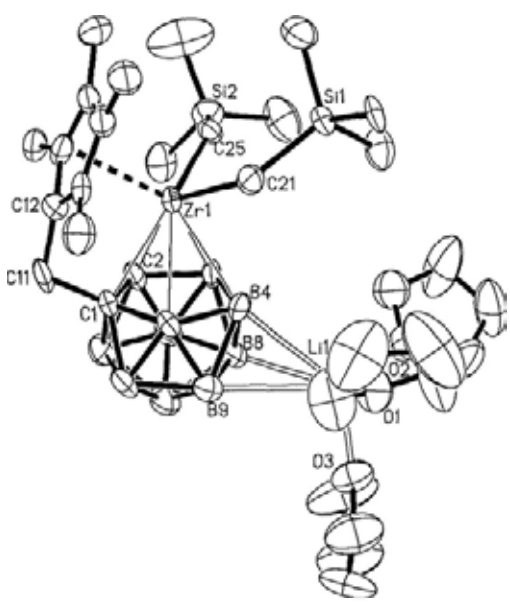


Figure 5.5. Molecular structure of

{[η^5:η^5-$H_2C(C_5Me_4)(C_2B_9H_{10})$]$Zr(CH_2TMS)_2$}{$Li(THF)_3$}(**V-7a**)

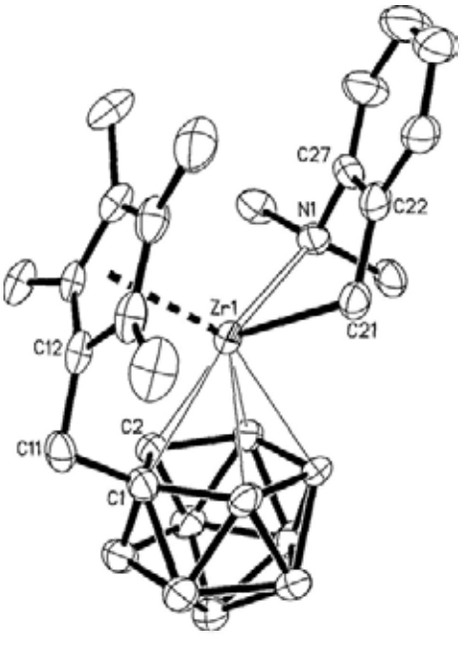


Figure 5.6. Molecular structure of

$[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr[\sigma:\eta^1\text{-}CH_2(NMe_2)\text{-}o\text{-}C_6H_4](THF)$ (**V-7b**)

5.4 Ethylene Polymerization.

The catalytic activity of complexes **V-4**, **V-6a**, **V-7a** and **V-7b** in ethylene polymerization was examined with methylalumoxane (MAO) as the co-catalyst in toluene at room temperature (1 atm of ethylene). The results were compiled in Table 5.2. All four complexes were active catalysts for polymerization of ethylene in the presence of MAO. Their activities were similar to the cyclopentadienyl analogues $[Me_2C(C_5H_4)(C_2B_9H_{10})]ZrX_2$,[115] but were higher than that of 7.2×10^4 g/mol·atm·h for $[(Cp^*)(C_2B_9H_{11})ZrMe]_n$.[40] However, the catalytic activity of **V-6a** dropped from 3.25×10^6 to 1.21×10^3 g/mol·atm·h as the Al/Zr molar ratio was decreased from 1500 to 750.

Only trace amount of polymer could be observed if this ratio was 200. Complex **V-7b** was inactive in the absence of MAO probably due to the very strong intramolecular coordination between the N atom and the Zr center. These results imply that a large excess of MAO is necessary to activate the pre-catalysts.

Table 5.2. Ethylene Polymerization Results.[a]

catalyst	activity (10^6 g/mol·atm·h)	$M_w/10^3$	M_w/M_n[b]	T_m[c] (°C)
V-4	**0.76**	**13.5**	**5.25**	**130.1**
V-6a	**3.25**	**32.1**	**6.10**	**131.0**
V-7a	**1.06**	**41.2**	**5.23**	**131.3**
V-7b	**4.38**	**49.3**	**6.15**	**132.0**

[a] Conditions: toluene (50 mL), 1 atm of ethylene, T = 25 °C, catalyst (3.0 μmol), MAO (4.5 mmol), Al/M = 1500, reaction time = 30 min. [b] Measured by GPC (using polystyrene standards in 1, 2, 4-trichlorobenzene at 150 °C). [c] Measured by DSC (heating rate: 10 °C / min).

5.5 Summary

A new CH_2-bridged tetramethylcyclopentadienyl-dicarbollyl ligand $[H_2C(C_5Me_4)(C_2B_9H_{10})]^{3-}$ was prepared. Several group 4 metal chloride/amide/oxide/alkyl complexes supported by this ligand were synthesized and structurally characterized. They share some common features with those supported by $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ and $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ ligands.[115,133] In the absence of p_π-d_π interactions between the central metal ion and the σ-ligand, all three *ansa*-ligands prefer to form *ate*-metallocene complex ions due to the high electron deficiency of the

central metal atoms. This work shows that the neutral metallocene alkyl can be achieved in the presence of an appended donor functionality, which can be ascribed to the intramolecular interactions between the central metal ion and the heteroatom. The results also suggest that π ligands which are bulkier than pentamethylcyclopentadienyl are required for the preparation of Lewis base-free neutral metallocene alkyls.

Preliminary results indicate that complexes **V-4**, **V-6a**, **V-7a** and **V-7b** are active catalysts for ethylene polymerization after activation with a large excess amount of MAO. Their activities are comparable to those of $[Me_2C(C_5H_4)(C_2B_9H_{10})]ZrX_2$,[115] and higher than $[Me_2C(C_9H_6)(C_2B_9H_{10})]ZrX_2$.[133] No catalytic activity is found for all complexes in the absence of MAO.

Chapter 6

Synthesis, Structural Characterization, and Alkyne Insertion of Zirconacarborane Alkyl Complexes

6.1 Introduction

Group 4 metallocene alkyl complexes of general type $(C_5R_5)_2M(R)^+$ have received great interests as they exhibit a rich insertion, olefin polymerization, and C-H bond activation chemistry, which is highly sensitive to the structural and electronic properties of $(C_5R_5)_2M$ fragment.[99,101] Replacement of a uninegative $C_5R_5^-$ ligand of cationic group 4 metal alkyls $(C_5R_5)_2M(R)^+$ by the isolobal, dinegative dicarbollide ligand to form a class of neutral mixed sandwich complexes $(C_5Me_5)(C_2B_9H_{11})M(R)$ was firstly reported by Jordan group.[40-46] The formed neutral species showed a variety of ligand exchange, insertion and ligand C-H activations characteristics of electrophilic metal alkyls.[40-46] However complex $(C_5Me_5)(C_2B_9H_{11})Zr(Me)$ is not stable even at 45 °C, which limits its applications.[40] In order to increase the stability of the zirconacarborane methyl complexes, we attempted to use carbon-bridged ligands $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$/$[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$/$[H_2C(C_5Me_4)(C_2B_9H_{10})]^{3-}$ in the hope to change the stability and reactivity of the resultant group 4 metal complexes.[115,133,144] As described in the previous chapters, all three ligands result in the isolation of group 4 metal complex anions. Only in the presence of donor atoms, a neutral complex $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr[\sigma:\eta^1\text{-}CH_2(NMe_2)\text{-}o\text{-}C_6H_4](THF)$

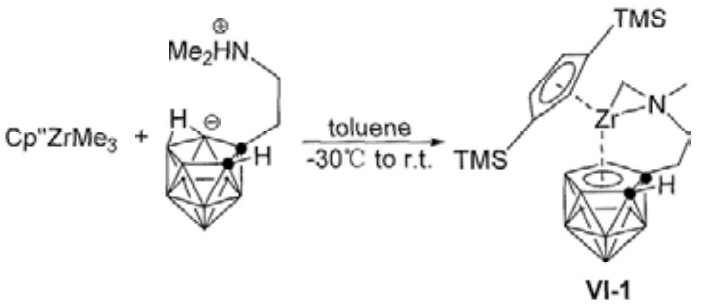
(**V-7b**) can be isolated, suggesting that a tethered donor atom on dicarbollide ligand may coordinate to the metal center and stabilize the neutral zirconacarborane alkyl complexes. A number of half-sandwich group 4 metallacarboranes bearing Lewis base functionalities have been prepared and studied since 2001.[51-57] The first half-sandwich metallacarborane alkyls was reported by our group.[56] In this chapter, full-sandwich zirconacarborane alkyl complexes bearing both $C_5H_3(TMS)_2^-$ and $Me_2NCH_2CH_2C_2B_9H_{10}^{2-}$ ligands will be described.

6.2 Synthesis of Zirconacarborane Alkyl Complex.

Alkane elimination is one of the most widely used methods for the preparation of metal alkyl complexes.[145] Treatment of (η^5-Cp'')$ZrMe_3$ (Cp'' = 1,3-$(Me_3Si)_2C_5H_3$) with 1 equiv of zwitterionic salt 7-$(Me_2NH)(CH_2)_2$-7,8-$C_2B_9H_{11}$[56,146] in toluene from -30℃ to room temperature overnight afforded, after recrystallization from toluene, a full-sandwich zirconacarborane alkyl complex [η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr(η^5-Cp'') (**VI-1**) in 80% isolated yield (Scheme 6.1). The reaction was monitored to the completion by ^{11}B NMR. The expected zirconacarborane methyl complex (η^5-Cp'')[η^1:η^5-$(Me_2NCH_2CH_2)C_2B_9H_{10}$]Zr(Me) was not isolated because of its instability at room temperature. However, it should serve as the intermediate of the alkane elimination reaction and subsequently eliminates one CH_4 molecule via the rupture of a C-H bond at one of the N-methyl groups to give the final product **VI-1**. Such an intramolecular C-H activation is normally observed at methylzirconocene cations[147] or [$(C_5Me_5)(C_2B_9H_{11})$]TiMe,[45] and firstly observed in

neutral metallocene alkyls $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]M(CH_2SiMe_3)(THF)$ (M = Zr, Hf).[56]

Scheme 6.1



VI-1

Cp" = 1,3-$(Me_3Si)_2C_5H_3$

The composition of **VI-1** was fully characterized by various spectroscopic techniques and elemental analyses. The ^{1}H NMR spectrum showed one broad singlet at 3.15 ppm attributable to the cage C*H*, two doublets at 2.21 and 2.19 ppm with J = 6.0 Hz assignable to CH_2 at the α positon of Zr atom in addition to the resonances corresponding to the protons on Cp'' ring, TMS group and substituted amino group CH_2CH_2NMe. The ^{13}C NMR spectrum was consistent with the above result. Its ^{11}B NMR spectrum showed a 1:1:2:1:2:1:1 pattern. The structure of **VI-1** was further confirmed by single-crystal X-ray diffraction analyses. The Zr atom is η^5-bound to both bistrimethylsilylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to one carbon atom from NCH_2 group and coordinated to the N atom of amino group in a distorted-tetrahedral geometry (Figure 6.1). The average Zr-C_5 ring distance of 2.509(4) Å (Table 6.1) is comparable to that of 2.548(4) Å in $(\eta^5\text{-Cp''})\{(^i PrN)_2C(NH^iPr)\}ZrCl_2$,[147] 2.554(3) Å in $(\eta^5\text{-Cp''})[3\text{-}MeC_4H_3BC_6F_5]Zr(C_6F_5)(OEt_2)$,[148] 2.517(5)/2.522(5) Å in

{(η^5-Cp'')$_2$ZrMe(μ-Me)B(C_6F_5)$_3$,[149] 2.523(3) Å in (η^5-Cp'')($C_4H_4BC_6F_5$)Zr(C_6F_5)(CN^{t}Bu),[150] 2.547(5) Å in (η^5-Cp'')(η^5-$C_4H_4BC_6F_5$)Zr(η^2-C_6F_5CN^{t}Bu),[150] and 2.530(5) Å in (η^5-Cp'')(η^5-$C_{13}H_9$)ZrCl_2.[151] The average Zr-cage atom distance of 2.522(4) Å is similar to that of 2.523(5) Å in [η^1:η^5-(Me_2NCH_2)$C_2B_9H_{10}$]$_2$Zr,[55] 2.538(5) Å in [η^1:η^5-($C_5H_4NCH_2$)$C_2B_9H_{10}$]Zr(NMe_2)$_2$,[52] 2.499 Å in (Cp*)($C_2B_9H_{11}$)Zr[C(Me)=CMe_2],[40] 2.535/2.533 Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2),[40] 2.568(4) Å in [η^1:η^5-(BzNCH_2)(CH_3)$C_2B_9H_{10}$]ZrCl_2(THF),[54] and 2.544(6) Å in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF).[56] The Zr-C σ bond distance of 2.271(4) Å is close to that of 2.271(5) Å in (η^5-Cp'')(η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)ZrH,[152] 2.320(2)/2.316(2) Å in (η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)$_2$Zr,[152] 2.282(2) Å in (η^5-Cp'')(η^5-C_5Me_5)ZrH(Me),[153] and 2.250(12) (Zr-C(sp^3)) Å in Cp_2Zr[(Ph)C=C(Ph)CH(C_6H_4)CH],[154] but is longer than that of 2.233(6)/2.242(6) Å (Zr-C(N)/Zr-C(TMS)) in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF),[56] 2.198(4) Å in (Cp*)($C_2B_9H_{11}$)Zr[C(Me)=CMe_2],[40] and 2.187(6)/2.176(7) Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2).[40] The Cent(C_5)-Zr-Cent(C_2B_3) angle of 140.0° is comparable to that of 141.3° in (Cp*)($C_2B_9H_{11}$)Zr[C(Me)=CMe_2],[40] but is a little larger than that of 134.9° in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2).[40]

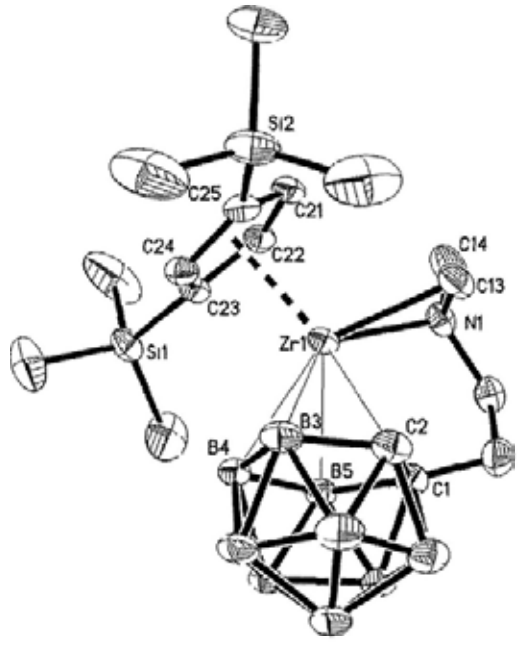


Figure 6.1. Molecular structure of (Cp'')[η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-1**)

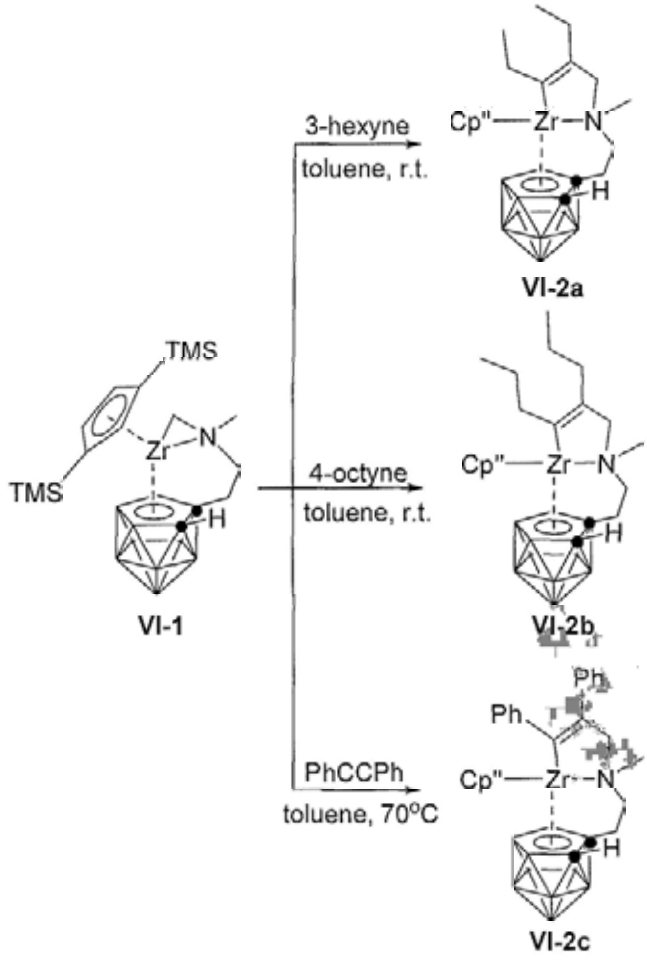
6.3 Reactivity of Zirconacarborane Alkyl Complex to Alkynes

6.3.1 Reactivity to Symmetrical Internal Alkynes.

Preliminary results showed that alkynes could insert into the Zr-C σ bond.[56,154] Treatment of symmetrical internal alkynes 3-hexyne or 4-octyne with complex **VI-1** in 1:1 molar ratio in toluene at room temperature afforded, after recrystallization from toluene, [η^1:σ:η^5-{MeN(CH_2(R)C=C(R))CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (R = Et (**VI-2a**), ^{n}Pr (**VI-2b**)) in ~ 70% isolated yields (Scheme 6.2). Only mono-insertion products were formed even in the presence of an excess amount of alkynes under refluxing condition. For more bulky PhC≡CPh, no insertion reaction proceeded at room temperature as monitored by ^{1}H NMR. When the reaction mixture was heated to 70 °C, the mono-insertion product

[η^1:σ:η^5-{MeN(CH_2(Ph)C=C(Ph))CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (**VI-2c**) was cleanly formed in 70% isolated yield (Scheme 6.2). It is noted that alkyne TMSC≡CTMS did not react with **VI-1** even after prolonged refluxing in toluene probably due to more bulky substituent of TMS over Ph group.[155]

Scheme 6.2



The compositions of three complexes were confirmed by various spectroscopic techniques and elemental analyses. The ^{1}H NMR spectra showed the signals corresponding to the protons of ethyl (**VI-2a**), propyl (**VI-2b**) and phenyl (**VI-2c**) groups, two doublets at 3.10 and 2.09 ppm with J = 15.0 Hz for **VI-2a**, 3.23 and 2.15 ppm with J

= 15.3 Hz for **VI-2b**, 3.68 and 2.62 ppm with J = 15.0 Hz for **VI-2c** attributable to NCH_2C_β in addition to the signals assignable to the protons on Cp'' ring, TMS group and substituted amino group CH_2CH_2NMe. The most characteristic vinyl carbons at 193.1/138.4 ppm (in **VI-2a**), 192.1/153.8 ppm (in **VI-2b**) and 194.5/149.7 ppm (in **VI-2c**) were observed in their ^{13}C NMR spectra, which are very comparable to the corresponding values of ~194 and ~142 ppm observed in $Cp_2Zr[C(R)=C(R)]_2$.[156] The three complexes showed different patterns, a 1:1:1:2:1:1:1:1 for **VI-2a**, a 1:1:2:1:1:1:1:1 for **VI-2b** and a 1:2:2:2:2 for **VI-2c** in their ^{11}B NMR spectra due to the different overlap of B signals. The structures of complexes **VI-2a** and **VI-2c** were further confirmed by single-crystal X-ray diffraction studies and shown in Figures 6.2 and 6.3, respectively. The Zr atom is η^5-bound to both bistrimethylsilylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to sp^2-C atom and coordinated to the N atom in a distorted-tetrahedral geometry. The average Zr-C(C_5 ring) and Zr-cage atom distances of 2.533(5) Å/2.537(6) Å in complex **VI-2a** and 2.559(2) Å/2.554(2) Å in **VI-2c** are close to each other and comparable to those of 2.509(4) Å/2.522(4) Å in complex **VI-1**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angles of 136.4° (in **VI-2a**) and 137.6° (in **VI-2c**) are similar to each other, but a little smaller than that of 140.0° in complex **VI-1**. The Zr-C σ bond distances of 2.329(5) Å (in **VI-2a**) and 2.295(2) Å (in **VI-2c**) are similar to each other and comparable to that of 2.271(4) Å in **VI-1**, 2.298(10) (Zr-C(sp^2)) Å in $Cp_2Zr[(Ph)C=C(Ph)CH(C_6H_4)CH]$,[154] but is longer than that of 2.198(4) Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$.[40]

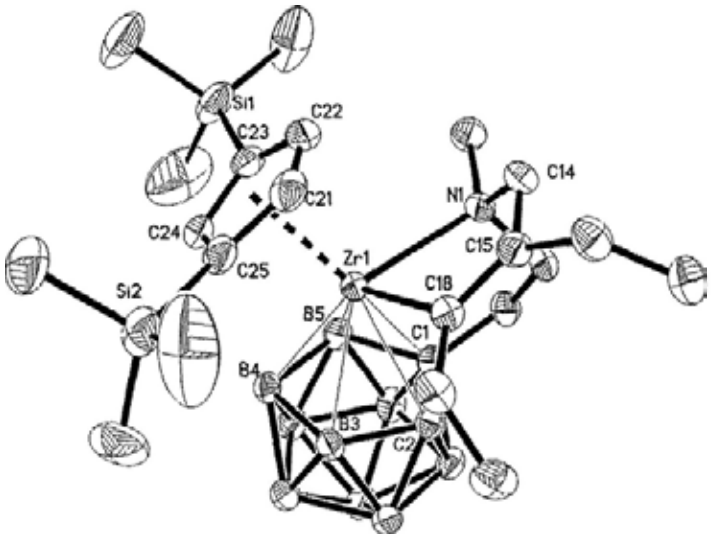


Figure 6.2. Molecular structure of

(Cp'')[η^1:σ:η^5-{MeN(CH_2EtC=CEt)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-2a**)

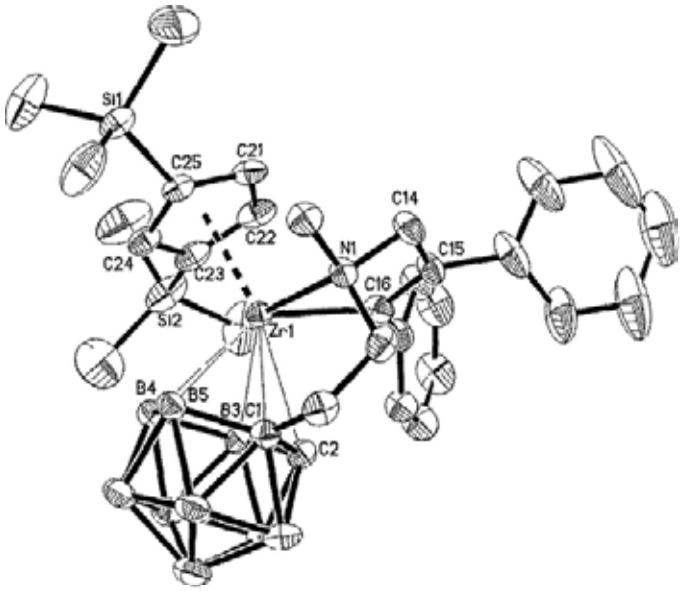


Figure 6.3. Molecular structure of

(Cp'')[η^1:σ:η^5-{MeN(CH_2PhC=CPh)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-2c**)

6.3.2 Reactivity to Unsymmetrical Internal Alkynes.

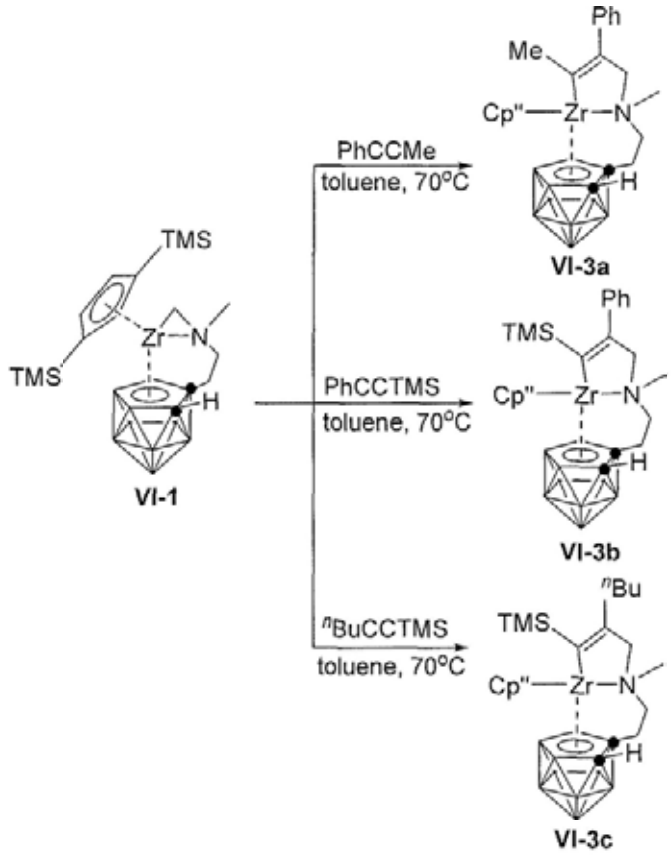
When unsymmetrical alkynes were used, regioselectivity should be considered. Treatment of complex **VI-1** with three different unsymmetrical internal alkynes (PhC≡CMe, PhC≡CTMS and ^{n}BuC≡CTMS) in 1:1 molecular ratio in toluene at 70 °C afforded, after recrystallization from toluene, the mono-insertion products $[\eta^1{:}\sigma{:}\eta^5$-{MeN($CH_2$($R^1$)C=C($R^2$))$CH_2CH_2$}$C_2B_9H_{10}$]Zr($\eta^5$-Cp'') ($R^1$ = Ph, R^2 = Me, **VI-3a**; R^1 = Ph, R^2 = TMS, **VI-3b**; R^1 = ^{n}Bu, R^2 = TMS, **VI-3c**) in ~ 80% isolated yields (Scheme 6.3). The regioselectivity of compound **VI-3a** may be best ascribed to the more steric hindrance of Ph over Me group as phenyl is often considered as an electron-withdrawing group.[157] Compounds **VI-3b** and **VI-3c** showed a totally different regioselectivity from that of **VI-3a**, in which the more bulky TMS group is closer to the Zr center. This result is rationalized on the basis of electronic effects[158] originating from the $SiMe_3$ group which can override the normal steric preference for 1,2-insertion of alkenes/alkynes into the Zr-C bonds. These results suggest that both electronic and steric factors affect the regioselectivity of the insertion reaction depending on the substituted groups on the alkynes.

Terminal alkynes 4-NO_2-C_6H_4C≡CH, 2-NO_2-C_6H_4C≡CH and 4-CF_3-C_6H_4C≡CH were also examined. However, the reactions were complicated from ^{1}H NMR spectra, and no pure products were isolated.

The compositions of three complexes were all confirmed by various spectroscopic techniques and elemental analyses. The ^{1}H NMR spectra showed the signals corresponding to the protons of methyl, phenyl (**VI-3a**), trimethylsilyl, phenyl (**VI-3b**) and trimethylsilyl, butyl (**VI-3c**) groups, two doublets at 3.42 and 2.44 ppm with J =

12.0 Hz for **VI-3a**, 4.58 and 3.24 ppm with J = 15.3 Hz for **VI-3b**, 3.40 and 2.35 ppm with J = 15.0 Hz for **VI-3c** attributable to NCH_2C_β in addition to the signals assignable to the protons on Cp'' ring, TMS group and substituted amino group CH_2CH_2NMe. The characteristic resonances at 191.3/141.5 ppm (in **VI-3a**), 202.2/153.0 ppm (in **VI-3b**) and 201.7/152.6 ppm (in **VI-3c**) corresponding to the alkenyl $ZrC_\alpha C_\beta$ were observed in the ^{13}C NMR spectra. The solid-state structures of **VI-3a - VI-3c** were further confirmed by single-crystal X-ray diffraction analyses and shown in Figures 6.4 - 6.6, respectively. The Zr atom is η^5-bound to both bistrimethylsilylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to sp^2-C atom and coordinated to one N atom in a distorted-tetrahedral geometry. The average Zr-C(C_5 ring)/Zr-cage atom distances and the Cent(C_5 ring)-Zr-Cent(C_2B_3) angles of 2.544(3) Å/2.551(3) Å/138.2° in **VI-3a**, 2.567(4) Å/2.554(5) Å/135.4° in **VI-3b**, and 2.565(4) Å/2.562(5) Å/135.3° in **VI-3c** are comparable to each other and similar to those of 2.533(5) Å/2.537(6) Å/136.4° in complex **VI-2a** and 2.559(2) Å/2.554(2) Å/137.6° in **VI-2c**. The Zr-C σ bond distances of 2.283(3) Å/2.338(4) Å/2.347(4) Å in **VI-3a/VI-3b/VI-3c** are close to each other and also comparable to that of 2.295(2) Å in **VI-2a** and 2.329(5) Å in **VI-2c**.

Scheme 6.3



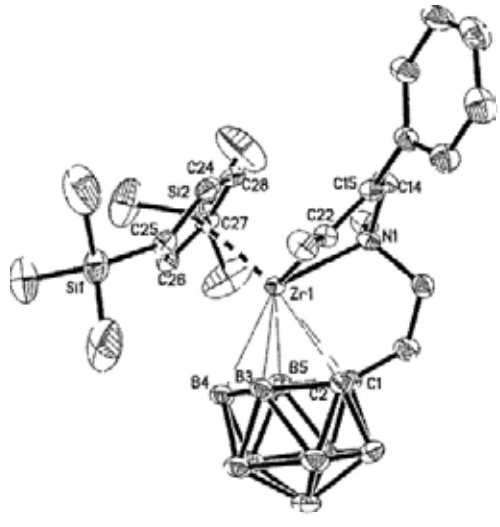


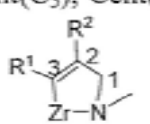
Figure 6.4. Molecular structure of

$(Cp'')[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2PhC{=}CMe)CH_2CH_2\}C_2B_9H_{10}]Zr$ (**VI-3a**)

Table 6.1. Selected Bond Lengths (Å) and Angles (deg) for VI-1, VI-2a, 2c, VI-3a – VI-3c, and VI-4a, 4c, 4d.

	VI-1	VI-2a	VI-2c	VI-3a	VI-3b	VI-3c	VI-4a	VI-4c	VI-4d
av. Zr-C_{ring}	2.509(4)	2.559(2)	2.533(5)	2.544(3)	2.567(4)	2.565(4)	2.537(6)	2.553(3)	2.538(4)
av. Zr-cage atom	2.522(4)	2.554(2)	2.537(6)	2.551(3)	2.554(5)	2.562(5)	2.551(7)	2.551(3)	2.561(5)
Zr-N	2.267(3)	2.368(2)	2.355(4)	2.353(2)	2.349(3)	2.352(3)	2.377(5)	2.379(2)	2.415(4)
Zr-C(3)[b]	2.271(4)	2.295(2)	2.329(5)	2.283(3)	2.338(4)	2.347(4)	2.278(6)	2.306(3)	2.190(5)
C(2)-C(3)[b]		1.339(3)	1.345(7)	1.336(4)	1.340(5)	1.354(5)	1.332(8)	1.341(4)	
C(1)-C(2)[b]		1.506(3)	1.498(7)	1.513(4)	1.521(5)	1.508(5)	1.500(8)	1.503(4)	
N-C(1)[b]		1.492(3)	1.495(7)	1.499(3)	1.480(5)	1.493(5)	1.499(8)	1.501(4)	
Zr-Cent(C_5)[a]	2.203	2.258	2.232	2.241	2.267	2.264	2.233	2.249	2.235
Zr-Cent(C_2B_3)[a]	2.075	2.116	2.100	2.111	2.114	2.121	2.108	2.106	2.121
Cent(C_5)-M-Cent(C_2B_3)	140.0	137.6	136.4	138.2	135.4	135.3	138.6	135.9	136.9

[a] Cent(C_5), Cent(C_2B_9): the centroid of the cyclopentadienyl ring and the C_2B_3 bonding face, respectively. [b] the number of C(1), C(2), C(3)

see: 

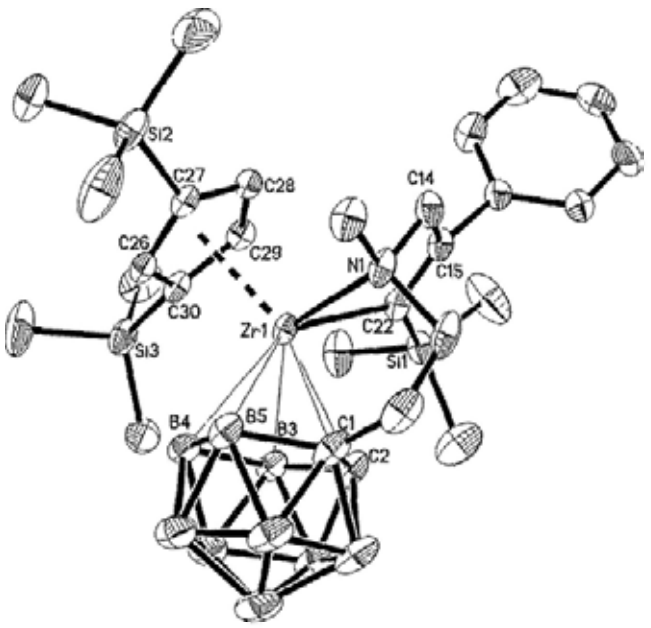


Figure 6.5. Molecular structure of

(Cp'')[η^1:σ:η^5-{MeN(CH_2PhC=CTMS)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-3b**)

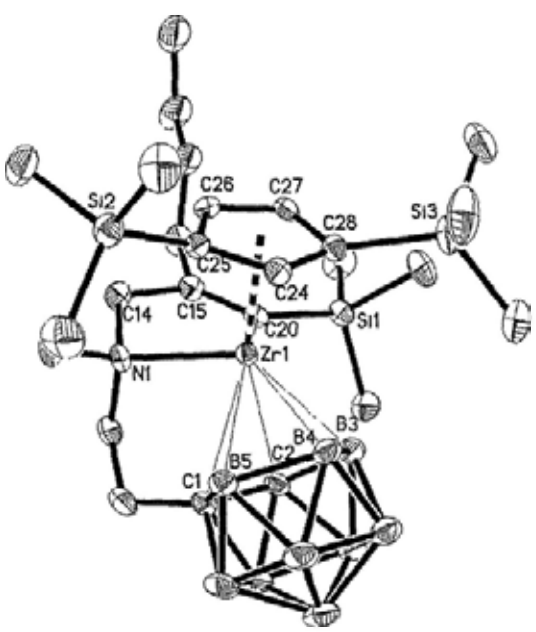


Figure 6.6. Molecular structure of

(Cp'')[η^1:σ:η^5-{MeN(CH_2^{n}BuC=CTMS)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-3c**)

6.3.3 Reactivity toward Terminal Alkynes.

The *sp*-CH protons in terminal alkynes are acidic. When treating the terminal alkynes with metal alkyls, either acid-base reaction or insertion reaction could happen. Treatment of zirconacarborane alkyl complex [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (**VI-1**) with 1 equiv of phenylacetylene/1-hexyne in toluene at room temperature afforded, after recrystallization from toluene, the mono-insertion zirconacarboranyl alkenyl complexes [η^1:σ:η^5-{MeN(CH_2R^1C=C(H))CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (R^1 = Ph, **VI-4a**; R^1 = ^{n}Bu, **VI-4b**) in ~ 80% isolated yields (Scheme 6.4). They did not react further with the second equivalent of alkynes even in refluxing toluene. The compositions of both **VI-4a** and **VI-4b** were confirmed by various spectroscopic techniques and elemental analyses. Except for the signals corresponding to Cp'', CH_2CH_2NMe and Ph (**VI-4a**), ^{n}Bu (**VI-4b**), one singlet at 7.07 ppm in **VI-4a** and 4.85 ppm in **VI-4b** attributable to the vinylic Zr$C_\alpha H$, two doublets at 3.45 and 2.85 ppm with J = 15.0 Hz in **VI-4a**, 3.07 and 2.12 ppm with J = 13.5 Hz in **VI-4b** assignable to NCH_2C(R) (R = Ph (**VI-4a**), ^{n}Bu (**VI-4b**)) were observed in the ^{1}H NMR spectra. The characteristic resonances at 187.5/141.8 ppm for **VI-4a** and 181.9/143.4 ppm for **VI-4b** assignable to the alkenyl Zr$C_\alpha C_\beta$ were observed in their ^{13}C NMR spetra. The ^{11}B NMR spectra of both compounds showed a 2:2:1:1:1:2 pattern. The structure of **VI-4a** was further revealed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both bistrimethylsilylcyclopentadienyl and dicarbollyl ligands, σ-bound to the sp^2-C atom and coordinated to the N atom of the amino group in a distorted-tetrahedral geometry (Figure 6.7). The average Zr-C(C_5 ring)/Zr-cage atom distances of 2.537(6) Å/2.551(1) Å are comparable to those of

2.509(4) Å/2.522(4) Å in **VI-1**, 2.533(5) Å/2.537(6) Å in **VI-2a**, and 2.559(2) Å/2.554(2) Å in **VI-2c**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 138.6° is comparable to that of 140.0° in **VI-1**, 136.4° in **VI-2a** and 137.6° in **VI-2c**. The Zr-C σ bond distance of 2.278(6) Å is similar to that of 2.271(4) Å in **VI-1**, 2.329(5) Å in **VI-2a**, 2.295(2) Å in **VI-2c** and 2.298(10) (Zr-C(sp^2)) Å in $Cp_2Zr[(Ph)C{=}C(Ph)CH(C_6H_4)CH]$.[154] From the NMR data and X-ray crystal structure, it is clear that the less bulky sp^2-C is connected to the Zr center. In view of the electron withdrawing property of Ph group and electron donating ability of ^{n}Bu, the regioselectivity of this insertion is dominated by steric factor.

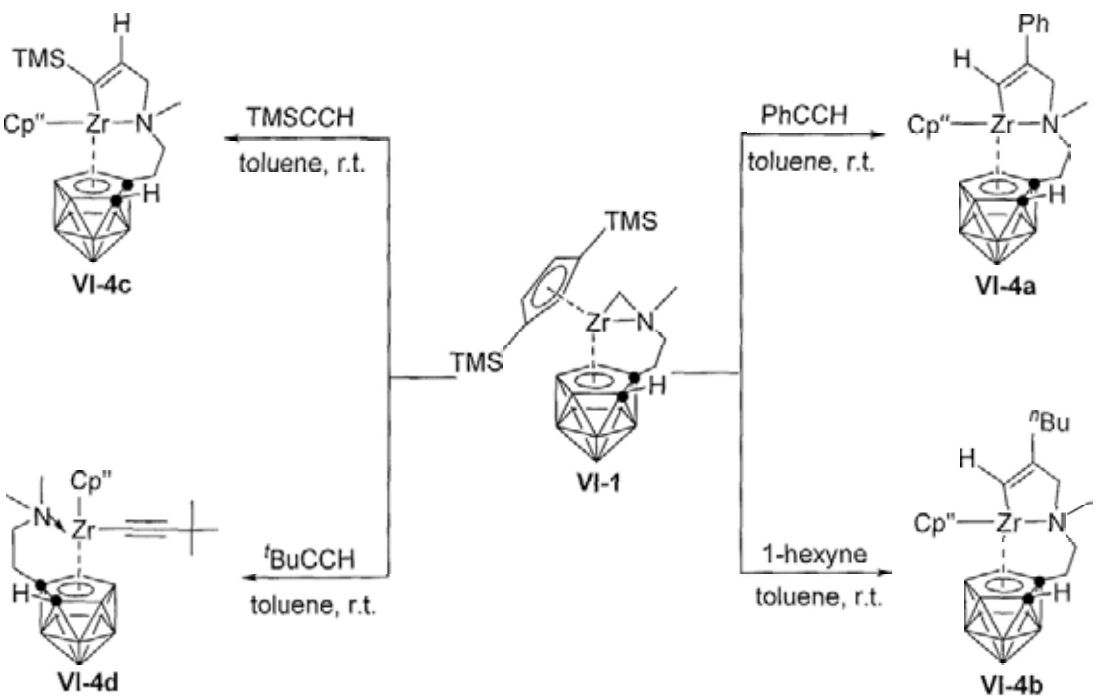
Treatment of complex **VI-1** with terminal alkyne TMSC≡CH in 1:1 molecular ratio in toluene at room temperature afforded, after recrystallization, mono-insertion product [η^1:σ:η^5-{MeN(CH_2(H)C=C(TMS))CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (**VI-4c**) in 78% isolated yield (Scheme 6.4). In compound **VI-4c**, the Zr atom is connected to the more bulky sp^2-C. This is established by a triplet at 6.43 ppm with J = 3.0 Hz corresponding to the vinylic proton of $ZrC_\alpha C_\beta H$ in the ^{1}H NMR spectrum, indicating this vinylic proton coupling to both CH_2 protons, the CH_2 protons show two doublets at 3.05 and 2.15 ppm with J = 15.0 Hz because of the stereochemistry. The ^{13}C NMR spectrum showed the characteristic alkenyl $ZrC_\alpha C_\beta$ resonances at 211.7 and 140.3 ppm. An X-ray crystal structure determination of **VI-4c** also confirms the regioselectivity of the insertion product **VI-4c** (Figure 6.8). The Zr atom is η^5-bound to both bistrimethylsilylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the sp^2-C atom and coordinated to the N atom of the amino group in a distorted-tetrahedral geometry. The average Zr-C(C_5 ring)/Zr-cage atom distances of 2.553(3) Å/2.551 (3) Å are

comparable to those of 2.537(6) Å/2.551(7) Å in **VI-4a**, and 2.509(4) Å/2.522(4) Å in **VI-1**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 135.9° is a little smaller than that of 140.0° in **VI-1** and 138.6° in **VI-4a**. The Zr-C σ bond distance of 2.306(3) Å is a little longer than that of 2.271(4) Å in **VI-1** and 2.278(6) Å in **VI-4a**. The result suggests that the regioselectivity of this insertion reaction was dominated by the electronic factor.

The reaction of complex **VI-1** with 1 equiv of *tert*-butylacetylene (3,3-dimethyl-1-butyne, ^{t}BuC≡CH) in toluene at room temperature produced, after recrystallization from toluene, zirconium alkyne complex (η^5-Cp'')[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(C≡C^{t}Bu) (**VI-4d**) in 75% isolated yield (Scheme 6.4). The ^{1}H NMR spectrum showed two singlets at 2.10 and 2.05 ppm corresponding to the NMe_2 protons which means the disappearance of the $ZrCH_2NMe$ in addition to the signals attributable to Cp'', CH_2CH_2 and ^{t}Bu groups. No characteristic signal of alkenyl Zr-C(sp^2) at low field was observed in the ^{13}C NMR spectrum, while a signal at 90.2 ppm assignable to Zr-C(*sp*) was shown. The solid-state structure of **VI-4d** was confirmed by single-crystal X-ray analyses. The Zr atom is η^5-bound to both bistrimethylsilylcyclopentadienyl and dicarbollyl ligands, σ-bound to the *sp*-C atom and coordinated to the nitrogen atom of the amino group in a distorted-tetrahedral geometry (Figure 6.9). The average Zr-C(C_5 ring)/Zr-cage atom distances and Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 2.538(4) Å/2.561(5) Å/136.9° are similar to those of 2.537(6) Å/2.551(7) Å/138.6° in **VI-4a**. The Zr-C σ bond distance of 2.190(5) Å is similar to that of 2.215 Å in $Cp_2Zr(\eta^1$-C≡C($CHCH_2CH_2$))$_2$,[159] and 2.227(4)/2.223(5) Å in (η^5-$C_5Me_4H)_2Zr(\eta^1$-C≡C$SiMe_3)_2$,[160] but a little shorter than that of 2.268(2) Å in (η^5-$C_5Me_5)_2Zr(\eta^1$-C≡C^{t}Bu)[η^3-C($SiMe_3$)=CH($SiMe_3$)],[161] 2.280(2) Å in

(η^5-$C_5Me_4H)_2Zr(\eta^1$-C≡CPh)[η^3-C(SiMe$_3$)=CH(SiMe$_3$)],[161] 2.310(5) Å in (η^5-$C_5Me_4H)_2Zr(\eta^1$-C≡CSiMe$_3$)[η^3-C(SiMe$_3$)=CH(SiMe$_3$)],[161] 2.231(3)/2.249(3) Å in (η^5-$C_5H_4SiMe_3)_2Zr(\eta^1$-C≡CPh)$_2$,[162] and 2.328(2) Å in $Cp_2Zr(\eta^1$-C≡CCO$_2$Me)(σ:η^1-C_6H_4C(P(N^{t}Pr$_2$)$_2$)=NH).[163] Acid-base reaction mechanism was proposed for the formation of **VI-4d**, and no insertion product was observed probably due to the bulkiness of ^{t}Bu group, which prohibits the insertion of C≡C bond into the Zr-C σ bond.

Scheme 6.4



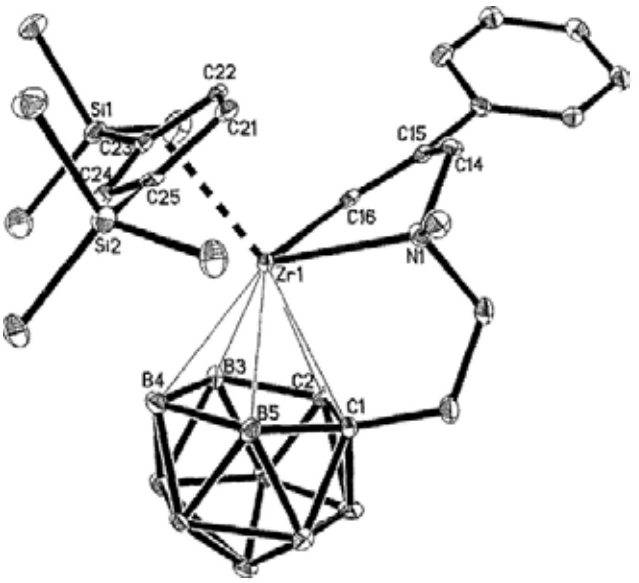


Figure 6.7. Molecular structure of

(Cp'')[η^1:σ:η^5-{MeN(CH_2PhC=CH)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-4a**)

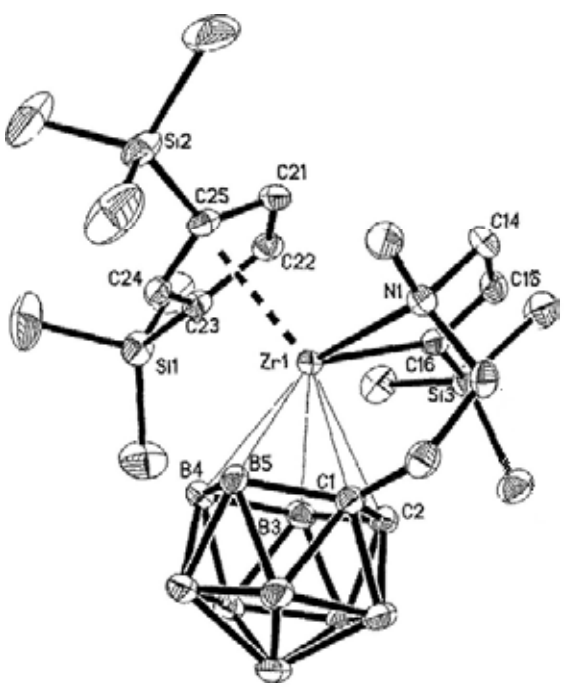


Figure 6.8. Molecular structure of

(Cp'')[η^1:σ:η^5-{MeN(CH_2HC=CTMS)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-4c**)

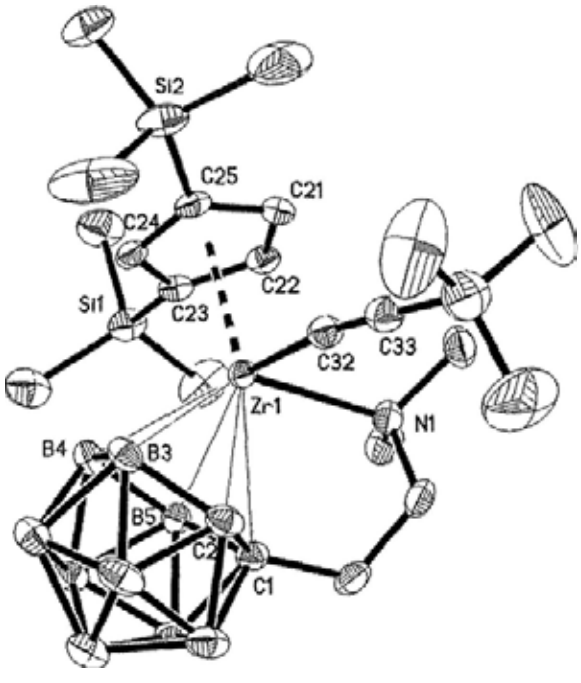


Figure 6.9. Molecular structure of

(Cp'')[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(C≡C^{t}Bu) (**VI-4d**)

6.5 Summary

Treatment of Cp''$ZrMe_3$ with 7-(Me_2NH)$(CH_2)_2$-7,8-$C_2B_9H_{11}$ afforded the full-sandwich zirconacarborane alkyl complex (η^5-Cp'')[η^1:σ:η^5-{MeN$(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**) via alkane elimination reaction. No expected zirconacarborane methyl complex was isolated because of the instability of (η^5-Cp'')[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) at room temperature which is believed to be the intermediate during the formation of **VI-1**.

Zirconacarborane alkyl complex **VI-1** showed no reactivity to alkenes even at harsh conditions, while alkynes can insert into the Zr-C σ bond of **VI-1**. Treatment of **VI-1** with symmetrical internal alkynes 3-hexyne, 4-octyne, and diphenylacetylene (PhC≡CPh)

gave the mono-insertion products $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2(R)C{=}C(R))CH_2CH_2\}C_2B_9H_{10}]Zr(\eta^5\text{-}Cp'')$ (R = Et (**VI-2a**), ^{n}Pr (**VI-2b**), Ph (**VI-2c**)). No further insertion reaction happened even with excess alkynes and at higher temperatures. For TMSC≡CTMS, no insertion product was formed because of the bulkiness of the TMS group. For unsymmetrical internal alkynes PhC≡CMe, TMSC≡CPh and TMSC≡C^{n}Bu, both electronic and steric factors affected the regioselectivity of the insertion process, and mono-insertion products $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2(R^1)C{=}C(R^2))CH_2CH_2\}C_2B_9H_{10}]Zr(\eta^5\text{-}Cp'')$ (R^1 = Ph, R^2= Me, **VI-3a**; R^1= Ph, R^2= TMS, **VI-3b**; R^1= ^{n}Bu, R^2= TMS, **VI-3c**) were generated. For the terminal alkynes PhC≡CH, ^{n}BuC≡CH and TMSC≡CH, mono-insertion metal alkenyl products $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2(R^1)C{=}C(R^2))CH_2CH_2\}C_2B_9H_{10}]Zr(\eta^5\text{-}Cp'')$ (R^1 = Ph, R^2= H, **VI-4a**; R^1= ^{n}Bu, R^2= H, **VI-4b**; R^1= H, R^2= TMS, **VI-4c**) were formed. But for the more bulky ^{t}BuC≡CH, metal alkynyl complex $(\eta^5\text{-}Cp'')[\eta^1{:}\eta^5\text{-}(Me_2NCH_2CH_2)C_2B_9H_{10}]Zr(C{\equiv}C^tBu)$ (**VI-4d**) was produced through acid-base reaction.

Chapter 7

Synthesis, Structural Characterization, and Alkynes Insertion Reaction of Zirconacarborane Methyl Complex $(\eta^5\text{-Cp}^*)[\eta^1:\eta^5\text{-}(Me_2NCH_2CH_2)C_2B_9H_{10}]Zr(Me)$

7.1 Introduction

In the previous chapter, $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(\eta^5\text{-Cp''})$ (**VI-1**) was synthesized by the alkane elimination reaction of $(\eta^5\text{-Cp''})ZrMe_3$ with 7-$(Me_2NH)(CH_2)_2$-7,8-$C_2B_9H_{11}$ followed by the elimination of CH_4. No expected zirconacarborane methyl complex was formed because of its instability at room temperature, which maybe ascribed to the less bulky Cp'' group. In this chapter, as a direct comparison with $Cp^*(C_2B_9H_9)ZrMe$, more bulky Cp* group was used to replace the Cp'' group in the hope to stabilize the formed zirconacarborane methyl complexes. $(\eta^5\text{-Cp}^*)[\eta^1:\eta^5\text{-}(Me_2NCH_2CH_2)C_2B_9H_{10}]Zr(Me)$ was then synthesized and its reactivity to alkynes, diynes and enyns was studied.

7.2 Synthesis of Zirconacarborane Methyl Complex.

Treatment of $(\eta^5\text{-Cp}^*)ZrMe_3$ ($Cp^* = C_5Me_5$) with 1 equiv of zwitterionic amino-dicarbollyl ligand 7-$(Me_2NH)(CH_2)_2$-7,8-$C_2B_9H_{11}$ in THF from -30 °C to room temperature overnight afforded a full-sandwich zirconacarborane methyl complex

(η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**) in 91% isolated yield (Scheme 7.1). Complex **VII-1** dissolved well in pyridine, showed low solubility in THF and toluene, and was insoluble in hexane. This is totally different from that of its Cp'' analogue [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (**VI-1**) and Cp*($C_2B_9H_{11}$)ZrMe, as both dissolved very well in toluene. Single-crystals suitable for X-ray analyses were grown from a mixture of toluene and THF solution. Complex **VII-1** is very stable at room temperature.

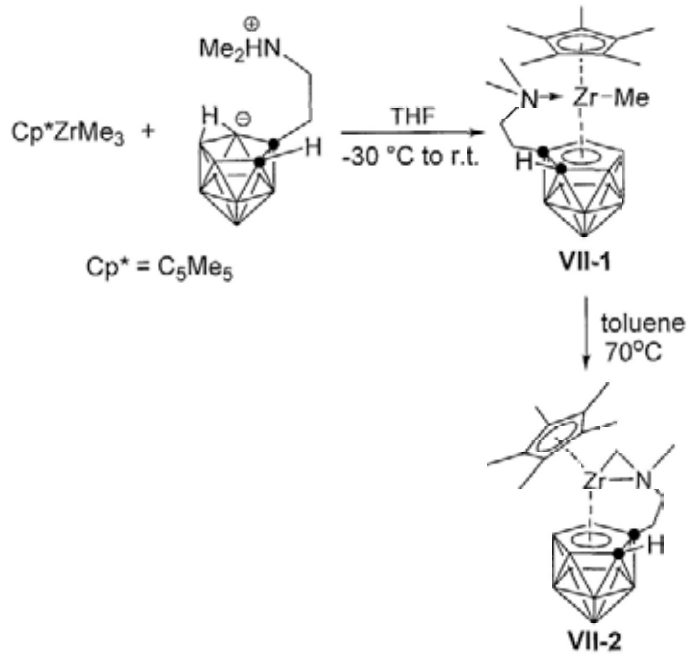
The composition of **VII-1** was characterized by various spectroscopic techniques and elemental analyses. Except for the signals of the methyl protons on Cp ring and Lewis base functionalities, a broad singlet at 4.23 ppm assignable to the cage *CH* and one singlet at 0.54 ppm attributable to the Zr-CH_3 protons were observed in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum was consistent with the above result. Its ^{11}B NMR spectrum showed a 1:1:1:1:1:1:1:1:1:1 pattern which is totally different from that of (Cp*)($C_2B_9H_{11}$)Zr(Me). The solid-state structure of **VII-1** was confirmed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the methyl group and coordinated to the N atom in a distorted-tetrahedral geometry (Figure 7.1). The average Zr-C_5 ring distance of 2.565(3) Å (Table 7.1) is comparable to that of 2.531/2.533 Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2),[40] 2.505 Å in (Cp*)($C_2B_9H_{11}$)Zr[C(Me)=CMe_2],[40] 2.538(7) Å in (C_5Me_5)$_2$Zr$CH_3^+CH_3B(C_6F_5)_3^-$,[173] 2.505(6) Å in (C_5Me_5)Zr(CH_3)$_2$($CB_{11}H_{12}$),[165] 2.534(9) Å in (Cp*)[Me_2C(Cp)($C_2B_{10}H_{11}$)]$ZrCl_2$,[166] 2.531(5) Å in (Cp*)[Me_2C(Cp)($MeC_2B_{10}H_{10}$)]$ZrCl_2$,[166] 2.538(9) Å in

(Cp*)[$Me_2C(Cp)(C_2B_{10}H_{10})$]ZrCl,[166] and 2.527(7) Å in (C_5Me_5)Zr(2,6-$OC_6H_3Me_2$)$_3$.[167] The average Zr-cage atom distance of 2.582(3) Å compares to that of 2.523(5) Å in [η^1:η^5-(Me_2NCH_2)$C_2B_9H_{10}$]$_2$Zr,[55] 2.538(5) Å in [η^1:η^5-($C_5H_4NCH_2$)$C_2B_9H_{10}$]Zr(NMe_2)$_2$,[52] 2.568(4) Å in [η^1:η^5-($BzNCH_2$)(CH_3)$C_2B_9H_{10}$]$ZrCl_2$(THF),[54] 2.601(5) Å in [η^1:η^5-(^{i}Pr$_2C_6H_3N$=CH)$C_2B_9H_{10}$]Zr(NMe_2)$_2$($NHMe_2$),[57] 2.535/2.533 Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2),[40] and 2.544(6) Å in [η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF).[56] The Zr-C σ bond distance of 2.300(3) Å is similar to that of 2.282(3)/2.270(2) Å in (η^5-C_5Me_5)Zr(2,4-^{t}Bu$_2$-6-(OCH_2CH_2N=CH)-C_6H_2O)Me_2,[168] 2.282(2) Å in (η^5-1,3-(Me_3Si)$_2C_5H_3$)(η^5-C_5Me_5)ZrH(Me),[153] and 2.270(3) Å in (C_5H_4Me)$_2$Zr(CH_3)($CB_{11}H_{12}$),[165] but is longer than that of 2.245(2)/2.236(2) Å in (C_5Me_5)Zr(CH_3)$_2$($CB_{11}H_{12}$),[165] 2.233(6) Å/2.242(6) Å (Zr-C(N)/Zr-C(TMS)) in [η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF),[56] 2.223(6) Å in (C_5Me_5)$_2$Zr$CH_3^+CH_3B(C_6F_5)_3^-$,[164] 2.198(4) Å in (Cp*)($C_2B_9H_{11}$)Zr[C(Me)=CMe_2],[40] and 2.187(6)/2.176(7) Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2).[40] The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 135.7° is comparable to that of 141.3° in (Cp*)($C_2B_9H_{11}$)Zr[C(Me)=CMe_2][40] and 134.9° in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2).[40]

After heating complex **VII-1** in toluene at 70 °C overnight, the yellow suspension was changed to a clear orange solution. After cooling down, crystalline solid (η^5-Cp*)[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VII-2**) was formed quantitatively via the elimination of one molecule of CH_4 (Scheme 7.1). The composition of **VII-2** was fully characterized by various spectroscopic techniques and elemental analyses. The

singlet at 0.54 ppm corresponding to Zr-CH_3 protons disappeared and two doublets at 2.25 and 2.31 ppm with ^2J = 5.7 Hz assignable to the Zr-CH_2 was observed in the ^{1}H NMR spectrum. The ^{13}C NMR data was consistent with the ^{1}H NMR result. The ^{11}B NMR spectrum showed a 1:1:1:1:1:1:1:1:1 pattern which is similar to the parent complex **VII-1**. The solid-state structure of complex **VII-2** was further revealed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the CH_2 and coordinated to the N atom in a distorted-tetrahedral geometry (Figure 7.2). The average Zr-C(C_5 ring)/Zr-cage distances of 2.543(3) Å/2.534(3) Å are a little shorter than those of 2.565(3) Å/2.582(3) Å in complex **VII-1**, but a little longer than those of 2.509(4) Å/2.522(4) Å in **VI-1**. The Zr-C σ bond distance of 2.260(3) Å is comparable to that of 2.300(3) Å in **VII-1**, 2.250(12) (Zr-C(sp^3)) Å in $Cp_2Zr[(Ph)C{=}C(Ph)CH(C_6H_4)CH]$,[154] and 2.271(4) Å in **VI-1**, but is longer than those of 2.187(6)/2.176(7) Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$.[40]. The Cent($C_5$ ring)-Zr-Cent(C_2B_3) angle of 138.3° is comparable to that of 135.7° in **VII-1**, 141.3° in $(Cp^*)(C_2B_9H_{11})Zr[C(Me){=}CMe_2]$,[40] and 140.0° in **VI-1**.

Scheme 7.1



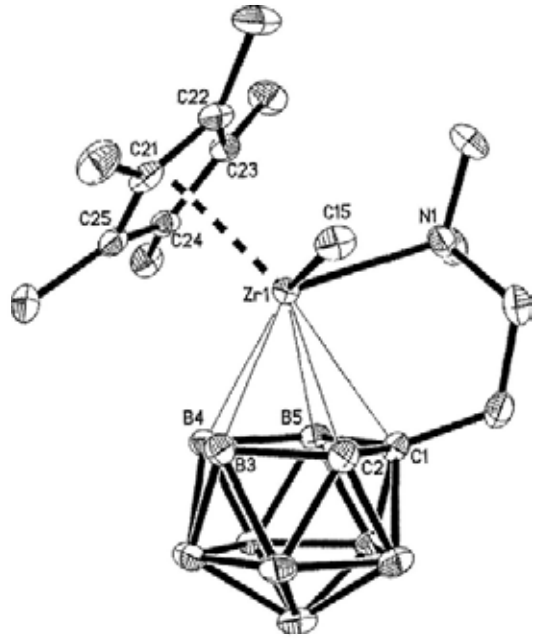


Figure 7.1. Molecular structure of (Cp*)[η^1:η^5-{$Me_2NCH_2CH_2$}$C_2B_9H_{10}$]Zr(Me)

(VII-1)

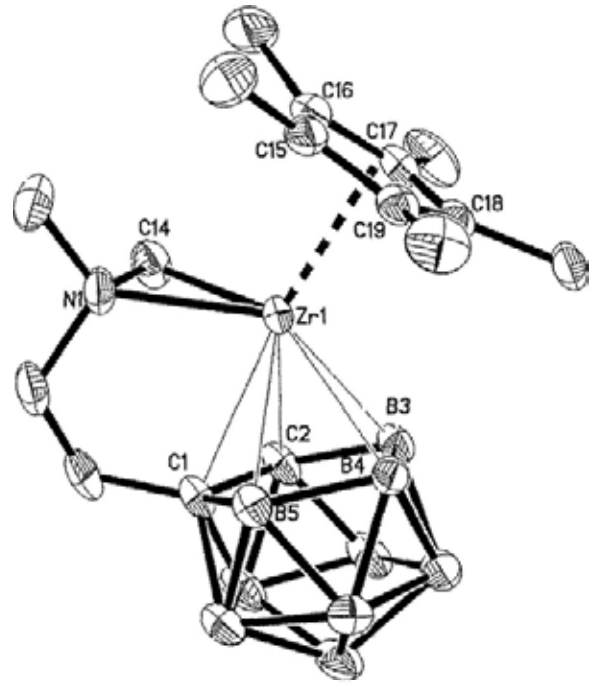


Figure 7.2. Molecular structure of (Cp*)[η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-2**)

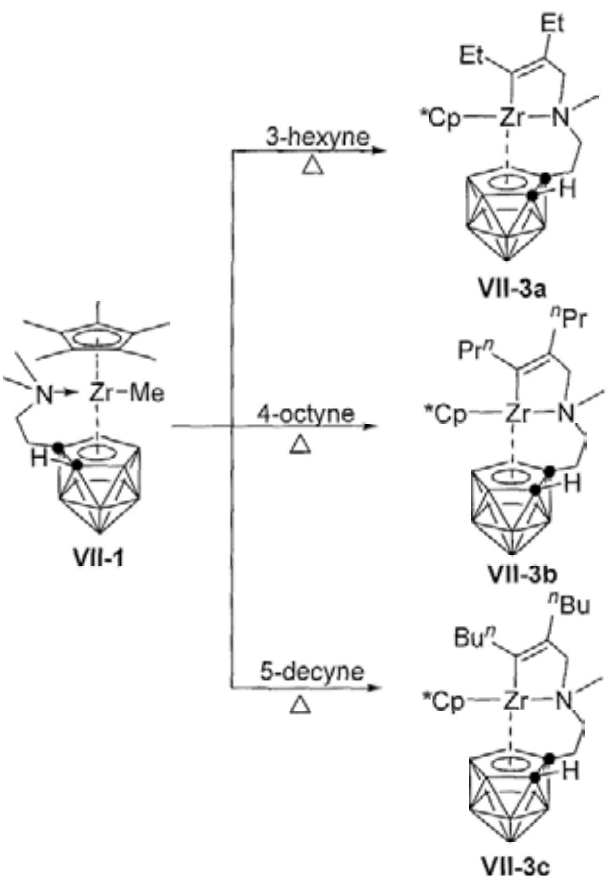
7.3 Reactivity of Zirconacarborane Methyl Complex

7.3.1 Reactivity to Symmetrical Internal Alkynes.

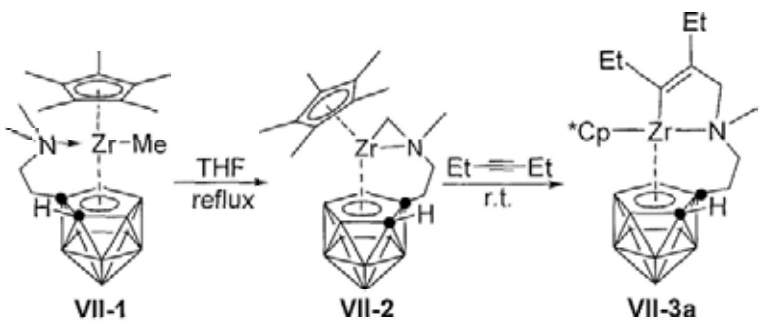
Treatment of complex **VII-1** with 1 equiv of symmetrical internal alkynes (3-hexyne, 4-octyne, and 5-decyne) in refluxing THF gave, after recrystallization from THF, the mono-insertion products (η^5-Cp*)[η^1:σ:η^5-{MeN[CH_2(R)C=C(R)]CH_2CH_2}$C_2B_9H_{10}$]Zr (R = Et, **VII-3a**; ^{n}Pr, **VII-3b**; ^{n}Bu, **VII-3c**) in 82-86% isolated yields (Scheme 7.2). No reaction was observed at room temperature. A reaction mechanism was proposed and shown in Scheme 7.3. Under refluxing condition, a methane molecule was eliminated from complex **VII-1** to form complex **VII-2**, the C≡C bond of alkyne then inserts into Zr-C bond of complex

VII-2 to form complex **VII-3a**. This proposal was confirmed by reaction of complex **VII-2** directly with one equiv of EtC≡CEt in THF at room temperature to afford complex **VII-3a** in 92% isolated yield. Complex **VII-2** showed higher reactivity than complex **VII-1** for the alkyne insertion reaction because of the presence of three-membered zirconacycle in **VII-2**.

Scheme 7.2



Scheme 7.3



VII-1 **VII-2** **VII-3a**

The compositions of complex **VII-3a**, **VII-3b** and **VII-3c** were fully characterized by various spectroscopic techniques and elemental analyses. The ^{1}H NMR spectra showed two doublets at 3.64 and 2.76 ppm with J = 15.9 Hz (in **VII-3a**), 3.67 and 2.78 ppm with J = 15.0 Hz (in **VII-3b**), 3.70 and 2.72 ppm with J = 15.6 Hz (in **VII-3c**) corresponding to the α'-CH_2 except for the signals assignable to Et (in **VII-3a**), ^{n}Pr (in **VII-3b**), ^{n}Bu (in **VII-3c**), methyl groups on Cp* ring and CH_2CH_2NMe. The characteristic resonances at low field of 196.8/196.0/195.9 ppm (C_α) and 138.2/137.5/137.4 ppm (C_β) in **VII-3a/VII-3b/VII-3c** for $ZrC_\alpha C_\beta$ (alkenyl carbon) were observed in the ^{13}C NMR spectra. The three complexes showed different ^{11}B NMR patterns: a 2:2:1:1:1:1:1 for **VII-3a**, a 3:1:1:1:1:2 for **VII-3b**, and a 1:1:1:2:2:2 for **VII-3c**. Single-crystal X-ray diffraction studies showed that in all three complexes, the Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the sp^2-C atom and coordinated to the N atom in a distorted-tetrahedral geometry (Figures 7.3, 7.4 and 7.5). The average Zr-C(C_5 ring)/Zr-cage atom distances and the Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 2.563(7) Å/2.566(7) Å/134.4° (in **VII-3a**), 2.562(4) Å/2.554(4) Å/134.2° (in **VII-3b**) and 2.573(4) Å/2.566(5) Å/134.6° (in **VII-3c**) are comparable to each other and similar to those of 2.565(3) Å/2.582(3) Å/135.7° in

VII-1 and 2.543(3) Å/2.534(3) Å/138.3° in **VII-2**. The Zr-C σ bond distances of 2.285(5) Å/2.286(3) Å/2.294(4) Å in **VII-3a/VII-3b/VII-3c** are similar to each other, and comparable to that of 2.300(3) Å in **VII-1** and 2.260(3) Å in **VII-2**.

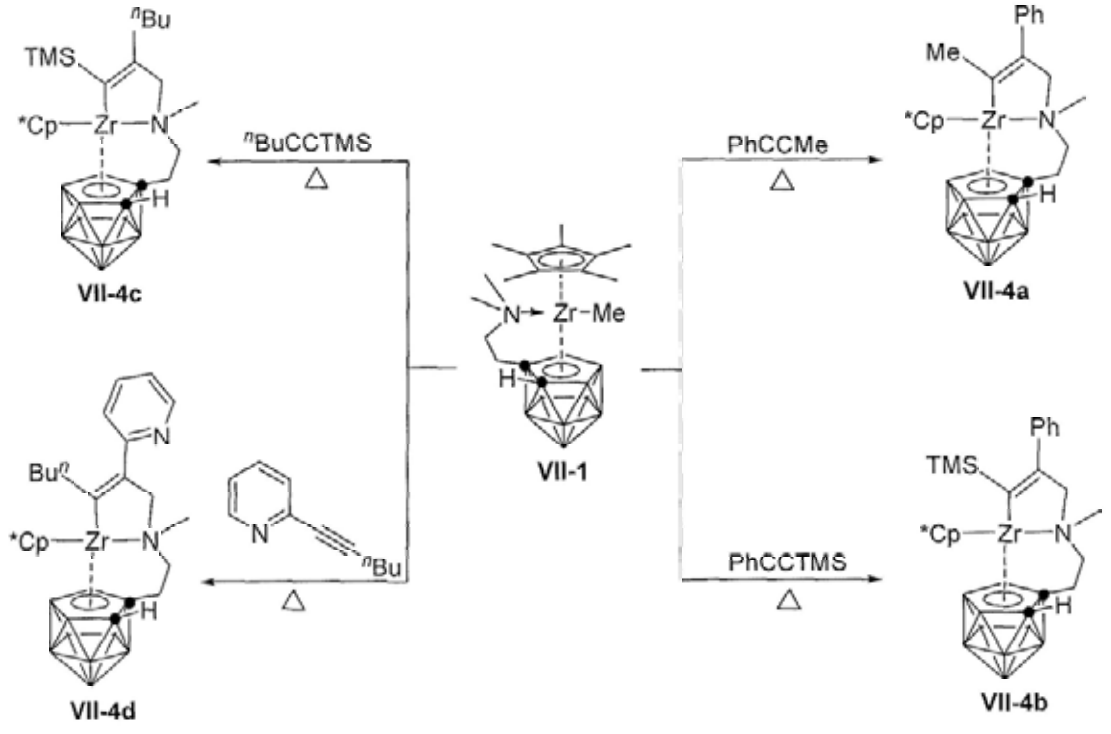
Both complexes **VII-1** and **VII-2** did not show any reactivity toward more bulky internal alkynes such as TMSC≡CTMS and PhC≡CPh even in refluxing toluene for 3 days.

7.3.2 Reactivity to Unsymmetrical Internal Alkynes.

For unsymmetrical internal alkynes such as PhC≡CMe, PhC≡CTMS, ^{n}BuC≡CTMS, and (2-Py)C≡C^{n}Bu, the regioselectivity will be interesting. Treatment of complex **VII-1** with unsymmetrical internal alkynes in refluxing THF produced, after recrystallization from THF, the mono-insertion products (η^5-Cp*)[η^1:σ:η^5-{MeN[CH_2(R^1)C=C(R^2)]CH_2CH_2}$C_2B_9H_{10}$]Zr (R^1 = Ph, R^2 = Me, **VII-4a**; R^1 = Ph, R^2 = TMS, **VII-4b**; R^1 = ^{n}Bu, R^2 = TMS, **VII-4c**; R^1 = 2-Py, R^2 = ^{n}Bu, **VII-4d**) in 75-88% isolated yields (Scheme 7.4). The compositions of four products were confirmed by various spectroscopic techniques and elemental analyses. The characteristic resonances of Zr$C_\alpha C_\beta$ (alkenyl) at 191.4/207.9/203.2/201.2 ppm (C_α) and 145.8/153.2/150.5/160.1 ppm (C_β) for **VII-4a/VII-4b/VII-4c/VII-4d** were observed in the ^{13}C NMR spectra. The solid-state structures of complexes **VII-4b**, **VII-4c** and **VII-4d** were further confirmed by single-crystal X-ray analyses. The Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the sp^2-*C* atom and coordinated to the N atom in a distorted-tetrahedral geometry, which is shown in Figures 7.6, 7.7 and 7.8, respectively. The average Zr-C(C_5 ring)/Zr-cage

atom/Zr-C σ bond distances and Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 2.574(5) Å/2.551(6) Å/2.322(5) Å/135.7° in **VII-4b**, 2.574(3) Å/2.547(3) Å/2.318(2) Å/134.9° in **VII-4c** and 2.572(8) Å/2.578(7) Å/2.313(6) Å/136.3° in **VII-4d** are comparable to each other and similar to those of 2.563(7) Å/2.566(7) Å/2.285(5) Å/134.4° in **VII-3a**, 2.562(4) Å/2.554(4) Å/2.286(3) Å/134.2° in **VII-3b** and 2.573(4) Å/2.566(5) Å/2.294(4) Å/134.6° in **VII-3c**. The regioselectivity observed in the reaction with **VII-1** is the same as that found in its Cp'' analogue **VI-1**. For the TMS substituted internal alkynes, the electronic effect of TMS plays a key role in the regioselectivity (**VII-4b** and **VII-4c**). For others, steric hindrance dominates the regioselectivity (**VII-4a** and **VII-4d**).

Scheme 7.4



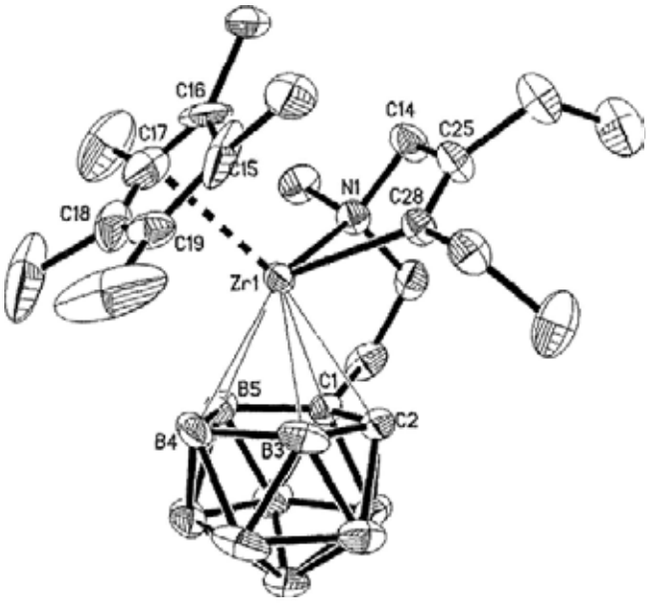


Figure 7.3. Molecular structure of

$(Cp^*)[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN[CH_2(Et)C{=}C(Et)]CH_2CH_2\}C_2B_9H_{10}]Zr$ (**VII-3a**)

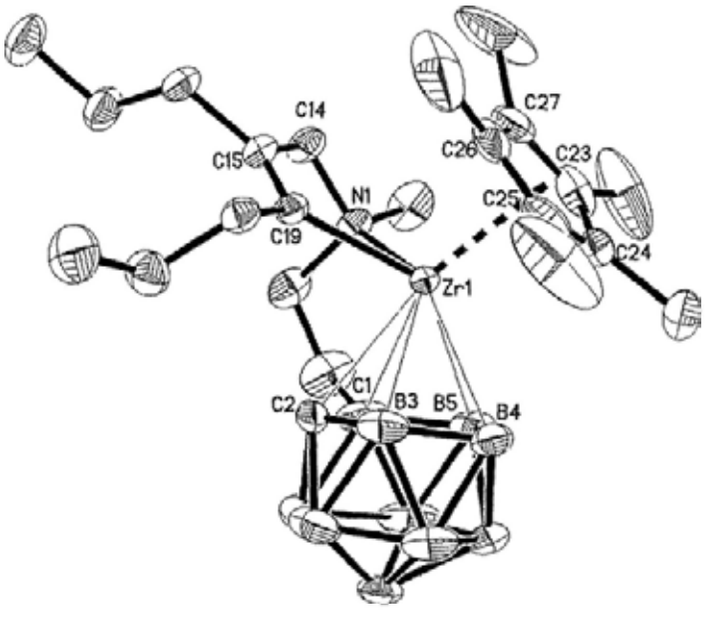


Figure 7.4. Molecular structure of

$(Cp^*)[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN[CH_2(^n Pr)C{=}C(^n Pr)]CH_2CH_2\}C_2B_9H_{10}]Zr$ (**VII-3b**)

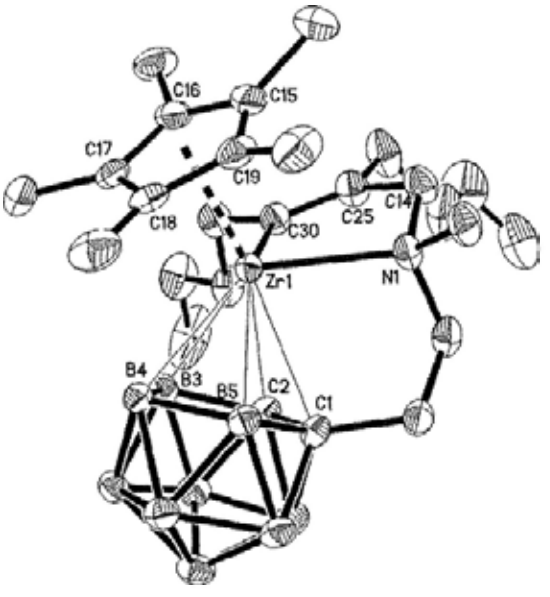


Figure 7.5. Molecular structure of

(Cp*)[η^1:σ:η^5-{MeN[CH_2(^{n}Bu)C=C(^{n}Bu)]CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-3c**)

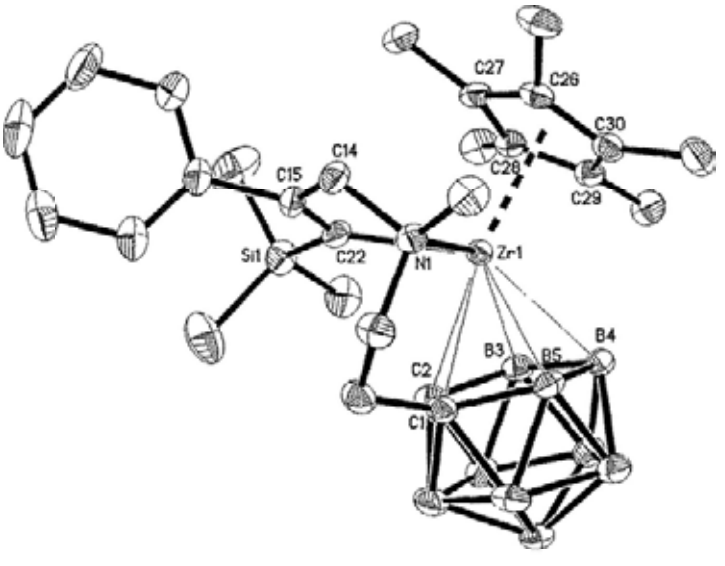


Figure 7.6. Molecular structure of

(Cp*)[η^1:σ:η^5-{MeN[CH_2(Ph)C=C(TMS)]CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-4b**)

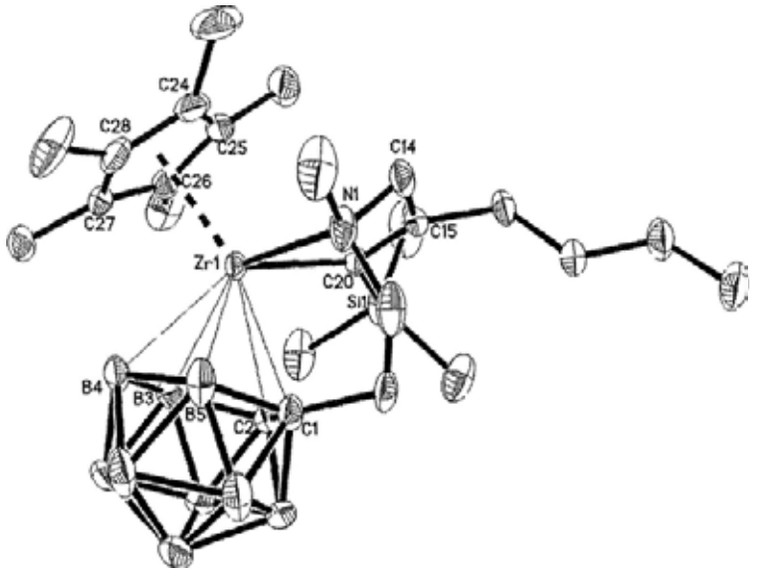


Figure 7.7. Molecular structure of

(Cp*)[η^1:σ:η^5-{MeN[CH_2(^{n}Bu)C=C(TMS)]CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-4c**)

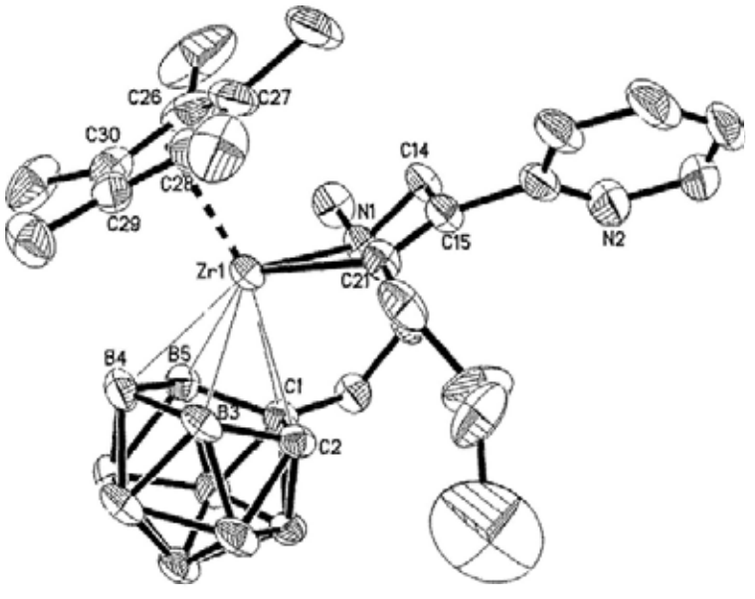
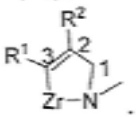


Figure 7.8. Molecular structure of

(Cp*)[η^1:σ:η^5-{MeN[CH_2(2-Py)C=C(^{n}Bu)]CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-4d**)

Table 7.1. Selected Bond Lengths (Å) and Angles (deg) for VII-1, VII-2 VII-3a – c, VII-4b - d and VII-5a - b

	VII-1	VII-2	VII-3a	VII-3b	VII-3c	VII-4b	VII-4c	VII-4d	VII-5a	VII-5b
av. Zr-C_{ring}	2.565(3)	2.543(3)	2.563(7)	2.562(4)	2.573(4)	2.574(5)	2.574(3)	2.572(8)	2.553(3)	2.558(4)
av. Zr-cage atom	2.582(3)	2.534(3)	2.566(7)	2.554(4)	2.566(7)	2.551(6)	2.547(3)	2.578(7)	2.569(3)	2.549(4)
Zr-N	2.267(3)	2.272(2)	2.379(5)	2.382(3)	2.383(4)	2.402(4)	2.376(2)	2.359(5)	2.379(2)	2.412(3)
Zr-C(3)[b]	2.300(3)	2.260(3)	2.285(5)	2.286(3)	2.285(5)	2.322(5)	2.318(2)	2.313(6)	2.217(3)	2.256(4)
C(2)-C(3)[b]			1.348(8)	1.345(4)	1.337(7)	1.350(7)	1.352(4)	1.318(9)	1.202(4)[c]	1.347(5)
C(1)-C(2)[b]			1.512(9)	1.507(5)	1.507(6)	1.519(7)	1.514(4)	1.526(9)		1.516(5)
N-C(1)[b]			1.513(8)	1.494(4)	1.496(5)	1.496(6)	1.487(5)	1.496(8)		1.501(5)
Zr-Cent(C_5)[a]	2.264	2.242	2.277	2.280	2.275	2.274	2.277	2.287	2.250	2.256
Zr-Cent(C_2B_3)[a]	2.147	2.090	2.137	2.128	2.131	2.113	2.107	2.146	2.132	2.106
Cent(C_5)-M-Cent(C_2B_3)	135.7	138.3	134.4	134.2	134.6	135.7	134.9	136.3	135.7	136.2

[a] Cent(C_5), Cent(C_2B_9): the centroid of the cyclopentadienyl ring and the C_2B_3 bonding face, respectively. [b] the number of C(1), C(2), C(3) see: 

. [c] Zr-C(3)C(2)^{t}Bu in **VII-5a**.

7.3.3 Reactivity to Terminal Alkynes.

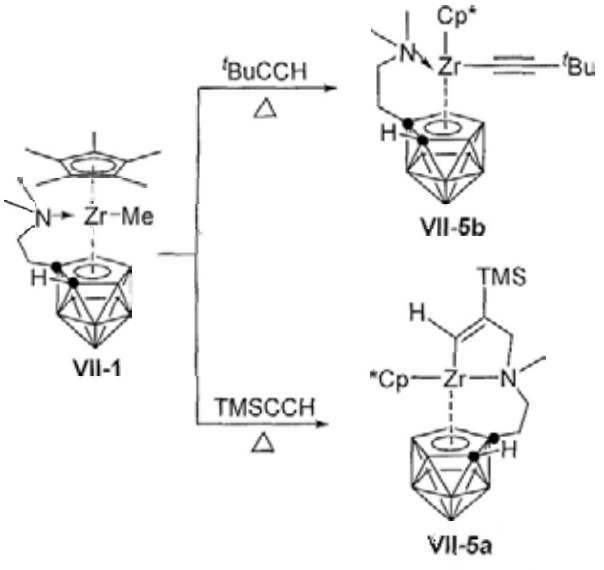
When treating complex **VII-1** with 1 equiv of TMSC≡CH in THF at room temperature for 3 days, the resulting yellow suspension showed no change in the ^{11}B NMR spectrum. When the suspension was heated to reflux overnight, a clear yellow solution was formed. Its ^{11}B NMR spectrum was different from that of complex **VII-1**. After recrystallization from THF, the mono-insertion product (η^5-Cp*)[η^1:σ:η^5-{MeN[CH_2(TMS)C=C(H)]CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-5a**) was obtained in 76% isolated yield (Scheme 7.5). Except for the resonances assignable to TMS group, methyl groups on Cp* ring and CH_2CH_2NMe, one singlet at 7.62 ppm attributable to vinylic proton Zr-C*H*, one broad singlet at 3.95 ppm corresponding to the cage proton *CH*, two doublets at 3.68 and 3.23 ppm with J = 15.0 Hz assignable to α'-CH_2 were observed in the ^1H NMR spectrum. The ^{13}C NMR data showed the characteristic resonance of Zr$C_\alpha C_\beta$(alkenyl) at low field of 210.6 and 137.2 ppm. These results indicated that C≡C did not insert into the Zr-methyl σ bond at room temperature, but such insertion proceeded at higher temperatures. The solid-state structure of **VII-5a** was confirmed by single-crystal X-ray analyses. The Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the sp^2-C atom and coordinated to the N atom in a distorted-tetrahedral geometry (Figure 7.9). The average Zr-C(C_5 ring)/Zr-cage atom distances of 2.553(3) Å/2.569(3) Å and the Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 135.7° are comparable to those of 2.565(3) Å/2.582(3) Å/ 135.7° in **VII-1**, 2.543(3) Å/2.534(3) Å/138.3° in **VII-2** and 2.553(3) Å /2.551(3) Å/135.9° in **VI-4c**. The Zr-C(sp^2) σ bond distance of 2.217(3) Å is much shorter than that of 2.300(3) Å in **VII-1**, 2.260(3) Å in **VII-2**, 2.298(10) (Zr-C(sp^2)) Å in

$Cp_2Zr[(Ph)C{=}C(Ph)CH(C_6H_4)CH]$[154] and 2.306(3) Å in **VI-4c**, but is comparable to that of 2.198(4) Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me){=}CMe_2]$.[40] Both the solid-state structure of **VII-5a** and splitting pattern of vinylic proton in the ^{1}H NMR spectrum indicated that the Zr atom is connected to the less bulky sp^2-C in complex **VII-5a**. The regioselectivity in this complex is totally different from that observed in its Cp'' analogue $[\eta^1{:}\sigma{:}\eta^5$-$\{MeN[CH_2(H)C{=}C(TMS)]CH_2CH_2\}C_2B_9H_{10}]Zr(\eta^5$-Cp'') (**VI-4c**). The electronic effect of the TMS group can not override the steric effect in this situation because of the more bulky pentamethylcyclopentadienyl ring than bis(trimethylsilyl)cyclopentadienyl ring and much smaller proton than TMS group.

Treatment of complex **VII-1** with 1 equiv of 3,3-dimethylbuta-1-yne (^{t}BuC≡CH) in refluxing THF gave zirconacarborane alkyne complex $(\eta^5$-Cp*$)[\eta^1{:}\eta^5$-$(Me_2NCH_2CH_2)C_2B_9H_{10}]Zr(C{\equiv}C^t$Bu) (**VII-5b**) in 83% isolated yield (Scheme 7.5). In refluxing THF, **VII-2** was initially formed, then acid-base reaction between complex **VII-2** and ^{t}BuCCH produced complex **VII-5b**. No characteristic signals of vinylic proton and alkenyl carbons connected to Zr atom were observed in the ^{1}H and ^{13}C NMR spectra. The ^{11}B NMR spectrum showed a 2:1:1:1:1:1:1:1 pattern. Single-crystal X-ray diffraction study revealed that the Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the *sp*-C atom and coordinated to the N atom in a distorted-tetrahedral geometry (Figure 7.10). The average Zr-C(C_5 ring)/Zr-cage atom distances of 2.558(4) Å/2.549(4) Å and the Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 136.2° are comparable to those of 2.565(3) Å/2.582(3) Å/ 135.7° in **VII-1**, 2.543(3) Å/2.534(3) Å/138.3° in **VII-2** and 2.538(4) Å/2.561(5) Å/136.9° in **VI-4d**. The Zr-C σ bond distance of 2.256(4) Å is comparable to that of

2.300(3) Å in **VII-1**, 2.260(3) Å in **VII-2**, 2.268(2) Å in $(\eta^5\text{-}C_5Me_5)_2Zr(\eta^1\text{-}C{\equiv}C^tBu)[\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)]$,[161] 2.280(2) Å in $(\eta^5\text{-}C_5Me_4H)_2Zr(\eta^1\text{-}C{\equiv}CPh)[\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)]$,[161] and 2.231(3)/2.249(3) Å in $(\eta^5\text{-}C_5H_4SiMe_3)_2Zr(\eta^1\text{-}C{\equiv}CPh)_2$,[162] but is longer than that of 2.190(5) Å in **VI-4d**.

Scheme 7.5



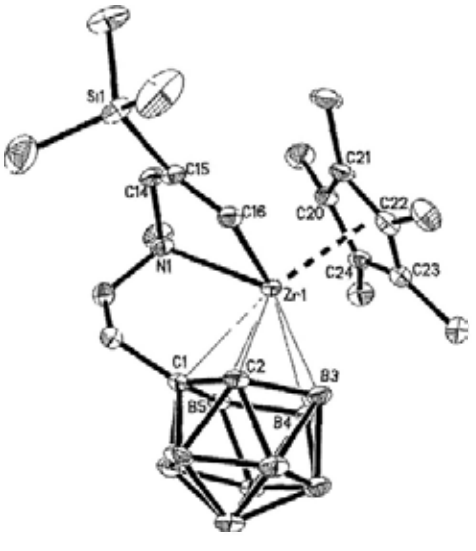


Figure 7.9. Molecular structure of

$(Cp^*)[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN[CH_2(TMS)C{=}C(H)]CH_2CH_2\}C_2B_9H_{10}]Zr$ (**VII-5a**)

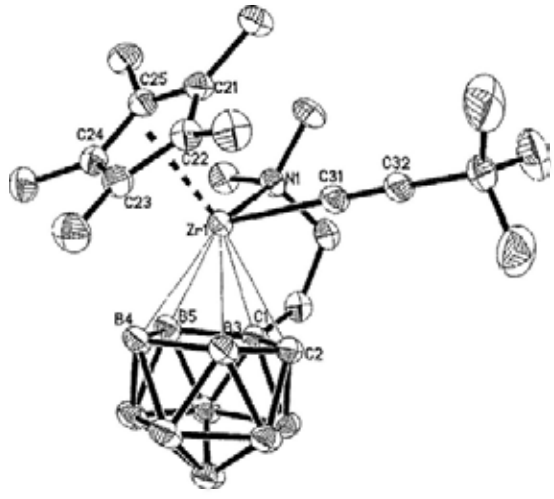


Figure 7.10. Molecular structure of (Cp*)[η^1:η^5-{$Me_2NCH_2CH_2$}$C_2B_9H_{10}$]Zr(C≡C^{t}Bu) **(VII-5b)**

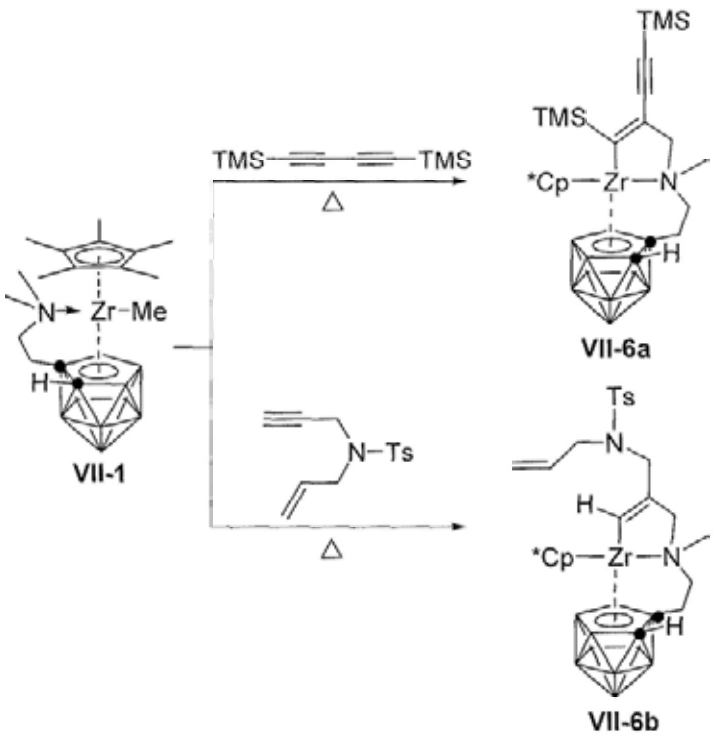
7.3.4 Reactivity to Diynes and Enynes.

Treatment of complex **VII-2** with 1 equiv of diynes TMSC≡CC≡CTMS in refluxing THF produced, after recrystallization from THF, the mono-insertion product (η^5-Cp*)[η^1:σ:η^5-{MeN[CH_2(TMSC≡C)C=C(TMS)]CH_2CH_2}$C_2B_9H_{10}$]Zr **(VII-6a)** in 72% isolated yield (Scheme 7.6). The composition of complex **VII-6a** was fully characterized by various spectroscopic techniques and elemental analyses. In addition to the resonances attributable to the methyl groups on Cp* ring and CH_2CH_2NMe, two singlets at 0.36 and 0.28 ppm corresponding to the two $SiMe_3$ groups and two doublets at 3.88 and 3.46 ppm with J = 16.2 Hz assignable to the α'-CH_2 were observed in the ^{1}H NMR spectrum. The characteristic resonances at low field of 228.1 and 133.7 ppm assignable to Zr$C_\alpha C_\beta$ alkenyl carbons and signals at 107.3 and 97.0 ppm corresponding to another sp-*C* of C≡C were shown in the ^{13}C NMR spectrum. The ^{11}B NMR spectrum showed a 1:3:1:1:1:1:1 pattern. Single-crystals suitable for X-ray analyses were not

obtained. Previous results showed that TMSC≡CTMS is too bulky to insert into the Zr-C σ bond of **VII-2.** The extended C≡C bond decreases the steric hindrance, which makes the insertion reaction possible. Only one C≡C bond can insert into the Zr-C σ bond to form the stable product **VII-6a** with a five-membered ring. Another C≡C bond can not insert into the second molecule of complex **VII-2** because of the steric reason. The more bulky sp^2-C connected with TMS group should be at α position of Zr atom according to the special electronic character of TMS substituent.

Reaction of complex **VII-2** with 1 equiv of enyne CH_2=$CHCH_2NTsCH_2C$≡CH in THF at room temperature gave (Cp*)[σ:η^1:η^5-{$(CH_3)[(CH_2)(CH_2CHCH_2NTsCH_2)C$=$C(H)]N(CH_2CH_2)C_2B_9H_{10}$}]Zr (**VII-6b**) in 81% isolated yield (Scheme 7.6). The ^{1}H NMR spectrum showed a broadened singlet at 6.84 ppm attributable to the vinylic proton at α-position of Zr atom, one multiplet at 5.76 ppm and one doublet of doublets at 5.17 ppm with ^1J = 16.2 Hz and ^2J = 3.0 Hz assignable to the three vinylic protons of the CH_2=CH moiety, one multiplet at 3.77 ppm and one doublet at 4.00 ppm with J = 6.6 Hz for the two CH_2 connected to NTs in addition to the resonances of the ligands and aryl H on Ts group. Signals at low field of 190.0 and 144.2 ppm assignable to alkenyl carbons of $ZrC_\alpha C_\beta$ and signals at 137.5 and 135.0 ppm attributable to the vinylic carbons were observed in the ^{13}C NMR spectrum. The composition of complex **VII-6b** was confirmed by elemental analyses. Crystals suitable for single-crystal X-ray diffraction study were not obtained yet. As the C≡C bond was more reactive than C=C double bond, the remaining C=C double bond is not active for the further insertion into the formed Zr-C(sp^2) bond or Zr-C(sp^3) bond of second molecule of **VII-2** even under refluxing condition.

Scheme 7.6



7.4 Summary

Zirconacarborane methyl complex (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**) was prepared by alkane elimination reaction. This complex was stable at room temperature and showed poor solubility in toluene and THF. Heating complex **VII-1** in toluene at 70°C gave (η^5-Cp*)[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VII-2**) by elimination of CH_4.

VII-1 showed no reactivity toward alkynes at room temperature. However, treatment of complex **VII-1** with symmetrical internal alkynes 3-hexyne, 4-octyne and 5-decyne in refluxing THF afforded the mono-insertion products [η^1:σ:η^5-{$MeN(CH_2(R)C{=}C(R))CH_2CH_2$}$C_2B_9H_{10}$]Zr($\eta^5$-Cp*) (R = Et, **VII-3a**; R = ^{n}Pr,

VII-3b; R = ^{n}Bu, **VII-3c**) in high yields. No insertion products were observed when bulky PhC≡CPh and TMSC≡CTMS were used even at 110 °C for 3 days. Treatment of the unsymmetrical internal alkynes PhC≡CMe, TMSC≡CPh, TMSC≡C^{n}Bu and 2-PyC≡C^{n}Bu with **VII-2** produced mono-insertion products [η^1:σ:η^5-{MeN(CH_2(Ph)C=C(Me))CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (R^1 = Ph, R^2= Me, **VII-4a**; R^1= Ph, R^2= TMS, **VII-4b**; R^1= ^{n}Bu, R^2= TMS, **VII-4c**; R^1 = 2-Py, R^2= ^{n}Bu, **VII-4d**). Both the steric and electronic factors affect the regioselectivity of the insertion reaction depending on the substituted group on alkynes. Reaction of complex **VII-1** with terminal alkynes TMSC≡C*H* and ^{t}BuC≡C*H* at 70 °C gave the mono-insertion product (η^5-Cp*)[η^1:σ:η^5-{MeN[CH_2(TMS)C=C(H)]CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-5a**) and acid-base reaction product (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(C≡C^{t}Bu) (**VII-5b**), respectively. Both the steric and electronic factors affect the regioselectivity of the insertion reaction depending on the substituted group on alkynes. For the diynes TMSC≡CC≡CTMS, only one C≡C bond was inserted into the Zr-C σ bond to form [η^1:σ:η^5-{MeN[CH_2(TMSC≡C)C=C(TMS)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (**VII-6a**). For the enynes HC≡CCH_2N(Ts)CH_2CH=CH_2, only C≡C bond was inserted into the Zr-C σ bond to produce [η^1:σ:η^5-{MeN[CH_2(CH_2=CHCH_2NTsCH_2)C=C(H)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (**VII-6b**), and the C=C bond remained intact.

Chapter 8

Reactivity Study of Full-Sandwich Metallacarborane Alkyl Complexes Bearing Both Substituted Cyclopentadienyl and Dicarbollyl Ligands

8.1 Introduction

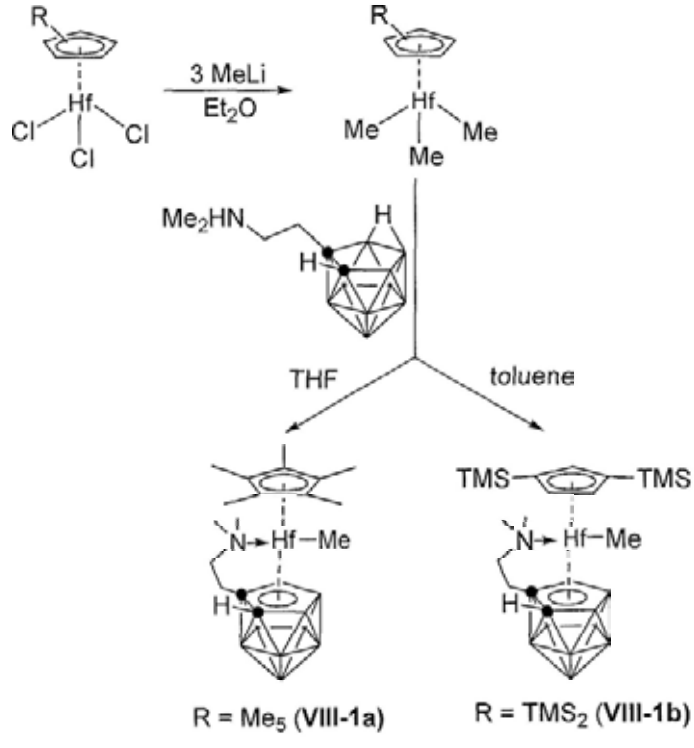
(η^5-Cp'')[η^1:σ:η^5-{MeN(CH_2)(CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VI-1**) and (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**) showed very similar reactivities toward alkynes. Only mono-insertion products were formed and no insertion reaction happened for alkenes. The Zr-C σ bond in **VI-1** and **VII-1** should be active for other polar unsaturated molecules such as nitriles, isocynides, ketones, etc. And Hafnacarborane alkyl complexes should be more stable than its Zr analogs, which may show a different reactivity pattern. This chapter will describe the synthesis of full sandwich hafnacarborane methyl complexes and insertion reaction of polar unsaturated molecules toward metallacarborane alkyl complexes.

8.2 Synthesis of Full-Sandwich Hafnacarborane Methyl Complex.

Treatment of Cp*$HfMe_3$ (Cp* = C_5Me_5) with 1 equiv of zwitterionic amino-dicarbollyl ligand 7-(Me_2NH)(CH_2)$_2$-7,8-$C_2B_9H_{11}$ in THF at room temperature overnight afforded the full-sandwich hafnacarborane methyl complex (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Hf(Me) (**VIII-1a**) in 82% isolated yield (Scheme 8.1). Complex **VIII-1a** was collected as a white solid from THF solution. It is soluble in pyridine and hot THF, almost insoluble in THF at room temperature, and

insoluble in toluene and hexane. Single-crystals suitable for X-ray analyses were grown from hot THF. Treatment of Cp''$HfMe_3$ (Cp'' = 1,3-$(TMS)_2$-C_5H_3) with 1 equiv of zwitterionic amino-dicarbollyl ligand 7-$(Me_2NH)(CH_2)_2$-7,8-$C_2B_9H_{11}$ in toluene at room temperature overnight afforded (η^5-Cp'')[η^1:η^5-$(Me_2NCH_2CH_2)C_2B_9H_{10}$]Hf(Me) (**VIII-1b**) in 57% isolated yield (Scheme 8.1). Complex **VIII-1b** showed very good solubility in toluene and did not dissolve in hexane. Complexes **VIII-1a** and **VIII-1b** were very thermally stable even at 100 °C, and no elimination of CH_4 was observed. This phenomenon is totally different from the corresponding $(Cp^*)(C_2B_9H_{11})$Hf(Me) which released one molecule of CH_4 when heating.

Scheme 8.1



The compositions of **VIII-1a** and **VIII-1b** were fully characterized by various spectroscopic techniques and elemental analyses. The ^{11}B NMR spectrum of **VIII-1a**

shows a 1:1:1:1:1:1:1:1:1 pattern, which is similar to its Zr analogue **VII-1**, whereas a 3:4:1:1 pattern was observed for **VIII-1b** due to the coincidence of B resonances. The singlet at 0.41 ppm for **VIII-1a** and 0.29 ppm for **VIII-1b** in the ^{1}H NMR spectra suggested the existence of Hf-CH_3 bond. The ^{13}C NMR spectra were consistent with the above results. The solid-state structures of both compounds were further confirmed by single-crystal X-ray diffraction studies and shown in Figures 8.1 and 8.2, respectively. In each structure, the Hf atom is η^5-bound to both substituted cyclopentadienyl ring and dicarbollyl ligand, σ-bound to the methyl group and coordinated to the N atom in a distorted-tetrahedral geometry. The average Hf-C(C_5 ring) distances of 2.544(5) Å in **VIII-1a** and 2.528(4) Å in **VIII-1b** are comparable to each other and similar to those of 2.530(14)/2.548(5) Å in $(Cp^*)_2(C_2B_9H_{11})_2Hf_2Me_2$,[41] and 2.509(9)/2.524(10) Å in $(Cp^*)_2(C_2B_9H_{11})_2Hf_2H_2$.[42] The average Hf-cage atom distances of 2.562(6) Å in **VIII-1a** and 2.561(4) Å in **VIII-1b** are similar to each other but are longer than that of 2.529(12) Å in $[\eta^1{:}\sigma{:}\eta^5$-{MeN($CH_2$)$CH_2CH_2$}$C_2B_9H_{10}$]Hf($CH_2SiMe_3$)(THF),[56] 2.503(10) Å in $[\sigma{:}\sigma{:}\eta^1{:}\eta^5$-{($CH_2$)[($CH_2$)PhC=CPh]N($CH_2CH_2$)$C_2B_9H_{10}$}]Hf(THF),[56] 2.505(7) Å in $(Cp^*)_2(C_2B_9H_{11})_2Hf_2Me_2$,[41] and 2.441(10)/2.516(11) Å in $(Cp^*)_2(C_2B_9H_{11})_2Hf_2H_2$.[42] The Hf-C σ bond distance of 2.295(6) Å in **VIII-1a** is a little longer than that of 2.246(4) Å in **VIII-1b**, while the Hf-C σ bond distance of **VIII-1b** is comparable to those of 2.226(11) Å/2.226(10) Å in $[\eta^1{:}\sigma{:}\eta^5$-{MeN($CH_2$)$CH_2CH_2$}$C_2B_9H_{10}$]Hf($CH_2SiMe_3$)(THF),[56] and 2.239(6)/2.228(6) Å in $(Cp^*)_2(C_2B_9H_{12})_2Hf_2Me_2$.[41] The Cent($C_5$ ring)-Hf-Cent(C_2B_3) angles of 136.4° in **VIII-1a** and 137.6° in **VIII-1b** are similar to each other and close to that of 135.4° in $(Cp^*)_2(C_2B_9H_{11})_2Hf_2Me_2$,[41] and 136.8°/137.2° in $(Cp^*)_2(C_2B_9H_{11})_2Hf_2H_2$.[42]

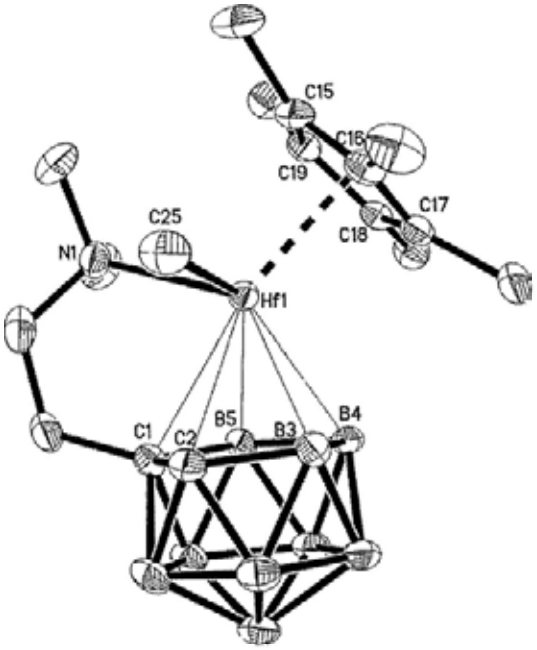


Figure 8.1. Molecular structure of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Hf(Me)

(VIII-1a)

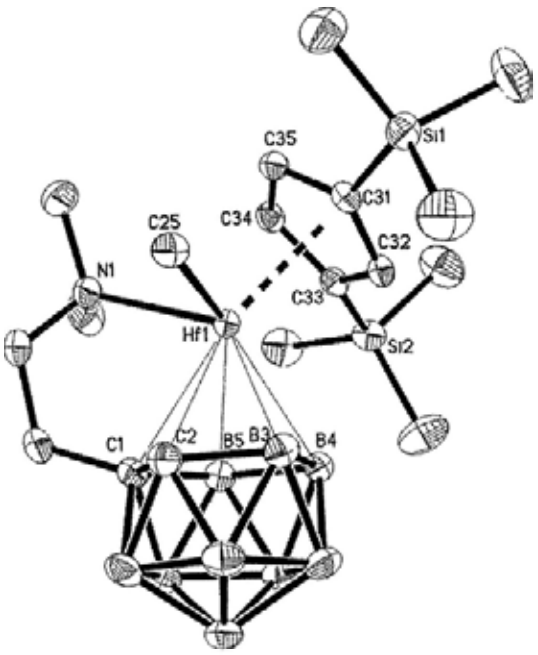


Figure 8.2. Molecular structure of (η^5-Cp'')[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Hf(Me)

(VIII-1b)

8.3 Reactivity of VI-1 toward Unsaturated Polar Molecules.

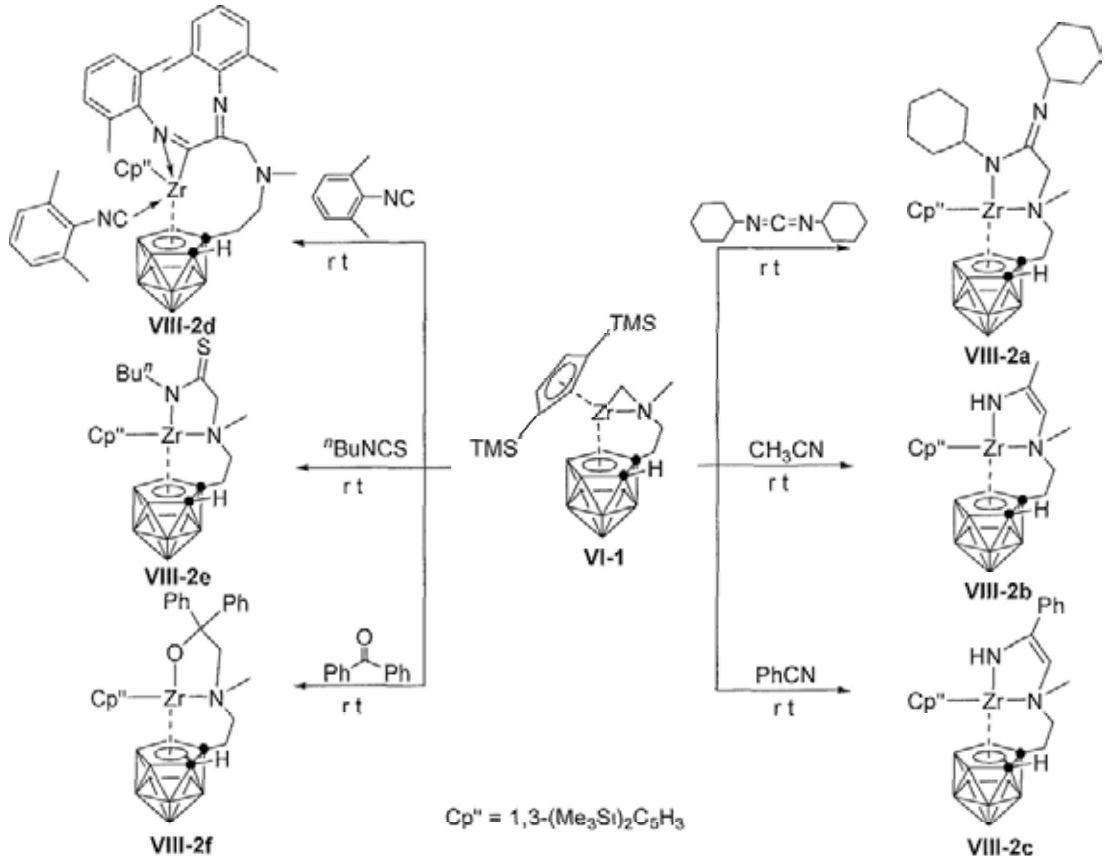
In the previous chapter, we have studied the reactivity of (η^5-Cp'')[η^1:σ:η^5-{MeN(CH_2)(CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VI-1**) (Cp'' = 1,3-$(TMS)_2$-C_5H_3) toward alkynes. Mono-insertion products were formed, in which electronic factor played a key role in the regioselectivity. The Zr-C σ bond should be also active for the polar unsaturated molecules.[18]

Treatment of complex **VI-1** with 1 equiv of Cy-N=C=N-Cy (DCC; Cy = C_6H_{11}) in toluene at room temperature afforded, after recrystallization from toluene, the mono-insertion product (η^5-Cp'')[η^1:σ:η^5-{MeN[CH_2C(=NCy)NCy](CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VIII-2a**) in 78% isolated yield (Scheme 8.2). The composition of **VIII-2a** was fully characterized by various spectroscopic techniques and elemental analyses. The ^{1}H NMR spectrum showed two doublets at 3.35 and 3.07 ppm with ^1J = 15.0 Hz corresponding to *a*'-CH_2, two multiplets at 3.33 and 3.15 ppm assignable to the C*H* protons on Cy ring connected to the N atom, and multiplets from 1.87 – 1.24 ppm attributable to other Cy protons in addition to the resonanes of the Cp'' ring and CH_2CH_2NMe. The characteristic N=*C*-N resonace at 155.4 ppm was observed in the ^{13}C NMR spectrum. Its ^{11}B NMR spectrum showed a 1:2:3:2:1 pattern. The solid-state structure of **VIII-2a** was confirmed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both bis(trimethylsilyl)cyclopentadienyl ring and dicarbollyl ligand, σ-bound to one nitrogen atom and coordinated to the N atom in a distorted-tetrahedral geometry (Figure 8.3). The average Zr-C(C_5 ring) distance of 2.571(2) Å (Table 8.1) is comparable to that of 2.548(4) Å in (η^5-Cp'')\{(^{i}PrN)$_2$C(NH^{i}Pr)\}$ZrCl_2$,[147] 2.554(3) Å in

(η^5-Cp'')[3-Me$C_4H_3BC_6F_5$]Zr(C_6F_5)(OEt_2),[148] 2.517(5)/2.522(5) Å in (η^5-Cp'')$_2$ZrMe(μ-Me)B(C_6F_5)$_3$,[149] 2.523(3) Å in (η^5-Cp'')($C_4H_4BC_6F_5$)Zr(C_6F_5)(CN^{t}Bu),[150] 2.547(5) Å in (η^5-Cp'')(η^5-$C_4H_4BC_6F_5$)Zr(η^2-C_6F_5CN^{t}Bu),[150] and 2.530(5) Å in (η^5-Cp'')(η^5-$C_{13}H_9$)$ZrCl_2$.[151] The average Zr-cage atom distance of 2.561(2) Å is also comparable to that of 2.523(5) Å in [η^1:η^5-(Me_2NCH_2)$C_2B_9H_{10}$]$_2$Zr,[55] 2.538(5) Å in [η^1:η^5-($C_5H_4NCH_2$)$C_2B_9H_{10}$]Zr(NMe_2)$_2$,[52] 2.535/2.533 Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2),[40] 2.568(4) Å in [η^1:η^5-(BzNCH$_2$)(CH_3)$C_2B_9H_{10}$]$ZrCl_2$(THF),[54] and 2.544(6) Å in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF).[56] The Zr-N σ bond distance of 2.152(2) Å is comparable to that of 2.130(4) Å in [η^5:η^5-$H_2C(C_5Me_4)(C_2B_9H_{10})$]Zr($NMe_2$)($NHMe_2$) (**V-4**), 2.111(9) Å in Cp*(2,4-^{t}Bu$_2$-6-(OCH_2CH(^{t}Bu)N=CH)-C_6H_2O)Zr(NMe_2)$_2$,[168] 2.078(2) Å in Cp_2Zr[σ:σ-CyNC(=NCy)($C_2B_{10}H_{10}$)],[15] and 2.077(4) Å in [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-{[^{i}PrNC(=N^{i}Pr)$C_2B_{10}H_{10}$}],[155] but is a little longer than that of 2.057(2) Å in [η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($NMe_2$)($NHMe_2$),[115] 2.016(8) Å in [$\eta^5$:$\sigma$-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$,[13] 2.036(4)/2.043(4) Å in [η^1:η^5-(^{i}Pr$_2C_6H_3N$=CH)$C_2B_9H_{10}$]Zr(NMe_2)$_2$($NHMe_2$),[57] 2.029(4)/2.020(4) Å in [η^5-($C_2B_9H_{10}$)(CH_2)$_2$NBz$_2$)]Zr(NMe_2)$_2$($NHMe_2$),[54] and 2.015(3)/2.018(3) Å in [η^1:η^5-($C_5H_4NCH_2$)$C_2B_9H_{10}$]Zr(NMe_2)$_2$.[52] The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 136.2° is similar to that of 140.0° in **VI-1**, 134.9° in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2),[40] and 135.7° in **VII-1**. In this insertion reaction, only one C=N bond of DCC inserted into the

Zr-C σ bond to form Zr-N σ bond, leaving another C=N bond inert, no η^3 coordination rotation is observed probably because of the formation of stable five-membered ring. The Zr-N-C angle of 127.5(1)° is much smaller than that of 143.8(1)° in **III-5c**,[115] and 150.1(3)° in **IV-4c**,[133] which means there is almost no $p_\pi(N)$-$d_\pi(Zr)$ interactions.

Scheme 8.2

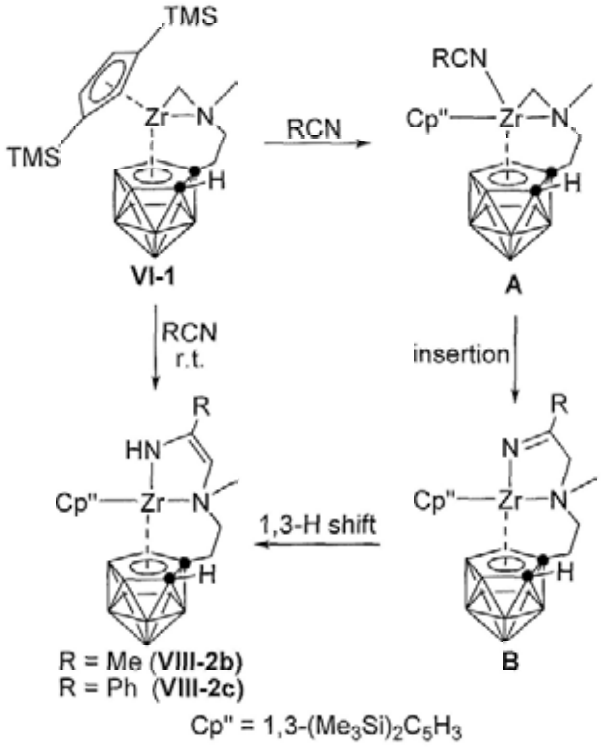


Treatment of complex **VI-1** with 1 equiv of acetonitrile (CH_3CN) or phenylnitrile (PhCN) in toluene at room temperature gave (η^5-Cp'')[η^1:σ:η^5-{MeN[(H)C=C(R)N(H)](CH$_2$CH$_2$)}$C_2B_9H_{10}$]Zr (R = Me (**VIII-2b**), Ph (**VIII-2c**)) in ~ 80% isolated yields (Scheme 8.2). The compositions of complex **VIII-2b** and **VIII-2c** were confirmed by various spectroscopic techniques and elemental

analyses. Broadened singlets at 7.10 ppm for **VIII-2b** and 7.23 ppm for **VIII-2c** corresponding to the vinylic protons C*H* and broad resonances at 3.76 ppm for **VIII-2b** and 4.43 ppm for **VIII-2c** assignable to the N*H* protons were observed in the ^{1}H NMR spectra. The mechanism of the formation of **VIII-2b** and **VIII-2c** was proposed and shown in Scheme 8.3. Firstly, one molecule of RCN coordinates to the Zr center to form intermediate **A**. The coordinated C≡N bond inserts into the Zr-C σ bond to give intermediate **B**. The thermodynamically favored metallacycles **VIII-2b** and **VIII-2c** were afforded after tautomerization (or vice versa) of **B**. Similar 1,3-hydrogen shifts have been observed in the related systems.[169] The insertion of C≡N bond into the Zr-C σ bond can form either Zr-N or Zr-C bond.[170] The formation of Zr-C bond is exceptional.[171] In this situation, the formation of Zr-N bond was proposed, otherwise no 1,3-H shift could happen. Only mono-insertion product was produced even an excess amount of CH_3CN was used at high temperature. The solid-state structure of complex **VIII-2b** was revealed by single-crystal X-ray analyses. The Zr atom is η^5-bound to both bis(trimethylsilyl)cyclopentadienyl ring and dicarbollyl ligand, σ-bound to one nitrogen atom and coordinated to another N atom in a distorted-tetrahedral geometry (Figure 8.4). The C(15)-N(2)/C(15)-C(14) bond distances of 1.376(4)/1.347(6) Å and C(14)-C(15)-N(2)/C(15)-C(14)-N(1)/C(14)-C(15)-C(16)/Zr(1)-N(2)-C(15) angles of 119.5(4)/120.8(3)/122.2(4)/111.8(2)° are consistent with the results of C(15)-N(2) single bond and C(14)-C(15) double bond. The Zr(1)-N(2)-C(15) angle of 111.8(2)° confirmed the sp^3 hybridization of N(2) atom. The average Zr-C_5 ring and Zr-cage atom distances of 2.550(4) Å and 2.535(4) Å (Table 8.1) are comparable to those of 2.509(4) Å and 2.522(4) Å in **VI-1**, and 2.571(2) Å and 2.561(2) Å in **VIII-2a**. The Cent(C_5

ring)-Zr-Cent(C_2B_3) angle of 135.8° is similar to that of 140.0° in **VI-1** and 136.2° in **VIII-2a**. The Zr-N bond distance of 2.212(3) Å is comparable to that of 2.184(5) Å in $Cp_2Zr[\sigma:\sigma\text{-}N{=}C(Ph)(C_2B_{10}H_{10})](PhCN)$,[111] and 2.152(2) Å in **VIII-2a**, but is much longer than that of 2.057(2) Å in **IV-2**,[133] 2.051(2) Å in $Cp_2Zr[N{=}C(Ph)CH(C_6H_4)CH]$,[170] 2.058(2)/2.063(2) Å in $Cp_2Zr(N{=}CPh_2)_2$,[172] 2.006(4) Å in $Cp_2ZrCl(N{=}C(^tBu)Ph)$,[173] 2.020(1) Å in $[Cp_2ZrCl(N{=}C(^tBu)Ph)]_{0.4}[Cp_2ZrMe(N{=}C(^tBu)Ph)]_{0.6}$,[173] 2.016(8) Å in $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$,[13] 2.036(4)/2.043(4) Å in $[\eta^1:\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] 2.029(4)/2.020(4) Å in $[\eta^5\text{-}(C_2B_9H_{10})(CH_2)_2NBz_2)]Zr(NMe_2)_2(NHMe_2)$,[54] and 2.015(3)/2.018(3) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$.[52] The longer Zr-N bond distance and smaller Zr-N-C angle of 111.8(2)° indicate there is no $p_\pi(N)$-$d_\pi(Zr)$ interaction. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 135.8° is similar to that of 136.2° in **VIII-2a**.

Scheme 8.3



Treatment of complex **VI-1** with 3 equiv of XyNC (2,6-$Me_2C_6H_3NC$) in toluene at room temperature afforded, after recrystallization from toluene, double-insertion product (η^5-Cp'')[η^2:η^5-{MeN[(CH_2)C(=NXy)C(=NXy)](CH_2CH_2)}$C_2B_9H_{10}$]Zr(CNXy) (**VIII-2d**) in 80% isolated yield (Scheme 8.2). The characteristic resonance at δ 242.3 ppm corresponding to the η^2-iminoacyl *a*-carbon atom was observed in the ^{13}C NMR spectrum. Except for the various spectroscopic techniques and elemental analyses, the structure of **VIII-2d** was further confirmed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both bis(trimethylsilyl)cyclopentadienyl ring and dicarbollyl ligand, σ-bound to one carbon atom and coordinated to carbon atom of 2,6-$Me_2C_6H_3NC$ molecule and N atom of C=N bond in a distorted-trigonal-bipyramidal geometry (Figure

8.5). The X-ray structure showed that double-insertion of carbene carbon of isocyanide into the Zr-C σ bond proceeded with the third molecule of isocaynide coordinating to the Zr center, making the N atom on the sidearm of the dicarbollyl ligand uncoordinated. Mono-insertion of isocyanide into the Zr-C σ bond is usually reported.[174] For the double-insertion, it is rare.[175] The average Zr-C_5 ring and Zr-cage atom distances of 2.574(5) Å and 2.577(5) Å (Table 8.1) are comparable to those of 2.571(2) Å and 2.561(2) Å in **VIII-2a**. The Zr-C(sp^2) σ bond distance of 2.250(5) Å is close to that of 2.231(2) Å in [Me_2Si(methylbenz[*e*]indenyl)(C_5H_4)]Zr(Bz)[C(Bz)=NXy],[174a] 2.223(8) Å in [CpZr(OC_6H_2-Ph-2-Bu^t_2-4,6)(η^2-Bu^tNCCH_2Ph)(CH_2Ph)],[174c] and 2.231(2) Å in Cp^*_2Zr[η^2:σ-^{t}BuN=CCH_2N(Me)CH_2N(Me)CH_2],[174e] but is longer than that of 2.163(8) Å in Cp_2Zr[σ:σ:η^1-1,2-C_6H_4(HC=C(PPh_2)(C=N^{t}Bu)],[174b] 2.162(3)/2.190(3) Å in [η^5:σ-Me_2C(C_5H_4)($C_2B_{10}H_{10}$)]Zr[η^2:η^2-XyN=CN(Me)$(CH_2)_3$N(Me)C=NXy],[26] and 2.196(2) Å in *anti*-[1,2-Me_2-(CCCH_2CH_2)-1,2-(C_9H_6)$_2$]Zr(Me)(η^2-Bu^tNCMe).[174d] The Zr-N(sp^2) bond distance of 2.308(4) Å is a little longer than that of 2.267(3) Å in **VI-1**, 2.259(4) Å in Zr(NMeCyc)$_2$[C(NAr)NMeCyc]$_2$,[174f] and 2.242(2) Å in *anti*-[1,2-Me_2-(CCCH_2CH_2)-1,2-(C_9H_6)$_2$]Zr(Me)(η^2-Bu^tNCMe).[174d]

Treatment of complex **VI-1** with 1 equiv of ^{n}BuNCS at room temperature afforded, after recrystallization from toluene, the mono-insertion product (η^5-Cp'')[η^1:σ:η^5-{MeN[CH_2(S=)C-N(^{n}Bu)](CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VIII-2e**) in 65% isolated yield (Scheme 8.2). There are two unsaturated bonds C=N and C=S, both of which can insert into the Zr-C σ bond of complex **VI-1**. From the result, we can see that the C=N is more active than the C=S group, and only complex **IX-2e** was formed chemoselecitively.[13,163] The composition of complex **VIII-2e** was confirmed by various

spectroscopic techniques and elemental analyses. The characteristic N-*C*=S resonance at 200.1 ppm was observed in the ^{13}C NMR spectrum. The structure was further revealed by single-crystal X-ray analyses. The Zr atom is η^5-bound to both bis(trimethylsilyl)cyclopentadienyl ring and dicarbollyl ligand, σ-bound to one nitrogen atom and coordinated to another N atom in a distorted-tetrahedral geometry (Figure 8.6). The average Zr-C(C_5 ring)/Zr-cage atom distances and Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 2.544(3) Å/2.552(4) Å and 135.8° (Table 8.1) are comparable to those of 2.571(2) Å/2.561(2) Å and 136.2° in **VIII-2a**. The Zr-N bond distance of 2.226(3) Å compares to that of 2.212(3) Å in **VIII-2b**.

Treatment of complex **VI-1** with 1 equiv of diphenylketone (Ph_2C=O) at room temperature in toluene gave, after recrystallization from toluene, (η^5-Cp'')[η^1:σ:η^5-{MeN[$(CH_2)(Ph)_2$C-O](CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VIII-2f**) in 66% isolated yield (Scheme 8.2). Complex **VIII-2f** did not dissolve in hexane, showed very bad solubility in toluene and dissolved well in THF. Complex **VIII-2f** was characterized by elemental analyses and various spectroscopic techniques. The structure of **VIII-2f** was further revealed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both bis(trimethylsilyl)cyclopentadienyl ring and dicarbollyl ligand, σ-bound to one oxygen atom and coordinated to the N atom in a distorted-tetrahedral geometry (Figure 8.7). The average Zr-C_5 ring/Zr-cage atom distances and Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 2.547(2) Å/2.544(2) Å/134.8° (Table 8.1) are comparable to those of 2.544(3) Å/2.552(4) Å/135.8° in **VIII-2e**. The Zr-O bond distance of 1.998(2) Å is comparable to that of 1.954(3) Å in [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-$(Ph)_2$C(O)$C_2B_{10}H_{10}$}],[155] 1.957 Å in (η^5-Cp*)(η^3-^{i}PrNC(Me)N^{i}Pr)Zr(CH_2C(=CH_2)CH_2C(Ph_2)O),[176] 1.954(2) Å in

$CpZr[NC_5H_4(CPh_2O)\text{-}2]Cl_2$,[177] 1.965(4) Å in $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_2)_2N(CH_3)_2\cdot THF$ (**V-5**),[143] 2.015(2) Å in $[4,6\text{-}^tBu_2\text{-}2\text{-}(\eta^5\text{-}C_9H_6)\text{-}C_6H_2O]_2Zr$,[130] and 1.979(3)/2.022(3) Å in $[meso\text{-}CH_2CH_2\text{-}(4,7\text{-}Me_2\text{-}C_9H_4)_2]Zr(OC_6F_5)_2$.[126] The Zr-O-C angle of 127.4(1)° is similar to that of 130.1(2)° in $CpZr[NC_5H_4(CPh_2O)\text{-}2]Cl_2$,[177] but is much smaller than that of 147.6° in $(\eta^5\text{-}Cp^*)(\eta^3\text{-}^iPrNC(Me)N^tPr)Zr(CH_2C(=CH_2)CH_2C(Ph_2)O)$,[176] 156.4(6)° in *trans*-$[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_3)(THF)$,[133] 152.2(3)° in $[meso\text{-}CH_2CH_2\text{-}(4,7\text{-}Me_2\text{-}C_9H_4)_2]Zr(OC_6F_5)_2$,[126] and 159.7(3)° in $[rac\text{-}\eta^5:\eta^5\text{-}CH_2CH_2\text{-}1,2\text{-}(C_9H_6)_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)][MeB(C_6F_5)_3]$,[129] suggestive of the absence of $p_\pi(O)\text{-}d_\pi(Zr)$ interactions and the sp^2 hybridization of O atom.

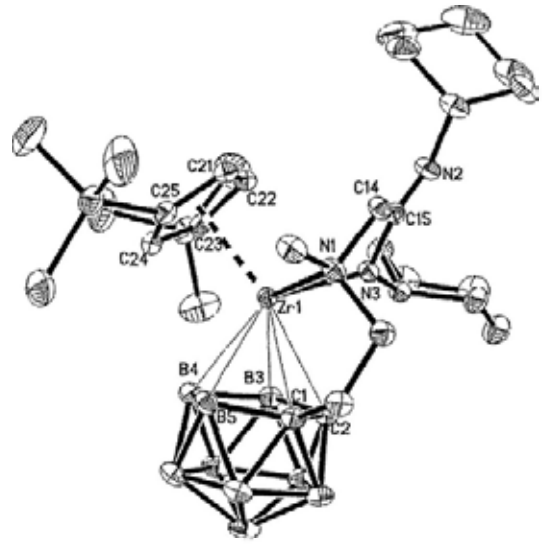


Figure 8.3. Molecular structure of $(\eta^5\text{-}Cp'')[\eta^1:\sigma:\eta^5\text{-}\{MeN[(CH_2)C(=N(Cy))N(Cy)]CH_2CH_2\}C_2B_9H_{10}]Zr$ (**VIII-2a**)

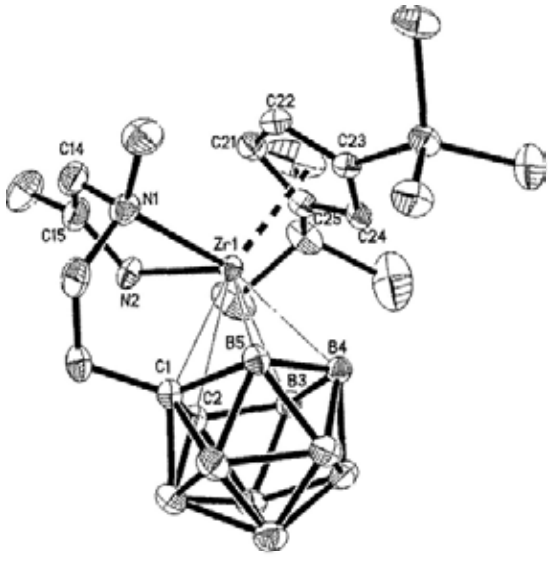


Figure 8.4. Molecular structure of

$(\eta^5$-Cp'')$[\eta^1{:}\sigma{:}\eta^5$-{MeN[HC=C($CH_3$)N(H)]($CH_2CH_2$)}$C_2B_9H_{10}$]Zr (**VIII-2b**)

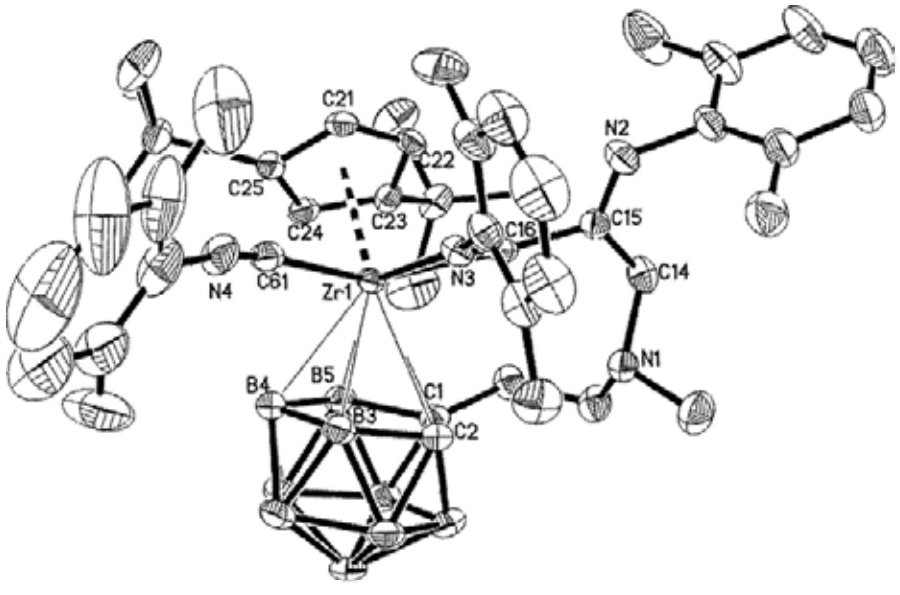


Figure 8.5. Molecular structure of

$(\eta^5$-Cp'')$[\eta^2{:}\eta^4$-{MeN[(CH_2)C(=NXy)C(=NXy)](CH_2CH_2)}$C_2B_9H_{10}$]Zr(CNXy)

(**VIII-2d**)

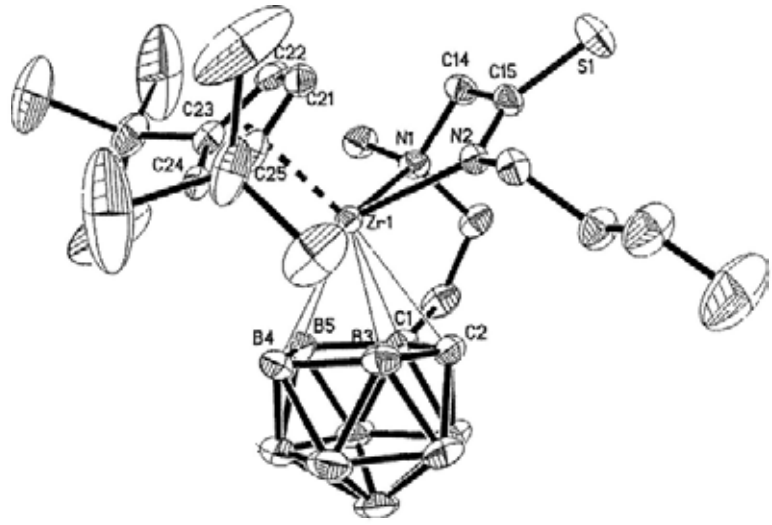


Figure 8.6. Molecular structure of

(η^5-Cp'')[η^1:σ:η^5-{MeN[(CH_2)C(=S)N^{n}Bu](CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VIII-2e**)

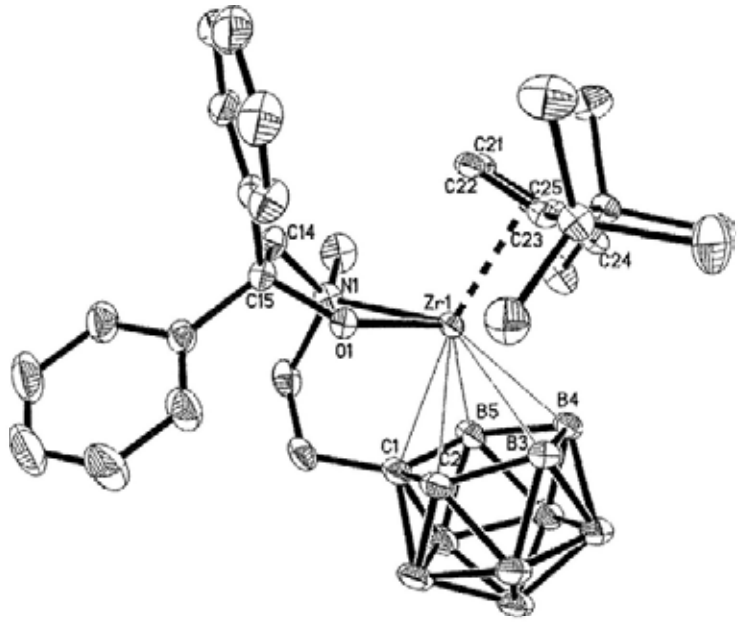


Figure 8.7. Molecular structure of

(η^5-Cp'')[η^1:σ:η^5-{MeN[(CH_2)C$(Ph)_2$O](CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VIII-2f**)

8.4 Reactivity of Complex VII-1.

Treatment of **VII-1** with 1 equiv of less bulky nitriles (CH_3CN, $(CH_2CH_2CH)CH_2CN$) at room temperature in THF afforded, after recrystallization from THF, the mono-insertion products (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr[N=C(Me)(R)] (R = Me, **VIII-3a**; R = $(CH_2CH_2CH)CH_2$, **VIII-3b**) in ~75% isolated yields (Scheme 8.4). The compositions of complex **VIII-3a** and **VIII-3b** were confirmed by various spectroscopic techniques and elemental analyses. In addition to the resonances assignable to the methyl groups on Cp* ring, $CH_2CH_2NMe_2$ and cyclopropyl group (in **VIII-3b**), two singlets at 2.00 ppm and 1.88 ppm corresponding to the two methyl groups N=C(CH_3)$_2$ in **VIII-3a**, and one singlet at 1.83 ppm corresponding to the methyl group N=C(CH_3), one doublet at 1.99 ppm with J = 9.6 Hz attributable to N=C(CH_2) in **VIII-3b** were observed in the ^{1}H NMR spectra. The characteristic signals at 128.9 ppm for **VIII-3a** and 129.7 ppm for **VIII-3b** attributable to the N=*C* carbon were observed in the ^{13}C NMR spectra. In thses complexes, the mono-insertion products with the Zr-N=C bond are stable at room temperature and no 1,3-H shift was observed. The resulting Zr-N bonds are stable and no further insertion reaction happened either to nitriles or other unsaturated molecules even under more harsh conditions. The structures of complexes **VIII-3a** and **VIII-3b** were further revealed by single-crystal X-ray diffraction studies. In both cases, the Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to one imido nitrogen atom and coordinated to another N atom on sidearm in a distorted-tetrahedral geometry (Figures 8.8 and 8.9). The N(2)-C(15)/C(15)-C(16)/C(15)-C(17) bond distances of 1.262(4)/1.504(5)/2.521(5) Å in

VIII-3a, N(2)-C(25)/C(25)-C(26) bond distances of 1.260(6)/1.515(7) Å, and C(25)-C(26)-C(27) angle of 113.1(5)° in **VIII-3b** compare to those of 1.376(4) Å/1.347(6) Å/111.8(2)° in **VIII-2b,** indicating the C=N double bond and C-C single bond in complexes **VIII-3a** and **VIII-3b**. The average Zr-C(C_5 ring)/Zr-cage atom distances and Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 2.560(3) Å/2.600(3) Å/135.0° (in **VIII-3a**) and 2.565(5) Å/2.601(5) Å/135.6° (in **VIII-3b**) are similar to each other and comparable to those of 2.565(3) Å/2.582(3) Å/135.7° in **VII-1**. The Zr-N bond distances of 2.016(2) Å/2.016(4) Å in **VIII-3a/VIII-3b** are close to each other and comparable to that of 2.057(2) Å in $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$,[133] 2.051(2) Å in $Cp_2Zr[N=C(Ph)CH(C_6H_4)CH]$,[170] 2.058(2)/2.063(2) Å in $Cp_2Zr(N=CPh_2)_2$,[172] 2.006(4) Å in $Cp_2ZrCl(N=C(^tBu)Ph)$,[173] 2.020(1) Å in $[Cp_2ZrCl(N=C(^tBu)Ph)]_{0.4}[Cp_2ZrMe(N=C(^tBu)Ph)]_{0.6}$,[173] 2.016(8) Å in $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$,[13] 2.036(4)/2.043(4) Å in $[\eta^1:\eta^5\text{-}(^iPr_2C_6H_3N=CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] 2.029(4)/2.020(4) Å in $[\eta^5\text{-}(C_2B_9H_{10})(CH_2)_2NBz_2)]Zr(NMe_2)_2(NHMe_2)$,[54] and 2.015(3)/2.018(3) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$.[52] The almost linear Zr-N-C angles of 167.3(2)° in **VIII-3a** and 168.1(4)° in **VIII-3b** suggest the presence of $p_\pi(N)$-$d_\pi(Zr)$ interactions.

For the more bulky PhCN, no reaction proceeded at room temperature. After refluxing in THF, the thermodynamically stable complex $(\eta^5\text{-}Cp^*)[\eta^1:\sigma:\eta^5\text{-}\{MeN[HC=C(Ph)N(H)](CH_2CH_2)\}C_2B_9H_{10}]Zr(PhCN)$ (**VIII-3c**) was isolated in 69% isolated yield (Scheme 8.4). Just like its Cp'' analogue, 1,3-H shift happened after the mono-insertion of C≡N into the Zr-C bond. The ^1H NMR spectrum showed a broad singlet at 5.62 ppm assignable to the vinylic proton and one broad

singlet at 5.00 ppm attributable to the N*H* in addition to the aryl protons and ligand protons. The characteristic resonance at 113.5 ppm corresponding to the N≡*C* unit in the ^{13}C NMR spectrum was observed. The structure of complex **VIII-3c** was also confirmed by single-crystal X-ray study. The Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to the amido nitrogen atom and coordinated to both C≡N nitrogen and the N atom on sidearm in a distorted-trigonal-bipyrimidal geometry (Figure 8.10). The N(2)-C(25)/C(14)-C(25) bond distances of 1.344(10)/1.331(11) Å and Zr(1)-N(2)-C(25)/C(14)-C(25)-N(2)/C(26)-C(25)-C(14)/C(25)-C(14)-N(1) angles of 125.5(5)/118.3(7)/118.5(5)/116.8(7)° indicate the C(25)-N(2) single bond, C(14)-C(25) double bond and sp^3 hybridization of N(2) atom. The average Zr-C_5 ring/Zr-cage atom distances and Cent(C_5)-Zr-Cent(C_2B_3) angles of 2.593(8) Å/2.642(9) Å/135.4° are comparable to those of 2.560(3) Å/2.600(3) Å/135.0° in **VIII-3a** and 2.565(5) Å/2.601(5) Å/135.6° in **VIII-3b**. The Zr-N2(amido) bond distance of 2.162(6) Å is a little shorter than that of 2.212(3) Å in **VIII-2a**. The Zr-N1(sidearm) bond distance of 2.510(8) Å is much longer than that of Zr-N3(imido) (2.330(7) Å), which indicates the weak coordination between the Zr atom and N1(sidearm) atom.

Complex **VII-1** did not react with DCC or DPC (^{i}PrN=C=N^{i}Pr) in THF at room temperature. After refluxing the mixture in THF for one day, the mono-insertion products with five-membered ring (η^5-Cp*)[η^1:σ:η^5-{MeN[(CH_2)C(=NR)NR](CH_2CH_2)}$C_2B_9H_{10}$]Zr (R = Cy, **VIII-3d**; ^{i}Pr, **VIII-3e**) were afforded in 71-77% isolated yield (Scheme 8.5). When TMSN=C=NTMS was used, no insertion product was formed even after prolonged

heating in toluene because of the streric hindrance of TMS group. The compositions of complexes **VIII-3d** and **VIII-3e** were confirmed by various spectroscopic techniques and elemental analyses. The structure of complex **VIII-3e** was further revealed by single-crystal X-ray analyses (Figure 8.11). The average Zr-C(C_5 ring)/Zr-cage atom distances of 2.580(3) Å/2.560(4) Å are comparable to those of 2.565(3) Å/2.582(3) Å in **VII-1**, 2.560(3) Å/2.600(3) Å in **VIII-3a** and 2.565(5) Å/2.601(5) Å in **VIII-3b**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 132.8° is a little smaller than that of 135.7° in **VII-1**, 135.0° in **VIII-3a** and 135.6° in **VIII-3b.** The Zr-N bond distance of 2.172(2) Å is similar to that of 2.152(2) Å in **VIII-2a** and 2.162(6) Å in **VIII-3c**, but is much longer than those of 2.016(2) Å/2.016(4) Å in **VIII-3a/VIII-3b**.

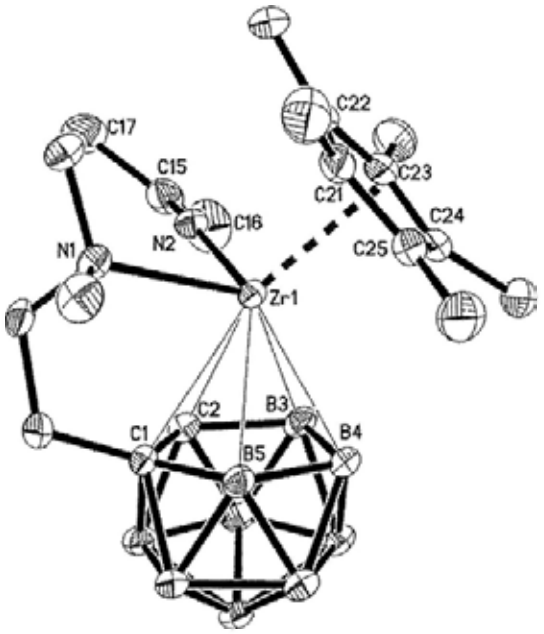
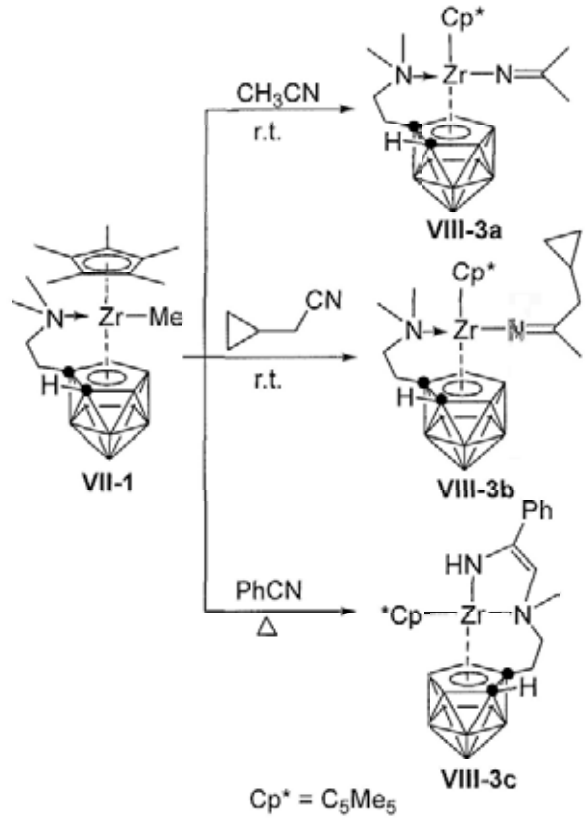


Figure 8.8. Molecular structure of

(η^5-Cp*)[η^1:η^5-{$Me_2NCH_2CH_2$}$C_2B_9H_{10}$]Zr(N=C(Me)$_2$ (**VIII-3a**)

Scheme 8.4



Treatment of complex **VII-1** with 1 equiv of MeOH in THF at room temperature afforded, after recrystallization from THF, (Cp*)[η^1:η^5-{$Me_2NCH_2CH_2$}$C_2B_9H_{10}$]Zr(OMe) (**VIII-3f**) in 76% isolated yield (Scheme 8.5). If an excess amount of MeOH was used, protonation of dicarbollyl ligand would happen as evidenced by the ^{11}B NMR. In addition to the resonances of the methyl groups on Cp* ring and $CH_2CH_2NMe_2$, one singlet at 3.87 ppm corresponding to the methoxyl group was observed in the ^{1}H NMR spectrum. The solid-state structure of complex **VIII-3f** was revealed by single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both pentamethylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to one methoxyl oxygen atom and coordinated to the N atom on sidearm in a

distorted-tetrahedral geometry (Figure 8.12). The average Zr-C(C_5 ring)/Zr-cage atom distances and Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 2.569(2) Å/2.605(3) Å/134.2° are comparable to those of 2.565(3) Å/2.582(3) Å/135.3° in **VII-1**, and 2.560(3) Å/2.600(3) Å/135.0° in **VIII-3a**. The Zr-O bond distance of 1.932(2) Å is a little shorter than that of 1.998(2) Å in **VIII-2f**, but is comparable to that of 1.930(5) Å in *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($OCH_2CH_2CH_2CH_3$)(THF),[133] 1.957 Å in (η^5-Cp*)(η^3-^{i}PrNC(Me)N^{i}Pr)Zr($CH_2C(=CH_2)CH_2C(Ph_2)O$),[176] 1.954(2) Å in CpZr[$NC_5H_4(CPh_2O)$-2]Cl_2,[177] 1.965(4) Å in **V-5**,[143] and 1.918(1) Å in [η^5-C_9H_5-1,3-$(SiMe_3)_2$]$_2$Zr($OCH_2CH_2CH_2CH_2$).[124]

Scheme 8.5

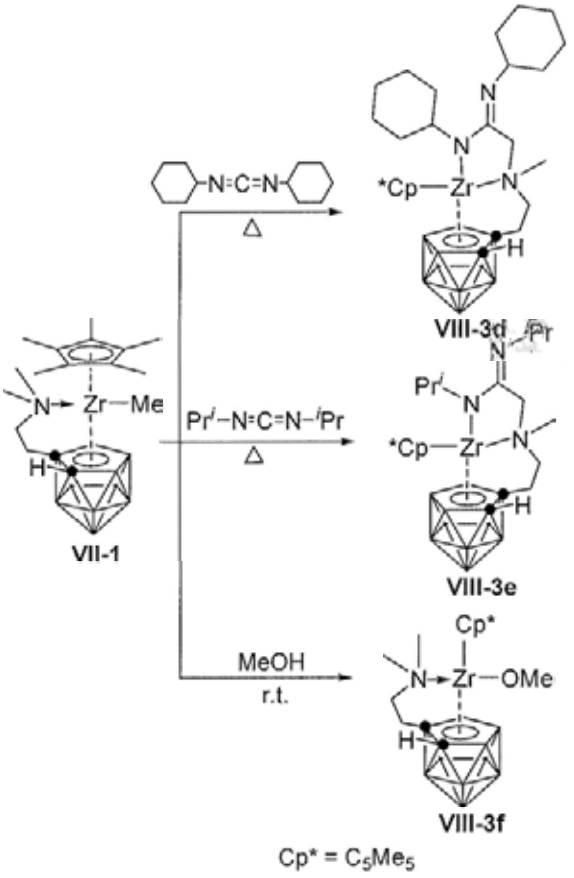
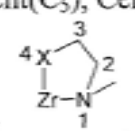


Table 8.1. Selected Bond Lengths (Å) and Angles (deg) for VIII-2a –VIII-3f

	VIII-2a	VIII-2b	VIII-2d	VIII-2e	VIII-2f	VIII-3a	VIII-3b	VIII-3c	VIII-3e	VIII-3f
av. Zr-C_{ring}	2.571(2)	2.550(4)	2.574(5)	2.544(3)	2.547(2)	2.562(4)	2.565(5)	2.593(8)	2.580(3)	2.569(2)
av. Zr-cage atom	2.561(2)	2.535(4)	2.577(5)	2.552(4)	2.544(2)	2.554(4)	2.601(5)	2.642(9)	2.560(4)	2.605(3)
Zr-N(1)	2.352(2)	2.384(3)	2.308(4)	2.353(2)	2.412(2)	2.382(3)	2.453(2)	2.506(6)	2.385(3)	2.420(2)
Zr-X	2.152(3) (X = N)	2.212(3) (X = N)	2.250(5) (X = C)	2.226(3) (X = N)	1.998(2) (X = O)	2.286(3) (X = N)	2.016(4) (X = N)	2.162(6) (X = N)	2.172(2) (X = N)	1.932(2) (X = O)
N(1)-C(2)[b]	1.502(2)	1.465(5)		1.498(4)	1.500(3)			1.489(10)	1.491(4)	
C(2)-C(3)[b]	1.531(3)	1.347(6)		1.499(5)	1.541(3)			1.331(11)	1.523(4)	
C(3)-X[b]	1.391(2)	1.376(4)		1.332(4)	1.432(3)			1.344(10)	1.387(4)	
Zr-Cent(C_5)[a]	2.272	2.247	2.278	2.245	2.244	2.258	2.265	2.295	2.280	2.270
Zr-Cent(C_2B_3)[a]	2.122	2.091	2.168	2.112	2.100	2.169	2.172	2.289	2.126	2.178
Cent(C_5)-M-Cent(C_2B_3)	136.2	135.8	135.3	137.6	134.8	135.0	135.6	135.4	132.8	134.2

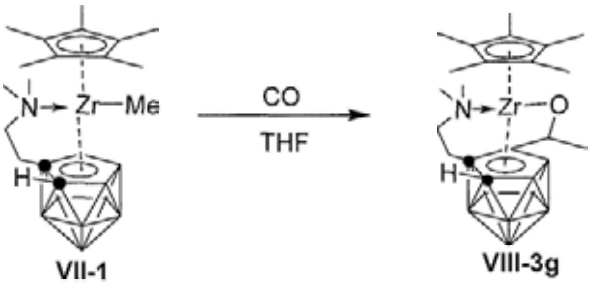
[a] Cent(C_5), Cent(C_2B_9): the centroid of the cyclopentadienyl ring and the C_2B_3 bonding face, respectively. [b] the number of N(1), C(2), C(3)



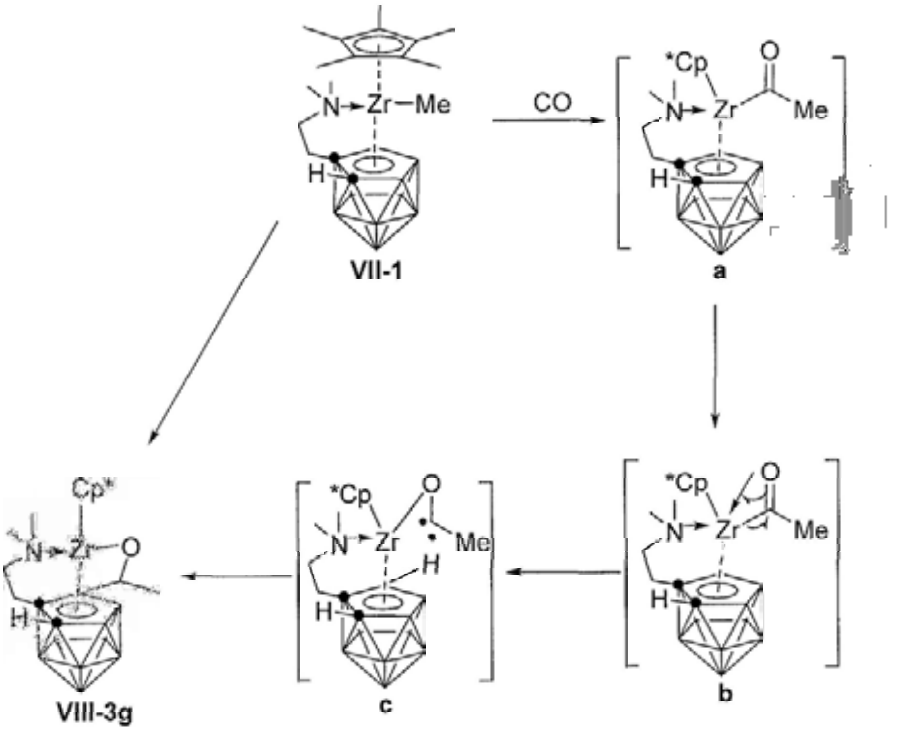
see: .

The reaction of **VII-1** with CO (1-2 atm) in THF (-78 to 50°C) for one day gave, after recrystallization from THF, (η^5-Cp*){η^1:η^5:σ-($Me_2N(CH_2CH_2)[O(CH_3)CH]C_2B_9H_9$}Zr (**VIII-3g**) in 56% isolated yield (Scheme 8.6). The complex **VIII-3g** contains a linked carborane-alkoxide ligand. The proposed mechanism was shown in Scheme 8.7. Firstly, CO inserts into the Zr-Me bond to form the acyl complex **a**, followed by net insertion of the acyl carbon into a B-H bond to produce **VIII-3g**. Intermediate **a** is not observed but is expected to adopt an η^2-acyl structure as other electron-deficient early transition metal acyl species do. The similar phenomena was also observed for the reaction of Cp*(η^5-$C_2B_9H_{11}$)TiMe with CO.[46] Only one product with the linker attached to a lateral boron (B5) was observed from the ^{11}B NMR spectrum and in the solid-state structure, while two products with linker attached to either central or lateral boron were found for Cp*(η^5-$C_2B_9H_{11}$)TiMe reactions. Single-crystal X-ray diffraction study showed that the Zr atom is η^5-bound to both substituted cyclopentadienyl ring and dicarbollyl ligand, σ-bound to the oxygen atom on the linkage and coordinated to the N atom on the dicarbollyl ligand in a distorted-tetrahedral geometry (Figure 8.13). The average Zr-C_5 ring and Zr-cage atom distances of 2.570(3) Å and 2.556(3) Å are similar to those of 2.565(3) Å and 2.582(3) Å in **VII-1**. The Zr-O bond distance of 1.977(2) Å is close to that of 1.932(2) Å in **VIII-2f**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 136.6° is similar to that of 135.3° in **VII-1**, and 134.2° in **VIII-3f**.

Scheme 8.6



Scheme 8.7



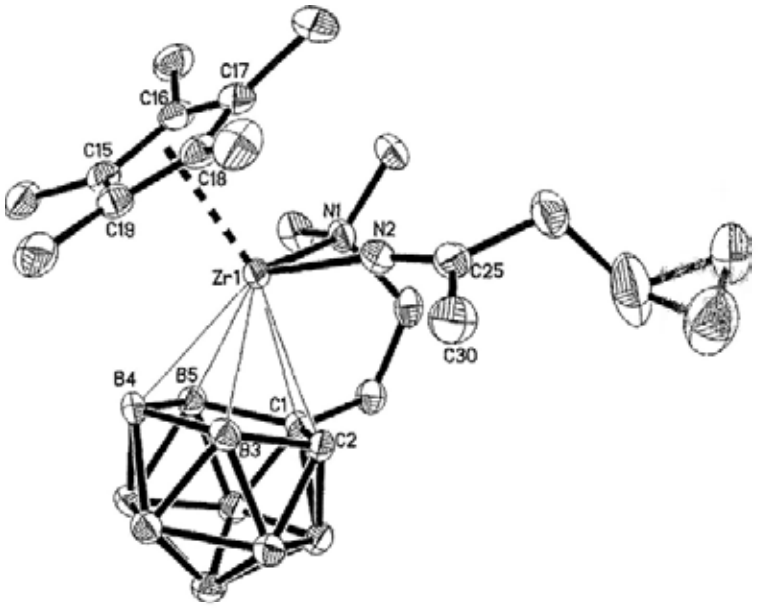


Figure 8.9. Molecular structure of

$(\eta^5$-Cp*)$[\eta^1:\eta^5$-$(Me_2NCH_2CH_2)C_2B_9H_{10}]Zr[N=C(Me)(CH_2CH(CH_2)_2)]$ (**VIII-3b**)

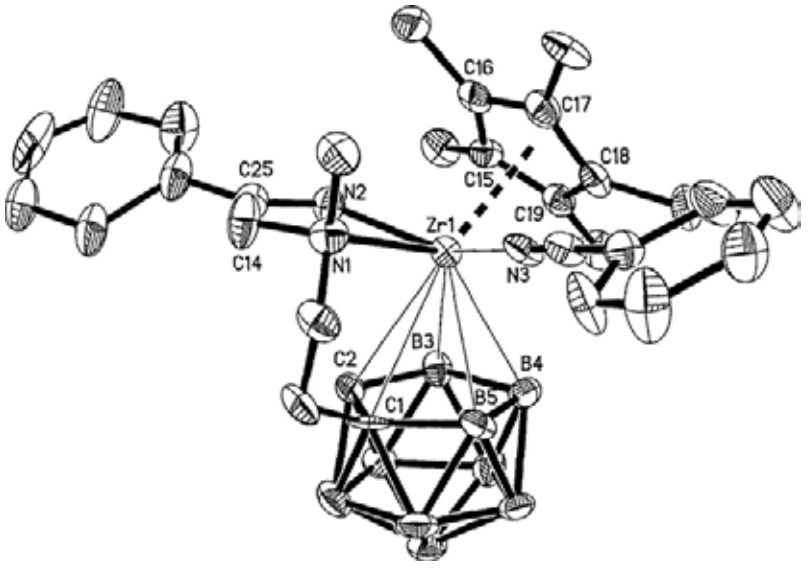


Figure 8.10. Molecular structure of

$(\eta^5$-Cp*)$[\eta^1:\eta^5$-$(Me_2NCH_2CH_2)C_2B_9H_{10}]Zr[N=C(Me)(Ph)]$ (**VIII-3c**)

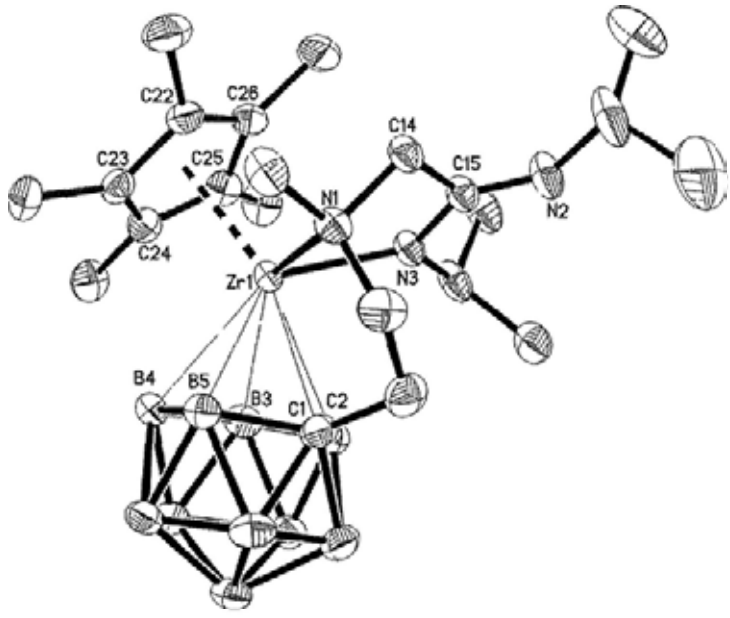


Figure 8.11. Molecular structure of

$(\eta^5$-Cp*)$[\eta^1{:}\sigma{:}\eta^5$-{MeN[$(CH_2)$C(=N^{i}Pr)N^{i}Pr]$(CH_2CH_2)$}$C_2B_9H_{10}$]Zr (**VIII-3e**)

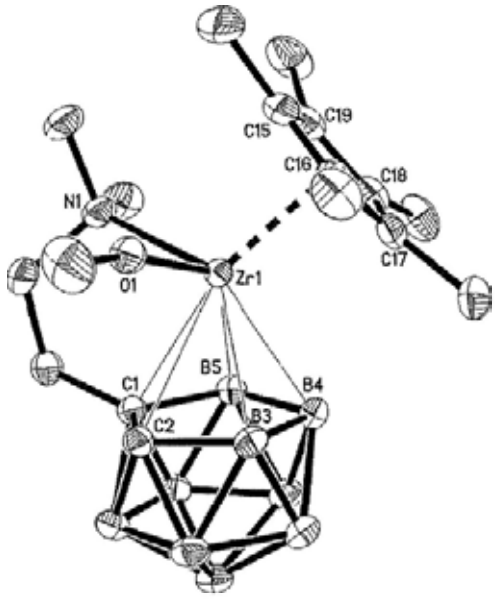


Figure 8.12. Molecular structure of $(\eta^5$-Cp*)$[\eta^1{:}\eta^5$-{$Me_2NCH_2CH_2$}$C_2B_9H_{10}$]Zr(OMe)

(VIII-3f)

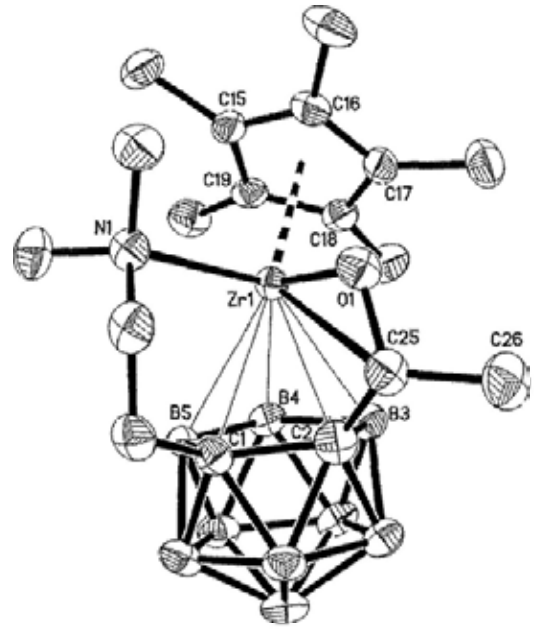


Figure 8.13. Molecular structure of

$(\eta^5$-Cp*$)\{\eta^1{:}\eta^5{:}\sigma$-$(Me_2N(CH_2CH_2)[O(CH_3)CH]C_2B_9H_9\}Zr$ (**VIII-3g**)

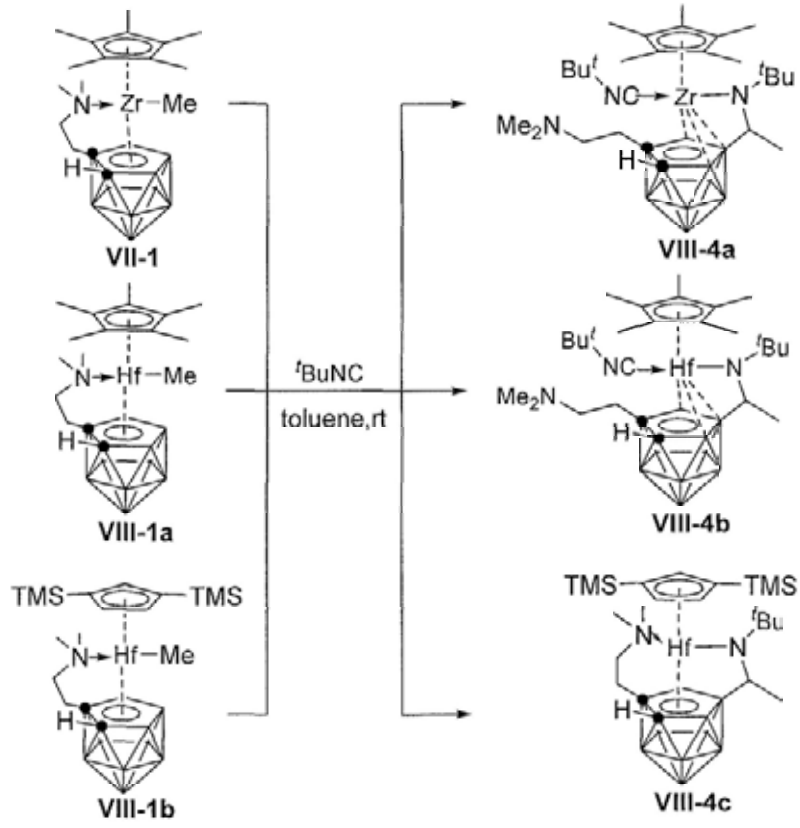
8.5 Reaction of Metallacarborane Methyl Complex with Isocyanides.

Similar reaction pathway was observed when treating the group 4 metal methyl complexes with isocyanides. Treatment of complexes **VII-1**, **VIII-1a**, **VIII-1b** with 2 equiv of *tert*-butyl isocyanide in toluene at room temperature afforded, after recrystallization from toluene, $(\eta^5$-Cp*$)\{\sigma{:}\eta^3$-$[(CH_3)_2N(CH_2CH_2)][^t BuN(CH_3)CH]C_2B_9H_9\}M(CN^t Bu)$ (M = Zr, **VIII-4a**; M = Hf, **VIII-4b**) and $(\eta^5$-Cp''$)\{\eta^1{:}\sigma{:}\eta^5$-$(Me_2NCH_2CH_2)[^t BuN(CH_3)CH]C_2B_9H_9\}Hf$ (**VIII-4c**) in 53 – 74% isolated yields (Scheme 8.8), respectively. The compositions of three compounds were all characterized by various spectroscopic techniques and elemental analyses. The ^{1}H

NMR spectra showed a quartet at 3.57 (**VIII-4a**), 3.25 (**VIII-4b**) and 2.96 (**VIII-4c**) ppm with J = 8.1, 9.0, 8.1 Hz assignable to the C*H* proton connecting to the cage B and doublet at 2.01 (**VIII-4a**), 2.62 (**VIII-4b**) and 2.39 (**VIII-4c**) ppm with J = 8.1, 9.0, 8.1 Hz contributable to the methyl group of $C_2B_9CH(CH_3)$ in addition to the signals of the Cp'', Cp*, $Me_2NCH_2CH_2$, and *tert*-butyl groups. The ^{13}C NMR spectra showed the characteristic resonances of 156.6 ppm and 156.5 ppm attributable to the $^tBuN{=}C$ unit in **VIII-4a** and **VIII-4b**, no signal was observed for **VIII-4c**. For complex **VIII-4a** and **VIII-4b**, a coordinated *tert*-butyl isocyanide was observed from the ^1H and ^{13}C NMR spectra, while for **VIII-4c** no coordinated isocyanide was observed. The ^{11}B NMR spectra showed 1:1:1:2:2:1:1, 1:1:2:2:2:1 and 1:1:1:2:2:2 patterns for **VIII-4a**, **VIII-4b** and **VIII-4c**, respectively. The resonances in lowest field (δ 14.0, 1B, **VIII-4a**; 19.5, 1B, **VIII-4b**; 13.5, 1B, **VIII-4c**) do not split in the ^1H-coupled ^{11}B NMR spectra, indicating that the corresponding B atoms do not have a hydrogen atom. The solid-state structures of complex **VIII-4a** and **VIII-4b** were also confirmed by single-crystal X-ray analyses (Figures 8.14 and 8.15). The metal is η^5-coordinated to the Cp*, η^3-coordianted to the C_2B_3 ring, σ-bound to the nitrogen atom of $^tBuNCHMe$ and coordinated to a free isocyanide in a distorted-tetrahedral geometry. The average M-C(C_5 ring) bond distances of 2.583(5) Å (M = Zr, **VIII-4a**) and 2.567(3) Å (M = Hf, **VIII-4b**) are similar to each other and comparable to that of 2.565(3) Å in **VII-1**, 2.544(5) Å in **VIII-1a**. The average Zr-B bond distance of 2.502(6) Å in **VIII-4a** is comparable to the average Hf-B bond distance of 2.488(3) Å in **VIII-4b**, 2.485(6) Å in $\{\eta^4{:}\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$,[49] but is shorter than that of 2.545(3) Å in **III-5a**. The Zr-N bond distance of 2.029(4) Å is shorter than that of

2.152(2) Å in **VIII-2a**, but is similar to that of 2.057(2) Å in $[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$,[133] 2.016(8) Å in $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$,[13] 2.036(4)/2.043(4) Å in $[\eta^1:\eta^5\text{-}(^tPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[57] 2.029(4)/2.020(4) Å in $[\eta^5\text{-}(C_2B_9H_{10})(CH_2)_2NBz_2)]Zr(NMe_2)_2(NHMe_2)$,[54] and 2.015(3)/2.018(3) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$.[52] The Hf-N bond distance of 2.015(2) Å is similar to that of 2.039(3) Å in $[Cp^*HfCl_2]_2[\mu\text{-}xyNCH{=}CHNxy]$,[178a] 2.044(3) Å in $\{[\eta:\sigma\text{-}(^iArNC(CH_2)C(CH_2){=}NAr^i)]Cp^*HfMe\}[Al(C_6F_5)_3]$,[178b] 2.030(7)/2.050(7) Å in $Hf(OC_6H_2\{\eta^5\text{-}2\text{-}Me\text{-}Ind\}\text{-}2\text{-}Bu^t_2\text{-}4,6)(NEt_2)_2$,[178c] 2.067(4) Å in $Cp^*Hf(NMe_2)[\eta^3:\sigma\text{-}(Ph)NC(NMe_2)NCH(Ph)CH_2O]$,[178d] 2.065(9) Å in $CpCp^*Hf(SnPh_3)(NMe_2)$,[178e] and 2.057(8) Å in $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)_2]Hf(SnPh_3)(NMe_2)$.[178f]

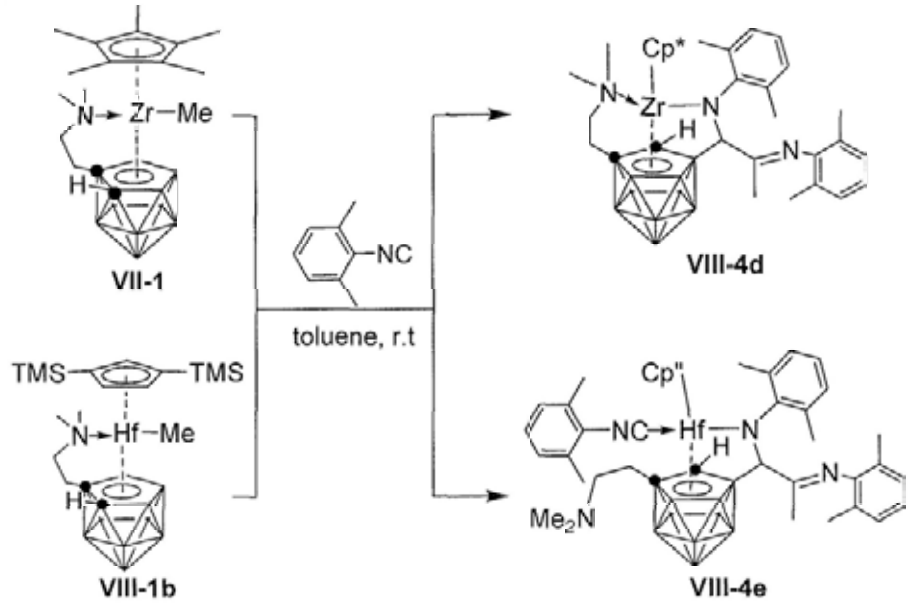
Scheme 8.8



Treatment of **VII-1** with 2 equiv of 2,6-dimethylphenylisocyanide (XyNC) in toluene at room temperature for one day gave, after recrystallization, (η^5-Cp*){σ:η^5-($Me_2NCH_2CH_2$)[$Me_2C_6H_3NCH(Me_2C_6H_3)N{=}C(CH_3)$]$C_2B_9H_9$}Zr (**VIII-4d**) in 71% isolated yield (Scheme 8.9). Reaction of **VIII-1b** with 3 equiv of 2,6-dimethylphenylisocyanide in toluene at room temperature afforded (η^5-Cp'')){σ:η^5-($Me_2NCH_2CH_2$)[$Me_2C_6H_3NCH(Me_2C_6H_3)N{=}C(CH_3)$]$C_2B_9H_9$}Hf(XyN-C) (**VIII-4e**) in 67% isolated yield (Scheme 8.9). The compositions of both compounds were characterized by various spectroscopic techniques and elemental analyses. The double insertion of XyNC into the M-C bonds proceeded before the insertion of the

carbene carbon into the B-H bond. From the ^{1}H and ^{13}C NMR data, there was an isocyanide coordinated to the Hf center in **VIII-4e**, while no coordination of isocyanide to the Zr atom was observed in **VIII-4d** probably due to the more bulkiness of Cp* than Cp'', which made the coordination of bulky isocyanide impossible. The solid-state structure of **VIII-4e** was further confirmed by single-crystal X-ray analyses. The Hf atom is η^5-bound to both bistrimethylsilylcyclopentadienyl ring and dicarbollyl ligand, σ-bound to an N atom and coordinated to an isocyanide molecule in a distorted-tetrahedral geometry (Figure 8.16). The average Hf-C(C_5 ring)/Hf-cage bond distances of 2.535(5) Å/2.549(6) Å are comparable to those of 2.528(4) Å/2.561(4) Å in **VIII-1b**. The Hf-N bond distance of 2.048(4) Å is close to that of 2.015(2) Å in **VIII-4b**. The Hf-C bond distance of 2.342(5) Å compares to that of 2.294(3) Å in **VIII-4b**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angle of 137.7° is similar to that of 137. 6° in **VIII-1b**.

Scheme 8.9



Cp'' = 1,3-$(Me_3Si)_2C_5H_3$, Cp* = C_5Me_5

Table 8.2. Selected Bond Lengths (Å) and Angles (deg) for VIII-1a –VIII-4e

	VIII-1a	VIII-1b	VIII-3g	VIII-4a	VIII-4b	VIII-4e
av. M-C_{ring}	2.544(5)	2.528(4)	2.569(3)	2.583(5)	2.567(3)	2.535(5)
av. M-cage atom	2.562(6)	2.561(4)	2.556(4)	2.502(6)	2.488(3)	2.549(6)
M-N	2.360(4)	2.395(3)	2.417(3)	2.332(6)[d]	2.294(3)[d]	2.342(5)[d]
M-C	2.295(6)	2.246(4)	1.977(2)[b]	2.029(4)[c]	2.015(2)[c]	2.048(4)[c]
M-Cent(C_5)[a]	2.239	2.222	2.272	2.285	2.266	2.232
M-Cent(C_2B_3)[a]	2.123	2.125	2.118			2.106
Cent(C_5)-M-Cent(C_2B_3)	136.4	137.6	136.6			137.7

[a] Cent(C_5), Cent(C_2B_3): the centroid of the cyclopentadienyl ring and the C_2B_3 bonding face, respectively. [b] Zr-O. [c] Zr-N. [d] Zr-C.

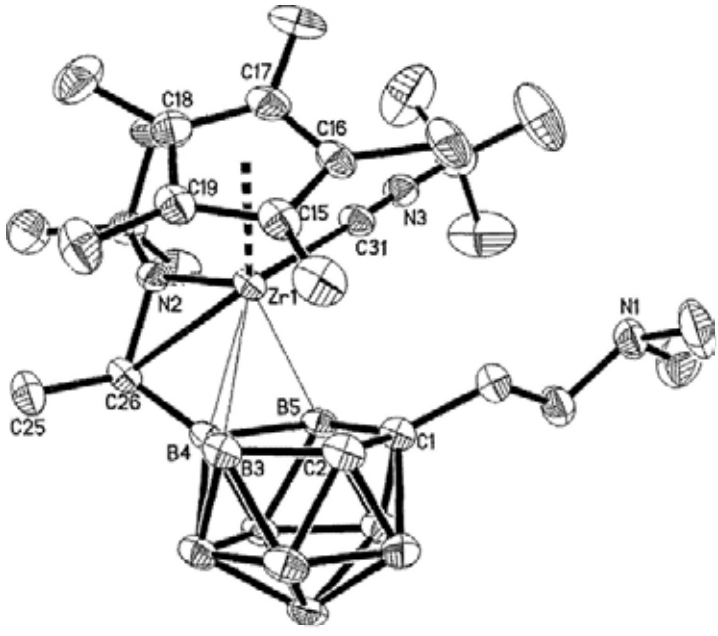


Figure 8.14. Molecular structure of

$(\eta^5$-Cp*$)\{\sigma{:}\eta^3$-$[(CH_3)_2N(CH_2CH_2)][^t BuN(CH_3)CH]C_2B_9H_9\}Zr(CN^tBu)$ (**VIII-4a**)

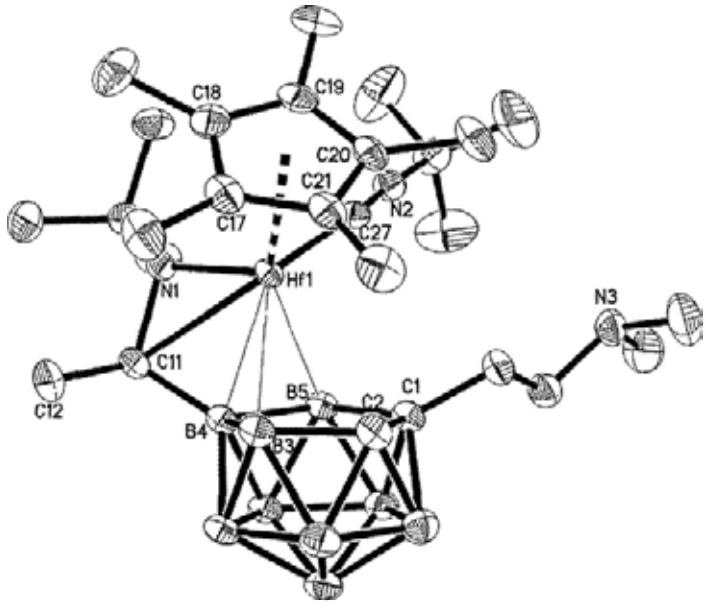


Figure 8.15. Molecular structure of

$(\eta^5$-Cp*$)\{\sigma{:}\eta^3$-$[(CH_3)_2N(CH_2CH_2)][^t BuN(CH_3)CH]C_2B_9H_9\}Hf(CN^tBu)$

(VIII-4b)

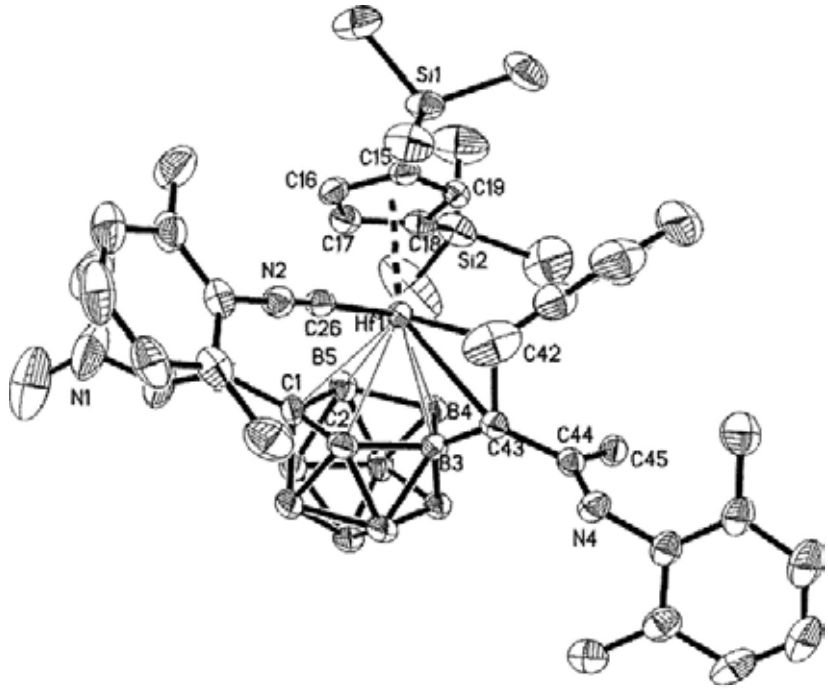


Figure 8.16. Molecular structure of

(η^5-Cp'')\{σ:η^5-($Me_2NCH_2CH_2$)[$Me_2C_6H_3NCH(Me_2C_6H_3)N{=}C(CH_3)$]$C_2B_9H_9$\}Hf-

($CNC_6H_3Me_2$) (**VIII-4e**)

8.6. Summary

Hafnacarborane methyl complexes (η^5-Cp')[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Hf(Me) (Cp' = Cp'', **VIII-1a;** Cp' = Cp*, **VIII-1b**) were synthesized by alkane elimination reaction of Cp''$HfMe_3$ or Cp*$HfMe_3$ with 1 equiv of 7-(Me_2NH)$(CH_2)_2$-7,8-$C_2B_9H_{11}$.

Treatment of (η^5-Cp'')[η^1:σ:η^5-\{$MeN(CH_2)(CH_2CH_2)$\}$C_2B_9H_{10}$]Zr (**VI-1**) with polar unsaturated molecules such as CyN=C=NCy (DCC; Cy = C_6H_{11}), Ph_2C=O and ^{n}BuNCS in toluene at room temperature produced the mono-insertion products **VIII-2a**, **VIII-2e** and **VIII-2f**. No further insertion reaction happened even at higher temperatures and for a longer reaction time. Reaction of **VI-1** with isocyanide 2,6-$Me_2C_6H_3NC$ (XyNC) provided the

double-insertion products **VIII-2d**. When treated **VI-1** with nitriles (CH_3CN, PhCN), **VIII-2b** and **VIII-2c** were formed through mono-insertion and 1,3-H shift.

For the zirconacarborane methyl complex **VII-1**, when treated with small unsaturated nitriles (CH_3CN and cyclopropylacetonitrile) at room temperature, mono-insertion products (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr[N=C(R)Me] (R = Me (**VIII-3a**), $CH_2CH(CH_2)_2$ (**VIII-3b**)) were produced and no 1,3-H shift was observed in such cases. For the more bulky molecules such as PhCN, DCC and ^{i}PrN=C=N^{i}Pr, no reaction happened at room temperature. In refluxing THF, (η^5-Cp*)[η^1:σ:η^5-{MeN[(H)C=C(Ph)N(H)](CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VIII-3c**), and (η^5-Cp*)[η^1:σ:η^5-{MeN[CH_2C(=NR)NR](CH_2CH_2)}$C_2B_9H_{10}$]Zr (R = C_6H_{11} (**VIII-3d**), ^{i}Pr (**VIII-3e**)) were formed. 1,3-H shift after the insertion reaction was observed during the formation of **VIII-3c**. **VII-1** can also react with MeOH to form (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(OMe) (**VIII-3f**) by the acid-base reaction to release CH_4 molecule. Treatment of **VII-1** with CO produced the unexpected product (η^5-Cp*){η^1:η^5:σ-($Me_2NCH_2CH_2$)[O(CH_3)CH]$C_2B_9H_9$}Zr (**VIII-3g**) through insertion and B-H activation. For **VI-1**, no reaction happened when treated with CO.

Treatment of metallacarborane methyl complexes **VII-1**, **VIII-1a**, **VIII-1b** with *tert*-butyl isocyanide at room temperature afforded (η^5-Cp*){σ:η^3-[$(CH_3)_2$N(CH_2CH_2)][^{t}BuN(CH_3)CH]$C_2B_9H_9$}M(CN^{t}Bu) (M = Zr, **VIII-4a**; M = Hf, **VIII-4b**) and (η^5-Cp'')){η^1:σ:η^5-($Me_2NCH_2CH_2$)[^{t}BuN(CH_3)CH]$C_2B_9H_9$}Hf (**VIII-4c**), respectively, via the mono-insertion and B-H activation. While reaction of **VII-1** or **VIII-1b** with XyNC afforded

(η^5-Cp*){σ:η^5-($Me_2NCH_2CH_2$)[$Me_2C_6H_3NCH(Me_2C_6H_3)N{=}C(CH_3)$]$C_2B_9H_9$}Zr (**VIII-4d**) or ($\eta^5$-Cp'')){$\sigma$:$\eta^5$-($Me_2NCH_2CH_2$)[$Me_2C_6H_3NCH(Me_2C_6H_3)N{=}C(CH_3)$]$C_2B_9H_9$}Hf(XyNC) (**VIII-4e**) through the sequential double-insertion of isocyanide and B-H activation.

Chapter 9

Conclusion

This thesis describes (1) synthesis and structure of late transition metal complexes bearing carbon-bridged cyclopentadienyl–carboranyl ligands and their reactivities, (2) synthesis and reactivity of group 4 metal chloride complexes bearing new carbon-bridged cyclopentadienyl-dicarbollyl ligands $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$, $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ and $[H_2C(C_5Me_4)(C_2B_9H_{10})]^{3-}$, (3) synthesis, structure and reactivity of metallacarborane alkyl complexes.

Late transition metal complexes $[Me_2C(C^R)(C_2B_{10}H_{10})]M(PPh_3)$ ($C^R = C_5H_4$, M = Co (**II-2a**), Ni (**II-2b**); $C^R = C_9H_6$, M = Co (**II-3a**), Ni (**II-3b**); $C^R = C_5H_3(CH_2CH_2NMe_2)$, M = Ni (**II-4**)) were synthesized by salt metathesis reaction of dilithium salts of bridged ligands with $MCl_2(PPh_3)_2$. The M-C_{cage} bonds in these complexes were inert toward unsaturated molecules due to the steric hindrance of carboranyl unit. Ligand exchange reaction happened when treated the metal complexes with isocyanide, carbene and phosphines.

Carbon-bridged ansa ligands $[Me_3NH][Me_2C(C_5H_5)(C_2B_9H_{11})]$ (**III-1**), $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**IV-1**) and $[Me_3NH][H_2C(C_5Me_4H)(C_2B_9H_{11})]$ (**V-2**) were synthesized by deboration reaction using an excess amount of piperidine as reagent. Treatment of the lithium/sodium salts of these ligands with $MCl_4(THF)_2$ afforded the ionic zirconacarborane chloride complexes $[\{\eta^5:\eta^5\text{-}R^1{}_2C(R^2)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (R^1 = Me, $R^2 = C_5H_4, C_9H_6$, R^1 = H, $R^2 = C_5Me_4$; M = Zr, Hf). The Zr-Cl bond can be replaced by alkyl, amide or oxo group. The neutral zirconacarborane alkyl complexes can not be formed even though bulky alkyl groups were introduced due to the more open coordination sphere

and increased electron deficiency of the metal center. On the other hand, neutral zirconium amide or oxide complexes can be prepared through $p_\pi(X)$-$d_\pi(Zr)$ interactions between the N/O atoms and Zr atom which can lower the acidity of the Zr center. Thus introduction of an amino group to alkyl unit can help to form the neutral zirconacarborane alkyl complex $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Zr[\sigma:\eta^1\text{-}CH_2(NMe_2)\text{-}o\text{-}C_6H_4](THF)$ (**V-7b**·THF). Neutral zirconacarborane amide complexes can also be produced through amine elimination reaction of ligands with $Zr(NMe_2)_4$. The zirconacarborane chloride/amide complexes showed good to moderate activity in ethylene polymerization in the presence of an excess amount of MAO.

Mixed sandwich metallacarborane alkyl/methyl complexes **VI-1**, **VII-1**, **VIII-1a** and **VIII-1b** were prepared by alkane elimination reaction of Cp^RMMe_3 (Cp^R = Cp'', Cp*, M = Zr, Hf) with 7-$(Me_2NH)(CH_2)_2$-7,8-$C_2B_9H_{11}$. The zirconacarborane alkyl/methyl complexes showed no reactivity to alkene. For alkynes, only mono-insertion products were formed. The regioselectivity of the insertion of unsymmetrical alkynes was determined by either steric hindrance or electronic factor depending on the substituents on C≡C. For terminal alkynes, either insertion or acid-base reaction produts were generated. Acid-base reaction can also happen between **VII-1** and MeOH. These complexes also showed reactivities toward RN=C=NR, RCN, RNC, Ph_2C=O and ^{n}BuNCS to afford the mono-insertion products. Treatment of **VI-1** with RNC provided the double-insertion products. For CO and RNC, sequential insertion into the M-C bond and B-H bond was observed.

Chapter 10

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 were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. $Me_2NCH_2CH_2Cl$,[179] $Me_2NCH_2CH_2C_5H_3CMe_2$,[180] $Me_2C(C_5H_5)(C_2B_{10}H_{11})$,[8,9] $Me_2C(C_9H_7)(C_2B_{10}H_{11})$,[11] $NiCl_2(PPh_3)_2$,[181] $CoCl_2(PPh_3)_2$,[182] C_5H_5Na,[183] $C_6H_5CH_2K$,[184] 2,6-$^iPr_2C_6H_3NHNa$,[185] $MCl_4(THF)_2$ (M = Zr, Hf),[186] 2,6-$Me_2C_6H_3NHNa$,[185] 1,2,3,4-Tetramethylpentafulvene,[187] $KCH_2(NMe_2)$-*o*-C_6H_4,[188] Cp''$ZrCl_3$,[189] Cp''$ZrMe_3$,[190] 7-$(Me_2NH)(CH_2)_2$-7,8-$C_2B_9H_{11}$,[146] PhC≡CMe,[191a] PhC≡CTMS,[191b] ^{n}BuC≡CTMS,[191c] Cp*$ZrCl_3$,[192] Cp*$ZrMe_3$,[192] 2-PyC≡C^{n}Bu,[191d] Cp''$HfCl_3$,[189] Cp''$HfMe_3$,[190] Cp*$HfCl_3$,[193a] Cp*$HfMe_3$[193b] were prepared according to literature methods. Other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR and ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 and 162.0 MHz. All chemical shifts are reported in δ units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts, and to external 85% H_3PO_4 (0.00 ppm) for phosphorus chemical shifts. Elemental analyses were performed by Shanghai Institute of Organic Chemistry, CAS, China.

$Me_2C(Me_2NCH_2CH_2C_5H_4)(C_2B_{10}H_{11})$ (II-1). To a toluene/Et_2O (2/1) solution (15 mL) of *o*-$C_2B_{10}H_{12}$ (1.44 g, 10.0 mmol) was added a 1.60 M solution of ^{n}BuLi in hexane (12.6 mL, 20.0 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. The resulting $Li_2C_2B_{10}H_{10}$ solution was then cooled to 0 °C, to which was slowly added a solution of dimethyl(dimethylaminoethyl)fulvene (2.12 g, 12.0 mmol) in a toluene/Et_2O (2/1) mixture (9 mL). The reaction mixture was maintained at 0 °C for 1 h, slowly warmed to room temperature and then refluxed overnight. After removal of the solvent, Et_2O was added. The solution was quenched with a saturated NH_4Cl solution. The organic layer was separated and washed with water, dried with anhydrous $MgSO_4$. After removal of the solvent by rotary evaporation, the residue was subject to column chromatography on silica gel to give **II-1** as an orange oil (2.66 g, 83%). ^{1}H NMR ($CDCl_3$): δ 6.25-5.70 (m, 3H) (vinylic *H*), 3.32 - 3.15 (m, 1H) (cage C*H*), 2.97 - 2.93 (m, 1H) (methane *H* on Cp), 2.53 (m, 2H) ($CH_2CH_2N(CH_3)_2$), 2.43 (m, 2H) ($CH_2CH_2N(CH_3)_2$), 2.28 - 2.25 (m, 6H) ($CH_2CH_2N(CH_3)_2$), 1.58 - 1.50 (m, 6H) ($C(CH_3)_2$) (a mixture of isomers). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.1, 149.2, 133.2, 130.9, 127.1, 126.9, 126.3, 126.1 (vinylic *C*), 84.8 (cage *C*), 63.9, 63.4 ($N(CH_3)_2$), 59.5, 58.8 ($CH_2CH_2N(CH_3)_2$), 45.5, 42.9 ($CH_2CH_2N(CH_3)_2$), 44.3, 42.1 (methane *C*), 42.1, 40.4 ($C(CH_3)_2$), 31.5, 30.8, 29.0, 28.3 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ -3.9 (2B), -8.9 (2B), -11.3 (2B), -13.5 (4B). IR (KBr, cm^{-1}): ν_{BH} 2521 (vs). EI-MS m/z (abundance): 320 (M^+).

Preparation of $[\eta^5:\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co(PPh_3)$ (II-2a). A 1.60 M ^{n}BuLi solution in hexane (1.2 mL, 2.0 mmol) was slowly added into a THF (10 mL) solution of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.25 g, 1.0 mmol) at -78 °C. The mixture was warmed up to room

temperature and stirred for 3 h. The resulting solution was slowly added into a THF suspension (10 mL) of $CoCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) at room temperature. The mixture was stirred for one day. After removal of the solvent, the residue was extracted with Et_2O (50 mL). The Et_2O solution was concentrated to *ca.* 10 mL. Complex **II-2a** was isolated as brown crystals after this solution stood at room temperature for 2 days (0.50 g, 87%). IR (KBr, cm^{-1}): ν_{BH} 2579 (vs). Anal. Calcd for $C_{28}H_{35}B_{10}CoP$ (**II-2a**): C, 59.04; H, 6.19. Found: C, 59.08; H, 6.61.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PPh_3$) (II-2b). This complex was prepared as green crystals from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.25 g, 1.0 mmol), ^{n}BuLi (1.60 M, 1.2 mL, 2.0 mmol) and $NiCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL), using the same procedure reported for **II-2a**: yield 0.53 g (93%). ^{1}H NMR (benzene-d_6): δ 7.62 (m, 6H), 7.01 (m, 9H) (C_6H_5), 5.96 (s, 2H), 3.70 (s, 2H) (C_5H_4), 1.39 (s, 6H) ($(CH_3)_2C$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 134.8, 134.7, 131.0, 128.9 (C_6H_5), 99.6, 88.2 (C_5H_4), 66.3 (cage *C*), 41.3 ($(CH_3)_2C$), 32.3 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -3.5 (3B), -7.0 (3B), -9.8 (4B). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 47.3. IR (KBr, cm^{-1}): ν_{BH} 2581 (vs). Anal. Calcd for $C_{28}H_{35}B_{10}NiP$ (**II-2b**): C, 59.07; H, 6.20. Found: C, 58.51; H, 6.25.

Preparation of [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Co($PPh_3$) (II-3a). This complex was prepared as brown crystals from $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol), ^{n}BuLi (1.60 M, 1.2 ml, 2.0 mmol) and $CoCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL), using the same procedure reported for **II-2a**: yield 0.49 g (79%). IR (KBr, cm^{-1}): ν_{BH} 2593 (vs). Anal. Calcd for $C_{32}H_{37}B_{10}CoP$ (**II-3a**): C, 62.03; H, 6.02. Found: C, 62.30; H, 6.17.

Preparation of [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Ni($PPh_3$) (II-3b). This complex was prepared as green crystals from $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol), ^{n}BuLi (1.60 M, 1.2 mL, 2.0 mmol) and $NiCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL), using the same procedure reported for **II-2a**: yield 0.43 g (69%). ^{1}H NMR (benzene-d_6): δ 7.75 (d, J = 7.8 Hz, 1H), 6.78 (t, J = 7.8 Hz, 2H), 6.45 (d, J = 3.6 Hz, 1H), 5.13 (d, J = 7.8 Hz, 1H), 3.88 (t, J = 3.6 Hz, 1H) (C_9H_6), 7.32 (m, 6H), 6.99 (m, 9H) (C_6H_5), 1,60 (s, 3H), 1.54 (s, 3H) ((CH_3)$_2$C). ^{13}C{^{1}H} NMR (benzene-d_6): δ 135.0, 135.8, 134.4, 132.8, 132.7, 131.9, 130.9, 129.6, 126.6, 125.3, 123.8, 121.9, 117.3 (C_9H_6 + C_6H_5), 64.5 (cage C), 44.1 ((CH_3)$_2C$), 32.3, 31.3 ((CH_3)$_2$C). ^{11}B{^{1}H} NMR (benzene-d_6): δ -3.2 (2B), -6.4 (3B), -9.3 (5B). ^{31}P{^{1}H} NMR (benzene-d_6): δ 33.8. IR (KBr, cm^{-1}): ν_{BH} 2581 (vs). Anal. Calcd for $C_{32}H_{37}B_{10}NiP$ (**II-3b**): C, 62.05; H, 6.02. Found: C, 62.07; H, 5.80.

Preparation of [η^5:σ-$Me_2C(C_5H_3CH_2CH_2NMe_2)(C_2B_{10}H_{10})$]Ni($PPh_3$) (II-4). This complex was prepared as green crystals from $Me_2C(C_5H_4CH_2CH_2NMe_2)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol), ^{n}BuLi (1.60 M, 1.2 mL, 2.0 mmol) and $NiCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL), using the same procedure reported for **II-2a**: yield 0.40 g (63%). ^{1}H NMR (benzene-d_6): δ 7.69 (m, 6H), 7.02 (m, 9H) (C_6H_5), 6.07 (m, 1H), 5.87 (s, 1H), 3.76 (m, 1H) (C_5H_3), 2.11 (m, 2H) ($CH_2CH_2NMe_2$), 1.90 (m, 2H) ($CH_2CH_2NMe_2$), 1.86 (s, 6H) (N(CH_3)$_2$), 1.45 (s, 3H), 1.40 (s, 3H) ((CH_3)$_2$C). ^{13}C{^{1}H} NMR (benzene-d_6): δ 135.4, 132.5, 132.1, 131.4, 125.6, 110.2, 109.8, 99.4, 97.7, (C_6H_5 + C_5H_3), 88.0 (cage C), 66.5 ($CH_2CH_2NMe_2$), 45.9 (N(CH_3)$_2$), 41.5 ($CH_2CH_2NMe_2$), 32.5 (C(CH_3)$_2$), 31.3, 30.7 (C(CH_3)$_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -3.6 (2B), -6.8 (3B), -9.5 (5B). ^{31}P{^{1}H} NMR

(benzene-d_6): δ 36.5. IR (KBr, cm^{-1}): ν_{BH} 2587 (vs). Anal. Calcd for $C_{32}H_{44}B_{10}NNiP$ (**II-4**): C, 60.01; H, 6.92; N, 2.19. Found: C, 60.35; H, 6.83; N, 2.06.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co(2,6-$Me_2$-$C_6H_3NC$) (II-5a). To a toluene (5 mL) solution of [$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co($PPh_3$) (**II-2a**; 0.29 g, 0.50 mmol) was added 2,6-Me_2-C_6H_3NC (0.07 g, 0.50 mmol) at room temperature. The reaction mixture was stirred at room temperature for one day. After removal of the solvent, the residue was extracted with Et_2O (20 mL). After filtration, the brown filtrate was concentrated to *ca.* 5 mL. Complex **II-5a** was isolated as brown crystals after this solution stood at room temperature for one day (0.17 g, 77%). IR (KBr, cm^{-1}): ν_{BH} 2575 (vs). Anal. Calcd for $C_{37}H_{56}B_{10}CoN_2$ (**II-5a**): C, 52.05; H, 6.67; N, 3.19. Found: C, 52.26; H, 6.70; N, 3.42.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni(2,6-$Me_2$-$C_6H_3NC$) (II-5b). This complex was prepared as green crystals from [$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PPh_3$) (**II-2b**; 0.29 g, 0.50 mmol) and 2,6-Me_2-C_6H_3NC (0.07 g, 0.50 mmol) in toluene (5 mL), using the same procedure reported for **II-5a**: yield 0.13 g (59%). ^{1}H NMR (benzene-d_6): δ 6.66 (t, J = 7.8 Hz, 1H), 6.51 (d, J = 7.8 Hz, 2H) (C_6H_3), 5.65 (t, J = 2.4 Hz, 2H), 4.47 (t, J = 2.4 Hz, 2H) (C_5H_4), 2.11 (s, 6H) ((CH_3)$_2C_6H_3$), 1.29 (s, 6H) ((CH_3)$_2$C). ^{13}C{^{1}H} NMR (benzene-d_6): δ 162.7 (N=*C*), 132.8, 132.7, 132.0, 129.2 (C_6H_3), 98.5, 88.4 (C_5H_4), 68.2, 66.3 (cage *C*), 32.3 ((CH_3)$_2$*C*), 30.6 ((CH_3)$_2C_6H_3$), 23.4((CH_3)$_2$C). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.03 (1B), -4.11 (2B), -6.79 (3B), -8.70 (4B). IR (KBr, cm^{-1}): ν_{BH} 2573 (vs). Anal. Calcd for $C_{32}H_{44}B_{10}NNi$ (**II-5b**): C, 52.07; H, 6.67; N, 3.20. Found: C, 52.52; H, 6.86; N, 3.28.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co[1,3-(2,6-^{i}Pr$_2$($C_6H_3$))$_2$-$C_3N_2H_2$] (II-6a). This complex was prepared as brown crystals from

$[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co(PPh_3)$ (**II-2a**; 0.29 g, 0.50 mmol) and 1,3-(2,6-^{i}Pr$_2$(C_6H_3))$_2$-$C_3N_2H_2$ (0.20 g, 0.50 mmol) in toluene (5 mL), using the same procedure reported for **II-5a**: yield 0.18 g (51%). IR (KBr, cm^{-1}): ν_{BH} 2570 (vs). Anal. Calcd for $C_{37}H_{56}B_{10}CoN_2$ (**II-6a**): C, 63.86; H, 8.11; N, 4.03. Found: C, 63.35; H, 7.67; N, 4.01.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ni[1,3-(2,6-^{i}Pr$_2$(C$_6$H$_3$))$_2$-C$_3$N$_2$H$_2$] (II-6b). This complex was prepared as green crystals from $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**II-2b**; 0.29 g, 0.50 mmol) and 1,3-(2,6-^{i}Pr$_2$(C_6H_3))$_2$-$C_3N_2H_2$ (0.20 g, 0.50 mmol) in toluene (5 mL), using the same procedure reported for **II-5a**: yield 0.21 g (60%). ^{1}H NMR (benzene-d_6): δ 7.25 (m, 4H), 7.12 (m, 2H) (C_6H_3), 6.47 (s, 2H) ($C_3N_2H_2$), 5.77 (m, 2H), 3.98 (m, 2H) (C_5H_4), 3.66 (m, 2H), 3.09 (m, 2H) ($(CH_3)_2CH$), 1.62 (d, J = 6.6 Hz, 6H), 1.27 (d, J = 6.6 Hz, 6H), 1.01 (d, J = 6.6 Hz, 6H), 0.80 (d, J = 6.6 Hz, 6H) ($(CH_3)_2CH$), 1.24 (s, 6H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 163.1 (carbene *C* of $C_3N_2H_2$), 146.7, 144.8, 138.9, 130.8, 126.8, 125.5, 124.5, 120.6 (C_6H_3 + vinylic *C* of $C_3N_2H_2$), 98.6, 89.2 (C_5H_4), 40.5 ($(CH_3)_2C$), 30.7 ($(CH_3)_2C$), 29.4, 29.0 ($(CH_3)_2CH$), 26.1, 25.7, 23.5, 22.6 ($(CH_3)_2CH$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -3.2 (2B), -6.3 (3B), -9.2 (5B). IR (KBr, cm^{-1}): ν_{BH} 2578 (vs). Anal. Calcd for $C_{32}H_{44}B_{10}NNiP$ (**II-6b**): C, 63.88; H, 8.11; N, 4.03. Found: C, 63.86; H, 8.19; N, 4.25.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ni(PCy$_3$)·THF (II-7·THF). To a toluene (5 mL) solution of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**II-2b**; 0.29 g, 0.50 mmol) was added PCy_3 (0.14 g, 0.50 mmol) at room temperature. The reaction mixture was heated to reflux for one day. After removal of the solvent, the residue was extracted with Et_2O (20

mL). After filtration, the filtrate was concentrated to *ca.* 5 mL. Complex **II-7**·THF was isolated as green crystals after this solution stood at room temperature for one day (0.18 g, 57%). ^{1}H NMR (benzene-d_6): δ 5.94 (m, 2H), 4.23 (m, 2H) (C_5H_4), 2.11-1.07 (m, 33H) ($HC(CH_2)_5$), 1.39 (s, 6H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 99.7, 90.2 (C_5H_4), 66.3 (cage *C*), 32.3, 31.2, 29.7, 28.1, 27.1, 23.4, 15.9 ($(CH_3)_2C$ + $P(C_6H_{11})_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.4 (5B), -6.0 (2B), -8.9 (3B). ^{31}P{^{1}H} NMR (benzene-d_6): δ 44.4. IR (KBr, cm^{-1}): ν_{BH} 2570 (vs). Anal. Calcd for $C_{30}H_{58}B_{10}O_{0.5}NiP$ (**II-7** + 0.5THF): C, 57.69; H, 9.36. Found: C, 58.09; H, 9.11.

Preparation of {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co}$_2$(dppe) (II-8). This complex was prepared as green crystals from $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co(PPh_3)$ (**II-6a**; 0.29 g, 0.50 mmol) and dppe (0.20 g, 0.50 mmol) in toluene (5 mL), using the same procedure reported for **II-7**: yield 0.19 g (62%). IR (KBr, cm^{-1}): ν_{BH} 2563 (vs). Anal. Calcd for $C_{46}H_{64}B_{20}Co_2P_2$ (**II-8**): C, 54.54; H, 6.37. Found: C, 54.24; H, 6.25.

Preparation of [Me_3NH][$Me_2C(C_5H_5)(C_2B_9H_{11})$] (III-1). To an ethanol (40 mL) solution of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.75 g, 3.0 mmol) was added piperidine (7.5 mL, 75.0 mmol), and the reaction mixture was heated to reflux for 2 days until the ^{11}B NMR spectrum of the solution showed the completion of the reaction. After removal of ethanol and the excess amount of piperidine under vacuum, the residue was dissolved in ethanol (5 mL). Addition of a saturated Me_3NHCl solution gave a sticky solid which was washed with water, reprecipitated from acetone to ether, and dried under vacuum. Compound **III-1** was then isolated as a pale yellow solid (0.72 g, 80%). ^{1}H NMR (acetone-d_6): δ 6.72 (m), 6.31 (m), 6.24 (m), 6.18 (m), 6.06 (m), 5.88 (m), 2.82 (m) (5H, C_5H_5, a mixture of isomers), 2.99

(s, 9H) ((C*H*$_3$)$_3$NH), 1.68 (s, 1H) (cage C*H*), 1.24 (s, 3H), 1.08 (s, 3H) ((C*H*$_3$)$_2$C), -2.70 (br s, 1H) (B-*H*-B). ^{13}C{^{1}H} NMR (acetone-d_6): δ 161.3, 158.1, 136.0, 132.5, 132.0, 131.0, 124.7, 124.0 (C_5H_5), 45.4 ((*C*H$_3$)$_3$NH), 42.9 (C_5H_5), 41.0, 31.3 ((*C*H$_3$)$_2$*C*). ^{11}B{^{1}H} NMR (acetone-d_6): δ -11.1 (2B), -16.1 (2B), -18.1 (1B), -19.4 (1B), -22.8 (1B), -33.4 (1B), -36.8 (1B). IR (KBr, cm^{-1}): ν_{BH} 2514 (vs), 2313 (w). Anal. Calcd for $C_{13}H_{32}B_9N$ (**III-1**): C, 52.10; H, 10.76; N, 4.67. Found: C, 51.78; H, 10.69; N, 4.88.

Preparation of [{[(μ-η^5):η^5-Me$_2$C(C$_5$H$_4$)(C$_2$B$_9$H$_{10}$)]Na(THF)}{Na(THF)$_3$}{Na(THF)$_2$}]$_2$·2THF (III-2·2THF). To a THF (30 mL) solution of [Me$_2$C(C$_5$H$_5$)(C$_2$B$_9$H$_{11}$)][Me$_3$NH] (0.48 g, 1.6 mmol) was added NaH (0.32 g, 13.3 mmol), and the reaction mixture was heated to reflux for 2 days. After removal of the excess amount of NaH by filtration, the resulting clear solution was concentrated to *ca.* 10 mL. Compound **III-2**·2THF was isolated as colorless crystals after this solution stood at room temperature for 3 days (0.62 g, 51%). ^{1}H NMR (pyridine-d_5): δ 6.58 (m, 2H), 6.37 (m, 2H) (C_5H_4), 3.66 (m, 28H) (THF), 2.10 (s, 1H) (cage C*H*), 1.90 (s, 3H), 1.65 (s, 3H) ((C*H*$_3$)$_2$C), 1.63 (m, 28H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 101.2, 100.9, 100.8 (C_5H_4), 67.2, 25.2 (THF), 61.4, 36.3 ($C_2B_9H_{10}$), 31.1, 30.2, 29.9 ((*C*H$_3$)$_2$*C*). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -21.0 (6B), -24.6 (2B), -44.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2503 (vs), 2350 (w). Anal. Calcd for $C_{60}H_{120}B_{18}Na_6O_{10}$ (**III-2** - 2THF): C, 54.02; H, 9.07. Found: C, 54.21; H, 9.01.

Preparation of [{η^5:η^5-Me$_2$C(C$_5$H$_4$)(C$_2$B$_9$H$_{10}$)}ZrCl$_2$][Na(DME)$_3$] (III-3a). To a THF (40 mL) solution of [Me$_2$C(C$_5$H$_5$)(C$_2$B$_9$H$_{11}$)][Me$_3$NH] (0.72 g, 2.4 mmol) was added NaH (0.46 g, 19.0 mmol), and the reaction mixture was heated to reflux for 2 days. The

resulting solution {[$Me_2C(C_5H_4)(C_2B_9H_{10})$]$Na_3(THF)_x$} was transferred via cannula to a suspension of $ZrCl_4(THF)_2$ (0.91 g, 2.4 mmol) in THF (10 mL) at -78°C, and the mixture was slowly warmed to room temperature and stirred for 2 days. After removal of the precipitate, the solvent was evaporated under vacuum leaving an oily residue that was recrystallized from DME to yield **III-3a** as colorless crystals (0.48 g, 29%). ^{1}H NMR (pyridine-d_5): δ 6.95 (m, 2H), 6.40 (m, 1H), 6.20 (m, 1H) (C_5H_4), 3.48 (s, 12H), 3.26 (s, 18H) (DME), 1.68 (s, 1H) (cage C*H*), 1.62 (s, 3H), 1.48 (s, 3H) ((CH_3)$_2$C). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.6, 124.9, 107.1, 104.7 (C_5H_4), 71.4, 58.0 (DME), 66.5, 51.2 ($C_2B_9H_{10}$), 37.8, 27.9, 26.8 ((CH_3)$_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.9 (1B), -3.1 (1B), -5.9 (3B), -12.2 (3B), -19.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2547 (vs). Anal. Calcd for $C_{18}H_{40}B_9Cl_2NaO_4Zr$ (**III-3a** - *DME*): C, 35.86; H, 6.69. Found: C, 35.93; H, 7.19.

Alternate Method. A THF solution (20 mL) of **III-2** (1.62 g, 2.0 mmol) was slowly added to a THF suspension (20 mL) of $ZrCl_4(THF)_2$ (0.75 g, 2.0 mmol) at -78°C, and the mixture was stirred at room temperature overnight. The resulting solution was treated using the same procedures reported above to give **III-3a** as colorless crystals (1.01 g, 73%).

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$HfCl_2$][Na(DME)$_3$] (III-3b). This complex was prepared as pale yellow crystals from [$Me_2C(C_5H_5)(C_2B_9H_{11})$][$Me_3NH$] (0.72 g, 2.4 mmol), NaH (0.50 g, 20.8 mmol) and $HfCl_4(THF)_2$ (1.12 g, 2.4 mmol) in THF (40 mL), using the same procedure reported for **III-3a**: yield 0.68 g (36%). ^{1}H NMR (pyridine-d_5): δ 6.92 (m, 1H), 6.87 (m, 1H), 6.26 (d, J = 2.7, 1H), 6.10 (m, 1H) (C_5H_4), 3.49 (s, 12H), 3.26 (s, 18H) (DME), 1.70 (s, 1H) (cage C*H*), 1.60 (s, 3H), 1.46 (s, 3H) ((CH_3)$_2$C). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.4, 124.7, 120.7, 105.2, 102.3 (C_5H_4), 71.4, 58.0 (DME),

66.3, 49.7 ($C_2B_9H_{10}$), 37.4, 27.7, 27.1 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 3.2 (1B), -4.2 (1B), -6.3 (2B), -7.4 (1B), -13.3 (2B), -14.3 (1B), -21.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2543 (vs). Anal. Calcd for $C_{18}H_{40}B_9Cl_2HfNaO_4$ (**III-3b** - DME): C, 31.32; H, 5.84. Found: C, 31.41; H, 6.50.

Alternate Method. Complex **III-3b** was also prepared in 70% yield from **III-2** (1.62 g, 2.0 mmol) and $HfCl_4(THF)_2$ (0.93 g, 2.0 mmol) in THF (40 mL) using the same procedure reported above.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][Li(DME)$_3$] (III-4). To a THF (10 mL) solution of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][Na(DME)$_3$] (**III-3a**; 0.21 g, 0.30 mmol) was added LiCl (0.01 g, 0.30 mmol) at room temperature, and the reaction mixture was stirred overnight. After removal of the solvent, the residue was extracted with toluene (5 mL x 3). The toluene solutions were evaporated under vacuum leaving an oily residue that was recrystallized from DME at -30°C to give **III-4** as pale yellow crystals (0.05 g, 25%). ^1H NMR (pyridine-d_5): δ 6.94 (m, 1H), 6.82 (m, 1 H), 6.40 (m, 1H), 6.20 (m, 1H) (C_5H_4), 3.49 (s, 12H), 3.26 (s, 18H) (DME), 1.70 (s, 1H) (cage C*H*), 1.59 (s, 3H), 1.47 (s, 3H) ($(CH_3)_2C$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 125.7, 120.0, 108.0, 105.0 (C_5H_4), 71.4, 57.9 (DME), 48.4 ($C_2B_9H_{10}$), 37.3, 27.9, 26.7 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 1.9 (1B), -3.4 (1B), -5.6 (1B), -6.9 (2B), -13.1 (1B), -15.0 (2B), -21.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2520 (vs). Anal. Calcd for $C_{20}H_{45}B_9Cl_2LiO_5Zr$ (**III-4** - 0.5DME): C, 38.01; H, 7.18. Found: C, 37.76; H, 7.34.

Alternate Method. To a THF (40 mL) solution of $[Me_2C(C_5H_5)(C_2B_9H_{11})][Me_3NH]$ (0.72 g, 2.4 mmol) was slowly added hexane solution of ^{n}BuLi (1.60M, 4.5 mL, 7.2 mmol)

at -78°C, and the mixture was stirred at room temperature for 3 h. The resulting $\{[Me_2C(C_5H_4)(C_2B_9H_{10})]Li_3(THF)_x\}$ solution was transferred via cannula to a suspension of $ZrCl_4(THF)_2$ (0.91 g, 2.4 mmol) in THF (10 mL) at -78°C, and the mixture was slowly warmed to room temperature and stirred overnight. After removal of the precipitate, the solvent was evaporated under vacuum leaving an oily residue that was recrystallized from DME to yield **III-4** as colorless crystals (0.68 g, 41%).

Preparation of $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_2\}$ (III-5a). To a THF (10 mL) solution of $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$ (**III-3a**; 0.20 g, 0.29 mmol) was slowly added a THF solution of C_5H_5Na (10.0 mL, 0.29 mmol) at -20°C, and the reaction mixture was stirred at room temperature for 2 days. After removal of the precipitate, the filtrate was evaporated to dryness under vacuum. The residue was dissolved in DME. The DME solution was then concentrated to *ca.* 6 mL, to which was added ether (1 mL). Complex **III-5a** was isolated as yellow crystals after this solution stood at -30°C for 3 days (0.09 g, 47%). ^{1}H NMR (pyridine-d_5): δ 6.85 (d, J = 2.7 Hz, 1H), 6.69 (m, 1H), 6.29 (m, 1H), 5.42 (d, J = 2.4, 1H) (C_5H_4), 6.39 (s, 5H) (C_5H_5), 3.48 (s, 8H), 3.25 (s, 12H) (DME), 2.55 (s, 1H) (cage C*H*), 1.39 (s, 3H), 1.33 (s, 3H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 113.9, 113.8, 112.8, 107.5, 104.8 (C_5H_4), 112.6 (C_5H_5), 95.8 ($C_2B_9H_{10}$), 71.4, 57.9 (DME), 35.4, 26.6, 25.2 ($(CH_3)_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -8.5 (1B), -9.3 (1B), -12.9 (1B), -13.5 (1B), -15.1 (1B), -18.7 (2B), -19.7 (1B), -34.5 (1B). IR (KBr, cm^{-1}): ν_{BH} 2517 (s). Anal. Calcd for $C_{19}H_{35}B_9ClNaO_2Zr$ (**III-5a** - DME): C, 42.07; H, 6.50. Found: C, 42.51; H, 7.19.

Preparation of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl(CH_2C_6H_5)$][$Na(DME)_3$] (III-5b). To a THF (15 mL) solution of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][$Na(DME)_3$] (**III-3a**; 0.55 g, 0.79 mmol) was slowly added a THF (10 mL) solution of $KCH_2C_6H_5$ (0.10 g, 0.79 mmol) at -78°C, and the reaction mixture was then warmed to room temperature and stirred for 4 h. After removal of the solvent, the residue was extracted with DME (5 mL x 3). The DME solutions were combined and concentrated to *ca.* 5 mL. Complex **III-5b** was isolated as orange crystals after this solution stood at -30°C for 3 days (0.21 g, 36%). ^{1}H NMR (benzene-d_6): δ 7.48 (m, 2H), 7.31 (m, 2H), 6.92 (m, 1H) ($CH_2C_6H_5$), 6.68 (m, 1H), 6.27 (m, 1H), 6.24 (m, 1H), 4.93 (m, 1H) (C_5H_4), 3.07 (s, 12H), 3.06 (s, 18H) (DME), 2.60 (br s, 2H) ($CH_2C_6H_5$), 1.99 (s, 1H) (cage C*H*), 1.41 (s, 3H), 0.84 (s, 3H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 155.0, 129.7, 127.1, 126.5, 122.8 ($CH_2C_6H_5$), 122.5, 121.6, 120.2, 108.6, 107.2 (C_5H_4), 71.5, 59.3 (DME), 68.3 ($CH_2C_6H_5$), 66.3, 51.6 ($C_2B_9H_{10}$), 38.2, 29.3, 26.3 ($(CH_3)_2C$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 3.6 (1B), -0.2 (1B), -2.7 (1B), -5.7 (2B), -7.7 (1B), -11.3 (1B), -12.5 (1B), -18.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2533 (s). Anal. Calcd for $C_{25}H_{47}B_9ClNaO_4Zr$ (**III-5b** - DME): C, 45.59; H, 7.19. Found: C, 45.87; H, 7.58.

Preparation of [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]$Zr(NHC_6H_3Pr^i_2)(THF)\cdot C_7H_8$ (III-5c·C_7H_8). To a THF (15 mL) solution of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][$Na(DME)_3$] (**III-3a**; 0.20 g, 0.29 mmol) was slowly added a THF (5 mL) solution of $NaNHC_6H_3Pr^i_2$ (0.06 g, 0.29 mmol) at -20°C, and the reaction mixture was stirred at room temperature for 2 days. After removal of solvent, the residue was extracted with toluene (15 mL x 3). The toluene solutions were combined and concentrated to *ca.* 10 mL. Complex **III-5c**·C_7H_8 was isolated as yellow crystals after this

solution stood at room temperature for 4 days (0.12 g, 62%). ^{1}H NMR (pyridine-d_5): δ 10.29 (s, 1H) (N*H*), 7.26-7.17 (m, 5H) ($C_6H_5CH_3$), 7.13 (d, J = 6.0 Hz, 2H), 6.90 (m, 1H) (aryl H), 6.58 (m, 1H), 6.45 (m, 2H), 6.02 (m, 1H) (C_5H_4), 3.64 (m, 4H), 1.60 (m, 4H) (THF), 3.18 (m, 2H) ($(CH_3)_2CH$), 2.20 (s, 3H) ($C_6H_5CH_3$), 1.78 (s, 1H) (cage C*H*), 1.56 (s, 3H), 1.51 (s, 3H) ($(CH_3)_2C$), 1.25 (s, 6H), 1.23 (s, 6H) ($CH_3)_2CH$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 141.5, 140.6, 131.7, 125.5, 128.7, 128.0, 125.1 (aryl *C*), 119.1, 118.8, 117.3, 108.2, 105.9 (C_5H_4), 67.2, 25.1 (THF), 38.2, 27.3, 26.4 ($(CH_3)_2C$), 27.3, 22.1 ($(CH_3)_2CH$), 20.6 ($C_6H_5CH_3$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 2.4 (1B), -3.5 (2B), -7.1 (3B), -13.2 (2B), -20.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2534 (s), 2312 (w). Anal. Calcd for $C_{25.5}H_{42}B_9NZr$ (**III-5c** - THF + 0.5C_7H_8): C, 55.57; H, 7.68; N, 2.54. Found: C, 55.33; H, 7.45; N, 2.55.

Preparation of [Me_3NH][$Me_2C(C_9H_7)(C_2B_9H_{11})$] (IV-1). To an ethanol (20 mL) solution of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol) was added piperidine (2.5 mL, 25.0 mmol), and the mixture was heated to reflux for 2 days until the ^{11}B NMR spectrum of the solution showed the completion of the reaction. After removal of ethanol and the excess amount of piperidine under vacuum, the residue was dissolved in ethanol (3 mL). Addition of a saturated Me_3NHCl solution gave a sticky solid which was washed with water, reprecipitated from acetone to ether, and dried under vacumm. Compound **IV-1** was then isolated as pale-yellow crystals (0.32 g, 91%). X-ray quality crystals were grown from ethanol solution. ^{1}H NMR (acetone-d_6): δ 7.90 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 6.19 (t, J = 2.1 Hz, 1H) (C_9H_7), 3.22 (m, 2H) (CH_2), 3.15 (s, 9H) ($CH_3)_3NH$), 1.84 (s, 1H) (C*H* of $C_2B_9H_{11}$), 1.47 (s, 3H), 1.34 (s, 3H) ($(CH_3)_2C$), -2.8 (br s, 1H) (B-*H*-B). ^{13}C{^{1}H} NMR (acetone-d_6): δ 155.1, 146.7, 146.0,

128.5, 126.2, 124.5, 124.4 (C_9H_7), 46.3 ($(CH_3)_3NH$), 40.3 (CH_2), 37.8, 32.0 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (acetone-d_6): δ -10.6 (2B), -15.7 (2B), -17.9 (1B), -18.8 (1B), -22.5 (1B), -32.7 (1B), -36.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2521 (vs). Anal. Calcd for $C_{17}H_{34}B_9N$ (**V-1**): C, 58.38; H, 9.80; N, 4.00. Found: C, 58.65; H, 9.55; N, 4.25.

Preparation of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NMe_2)(NHMe_2)$ (IV-2). To a DME (10 mL) solution of $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**IV-1**; 0.20 g, 0.57 mmol) was slowly added a DME (5 mL) solution of $Zr(NMe_2)_4$ (0.16 g, 0.60 mmol) at room temperature, and the reaction mixture was stirred overnight to give a brown solution. After removal of the solvent under vacuum, the residue was extracted with DME (2 x 5 mL). The combined solutions were concentrated to *ca.* 5 mL. Complex **IV-2** was isolated as yellow crystals after this solution stood at room temperature for 5 days (0.14 g, 54%). ^1H NMR (pyridine-d_5): δ 7.71 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 3.3 Hz, 1H), 6.89 (d, J = 3.3 Hz, 1H), 6.56 (t, J = 8.2 Hz, 1H), 6.26 (t, J = 8.2 Hz, 1H) (C_9H_6), 3.22 (s, 6H) ($(CH_3)_2N$), 2.32 (s , 6H) ($(CH_3)_2NH$), 1.98 (s, 3H), 1.76 (s, 3H) ($(CH_3)_2C$), 1.46 (s, 1H) (C*H* of $C_2B_9H_{10}$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 127.7, 126.2, 125.0, 124.7, 124.6, 122.0, 113.4, 111.8 (C_9H_6), 68.2 ($C_2B_9H_{10}$), 39.8, 38.2 ($(CH_3)_2NH$ + $(CH_3)_2N$), 48.0, 29.5, 28.5 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 0.9 (1B), -5.3 (2B), -8.6 (3B), -12.7 (2B), -21.5 (1B) (Note that the integral 2 or 3 boron resonances are due to coincidence.). IR (KBr, cm^{-1}): ν_{BH} 2524 (vs). Anal. Calcd for $C_{18}H_{35}B_9N_2Zr$ (**IV-2**): C, 46.20; H, 7.54; N, 5.99. Found: C, 45.91; H, 7.46; N, 6.01.

Preparation of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][$Na(DME)_3$] (IV-3a). To a THF (40 mL) solution of $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**IV-1**; 0.64 g, 1.83 mmol)

was added NaH (0.32 g, 13.3 mmol), and the reaction mixture was heated to reflux for 2 days. The excess NaH was filtered off and washed with THF (3 mL). The resulting solution $[Me_2C(C_9H_6)(C_2B_9H_{10})]Na_3(THF)_x$ was slowly added to a suspension of $ZrCl_4(THF)_2$ (0.69 g, 1.82 mmol) in THF (10 mL) at -78°C, and the mixture was slowly warmed to room temperature and stirred for 2 days. After removal of the precipitate, the solvent was evaporated under vacuum leaving an oily residue which was extracted with DME (2 x 10 mL). The DME solutions were combined and concentrated to *ca.* 8 mL, to which was added hexane (10 mL). Complex **IV-3a** was isolated as a pale-yellow crystalline solid after this solution stood at room temperature for 3 days (0.89 g, 60%). ^{1}H NMR (pyridine-d_5): δ 7.71 (d, J = 8.2 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.34 (m, 1H), 6.90 (m, 1H), 6.75 (s, 1H), 6.66 (s, 1H) (C_9H_6), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 1.80 (s, 1H) (C*H* of $C_2B_9H_{10}$), 1.85 (s, 3H), 1.74 (s, 3H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 130.4, 126.6, 125.6, 125.0, 124.4, 120.2, 113.8, 110.9 107.1 (C_9H_6), 71.4, 57.9 (DME), 66.3, 52.1 ($C_2B_9H_{10}$), 40.5, 30.0, 29.1 ($(CH_3)_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.7 (1B), -2.1 (1B), -5.7 (3B), -11.3 (3B), -18.8 (1B). IR (KBr, cm^{-1}): ν_{BH} 2530 (vs). Anal. Calcd for $C_{26}H_{52}B_9Cl_2NaO_6Zr$ **(V-3a)**: C, 42.02; H, 7.05. Found: C, 42.00; H, 7.21.

Preparation of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$HfCl_2$][Na(DME)$_3$] (IV-3b). This compound was prepared as a pale-yellow solid from $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**IV-1**; 0.63 g, 1.81 mmol), NaH (0.32 g, 13.3 mmol) and $HfCl_4(THF)_2$ (0.84 g, 1.81 mmol) in THF (50 mL) using the same procedure reported for **IV-3a**: yield 0.81 g (54%). ^{1}H NMR (pyridine-d_5): δ 7.96 (d, J = 8.3 Hz, 1H), 7.69 (m, 1H), 7.37 (m, 1H), 7.07 (m, 1H), 6.83 (d, J = 3.6 Hz, 1H), 6.73 (d, J = 3.6 Hz, 1H) (C_9H_6), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 1.80

(s, 1H) (C*H* of $C_2B_9H_{10}$), 1.83 (s, 3H), 1.71 (s, 3H) ((CH_3)$_2$C). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 129.4, 125.5, 125.2, 124.8, 124.7, 118.3, 112.2, 109.1, 106.5 (C_9H_6), 71.4, 58.0 (DME), 66.7, 50.2 ($C_2B_9H_{10}$), 40.1, 30.2, 28.5 ((CH_3)$_2$*C*). $^{11}B\{^1H\}$NMR (pyridine-d_5): δ 3.1 (1B), -3.0 (1B), -5.8 (3B), -13.2 (3B), -20.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). Anal. Calcd for $C_{26}H_{52}B_9Cl_2NaO_6Hf$ **(IV-3b)**: C, 37.61; H, 6.31. Found: C, 37.32; H, 6.16.

Preparation of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}ZrCl($CH_2C_6H_5$)][Na(DME)$_3$] (IV-4a). To a THF (15 mL) solution of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][Na(DME)$_3$] (**IV-3a**; 0.50 g, 0.86 mmol) was added a THF (10 mL) solution of $KCH_2C_6H_5$ (0.11 g, 0.86 mmol) at -78°C, and the reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was evaporated under vacuum and the residue was extracted with DME (5 mL x 3). The DME solutions were combined and concentrated to *ca.* 5 mL. Complex **IV-4a** was isolated as orange crystals after this solution stood at -30°C for 4 days (0.20 g, 29%). ^1H NMR (pyridine-d_5): δ 7.74 (d, J = 8.2 Hz, 1H), 7.49 (m, 2H), 7.39 (m, 2H), 7.23 - 6.80 (m, 4H), 6.71 (d, J = 3.6 Hz, 1H), 5.27 (d, J = 3.6 Hz, 1H) ($CH_2C_6H_5$ + C_9H_6), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 2.60 (s, 2H) (CH_2C$_6$H$_5$), 2.20 (s, 1H) (C*H* of $C_2B_9H_{10}$), 1.81 (s, 3H), 1.12 (s, 3H) ((CH_3)$_2$C). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 154.8, 130.3, 129.3, 127.0, 126.5, 126.0, 125.6, 124.6, 123.9, 122.1, 121.3, 115.8, 112.4, 104.6 ($CH_2C_6H_5$ + C_9H_6), 71.1, 58.8 (DME), 70.3 (*C*H$_2$C$_6$H$_5$), 65.3, 52.0 ($C_2B_9H_{10}$), 40.7, 29.7, 29.4 ((CH_3)$_2$*C*). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 0.9 (1B), -0.8 (1B), -2.7 (1B), -5.5 (1B), -7.0 (2B), -11.3 (1B), -13.3 (1B), -20.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2533 (vs). Anal. Calcd for $C_{27}H_{44}B_9ClNaO_3Zr$ (**IV-4a** - 1.5 DME): C, 48.87; H, 6.68. Found: C, 48.97; H, 7.06.

Preparation of *trans*-[{η^1:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl(\eta^5$-$C_5H_5)$][$Na(DME)_3$] (IV-4b). To a DME (10 mL) solution of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][$Na(DME)_3$] (**IV-3a**; 0.25 g, 0.34 mmol) was slowly added a DME (5 mL) solution of C_5H_5Na (0.03 g, 0.34 mmol) at -20°C, and the reaction mixture was stirred at room temperature for 2 days. After removal of the precipitate, the DME solution was concentrated to *ca.* 6 mL under vacuum, to which was added toluene (1 mL). Complex **IV-4b** was isolated as red crystals after this solution stood at room temperature for 3 days (0.14 g, 53%). ^{1}H NMR (pyridine-d_5): δ 8.38 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.38 (m, 2H), 6.98 (m, 1H), 6.35 (m, 1H) (C_9H_6), 6.08 (s, 5H) (C_5H_5), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 2.61 (s, 1H) (C*H* of $C_2B_9H_{10}$), 1.85 (s, 3H), 1.71 (s, 3H) ((CH_3)$_2$C). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 153.8, 144.8, 127.7, 125.3, 123.7, 120.3, 119.9, 119.6, 119.4 (C_9H_6), 115.4 (C_5H_5), 84.2 ($C_2B_9H_{10}$), 71.3, 57.9 (DME), 36.7, 31.1, 28.2 ((CH_3)$_2$*C*). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 3.8 (1B), -3.6 (1B), -4.9 (1B), -6.4 (2B), -10.6 (1B), -12.4 (1B), -16.2 (2B). IR (KBr, cm^{-1}): ν_{BH} 2520 (s). Anal. Calcd for $C_{31}H_{57}B_9ClNaO_6Zr$ (**IV-4b**): C, 48.18; H, 7.43. Found: C, 48.01; H, 7.45.

Preparation of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NHC_6H_3Me_2$-2,6)(THF) (IV-4c). To a THF (20 mL) solution of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][$Na(DME)_3$] (**IV-3a**; 0.71 g, 0.96 mmol) was slowly added a THF (5 mL) solution of $NaNHC_6H_3Me_2$-2,6 (0.14 g, 0.96 mmol) at -78°C, and the reaction mixture was stirred at room temperature for 2 days. After removal of the solvent, the residue was extracted with toluene (15 mL x 3). The toluene solutions were combined and concentrated to *ca.* 10 mL. Complex **IV-4c** was isolated as yellow crystals

after this solution stood at room temperature for 3 days (0.32 g, 54%). X-ray quality crystals were grown from a benzene solution. ^{1}H NMR (pyridine-d_5): δ 9.38 (s, 1H) (N*H*), 7.86 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 6.96 (m, 1H), 6.91 (m, 1H), 6.86 - 6.75 (m, 2H) (C_9H_6), 7.04 (d, J = 7.5 Hz, 2H), 6.41 (m, 1H) ($NHC_6H_3(CH_3)_2$)), 3.64 (m, 4H), 1.59 (m, 4H) (THF), 2.31 (s, 6H) ($NHC_6H_3(CH_3)_2$), 1.99 (s, 3H), 1.70 (s, 3H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 154.0, 129.8, 127.7, 126.5, 125.3, 124.7, 123.8, 121.9, 120.8, 118.9, 114.7, 111.8, 110.3, 108.9 (aromatic *C*), 67.1, 25.1 (THF), 51.1 ($C_2B_9H_{10}$), 40.7, 29.0, 28.9 ($(CH_3)_2C$), 20.1, 17.3 ($NHC_6H_3(CH_3)_2$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.5 (1B), -3.3 (1B), -4.6 (1B), -6.7 (2B), -11.5 (3B), -18.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2524 (s). Anal. Calcd for $C_{24}H_{36}B_9NO_{0.5}Zr$ (**IV-4c** — 0.5THF): C, 53.87; H, 6.78; N, 2.62. Found: C, 53.55; H, 6.66; N, 2.36.

Preparation of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($OCH_2CH_2CH_2CH_3$)(THF) (IV-4d). To a THF solution (15 mL) of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][Na(DME)$_3$] (**IV-3a**; 0.37 g, 0.5 mmol) was added NaH (48 mg, 2.0 mmol), and the mixture was refluxed for 2 days. After removal of excess NaH, the clear solution was evaporated to dryness. The residue was extracted with toluene (8 mL x 3). The toluene solutions were combined and concentrated to *ca.* 15 mL. Complex **IV-4d** was isolated as pale-yellow crystals after this solution stood at room temperature for 5 days (0.09 g, 33%). X-ray quality crystals were grown from a benzene solution. ^{1}H NMR (pyridine-d_5): δ 8.37 (d, J = 7.8 Hz, 1H), 7.97 (m, 1H), 6.90 (s, 2H), 6.66 (m, 1H), 6.35 (m, 1H) (C_9H_6), 3.64 (m, 4H) (THF), 3.51 (t, J = 7.5 Hz, 2H) (OCH_2), 2.61 (s, 1H) (*CH* of $C_2B_9H_{10}$), 2.07 (s, 3H), 1.78 (s, 3H) ($(CH_3)_2C$), 1.62 (m, 2H), 1.20 (m, 2H),

0.84 (t, J = 7.0 Hz, 3H) ($OCH_2CH_2CH_2CH_3$), 1.59 (m, 4H) (THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 130.0, 127.7, 127.1, 125.3, 124.7, 113.7, 111.0 106.9 (C_9H_6), 84.9, 50.3 ($C_2B_9H_{10}$), 74.1 ($OCH_2CH_2CH_2CH_3$), 37.0, 20.6, 17.0 ($OCH_2CH_2CH_2CH_3$), 67.2, 25.1 (THF), 41.1 ($(CH_3)_2C$), 30.2, 28.6 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 2.0 (1B), -1.9 (1B), -6.7 (3B), -10.0 (1B), -12.9 (1B), -15.0 (1B), -20.0 (1). IR (KBr, cm^{-1}): ν_{BH} 2539 (vs). Anal. Calcd for $C_{22}H_{39}B_9O_2Zr$ (**IV-4d**): C, 50.42; H, 7.50. Found: C, 50.23; H, 7.39.

Preparation of $[H_2C(C_5Me_4)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ (V-1). To a toluene/Et_2O (2/1) solution (45 mL) of *o*-$C_2B_{10}H_{12}$ (3.20 g, 22.2 mmol) was added an ^{n}BuLi solution in hexane (1.60 M, 27.8 mL, 44.4 mmol) at -78 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The resulting $Li_2C_2B_{10}H_{10}$ solution was then cooled to -78 °C, to which was slowly added a toluene/Et_2O (2:1) solution (30 mL) of 1,2,3,4-tetramethylpentafulvene (3.64 g, 27.1 mmol). The orange mixture was stirred at room temperature for 3 h, and then at 60 °C overnight to give a white suspension. Compound **V-1** was obtained as a white solid after filtration (8.82 g, 91%). ^1H NMR (pyridine-d_5): δ 3.91 (s, 2H) (CH_2), 3.35 (q, J = 6.9 Hz, 8H) ($O(CH_2CH_3)_2$), 2.47 (s, 6H), 2.25 (s, 6H) ($C_5(CH_3)_4$), 1.12 (t, J = 6.9 Hz, 12H) ($O(CH_2CH_3)_2$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 108.6, 108.1, 107.0, 106.5, 106.1 ($C_5(CH_3)_4$), 65.1 ($O(CH_2CH_3)_2$), 36.6 (CH_2), 14.9 ($O(CH_2CH_3)_2$), 12.8, 12.2, 11.4, 11.1 ($C_5(CH_3)_4$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ -3.6 (1B), -4.9 (4B), -7.1 (2B), -8.5 (2B), -9.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2569 (vs). Anal. Calcd for $C_{20}H_{44}B_{10}Li_2O_2$ (**V-1**): C, 54.78; H, 10.11. Found: C, 54.45; H, 10.32.

Preparation of $H_2C(C_5Me_4H)(C_2B_{10}H_{11})$ (V-2). To a diethyl ether suspension (100 mL) of **V-1** (8.82 g, 20.1 mmol) was added a cooled saturated NH_4Cl solution (50 mL) with

stirring. The organic layer was separated, and the aqueous solution was extracted with Et_2O (3 x 20 mL). The combined organic solutions were washed with saturated $NaHCO_3$ aqueous solution (30 mL) and brine (30 mL), and then dried with anhydrous $MgSO_4$. Removal of the solvent gave **V-2** as a white solid (5.40 g, 97%). ^{1}H NMR ($CDCl_3$): δ 3.42 (br s, 1H) (cage C*H*), 3.16 - 2.98 (m, 2H) (CH_2), 2.55 (m, 1H) ($C_5H(CH_3)_4$), 1.86 - 1.80 (m, 9H), 1.05 - 0.94 (m, 3H) ($C_5H(CH_3)_4$) (a mixture of isomers). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.5, 142.3, 141.8, 138.5, 138.9, 134.6, 133.8, 129.0, 128.2 ($C_5H(CH_3)_4$)), 75.3, 59.5 (cage *C*), 51.9, 49.9, 34.8, 33.9, 33.5, 14.2, 12.8, 12.3, 11.8, 11.2, 10.9 ($CH_2C_5H(CH_3)_4$). ^{11}B{^{1}H} NMR ($CDCl_3$): δ -3.8 (1B), -7.1 (1B), -10.8 (2B), -12.0 (2B), -13.5 (2B), -14.4 (2B). IR (KBr, cm^{-1}): ν_{BH} 2586 (vs). EI-MS m/z (abundance): 278 (M^+) (58%), 264 (M^+-CH_3) (50%), 136 ($C_5HMe_5^+$) (100%). Anal. Calcd for $C_{12}H_{26}B_{10}$(**V-2**): C, 51.76; H, 9.41. Found: C, 51.41; H, 9.69.

Preparation of [$H_2C(C_5Me_4H)(C_2B_9H_{11})$][$Me_3NH$] (V-3) To an ethanol (20 mL) solution of [$H_2C(C_5Me_4H)(C_2B_{10}H_{11})$] (**V-2**; 0.28 g, 1.0 mmol) was added piperidine (2.5 mL, 25.0 mmol). The mixture was heated to reflux for 2 days until the ^{11}B NMR spectrum of the reaction solution showed a complete conversion. Removal of the solvent and piperidine under vacuum gave a residue which was re-dissolved in ethanol (5 mL). Addition of a saturated Me_3NHCl solution produced a sticky solid. It was washed with water, and recrystallized from ethanol to afford **V-3** as a yellow solid (0.26 g, 79%). ^{1}H NMR ($CDCl_3$): δ 3.13 (s, 9H) ($NH(CH_3)_3$), 3.18 (m, 2H) (CH_2), 2.05 (m, 1H) (C_5HMe_4), 1.83 - 1.67 (m, 12H) ($C_5(CH_3)_4$), -2.52 (br s, 1H) (B-*H*-B) (a mixture of isomers). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.3, 138.5, 138.8, 136.9, 136.4, 131.9, 131.6 (C_5Me_4), 63.7 (cage *C*), 48.2, 47.8, 45.6, 43.4, 33.7, 13.5, 13.1, 12.5, 10.2, 9.4, 8.8 ($N(CH_3)_3$ + CH_2 + $C_5H(CH_3)_4$). ^{11}B{^{1}H} NMR

($CDCl_3$): δ -9.9 (1B), -10.9 (1B), -14.0 (1B), -16.9 (1B), -18.3 (1B), -19.1 (1B), -22.3 (1B), -33.4 (1B), -36.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2508 (vs). Anal. Calcd for $C_{15}H_{36}B_9N$ (**V-3**): C, 54.97; H, 11.07; N, 4.27. Found: C, 54.68; H, 11.23; N, 4.31.

Preparation of [η^5:η^5-$H_2C(C_5Me_4)(C_2B_9H_{10})$]Zr($NMe_2$)($NHMe_2$) (V-4). To a DME (10 mL) solution of [$H_2C(C_5Me_4H)(C_2B_9H_{11})$][$Me_3NH$] (**V-3**; 0.25 g, 0.77 mmol) was added $Zr(NMe_2)_4$ (0.21 g, 0.77 mmol), and the reaction mixture was stirred at room temperature for 1 h. After filtration, the clear brownish filtrate was concentrated to *ca.* 6 mL. Complex **V-4** was isolated as yellow crystals after this solution stood at room temperature for 5 days (0.18 g, 53%). ^{1}H NMR (pyridine-d_5): δ 3.39 (d, J = 14.1 Hz, 1H), 3.19 (d, J = 14.1 Hz, 1H) (CH_2), 3.22 (s, 6H) ((CH_3)$_2$N-Zr), 2.32 (d, J = 6.0 Hz, 6H) ((CH_3)$_2$NH), 2.21 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H) ($C_5(CH_3)_4$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 132.0, 131.1, 122.6, 115.2, 108.5 ($C_5(CH_3)_4$), 78.3, 55.9, (cage *C*), 40.1, 38.2 ((CH_3)$_2$NH + (CH_3)$_2$N), 35.2 (CH_2), 14.6, 12.3, 12.2, 11.5 ($C_5(CH_3)_4$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 2.0 (1B), -3.2 (1B), -5.8 (1B), -7.3 (2B), -12.1 (1B), -15.3 (2B), 20.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2562 (vs). Anal. Calcd for $C_{16}H_{37}B_9N_2Zr$ (**V-4**): C, 43.09; H, 8.36; N, 6.28. Found: C, 43.43; H, 8.00; N, 6.04.

Preparation of [η^5:η^5-$H_2C(C_5Me_4)(C_2B_9H_{10})$]Zr($OCH_2CH_2CH_2CH_2$)$_2$N($CH_3$)$_2$·THF (V-5·THF). To a DME (10 mL) solution of [$H_2C(C_5Me_4H)(C_2B_9H_{11})$][$Me_3NH$] (**V-3**; 0.20 g, 0.61 mmol) was added $Zr(NMe_2)_4$ (0.16 g, 0.61 mmol), and the reaction mixture was stirred at room temperature for 1 h. Removal of the solvent gave a yellow solid which was dissolved in hot THF (20 mL). Slow evaporation at room temperature afforded **V-5**·THF as colorless

crystals (0.18 g, 48%). ^{1}H NMR (pyridine-d_5): δ 4.55 (m, 2H), 4.39 (m, 2H) (OCH_2), 3.61 (m, 4H) (THF), 3.60-3.45 (m, 4H) (CH_2N), 3.39 (d, J = 14.1 Hz, 1H), 3.19 (d, J = 14.1 Hz, 1H) (bridging CH_2), 3.15 (s, 3H), 3.01 (s, 3H) (N(CH_3)$_2$), 2.46 (br s, 1H) (cage CH), 2.30-2.12 (m, 4H) (OCH$_2$CH_2CH$_2$CH$_2$N), 2.21 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H) (C$_5$(CH_3)$_4$), 1.78-1.67 (m, 2H), 1.50 (m, 2H) (OCH$_2$CH$_2$CH_2CH$_2$N), 1.59 (m, 4H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.4, 121.6, 112.8, 112.2, 108.4 (*C*$_5$(CH$_3$)$_4$), 67.1, 25.1 (THF), 66.9, 66.7 (O*C*H$_2$CH$_2$CH$_2$CH$_2$N), 62.2, 61.1 (OCH$_2$CH$_2$CH$_2$*C*H$_2$N), 59.0, 45.6 (cage *C*), 51.7, 51.4 (N(*C*H$_3$)$_2$), 32.8 (*C*H$_2$), 30.5, 29.0 (OCH$_2$*C*H$_2$CH$_2$CH$_2$N), 17.6, 17.0 (OCH$_2$CH$_2$*C*H$_2$CH$_2$N), 12.8, 11.7, 10.6, 10.5 (C$_5$(*C*H$_3$)$_4$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -3.9 (1B), -6.1 (1B), -11.5 (4B), -15.3 (2B), -25.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). Anal. Calcd for $C_{26}H_{54}B_9NO_3Zr$ (**V-5** + THF): C, 50.59; H, 8.82; N, 2.27. Found: C, 50.19; H, 8.61; N, 2.24.

Preparation of [η^5:η^5-H$_2$C(C$_5$Me$_4$)(C$_2$B$_9$H$_{10}$)]Zr(μ-Cl)$_2$Li(THF)$_2$ (V-6a). To a THF (15 mL) solution of [H$_2$C(C$_5$Me$_4$H)(C$_2$B$_9$H$_{11}$)][Me$_3$NH] (**V-3**; 0.62 g, 1.90 mmol) was added a hexane solution of ^{n}BuLi (1.60 M, 3.6 mL, 5.80 mmol) at -78°C. The mixture was allowed to slowly warm to room temperature, and stirred overnight. The resulting clear yellow solution was added to a THF suspension (15 mL) of ZrCl$_4$(THF)$_2$ (0.72 g, 1.90 mmol) at -78°C, and the mixture was stirred at room temperature for two days. Removal of the solvent under vacuum gave a brown residue which was extracted with toluene (20 mL x 3). The combined toluene solutions were concentrated to *ca.* 10 mL. Complex **V-6a** was isolated as colorless crystals after this solution stood at room temperature for 3 days (0.58 g, 53%). ^{1}H NMR (benzene-d_6): δ 3.52 (m, 8H) (THF), 3.46 (d, J = 14.7 Hz, 1H), 3.12 (d, J =

14.7 Hz, 1H) (CH_2), 2.48 (s, 1H) (cage C*H*), 2.04 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.42 (s, 3H) ($C_5(CH_3)_4$), 1.37 (m, 8H) (THF). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 134.1, 130.1, 122.1, 117.4, 106.5 ($C_5(CH_3)_4$), 78.1, 55.6 (cage *C*), 68.7, 25.3 (THF), 33.5 (CH_2), 14.9, 12.6, 12.1, 11.8 ($C_5(CH_3)_4$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 1.9 (1B), -2.5 (1B), -4.8 (2B), -7.9 (2B), -9.7 (1B), -12.7 (1B), -17.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2536 (vs). Anal. Calcd for $C_{20}H_{40}B_9Cl_2LiO_2Zr$ (**V-6a**): C, 41.50; H, 6.96. Found: C 41.79; H, 7.07.

Preparation of $[\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})]Hf(\mu\text{-}Cl)_2Li(THF)_2$ (V-6b). This compound was prepared as a pale-yellow solid from $[H_2C(C_5Me_4H)(C_2B_9H_{11})][Me_3NH]$ (**V-3**; 0.65 g, 1.98 mmol), a hexane solution of ^{n}BuLi (1.60 M, 3.75 mL, 6.00 mmol) and $HfCl_4(THF)_2$ (0.92 g, 1.98 mmol) in THF (40 mL), using the same procedure reported for **V-6a**: yield 0.55 g (42%). ^1H NMR (benzene-d_6): δ 3.52 (m, 8H) (THF), 3.28 (d, J = 14.7 Hz, 1H), 3.12 (d, J = 14.7 Hz, 1H) (CH_2), 2.49 (s, 1H) (cage C*H*), 2.18 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H), 1.61 (s, 3H) ($C_5(CH_3)_4$), 1.41 (m, 8H) (THF). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 131.8, 118.0, 113.5, 107.4 ($C_5(CH_3)_4$), 68.5, 25.4 (THF), 53.1 (cage *C*), 33.0 (CH_2), 14.6, 12.5, 12.1, 11.8 ($C_5(CH_3)_4$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 0.7 (1B), -3.5 (1B), -5.6 (1B), -6.4 (1B), -8.4 (2B), -10.7 (1B), -13.4 (1B), -19.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2536 (vs). Anal. Calcd for $C_{20}H_{40}B_9Cl_2LiO_2Hf$ (**V-6b**): C, 36.06; H, 6.05. Found: C, 36.68; H, 6.16.

Preparation of $[\{\eta^5:\eta^5\text{-}H_2C(C_5Me_4)(C_2B_9H_{10})\}ZrCl_2][Li(DME)_2]$ (V-6c). To a THF solution (15 mL) of $[H_2C(C_5Me_4H)(C_2B_9H_{11})][Me_3NH]$ (**V-3**; 0.62 g, 1.90 mmol) was added a hexane solution of ^{n}BuLi (1.60 M, 3.6 mL, 5.80 mmol) at −78°C. The mixture was allowed to slowly warm to room temperature, and stirred overnight. The resulting clear yellow solution was added to a THF suspension (15 mL) of $ZrCl_4(THF)_2$ (0.72 g, 1.90

mmol) at −78°C, and the mixture was stirred at room temperature for two days. Removal of the solvent under vacuum gave a brown residue which was extracted with toluene (15 mL × 3). The combined toluene solution was concentrated to dryness to afford a pale-yellow residue which was dissolved in DME (5 mL). After filtration, the filtrate was diffused with hexane to give **V-6c** as colorless crystals (0.53 g, 45%). ^{1}H NMR (benzene-d_6): δ 3.43 (d, J = 14.4 Hz, 1H), 3.06 (d, J = 14.4 Hz, 1H) (CH_2), 3.09 (s, 8H), 2.98 (s, 12H) (DME), 2.48 (s, 1H) (cage C*H*), 2.15 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.54 (s, 3H) ($C_5(CH_3)_4$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 133.3, 129.6, 120.9, 116.6, 106.7 ($C_5(CH_3)_4$), 70.4, 59.3 (DME), 65.9, 54.0 (cage *C*), 33.5 (CH_2), 15.1, 12.8, 12.4, 12.1 ($C_5(CH_3)_4$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.3 (1B), -2.9 (1B), -5.4 (2B), -8.6 (2B), -10.1 (1B), -12.7 (1B), -18.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2540 (vs). Anal. Calcd for $C_{20}H_{44}B_9Cl_2LiO_4Zr$ (**V-6c**): C, 39.06; H, 7.21. Found: C, 38.73; H, 6.94.

Preparation of {[η^5:η^5-H$_2$C(C$_5$Me$_4$)(C$_2$B$_9$H$_{10}$)]Zr(CH$_2$TMS)$_2$}{Li(THF)$_3$} (V-7a). To a THF solution (20 mL) of [η^5:η^5-$H_2C(C_5Me_4)(C_2B_9H_{10})$]Zr($\mu$-Cl)$_2$Li(THF)$_2$ (**V-6a**; 0.75 g, 1.30 mmol) was added a pentane solution of $LiCH_2SiMe_3$ (1.0 M, 1.3 mL, 1.30 mmol) at –78°C with stirring. The reaction mixture was allowed to slowly warm to room temperature, and stirred overnight. Removal of the solvent under vacuum afforded a residue which was extracted with toluene (10 mL x 3). The combined toluene solution was filtered, and the filtrate was concentrated to *ca.* 5 mL. Complex **V-7a** was isolated as yellow crystals after this solution stood at room temperature for 3 days (0.35 g, 36%). ^{1}H NMR (benzene-d_6): δ 3.53 (m, 12H) (THF), 2.95 (d, J = 14.7 Hz, 1H), 2.63 (d, J = 14.7 Hz, 1H) (CH_2), 2.14 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.69 (s, 3H) ($C_5(CH_3)_4$), 1.38 (m, 12H)

(THF), 0.81 (d, J = 11.0 Hz, 1H), 0.67 (d, J = 11.0 Hz, 1H), 0.63 (d, J = 11.0 Hz, 1H), 0.57 (d, J = 11.0 Hz, 1H) (CH_2TMS), 0.38 (s, 9H), 0.36 (s, 9H) (Si(CH_3)$_3$). $^{13}C\{^1H\}$ (benzene-d_6): δ 124.2, 122.9, 116.8, 113.4, 103.9 (C_5Me_4), 68.8, 26.1 (THF), 61.9 (Zr-CH_2TMS), 49.0 (cage C), 33.3 (CH_2), 14.1, 12.8, 12.5, 12.4 ($C_5(CH_3)_4$), 4.2, 3.8, 1.5 ($CH_2Si(CH_3)_3$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 0.1 (1B), -6.2 (1B), -10.1 (2B), -13.7 (2B), -15.9 (1B), -18.9 (1B), -22.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2542 (vs). Anal. Calcd for $C_{32}H_{70}B_9LiO_3Si_2Zr$ (**V-7a**): C, 50.89; H, 9.28. Found: C, 50.78; H, 9.24.

Preparation of [η^5:η^5-$H_2C(C_5Me_4)(C_2B_9H_{10})$]Zr[$\sigma$:$\eta^1$-$CH_2(NMe_2)$-$o$-$C_6H_4$](THF) (V-7b·THF). To a THF solution (10 mL) of [η^5:η^5-$H_2C(C_5Me_4)(C_2B_9H_{10})$]Zr($\mu$-Cl)$_2$Li(THF)$_2$ (**V-6a**; 0.29 g, 0.50 mmol) was added a THF solution (5 mL) of $KCH_2(NMe_2)$-o-C_6H_4 (0.09 g, 0.50 mmol) at -78°C with stirring. The reaction mixture was allowed to warm to room temperature, and stirred overnight. After filtration, the orange filtrate was concentrated to *ca.* 5 mL. Complex **V-7b**·THF was isolated as orange crystals after this solution stood at room temperature for 3 days (0.16 g, 57%). ^1H NMR (pyridine-d_5): δ 7.26 (m, 2H), 7.02 (m, 2H) (C_6H_4), 3.65 (m, 4H) (THF), 3.52 (d, J = 14.4 Hz, 1H), 3.43 (d, J = 14.4 Hz, 1H) (bridging CH_2), 2.57 (br s, 2H) (ZrCH_2), 2.54 (s, 6H) (N(CH_3)$_2$), 2.29 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H), 1.59 (s, 3H) ($C_5(CH_3)_4$), 1.45 (m, 4H) (THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 152.6, 137.4, 130.8, 128.7, 128.0, 126.2, 125.1, 122.3, 118.2 (aromatic CH + C_5Me_4), 72.5 (Zr-CH_2), 67.2, 22.2 (THF), 65.1 (cage C), 48.6 (N(CH_3)$_2$), 33.8 (CH_2), 15.0, 12.7, 12.4, 11.9 ($C_5(CH_3)_4$) $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 1.7 (1B), -4.0 (1B), -6.6 (2B), -9.0 (2B), -11.4 (1B), -16.4 (1B), -22.0 (1B).

IR (KBr, cm^{-1}): ν_{BH} 2577 (vs). Anal. Calcd for $C_{23}H_{40}B_9NO_{0.5}Zr$ (**V-7b** + 0.5 THF): C, 52.41; H, 7.65; N, 2.66. Found: C, 52.23; H, 7.95; N, 2.65.

Ethylene Polymerization. This experiment was carried out in a 150 mL glass reactor equipped with a magnetic stirrer and gas inlets. The reactor was charged with the catalyst together with MAO and toluene (50 mL). The mixture was stirred at room temperature for 0.5 h. Ethylene gas was then introduced to the reactor, and its pressure was maintained continuously at 1 atm by means of bubbling. The polymerization was terminated by addition of acidic ethanol (100 mL). The white precipitate was filtered off and washed with ethanol and acetone. The resulting powder was finally dried in a vacumm oven at 80°C overnight.

Preparation of (η^5-Cp'')[η^1:σ:η^5-{MeN(CH$_2$)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (VI-1). To a Et_2O (25 mL) suspension of Cp''$ZrCl_3$ (2.04 g, 5.0 mmol) was added a Et_2O solution of MeLi (1.4 M, 10.7 mL, 15.0 mmol) at -78 °C with stirring. The reaction mixture was allowed to slowly warm to -20 °C, and stirred for 2 h. Removal of the solvent under vacuum gave a pale-yellow residue which was extracted with hexane (50 mL). After filtration, the filtrate was concentrated to dryness to afford Cp''$ZrMe_3$ as a yellow crystalline solid (1.21 g, 3.5 mmol). The white solid 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (0.72 g, 3.5 mmol) was added into the toluene solution (15 mL) of Cp''$ZrMe_3$ (1.21 g, 3.5 mmol) in portions at -30 °C with stirring. The orange suspension was allowed to warm to room temperature, and stirred overnight. After filtration, the organe filtrate was concentrated to *ca.* 10 mL. Complex **VI-1** was isolated as orange crystals after this solution stood at room temperature for 2 days (1.41 g, 56%). ^{1}H NMR (benzene-d_6): δ 7.68 (m, 1H), 7.11 (m, 1H), 6.28 (m, 1H)

($C_5H_3(Si(CH_3)_3)_2$), 3.15 (br s, 1H) (cage C*H*), 2.21 (m, 2H) (CH_2CH_2NMe), 2.08 (s, 3H) (NCH_3), 2.01 (m, 2H) (CH_2CH_2NMe), 2.21 (d, J = 6.0 Hz, 1H), 2.19 (d, J = 6.0 Hz, 1H) (Zr-CH_2), 0.28 (s, 9H), -0.04 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 132.4, 131.5, 130.7, 129.7, 124.2 (C_5H_3), 73.2 (Zr-CH_2), 68.2 (CH_2CH_2NMe), 63.7 (cage *C*), 54.4 (NCH_3), 38.3 (CH_2CH_2NMe), 1.1, -0.2 ($Si(CH_3)_3$) $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 2.1 (1B), 0.9 (1B), -2.2 (2B), -4.9 (1B), -7.9 (2B), -13.9 (1B), -18.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{17}H_{40}B_9NSi_2Zr$ (**VI-1**): C, 40.58; H, 8.01; N, 2.78. Found: C, 40.73; H, 8.08; N, 2.81.

Preparation of (η^5-Cp'')[σ:η^1:η^5-{$(CH_3)[(CH_2)EtC=CEt]N(CH_2CH_2)C_2B_9H_{10}$}]Zr (VI-2a). To a toluene (5 mL) solution of (η^5-Cp'')[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) was added 3-hexyne (0.02 g, 0.20 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. After filtration, the orange filtrate was concentrated to *ca.* 2 mL. Complex **VI-2a** was isolated as orange crystals after this solution stood at room temperature for 3 days (0.09 g, 73%). ^1H NMR (benzene-d_6): δ 7.94 (m, 1H), 7.11 (m, 1H), 6.20 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 4.44 (br s, 1H) (cage C*H*), 3.10 (d, J = 15.0 Hz, 1H), 2.09 (d, J = 15.0 Hz, 1H) ($MeNCH_2CEt$), 3.00 (m, 2H) (CH_2CH_2NMe), 1.83 (q, J = 7.5 Hz, 2H), 1.76 (q, J = 7.5 Hz, 2H) (CH_2CH_3), 1.71 (m, 2H) (CH_2CH_2NMe), 1.45 (s, 3H) (NCH_3), 0.98 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 7.5 Hz, 3H) (CH_2CH_3), 0.25 (s, 9H), 0.23 (s, 9H) ($Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 193.1 (Zr-C_α), 138.4 (Zr-$C_\alpha C_\beta$), 137.8, 131.7, 130.9, 129.7, 121.6 ($C_5H_3(Si(CH_3)_3)_2$), 88.0, 86.2 (cage *C*), 67.8 ($MeNCH_2CEt$), 64.5 (CH_2CH_2NMe), 46.8 (NCH_3), 37.2 (CH_2CH_2NMe), 32.3, 30.4 (CH_2CH_3), 15.8, 13.3 (CH_2CH_3), 1.1, 1.0

($Si(CH_3)_3$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 2.4 (1B), 0.9 (1B), -1.6 (1B), -3.3 (2B), -5.2 (1B), -8.5 (1B), -12.5 (1B), -16.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{23}H_{50}B_9NSi_2Zr$ (**VI-2a**): C, 47.20; H, 8.61; N, 2.39. Found: C, 47.24; H, 8.36; N, 2.53.

Preparation of (Cp'')[σ:η^1:η^5-{$(CH_3)[(CH_2)^nPrC{=}C^nPr]N(CH_2CH_2)C_2B_9H_{10}$}]Zr (VI-2b). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and 4-octyne (0.02 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2a**: yield 0.09 g (73%). ^1H NMR (benzene-d_6): δ 7.96 (m, 1H), 7.24 (m, 1H), 6.33 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 4.40 (br s, 1H) (cage C*H*), 3.23 (d, J = 15.3 Hz, 1H), 2.15 (d, J = 15.3 Hz, 1H) ($MeNCH_2C^nPr$), 3.12 (m, 2H) (CH_2CH_2NMe), 2.36 (m, 2H) (CH_2CH_2NMe), 1.91 (m, 4H) ($CH_2CH_2CH_3$), 1.69 (m, 4H) ($CH_2CH_2CH_3$), 1.50 (s, 3H) (NCH_3), 0.94 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H) ($CH_2CH_2CH_3$), 0.28 (s, 9H), 0.24 (s, 9H) ($Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 192.1 (Zr-C_α), 153.8 (Zr-$C_\alpha C_\beta$), 137.7, 137.3, 131.2, 130.5, 121.1 ($C_5H_3(Si(CH_3)_3)_2$), 74.2 (cage *C*), 68.0 ($MeNCH_2C^nPr$), 64.1 (CH_2CH_2NMe), 46.3 (NCH_3), 40.2 (CH_2CH_2NMe), 36.8, 34.3 ($CH_2CH_2CH_3$), 25.7, 24.1 ($CH_2CH_2CH_3$), 15.4, 14.7 ($CH_2CH_2CH_3$), 0.8, 0.7 ($Si(CH_3)_3$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 2.8 (1B), 1.0 (1B), -1.6 (2B), -3.3 (1B), -5.7 (1B), -9.5 (1B), -12.3 (1B), -16.5 (1B). IR (KBr, cm^{-1}): ν_{BH} 2543 (vs). Anal. Calcd for $C_{25}H_{54}B_9NSi_2Zr$ (**VI-2b**): C, 48.95; H, 8.87; N, 2.28. Found: C, 48.51; H, 8.56; N, 2.35.

Preparation of (Cp'')[σ:η^1:η^5-{$(CH_3)[(CH_2)PhC{=}CPh]N(CH_2CH_2)C_2B_9H_{10}$}]Zr·$C_7H_8$ (VI-2c·C_7H_8). To a toluene (5 mL) solution of (η^5-Cp'')[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**;

0.10 g, 0.20 mmol) was added diphenylacetylene (0.04 g, 0.20 mmol) at room temperature. The reaction mixture was heated to 70 °C and stirred overnight. After filtration, the orange filtrate was concentrated to *ca.* 2 mL. **VI-2c**·C_7H_8 was collected as orange crystals after this solution stood at room temperature for 4 days (0.11 g, 70%). ^{1}H NMR (benzene-d_6): 8.21 (m, 1H), 7.54 (m, 1H), 6.61 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 7.00 (m, 5H), 6.92 (m, 3H), 6.78 (m, 2H) (C_6H_5), 4.67 (br s, 1H) (cage C*H*), 3.68 (d, J = 15.0 Hz, 1H), 2.62 (d, J = 15.0 Hz, 1H) (C(Ph)CH_2NMe), 3.38 (m, 2H) (CH_2CH_2NMe), 2.10 (s, 3H) (NCH_3), 1.63 (m, 2H) (CH_2CH_2NMe), 0.19 (s, 9H), 0.04 (s, 9H) (Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 194.5 (Zr-C_a), 149.7 (Zr-C_aC_β), 141.7, 140.2, 138.4, 131.7, 130.7, 129.4, 129.3, 127.7, 126.5, 125.6, 125.0, 122.6 (C_6H_5 + $C_5H_3(Si(CH_3)_3)_2$), 89.8 (cage *C*), 69.3 (C(Ph)CH_2NMe), 64.1 (CH_2CH_2NMe), 46.2 (NCH_3), 36.5 (CH_2CH_2NMe), 0.9, 0.6 (Si(CH_3)$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 5.2 (1B), -0.2 (2B), -1.6 (2B), -11.2 (2B), -14.1 (2B). IR (KBr, cm^{-1}): ν_{BH} 2544 (vs). Anal. Calcd for $C_{34.5}H_{54}B_9NSi_2Zr$ (**VI-2c** + 0.5 toluene): C, 56.96; H, 7.48; N, 1.93. Found: C, 57.16; H, 7.54; N, 2.26.

Preparation of (Cp'')[σ:η^1:η^5-{(CH$_3$)[(CH$_2$)PhC=CMe]N(CH$_2$CH$_2$)C$_2$B$_9$H$_{10}$}]Zr (VI-3a). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{MeN(CH$_2$)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and phenylmethylacetylene (0.023 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2c**: yield 0.10 g (81%). ^{1}H NMR (benzene-d_6): δ 7.89 (m, 1H), 7.19 (m, 1H), 6.26 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 7.25 (t, J = 7.6 Hz, 3H), 6.91 (d, J = 7.6 Hz, 2H) (C_6H_5), 3.98 (br s, 1H) (cage C*H*), 3.42 (d, J = 15.6 Hz, 1H), 2.44 (d, J = 15.6 Hz, 1H) (MeNCH_2C(Ph)), 3.18 (m, 2H) (CH_2CH_2NMe), 2.19 (m, 2H) (CH_2CH_2NMe), 1.75 (s, 3H)

(NCH_3), 1.47 (s, 3H) (ZrC(CH_3)), 0.28 (s, 9H), 0.22 (s, 9H) (Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 191.4 (Zr-C_α), 141.5 (Zr-$C_\alpha C_\beta$), 137.0, 136.5, 132.4, 130.5, 129.0, 128.8, 127.8, 127.2, 122.3 (C_6H_5 + C_5H_3(Si(CH$_3$)$_3$)$_2$), 69.7 (PhC*C*H$_2$NMe), 64.4, (CH$_2$*C*H$_2$NMe), 46.4 (N*C*H$_3$), 37.5 (*C*H$_2$CH$_2$NMe), 26.0 (ZrC(*C*H$_3$)), 0.9, 0.7 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.3 (1B), 0.1 (1B), -1.5 (2B), -3.3 (1B), -5.8 (1B), -9.9 (1B), -16.3 (2B). IR (KBr, cm^{-1}): ν_{BH} 2553 (vs). Anal. Calcd for: $C_{26}H_{48}B_9NSi_2Zr$ (**VI-3a**): C, 50.42; H, 7.81; N, 2.26. Found: C, 50.05; H, 7.29; N, 2.76.

Preparation of (Cp'')[σ:η^1:η^5-{(CH$_3$)[(CH$_2$)PhC=CTMS]N(CH$_2$CH$_2$)C$_2$B$_9$H$_{10}$}]Zr (VI-3b). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{MeN(CH$_2$)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and trimethylsilylphenylacetylene (0.023 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2c**: yield 0.10 g (76%). ^{1}H NMR (pyridine-d_5): δ 8.10 (m, 1H), 7.65 (m, 1H), 7.54(m, 1H) (C$_5H_3$(Si(CH$_3$)$_3$)$_2$), 7.37 (t, J = 6.0 Hz, 2H), 7.26 (m, 1H), 7.16 (t, J = 6.0 Hz, 2H) (C$_6H_5$), 4.56 (br s, 1H) (cage C*H*), 3.85 (m, 2H) (CH$_2$C*H*$_2$NMe), 4.58 (d, J = 15.0 Hz, 1H), 3.24 (d, J = 15.0 Hz, 1H) (PhCC*H*$_2$NMe), 2.45 (s, 3H) (NC*H*$_3$), 2.26 (m, 2H) (C*H*$_2$CH$_2$NMe), 0.45 (s, 9H), 0.34 (s, 9H) (C$_5$H$_3$(Si(C*H*$_3$)$_3$)$_2$), -0.03 (s, 9H) (Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 202.2 (Zr-C_α), 153.0 (Zr-$C_\alpha C_\beta$), 145.7, 137.0, 132.8, 130.0, 128.3, 127.6, 126.8, 126.3, 124.9 (C_6H_5 + C_5H_3(Si(CH$_3$)$_3$)$_2$), 70.8 (PhC*C*H$_2$NMe), 64.8 (CH$_2$*C*H$_2$NMe), 47.3 (N*C*H$_3$), 35.8 (*C*H$_2$CH$_2$NMe), 3.1 (Si(*C*H$_3$)$_3$), 0.3, -0.1 (C$_5$H$_3$(Si(*C*H$_3$)$_3$)$_2$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.9 (1B), -2.3 (2B), -4.0 (2B), -9.8 (1B), -11.6 (1B), -16.5 (2B). IR (KBr, cm^{-1}): ν_{BH} 2558 (vs). Anal. Calcd for $C_{28}H_{54}B_9NSi_3Zr$ (**VI-3b**): C, 49.64; H, 8.03; N, 2.07. Found: C, 49.63; H, 8.09; N, 1.79.

Preparation of (Cp'')[σ:η^1:η^5-{$(CH_3)[(CH_2)^nBuC{=}CTMS]N(CH_2CH_2)C_2B_9H_{10}$}]Zr (VI-3c). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and 1-trimethylsilyl-1-hexyne (0.03 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2c**: yield 0.11 g (81%). ^{1}H NMR (benzene-d_6): δ 7.34 (m, 1H), 7.20 (m, 1H), 6.45 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 4.08 (br s, 1H) (cage C*H*), 3.40 (d, J = 15.0 Hz, 1H), 2.35 (d, J = 15.0 Hz, 1H) (MeNCH_2C^{n}Bu), 2.49 (m, 2H) (CH_2CH_2NMe), 2.05 (t, J = 6.0 Hz, 2H) ($CH_2CH_2CH_2CH_3$), 1.82 (m, 2H) (CH_2CH_2NMe), 1.77 (s, 3H) (NCH_3), 1.31 – 1.27 (m, 4H) ($CH_2CH_2CH_2CH_3$), 0.96 (t, J = 9.0 Hz, 3H) ($CH_2CH_2CH_2CH_3$), 0.30 (s, 9H) ($Si(CH_3)_3$), 0.20 (s, 9H), 0.18 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 201.7 (Zr-C_α), 152.6 (Zr-$C_\alpha C_\beta$), 135.0, 133.2, 131.4, 128.9, 125.4 ($C_5H_3(Si(CH_3)_3)_2$), 68.9 (^{n}BuCCH_2NMe), 67.5 (CH_2CH_2NMe), 58.6 (cage *C*), 50.5 (NCH_3), 40.7 ($CH_2CH_2CH_2CH_3$), 37.9 (CH_2CH_2NMe), 30.8, 23.5, 14.2 ($CH_2CH_2CH_2CH_3$), 4.0, 1.0, 0.9 ($CSi(CH_3)_3$ + $C_5H_3(Si(CH_3)_3)_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 1.4 (1B), -2.1 (2B), -3.7 (1B), -7.4 (2B), -10.4 (1B), -15.2 (2B). IR (KBr, cm^{-1}): ν_{BH} 2548 (vs). Anal. Calcd for $C_{26}H_{58}B_9NSi_3Zr$ (**VI-3c**): C, 47.49; H, 8.89; N, 2.13. Found: C, 47.83; H, 9.11; N, 2.79.

Preparation of (η^5-Cp'')[σ:η^1:η^5-{$(CH_3)[(CH_2)PhC{=}CH]N(CH_2CH_2)C_2B_9H_{10}$}]Zr (VI-4a). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and phenylacetylene (0.02 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2a**: yield 0.09 g (75%). ^{1}H NMR (benzene-d_6): δ 7.88 (m, 1H), 7.47 (m, 1H), 6.11

(m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 7.22 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 5.1 Hz, 3H) (C_6H_5), 7.07 (s, 1H) (Zr-C*H*), 3.90 (br s, 1H) (cage C*H*), 3.45 (d, J = 15.0 Hz, 1H), 2.85 (d, J = 15.0 Hz, 1H) (MeNCH_2CPh), 2.56 (m, 2H) (CH_2CH_2NMe), 1.77 (m, 2H) (CH_2CH_2NMe), 1.53 (s, 3H) (NCH_3), 0.32 (s, 9H), 0.16 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 187.5 (Zr-C_α), 141.8 (Zr-$C_\alpha C_\beta$), 140.1, 135.3, 132.3, 131.0, 129.2, 127.8, 125.2, 123.4, 122.3 (C_6H_5 + $C_5H_3(Si(CH_3)_3)_2$), 68.6 ((Ph)CCH_2NMe), 65.9 ($CH_2CH_2NCH_3$), 59.3 (cage *C*), 47.9 (NCH_3), 38.3 (CH_2CH_2NMe), 1.1, 0.5 ($C_5H_3(Si(CH_3)_3)_2$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -0.2 (2B), -2.4 (2B), -6.3 (2B), -9.5(2B), -15.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2550 (vs). Anal. Calcd for $C_{25}H_{45}B_9NSi_2Zr$ (**VI-4a**): C, 49.69; H, 7.51; N, 2.32. Found: C, 49.15; H, 7.60; N, 2.46.

Preparation of (η^5-Cp'')[σ:η^1:η^5-{$(CH_3)[(CH_2)(CH_3(CH_2)_3)C$=$C(H)]N(CH_2CH_2)C_2B_9H_{10}$}]Zr (VI-4b). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and 1-hexyne (0.02 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2a**: yield 0.09 g (81%). ^{1}H NMR (benzene-d_6): δ 7.81 (m, 1H), 6.46 (m, 1H), 6.13 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 4.85 (s, 1H) (Zr-C*H*), 3.94 (br s, 1H) (cage C*H*), 3.07 (d, J = 13.5 Hz, 1H), 2.12 (d, J = 13.5 Hz, 1H) (MeNCH_2C^{n}Bu), 2.47 (m, 2H) (CH_2CH_2NMe), 2.28 (m, 2H) (CH_2CH_2NMe), 1.55 (s, 3H) (NCH_3), 1.31 - 0.99 (m, 6H) ((CH_2)$_3$CH$_3$), 0.97 (t, J = 6.9 Hz, 3H) ((CH$_2$)$_3$CH_3), 0.34 (s, 9H), 0.19 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 181.9 (Zr-C_α), 143.4 (Zr-$C_\alpha C_\beta$), 134.6, 131.9, 131.5, 125.8, 123.2 ($C_5H_3(TMS)_2$), 69.6 (^{n}BuCCH_2NMe), 66.3 (CH_2CH_2NMe), 48.6 (NCH_3), 45.3

($CH_2CH_2CH_2CH_3$), 38.7 (CH_2CH_2NMe), 30.4, 23.5 14.6 ($CH_2CH_2CH_2CH_3$), 1.2, 0.6 ($C_5H_3(Si(CH_3)_3)_2$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -0.4 (2B), -2.8 (2B), -6.7 (1B), -9.8 (1B), -11.5 (1B), -16.5 (2B). IR (KBr, cm^{-1}): ν_{BH} 2547 (vs). Anal. Calcd for $C_{23}H_{50}B_9NSi_2Zr$ (**VI-4b**): C, 47.20; H, 8.61; N, 2.39. Found: C, 47.05; H, 9.07 N, 2.99.

Preparation of (η^5-Cp'')[σ:η^1:η^5-{$(CH_3)[(CH_2)HC$=$CTMS]N(CH_2CH_2)C_2B_9H_{10}$}]Zr (VI-4c). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and trimethylsilylacetylene (0.02 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2a**: yield 0.09 g (78%). ^1H NMR (benzene-d_6): δ 7.63 (m, 1H), 6.86 (m, 1H), 6.71 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 6.43 (t, J = 3.0 Hz, 1H) ($CH_2CHCTMS$), 4.10 (br s, 1H) (cage CH), 3.05 (d, J = 15.0 Hz, 1H), 2.15 (d, J = 15.0 Hz, 1H) ($MeNCH_2CH$), 2.73 (m, 2H) (CH_2CH_2NMe), 1.60 (m, 2H) (CH_2CH_2NMe) 1.47 (s, 3H) (NCH_3), 0.34 (s, 9H), 0.21 (s, 9H) ($C_5H_3Si(CH_3)_3$), 0.12 (s, 9H) ($Si(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 211.7 (ZrC_α), 140.3 ($ZrC_\alpha C_\beta$), 137.1, 133.1, 132.2, 129.4, 129.2 ($C_5H_3(TMS)_2$), 66.9 ($HCCH_2NMe$), 64.5 (CH_2CH_2NMe), 51.9 (cage C), 46.9 (NCH_3), 36.8 (CH_2CH_2NMe), 1.2, 0.9 ($C_5H_3(Si(CH_3)_3)_2$), -0.8 ($Si(CH_3)_3$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 2.2 (1B), -2.7 (3B), -3.7 (1B), -6.5 (1B), -9.6 (1B), -13.4 (1B), -16.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2522 (vs). Anal. Calcd for $C_{22}H_{50}B_9NSi_3Zr$ (**VI-4c**): C, 43.94; H, 8.38; N, 2.33. Found: C, 43.80; H, 7.98; N, 1.95.

Preparation of (η^5-Cp'')[η^1:η^5-$Me_2NCH_2CH_2C_2B_9H_{10}$}]Zr(C≡C(^{t}Bu)) (VI-4d). This complex was prepared as orange crystals from

(η^5-Cp'')[η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and 3,3-dimethyl-1-butyne (0.02 g, 0.20 mmol) in toluene (10 mL), using the same procedure reported for **VI-2a**: yield 0.9 g (75%). ^{1}H NMR (benzene-d_6): δ 7.50 (m, 1H), 7.06 (m, 1H), 5.64 (m, 1H) (C_5H_3(Si(CH_3)$_3$)$_2$), 5.12 (br s, 1H) (cage C*H*), 3.31 (m, 2H) ($CH_2CH_2NMe_2$), 2.10 (s, 3H), 2.05 (s, 3H) (N(CH_3)$_2$), 1.85 (m, 2H) ($CH_2CH_2NMe_2$), 1.08 (s, 9H) (C(CH_3)$_3$), 0.38 (s, 9H), 0.34 (s, 9H) ($C_5H_3Si(CH_3)_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 131.9, 131.4, 129.6, 126.6, 126.0, 125.6 (C_5H_3(Si(CH_3)$_3$)$_2$ + ZrC_α), 90.2 (Zr$C_\alpha C_\beta$), 65.0 ($CH_2CH_2NMe_2$), 59.3 (cage *C*), 53.3, 47.7 (N(CH_3)$_2$), 36.7 (CH_2CH_2NMe), 32.3 ($C(CH_3)_3$), 31.2 (C(CH_3)$_3$), 1.3, 1.4 (C_5H_3(Si(CH_3)$_3$)$_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.2 (1B), -0.5 (1B), -1.9 (2B), -3.8 (1B), -6.4 (1B), -9.5 (1B), -12.6 (1B), -16.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2557 (vs). Anal. Calcd for $C_{26.5}H_{54}B_9NSi_2Zr$ (**VI-4d** + 0.5Toluene): C, 50.41; H, 8.62; N, 2.22. Found: C, 50.28; H, 8.14; N, 1.79.

Preparation of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (VII-1). To a Et_2O (25 mL) suspension of Cp^*ZrCl_3 (1.66 g, 5.0 mmol) was added a Et_2O solution of MeLi (1.40 M, 10.7 mL, 15.0 mmol) at -78 °C with stirring. The reaction mixture was allowed to slowly warm to -20 °C, and stirred for 2 h. Removal of the solvent under vacuum gave a pale-yellow residue which was extracted with hexane (50 mL). After filtration, the filtrate was concentrated to driness to afford Cp^*ZrMe_3 as a pale-yellow crystalline solid (1.09 g, 4.0 mmol). The white solid 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (0.81 g, 4.0 mmol) was added into the THF solution (20 mL) of Cp^*ZrMe_3 (1.09 g, 4.0 mmol) at -30 °C with stirring. The yellow suspension was allowed to warm to room temperature, and stirred overnight to give a yellow suspension. The ^{11}B NMR spectrum showed complete conversion of the ligand.

After filtration, the yellow filtrate was concentrated to *ca.* 10 mL, and 5 mL toluene was added. Pale-yellow crystals suitable for X-ray analyses were collected after this solution stood at room temperature for 3 days. Complex **VII-1** was collected as pale-yellow solids and pale-yellow crystals (1.62 g, 91%). ^{1}H NMR (pyridine-d_5): δ 4.23 (br s, 1H) (cage C*H*), 3.17 (m, 2H) ($CH_2CH_2NMe_2$), 2.34 (m, 2H) ($CH_2CH_2NMe_2$), 2.15 (s, 3H), 2.07 (s, 3H) ($N(CH_3)_2$), 2.09 (s, 15H) ($C_5(CH_3)_5$), 0.54 (s, 3H) ($ZrCH_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.5 (C_5Me_5), 68.2 ($CH_2CH_2NMe_2$), 66.2 (Zr-CH_3), 50.7 (cage *C*), 48.3, 45.6 ($N(CH_3)_2$), 36.8 ($CH_2CH_2NMe_2$), 13.7 ($C_5(CH_3)_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.5 (1B), 0.4 (1B), -1.9 (1B), -3.1 (1B), -4.3 (1B), -7.8 (1B), -9.6 (1B), -10.9 (1B), -18.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2534 (vs). Anal. Calcd for $C_{17}H_{38}B_9NZr$ (**VII-1**): C, 45.81; H, 8.60; N, 3.14. Found: C, 45.71; H, 8.81; N, 2.99.

Preparation of (η^5-Cp*)[η^1:σ:η^5-{MeN(CH$_2$)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (VII-2). A toluene (10 mL) suspension of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.22 g, 0.50 mmol) was heated to reflux overnight to give a clear orange solution. After hot filtration, the orange filtrate was cooled down to room temperature. Complex **VII-2** was isolated as orange crystals after this solution stood at room temperature for 1 day (0.19 g, 89%). ^{1}H NMR (benzene-d_6): δ 2.95 (br s, 1H) (cage C*H*), 2.52 (m, 2H) (CH_2CH_2NMe), 2.25 (d, J = 5.7 Hz, 1H), 2.31 (d, J = 5.7 Hz, 1H) ($MeNCH_2Zr$), 2.06 (m, 2H) (CH_2CH_2NMe), 1.95 (s, 3H) (NCH_3), 1.80 (s, 15H) ($C_5(CH_3)_5$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 123.7 ($C_5(CH_3)_5$), 71.9 ($MeNCH_2Zr$), 68.0 (cage *C*), 65.3 (CH_2CH_2NMe), 51.7 (NCH_3), 38.3 (CH_2CH_2NMe), 13.1 ($C_5(CH_3)_5$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 3.5 (1B), 0.4 (1B), -2.4 (1B), -4.0 (1B), -5.1 (1B), -6.3 (1B), -7.2 (1B), -13.7 (1B), -19.0 (1B). IR (KBr, cm^{-1}):

ν_{BH} 2539 (vs). Anal. Calcd for $C_{16}H_{34}B_9NZr$ (**VII-2**): C, 44.73; H, 7.98; N, 3.26. Found: C, 45.11; H, 8.15; N, 2.94.

Preparation of [η^1:σ:η^5-{MeN(CH$_2$EtC=CEt)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr(η^5-Cp*) (VII-3a). To a THF (10 mL) suspension of (η^5-Cp*)[η^1:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$]Zr(Me) (**VII-1**; 0.089 g, 0.20 mmol) was added 3-hexyne (0.016 g, 0.20 mmol) at room temperature. The reaction mixture was heated to reflux for one day to give a clear yellow solution. After filtration, the filtrate was concentrated to *ca.* 3 mL. Complex **VII-3a** was isolated as yellow crystals after this solution stood at room temperature for 3 days (0.088 g, 86%). ^{1}H NMR (pyridine-d_5): δ 4.43 (br s, 1H) (cage C*H*), 3.64 (d, J = 15.9 Hz, 1H), 2.76 (d, J = 15.9 Hz, 1H) (MeNC*H*$_2$CEt), 3.40 (m, 2H) (CH$_2$C*H*$_2$NMe), 2.41 (m, 2H) (C*H*$_2$CH$_2$NMe), 2.15 (s, 3H) (NC*H*$_3$), 2.09 (s, 15H) (C$_5$(C*H*$_3$)$_5$), 1.96 (q, J = 7.5 Hz, 2H), 1.68 (q, J = 7.5 Hz, 2H) (C*H*$_2$CH$_3$), 0.98 (t, J = 7.5 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H) (CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 196.8 (Zr*C*$_\alpha$), 138.2 (ZrC$_\alpha$*C*$_\beta$), 126.8 (*C*$_5$(CH$_3$)$_5$), 67.3 (MeNCH$_2$CEt), 67.0 (CH$_2$CH$_2$NMe), 51.2 (cage *C*), 42.5 (N*C*H$_3$), 37.5 (*C*H$_2$CH$_2$NMe), 30.5, 25.6 (*C*H$_2$CH$_3$), 15.8, 13.7 (CH$_2$*C*H$_3$), 14.1 (C$_5$(*C*H$_3$)$_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 5.6 (2B), 4.7 (2B), 1.0 (1B), -1.9 (1B), -5.3 (1B), -6.67 (1B), -12.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2551 (vs). Anal. Calcd for $C_{22}H_{44}B_9NZr$ (**VII-3a**): C, 51.63; H, 8.67; N, 2.74. Found: C, 51.19; H, 8.76; N, 2.67.

Alternate Method. To a THF solution (10 mL) of (η^5-Cp*)[η^1:σ:η^5-{MeN(CH$_2$)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) was added 3-hexyne (0.016 g, 0.20 mmol) at room temperature. The reaction mixture stirred at room

temperature overnight. The resulting yellow solution was treated using the same procedure reported above to give **VII-3a** as yellow crystals (0.092 g, 90%).

Preparation of [η^1:σ:η^5-{MeN($CH_2{}^n$PrC=C^{n}Pr)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (VII-3b). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.089 g, 0.20 mmol) and 4-octyne (0.022 g, 0.20 mmol) in THF (10 mL), using the same procedure reported for **VII-3a**: yield 0.091 g (84%). ^{1}H NMR (pyridine-d_5): δ 4.40 (br s, 1H) (cage C*H*), 3.67 (d, J = 15.6 Hz, 1H), 2.78 (d, J = 15.6 Hz, 1H) (MeNCH_2C^{n}Pr), 3.43 (m, 2H) (CH_2CH_2NMe), 2.30 (m, 2H) (CH_2CH_2NMe), 2.18 (m, 4H) ($CH_2CH_2CH_3$), 2.17 (s, 3H) (NCH_3), 2.12 (s, 15H) ($C_5(CH_3)_5$), 2.03 (m, 4H) ($CH_2CH_2CH_3$), 0.98 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H) ($CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 196.0 (ZrC_α), 137.5 (Zr$C_\alpha C_\beta$), 126.8 ($C_5(CH_3)_5$), 67.8 (MeNCH_2C^{n}Pr), 67.0 (CH_2CH_2NMe), 51.5 (cage *C*), 46.0 (NCH_3), 40.8, 37.5 ($CH_2CH_2CH_3$), 35.6 (CH_2CH_2NMe), 24.8, 22.9 ($CH_2CH_2CH_3$), 15.9, 15.4 ($CH_2CH_2CH_3$), 14.2 ($C_5(CH_3)_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -0.3 (3B), -4.8 (1B), -7.4 (1B), -10.5 (1B), -12.9 (1B), -18.1 (2B). IR (KBr, cm^{-1}): ν_{BH} 2550 (vs). Anal. Calcd for $C_{24}H_{48}B_9NZr$ (**VII-3b**): C, 53.40; H, 8.97; N, 2.60. Found: C, 53.32; H, 8.94; N, 2.48.

Preparation of [η^1:σ:η^5-{MeN($CH_2{}^n$BuC=C^{n}Bu)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (VII-3c). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.089 g, 0.20 mmol) and 5-decyne (0.028 g, 0.20 mmol) in THF (10 mL), using the same procedure reported for **VII-3a**: yield 0.093 g (82%). ^{1}H NMR (pyridine-d_5): δ 4.45 (br s, 1H) (cage C*H*), 3.70 (d, J = 15.6 Hz, 1H), 2.82 (d, J = 15.6 Hz, 1H) (MeNCH_2C^{n}Bu), 3.51 (m, 2H) (CH_2CH_2NMe), 2.49 (m, 2H)

(CH_2CH_2NMe), 2.19 (s, 3H) (NCH_3), 2.13 (s, 15H) ($C_5(CH_3)_5$), 2.02 (m, 4H) ($CH_2CH_2CH_2CH_3$), 1.35 (m, 4H) ($CH_2CH_2CH_2CH_3$), 1.28 (m, 4H) ($CH_2CH_2CH_2CH_3$), 1.10 (t, J = 6.6 Hz, 3H), 0.88 (t, J = 6.6 Hz, 3H) ($CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 195.9 (ZrC_α), 137.4 ($ZrC_\alpha C_\beta$), 126.8 ($C_5(CH_3)_5$), 67.8 ($MeNCH_2C^nBu$), 67.0 (CH_2CH_2NMe), 68.2, 66.1 (cage C), 46.0 (NCH_3), 38.1, 37.5 ($CH_2CH_2CH_2CH_3$), 33.7, 32.9 ($CH_2CH_2CH_2CH_3$), 31.6 (CH_2CH_2NMe), 24.5, 24.1 ($CH_2CH_2CH_2CH_3$), 14.6, 14.5 ($CH_2CH_2CH_2CH_3$), 14.2 ($C_5(CH_3)_5$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 2.0 (1B), -0.0 (1B), -1.6 (1B), -3.1 (2B), -9.6 (2B), -16.7 (2B). IR (KBr, cm^{-1}): ν_{BH} 2554 (vs). Anal. Calcd for $C_{26}H_{52}B_9NZr$ (**VII-3c**): C, 54.99; H, 9.24; N, 2.47. Found: C, 54.47; H, 9.21; N, 2.36.

Preparation of [η^1:σ:η^5-{MeN(CH_2PhC=CMe)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (VII-4a). To a THF (10 mL) solution of (η^5-Cp*)[η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) was added phenylmethylacetylene (0.023 g, 0.20 mmol) at room temperature. The reaction mixture was heated to reflux for one day. After filtration, the yellow filtrate was concentrated to *ca.* 3 mL. Complex **VII-4a** was isolated as yellow crystals after this solution stood at room temperature for 2 days (0.096 g, 88%). ^1H NMR (pyridine-d_5): δ 7.47 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 6.9 Hz, 2H) (C_6H_5), 4.01 (br s, 1H) (cage CH), 3.98 (d, J = 15.6 Hz, 1H), 3.12 (d, J = 15.6 Hz, 1H) ($MeNCH_2C(Ph)$), 3.61 (m, 2H) (CH_2CH_2NMe), 2.62 (m, 2H) (CH_2CH_2NMe), 2.23 (s, 3H) (NCH_3), 2.14 (s, 15H) ($C_5(CH_3)_5$), 1.74 (s, 3H) ($C(CH_3)$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 191.4 (ZrC_α), 145.8 ($ZrC_\alpha C_\beta$), 124.4, 124.1, 122.6, 122.0 (C_6H_5), 119.9 ($C_5(CH_3)_5$), 64.9 ($MeNCH_2C(Ph)$), 63.4 (CH_2CH_2NMe), 61.4 (cage C), 41.7 ($N(CH_3)$), 33.7 (CH_2CH_2NMe), 20.1 ($C(CH_3)$), 9.2 ($C_5(CH_3)_5$). $^{11}B\{^1H\}$ NMR

(pyridine-d_5): δ -0.6 (3B), -4.4 (1B), -7.5 (1B), -10.0 (3B), -17.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2563 (vs). Anal. Calcd for $C_{25}H_{42}B_9NZr$ (**VII-4a**): C, 55.01; H, 7.76; N, 2.57. Found: C, 55.48; H, 7.99; N, 2.30.

Preparation of [η^1:σ:η^5-{MeN(CH$_2$PhC=CTMS)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr(η^5-Cp*) (VII-4b). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:σ:η^5-{MeN(CH$_2$)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) and phenyltrimethylsilylacetylene (0.035 g 0.20 mmol) in THF (10 mL), using the same procedure reported for **VII-4a**: yield 0.104 g (80%). ^{1}H NMR (pyridine-d_5): δ 7.42 (t, J = 7.2 Hz, 2H), 7.35 (d, J = 6.9 Hz, 1H), 7.24 (t, J = 7.2 Hz, 2H) (C$_6H_5$), 4.18 (br s, 1H) (cage C*H*), 4.00 (d, J = 16.5 Hz, 1H), 2.97 (d, J = 16.5 Hz, 1H) (MeNCH_2C(Ph)), 3.50 (m, 2H) (CH$_2$CH_2NMe), 2.75 (m, 2H) (CH_2CH$_2$NMe), 2.26 (s, 3H) (NCH_3), 2.23 (s, 15H) (C$_5$(CH_3)$_5$), -0.09 (s, 9H) (Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 207.9 (ZrC$_\alpha$), 153.2 (ZrC$_\alpha$C$_\beta$), 147.1, 129.8, 129.0, 128.5, 127.7, 127.4, 126.1 (aryl *C* + *C*$_5$(CH$_3$)$_5$), 70.8 (MeNCH$_2$C(Ph)), 69.1 (CH$_2$CH$_2$NMe), 73.2, 55.9 (cage *C*), 47.8 (NCH$_3$), 38.0 (CH$_2$CH$_2$NMe), 14.5 (C$_5$(CH$_3$)$_5$), 5.1 (Si(CH$_3$)$_3$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.2 (1B), -1.6 (3B), -5.0 (1B), -7.6 (1B), -10.1 (2B), -17.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{30.50}H_{52}B_9NSiZr$ (**VII-4b** + 0.5 C_7H_8): C, 56.42; H, 8.07; N, 2.16. Found: C, 56.30; H, 8.14; N, 2.10.

Preparation of [η^1:σ:η^5-{MeN(CH$_2$^{n}BuC=CTMS)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr(η^5-Cp*) (VII-4c). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:σ:η^5-{MeN(CH$_2$)CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) and *n*-butyltrimethylsilylacetylene (0.031 g 0.20 mmol) in THF (10 mL), using the same

procedure reported for **VII-4a**: yield 0.099 g (85%). ^{1}H NMR (pyridine-d_5): δ 3.82 (br s, 1H) (cage C*H*), 3.60 (d, J = 15.3 Hz, 1H), 3.02 (d, J = 15.3 Hz, 1H) (MeNCH_2C^{n}Bu), 2.77 (m, 2H) (CH_2CH_2NMe), 2.62 (m, 2H) (CH_2CH_2NMe), 2.32 (s, 3H) (NCH_3), 2.10 (s, 15H) ($C_5(CH_3)_5$), 1.79 (t, J = 7.5 Hz, 2H) ($CH_2CH_2CH_2CH_3$), 1.34 (m, 4H) ($CH_2CH_2CH_2CH_3$), 0.79 (t, J = 6.9 Hz, 3H) ($CH_2CH_2CH_2CH_3$), 0.16 (s, 9H) (Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 203.2 (ZrC_α), 150.5 ($ZrC_\alpha C_\beta$), 123.5 ($C_5(CH_3)_5$), 66.9 (MeNCH_2C^{n}Bu), 63.8 (CH_2CH_2NMe), 56.3 (cage *C*), 45.3 (NCH_3), 38.9 (CH_2CH_2NMe), 35.7 ($CH_2CH_2CH_2CH_3$), 27.4 ($CH_2CH_2CH_2CH_3$), 20.7 ($CH_2CH_2CH_2CH_3$), 11.2 ($CH_2CH_2CH_2CH_3$), 11.0 ($C_5(CH_3)_5$), 1.2 (Si(CH_3)$_3$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 2.7 (1B), -2.4 (1B), -5.1 (1B), -6.8 (1B), -8.6 (1B), -9.7 (1B), -16.9 (1B), -18.0 (1B), -20.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2557 (vs). Anal. Calcd for $C_{25}H_{52}B_9NSiZr$ (**VII-4c**): C, 51.42; H, 8.98; N, 2.40. Found: C, 51.72; H, 8.53; N, 2.13.

Preparation of [η^1:σ:η^5-{MeN[CH$_2$(2-Py)C=C^{n}Bu]CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr(η^5-Cp*) (VII-4d). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) and 2-(hex-1-ynyl)pyridine (0.035 g, 0.20 mmol) in THF (10 mL), using the same procedure reported for **VII-4a**: yield 0.094 g (75%). ^{1}H NMR (pyridine-d_5): δ 8.80 (d, J = 4.2 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.56 (d, J = 6.0 Hz, 1H). 7.19 (t, J = 6.0 Hz, 1H) (C_5NH_4), 4.51 (br s, 1H) (cage C*H*), 4.07 (d, J = 15.9 Hz, 1H), 3.47 (d, J = 15.9 Hz, 1H) (MeNCH_2CPy-2), 3.88 (m, 2H), (CH_2CH_2NMe), 3.63 (m, 4H) (THF), 2.75 (m, 2H) (CH_2CH_2NMe), 2.52 (m, 4H) ($CH_2CH_2CH_2CH_3$), 2.24 (s, 15H) ($C_5(CH_3)_5$), 2.14 (s, 3H) (NCH_3), 1.83 (m, 2H) ($CH_2CH_2CH_2CH_3$), 1.61 (m, 4H) (THF), 0.63 (t, J = 6.9 Hz, 3H) ($CH_2CH_2CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 201.2 (ZrC_α), 160.1 ($ZrC_\alpha C_\beta$), 127.3 ($C_5(CH_3)_5$), 138.0, 136.7, 127.3, 124.2, 122.3 (C_5NH_4), 68.6 ($MeNCH_2CPy$-2), 68.2, 26.2 (THF), 67.3 (CH_2CH_2NMe), 51.6 (cage *C*), 46.0 (NCH_3), 38.2 (CH_2CH_2NMe), 37.6 ($CH_2CH_2CH_2CH_3$), 33.3 ($CH_2CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$), 14.2 ($C_5(CH_3)_5$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ -0.2 (3B), -4.8 (2B), -10.9 (2B), -17.8 (2B). IR (KBr, cm^{-1}): ν_{BH} 2553 (vs). Anal. Calcd for $C_{29}H_{51}B_9N_2O_{0.5}Zr$ (**VII-4d** + 0.5 THF): C, 55.73; H, 8.23; N, 4.49. Found: C, 55.94; H, 7.78; N, 4.52.

Preparation of (η^5-Cp*)[η^1:σ:η^5-{$(CH_3)N[(CH_2)(TMS)C=CH](CH_2CH_2)C_2B_9H_{10}$}]Zr (VII-5a). To a THF (10 mL) suspension of (η^5-Cp*)[η^1:η^5-$(Me_2NCH_2CH_2)C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.089 g, 0.20 mmol) was added trimethylsilylacetylene (0.020 g, 0.20 mmol) at room temperature. The reaction mixture was heated to reflux for one day to give a clear yellow solution. After filtration, the yellow filtrate was concentrated to *ca.* 3 mL. Complex **VII-5a** was isolated as pale-yellow crystals after this solution stood at room temperature for 2 days (0.080 g, 76%). ^1H NMR (pyridine-d_5): δ 7.62 (s, 1H), ($ZrCHCTMS$), 3.95 (br s, 1H) (cage C*H*), 3.68 (d, J = 15.0 Hz, 1H), 3.23 (d, J = 15.0 Hz, 1H) ($TMSCCH_2NMe$), 3.12 (m, 2H) (CH_2CH_2NMe), 2.60 (m, 2H) (CH_2CH_2NMe), 2.24 (s, 3H) (NCH_3), 2.08 (s, 15H) ($C_5(CH_3)_5$), 0.11 (s, 9H) ($Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 210.6 (ZrC_α), 137.2 ($ZrC_\alpha C_\beta$), 125.8 ($C_5(CH_3)_5$), 69.0 ($TMSCCH_2NMe$), 68.6 (CH_2CH_2NMe), 60.2 (cage *C*), 47.8 (NCH_3), 38.5 (CH_2CH_2NMe), 13.6 ($C_5(CH_3)_5$), -1.3 ($Si(CH_3)_3$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ -0.4 (1B), -3.8 (1B), -4.9 (1B), -10.5 (2B), -13.7(1B), -16.0 (1B), -18.2 (1B), -21.4 (1B). IR (KBr,

cm^{-1}): ν_{BH} 2562 (vs). Anal. Calcd for $C_{21}H_{44}B_9NSiZr$ (**VII-5a**): C, 47.79; H, 8.41; N, 2.66. Found: C, 48.08; H, 8.19; N, 2.62.

Alternate Method. To a THF solution (10 mL) of (η^5-Cp*)[η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) was added trimethylsilylacetylene (0.020 g, 0.20 mmol) with stirring. The reaction mixture was stirred at room temperature overnight. The resulting solution was treated using the same procedure reported above to give **VII-5a** as pale-yellow crystals (0.090 g, 85%).

Preparation of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(C≡C^{t}Bu) (VII-5b). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.089 g, 0.20 mmol) and 3,3-dimethyl-1-butyne (0.016 g 0.20 mmol) in THF (10 mL), using the same procedure reported for **VII-5a**: yield 0.097 g (83%). ^{1}H NMR (pyridine-d_5): δ 5.00 (br s, 1H) (cage *CH*), 3.91 (m, 2H) ($CH_2CH_2NMe_2$), 3.63 (m, 4H), 1.59 (m, 4H) (THF), 2.72 (s, 3H), 2.21 (s, 3H) ($N(CH_3)_2$), 2.28 (m, 2H) ($CH_2CH_2NMe_2$), 2.23 (s, 15H) ($C_5(CH_3)_5$), 1.16 (s, 9H) ($C(CH_3)_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 140.3 (ZrC_α), 127.4 ($ZrC_\alpha C_\beta$), 127.0 ($C_5(CH_3)_5$), 68.2, 26.2 (THF), 66.3 ($CH_2CH_2NMe_2$), 57.2 (cage *C*), 52.8, 45.8 ($N(CH_3)_2$), 36.6 ($CH_2CH_2NMe_2$), 26.2 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$), 14.2 ($C_5(CH_3)_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 3.1 (2B), 1.0 (1B), -0.4 (1B), -1.4 (1B), -4.8 (1B), -6.5 (1B), -8.0 (1B), -15.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{26}H_{52}B_9NOZr$ (**VII-5b** + THF): C, 53.55; H, 8.99; N, 2.74. Found: C, 54.04; H, 9.20; N, 2.42.

Preparation of [η^1:σ:η^5-{$(CH_3)N[(CH_2)(TMSC≡C)C=C(TMS)](CH_2CH_2)C_2B_9H_{10}$}]Zr($\eta^5$-Cp*)

(VII-6a). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) and 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.039 g, 0.20 mmol) in THF (10 mL), using the same procedure reported for **VII-4a**: yield 0.090 g (72%). ^{1}H NMR (pyridine-d_5): δ 3.88 (d, J = 15.6 Hz, 1H), 3.46 (d, J = 15.6 Hz, 1H) (MeNCH_2CCTMS), 3.79 (br s, 1H) (cage CH), 3.12 (m, 2H) (CH_2CH_2NMe), 2.68 (m, 2H) (CH_2CH_2NMe), 2.30 (s, 3H) (NCH_3), 2.10 (s, 15H) ($C_5(CH_3)_5$), 0.36 (s, 9H), 0.28 (s, 9H) (Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 228.1 (ZrC_α), 133.7 (Zr$C_\alpha C_\beta$), 127.4 ($C_5(CH_3)_5$), 107.3, 97.0 (alkyne C), 69.8 (MeNCH_2CCTMS). 58.5 (CH_2CH_2NMe), 47.8 (NCH_3), 38.7 (CH_2CH_2NMe), 14.1 ($C_5(CH_3)_5$), 2.5, 0.0 (Si(CH_3)$_3$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -1.9 (1B), -6.1 (3B), -9.4 (1B), -11.4 (1B), -14.0 (1B), -16.1 (1B), -21.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2523 (vs). Anal. Calcd for $C_{26}H_{52}B_9NSi_2Zr$ (**VII-6a**): C, 50.05; H, 8.41; N, 2.25. Found: C, 50.24; H, 8.25; N, 2.03.

Preparation of [η^1:σ:η^5-{(CH_3)N[$(CH_2)(CH_2$=CHCH_2NTsCH_2)C=C(H)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (VII-6b). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr (**VII-2**; 0.086 g, 0.20 mmol) and *N*-(prop-2-ynyl)-*N*-tosylprop-2-en-1-amine (0.050 g, 0.20 mmol) in THF (10 mL), using the same procedure reported for **VII-4a**: yield 0.10 g (74%). ^{1}H NMR (pyridine-d_5): δ 7.97 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H) (C_6H_4), 6.84 (s, 1H) (ZrCH), 5.76 (m, 1H) (CH_2=CH), 5.17 (dd, ^1J = 16.2 Hz, ^2J = 3.0 Hz, 2H) (CH_2=CH), 4.02 (br s, 1H) (cage CH), 4.00 (d, J = 6.6 Hz, 2H) (TsNCH_2CH), 3.77 (m, 2H) (TsNCH_2CCH), 3.93 (d, J = 15.9 Hz, 1H), 3.35 (d, J = 15.9 Hz, 1H) (MeNCH_2C_β), 3.12 (m, 2H) (CH_2CH_2NMe), 2.59 (m, 2H)

(CH_2CH_2NMe), 2.21 (s, 3H) (NCH_3), 2.20 (s, 3H) ($C_6H_4CH_3$), 2.10 (s, 15H) ($C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 190.0 (ZrC_α), 144.2 ($ZrC_\alpha C_\beta$), 137.6, 137.5 (vinylic *C*), 134.0, 130.6, 128.1, 119.1 (C_6H_4), 126.2 ($C_5(CH_3)_5$), 68.4 ($TsNCH_2CH$), 68.2 ($TsNCH_2CCH$), 59.7 (cage *C*), 54.4 ($C_\beta CH_2NMe$), 52.3 (CH_2CH_2NMe), 48.0 (NCH_3), 38.2 (CH_2CH_2NMe), 26.1 ($C_6H_4CH_3$), 13.7 ($C_5(CH_3)_5$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 0.3 (1B), -2.7 (2B), -7.9 (2B), -11.5 (1B), -13.8 (1B), -17.2 (1B), -20.8 (1B). IR (KBr, cm^{-1}): ν_{BH} 2543 (vs). Anal. Calcd for $C_{29}H_{49}B_9SO_2N_2Zr$ (**VII-6b**): C, 51.30; H, 7.28; N, 4.13. Found: C, 51.65; H, 6.90; N, 4.71.

Preparation of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]HfMe (VIII-1a). To a Et_2O (25 mL) suspension of Cp^*HfCl_3 (2.10 g, 5.0 mmol) was added a Et_2O solution of MeLi (1.40 M, 10.7 mL, 15.0 mmol) at -40 °C. The suspension was allowed to slowly warm to room temperature, and stirred for 1 h. After removal of the solvent, the residue was extracted with toluene (50 mL). After filtration, the filtrate was concentrated to driness under vacumm and Cp^*HfMe_3 was afforded as a white crystalline solid (1.40 g, 3.9 mmol). To a THF (20 mL) solution of Cp^*HfMe_3 (1.40 g, 3.9 mmol) was added 7-(Me_2NH)$(CH_2)_2$-7,8-$C_2B_9H_{11}$ (0.80 g, 3.9 mmol) in portions with stirring. The reaction mixture was stirred at room temperature overnight to give a white suspension. After filtration, the white solid was washed with THF and collected as complex **VIII-1a** (1.70 g, 82%). The crystals suitable for X-ray analyses were grown up from hot THF solution. ^1H NMR (pyridine-d_5): δ 3.96 (br s, 1H) (cage C*H*), 2.42 (m, 2H) ($CH_2CH_2NMe_2$), 2.23 (s, 3H), 2.20 (s, 3H) ($N(CH_3)_2$), 2.16 (s, 15H) ($C_5(CH_3)_5$), 1.93 (m, 2H) ($CH_2CH_2NMe_2$), 0.41 (s, 3H) (Hf-CH_3). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 128.4 (C_5Me_5), 66.2 (Hf-CH_3), 51.0 (cage *C*),

50.8 ($CH_2CH_2NMe_2$), 45.6, 44.5 ($N(CH_3)_2$), 36.4 ($CH_2CH_2NMe_2$), 13.6 ($C_5(CH_3)_5$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 3.1 (1B), -0.3 (1B), -3.1 (1B), -4.6 (1B), -5.9 (1B), -6.8 (1B), -7.8 (1B), -14.3 (1B), -19.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). Anal. Calcd for $C_{17}H_{38}B_9NHf$ (**VIII-1a**): C, 38.36; H, 7.20; N, 2.63. Found: C, 38.80; H, 7.15; N, 2.34.

Preparation of (η^5-Cp'')[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]HfMe (VIII-1b). To a Et_2O (25 mL) suspension of Cp''$HfCl_3$ (2.47 g, 5.0 mmol) was added a Et_2O solution of MeLi (1.40 M, 10.7 mL, 15.0 mmol) with stirring at -40 °C. The suspension was allowed to slowly warm to room temperature, and stirred for 1 h. After removal of the solvent, the residue was extracted with hexane (50 mL). After filtration, the filtrate was concentrated to driness under vacumm and Cp''$HfMe_3$ was afforded as a pale-yellow crystalline solid (1.52 g, 3.5 mmol). To a toluene (30 mL) solution of Cp''$HfMe_3$ (1.52 g, 3.5 mmol) was added 7-(Me_2NH)$(CH_2)_2$-7,8-$C_2B_9H_{11}$ solid (0.72 g, 3.5 mmol) in portions with stirring. The reaction mixture was stirred at room temperature overnight. After filtration, the filtrate was concentrated to *ca.* 10 mL. Pale-yellow crystals was got after this solution stood at room temperature for 3 days (1.21 g, 57%). ^1H NMR (benzene-d_6): δ 7.38 (m, 1H), 6.80 (m, 1H), 5.71 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 3.79 (br s, 1H) (cage C*H*), 2.21 (m, 2H) ($CH_2CH_2NMe_2$), 1.92 (m, 2H) ($CH_2CH_2NMe_2$), 1.54 (s, 6H) ($N(CH_3)_2$), 0.29 (s, 3H) (Hf-CH_3), 0.36 (s, 9H), 0.24 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 132.3, 127.8, 127.3, 123.2, 122.9 ($C_5H_3(Si(CH_3)_3)_2$), 65.9 (cage *C*), 65.2 (Hf-CH_3), 49.0 ($CH_2CH_2NMe_2$), 47.5 ($CH_2CH_2N(CH_3)_2$), 36.0 ($CH_2CH_2NMe_2$), 0.8, 0.5 ($C_5H_3(Si(CH_3)_3)_2$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -0.1 (3B), -3.9 (4B), -10.0 (1B), -18.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2525 (vs).

Anal. Calcd for $C_{18}H_{44}B_9HfNSi_2$ (**VIII-1b**): C, 37.12; H, 7.31; N, 2.31. Found: C, 37.58; H, 7.74; N, 2.14.

Preparation of (η^5-Cp'')[η^1:σ:η^5-{MeN[(CH$_2$)C(=N(Cy))N(Cy)]CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr (VIII-2a). To a toluene (10 mL) solution of (η^5-Cp'')[η^1:σ:η^5-{MeN(CH$_2$)(CH$_2$CH$_2$)}C$_2$B$_9$H$_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) was added dicyclohexylcarbondiimide (CyN=C=NCy) (0.041 g, 0.20 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 days. After filtration, the orange filtrate was concentrated to *ca.* 3 mL. Complex **VIII-2a** was isolated as orange crystals after this solution stood at room temperature for 3 days (0.11 g, 78%). ^{1}H NMR (benzene-d_6): δ 8.38 (m, 1H), 7.09 (m, 1H), 6.08 (m, 1H) (C$_5H_3$(Si(CH$_3$)$_3$)$_2$), 3.90 (br s, 1H) (cage C*H*), 3.37 (d, J = 15.0 Hz, 1H), 3.05 (d, J = 15.0 Hz, 1H) (MeNCH_2CNCy), 3.33 (m, 1H), 3.15 (m, 1H) (NC*H*(CH$_2$)$_5$), 2.16 (m, 2H) (CH$_2$CH_2NMe), 1.87 - 1.24 (m, 22H) (NCH(CH_2)$_5$ + CH_2CH$_2$NMe), 1.63 (s, 3H) (NCH_3), 0.29 (s, 9H), 0.24 (s, 9H) (C$_5$H$_3$(Si(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 155.4 (*C*=N), 143.7, 132.7, 129.5, 129.3, 125.7 (*C*$_5$H$_3$(Si(CH$_3$)$_3$)$_2$), 66.4 (MeN*C*H$_2$CNCy), 64.9, 64.2 (N*C*H(CH$_2$)$_5$), 57.5 (CH$_2$*C*H$_2$NMe), 55.4 (cage *C*), 47.3 (N*C*H$_3$), 37.1, 36.3, 36.0, 32.7, 27.9, 26.9, 25.4, 25.3 (NCH(*C*H$_2$)$_5$ + *C*H$_2$CH$_2$NMe), 1.40, 1.11 (C$_5$H$_3$(Si(*C*H$_3$)$_3$)$_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 4.8 (1B), 0.8 (2B), -2.7 (3B), -8.9 (2B), -17.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2553 (vs). Anal. Calcd for $C_{30}H_{62}B_9N_3Si_2Zr$ (**VIII-2a**): C, 50.78; H, 8.81; N, 5.92. Found: C, 50.23; H, 8.69; N, 5.98.

Preparation of (η^5-Cp'')[η^1:σ:η^5-{MeN[HC=C(CH$_3$)N(H)](CH$_2$CH$_2$)}C$_2$B$_9$H$_{10}$]Zr (VIII-2b). This complex was prepared as pale-orange crystals from

(η^5-Cp'')[η^1:σ:η^5-{MeN(CH_2)(CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VI-1**; 0.20 g, 0.40 mmol) and CH_3CN (0.016 g, 0.40 mmol) in toluene (10 mL) using the same procedure reported for **VIII-2a**: yield 0.18 g (83%). ^{1}H NMR (benzene-d_6): δ 8.10 (m, 1H), 6.28 (m, 1H), 6.17 (m, 1H) (C_5H_3(Si(CH_3)$_3$)$_2$), 7.10 (s, 1H) (*H*C=C(CH_3)), 3.76 (br s, 1H) (Zr-N*H*), 3.13 (br s, 1H) (cage C*H*), 2.84 (m, 2H) (CH_2CH_2NMe), 2.10 (s, 3H) (NCH_3), 2.04 (m, 2H) (CH_2CH_2NMe), 1.27 (s, 3H) (C(CH_3)), 0.36 (s, 9H), 0.12 (s, 9H) (C_5H_3(Si(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 144.5, 134.1, 131.8, 129.7, 127.0, 125.9, 112.3 (C_5H_3(Si(CH_3)$_3$)$_2$ + vinylic *C*), 67.8 (CH_2CH_2NMe), 50.9 (cage *C*), 38.4 (NCH_3), 32.3 (CH_2CH_2NMe), 19.3 (C(CH_3)), 1.4, 0.7 (C_5H_3(Si(CH_3)$_3$)$_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 1.6 (1B), -1.8 (3B), -6.2 (3B), -12.8 (1B), -17.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs), ν_{NH} 3367 (vs). Anal. Calcd for $C_{19}H_{43}B_9N_2Si_2Zr$ (**VIII-2b**): C, 41.93; H, 7.96; N, 5.15. Found: C, 41.76; H, 8.10; N, 4.91.

Preparation of (η^5-Cp'')[η^1:σ:η^5-{MeN[HC=C(Ph)N(H)](CH_2CH_2)}$C_2B_9H_{10}$]Zr (VIII-2c). This complex was prepared as pale-orange crystals from (η^5-Cp'')[η^1:σ:η^5-{MeN(CH_2)(CH_2CH_2)}$C_2B_9H_{10}$]Zr (**VI-1**; 0.20 g, 0.40 mmol) and PhCN (0.041 g, 0.40 mmol) in toluene (5 mL), using the same procedure reported for **VIII-2a**: yield 0.18 g (74%). ^{1}H NMR (benzene-d_6): δ 8.25 (m, 1H), 6.36 (m, 1H), 6.19 (m, 1H) (C_5H_3(Si(CH_3)$_3$)$_2$), 7.24 (m, 2H), 6.99 (t, J = 7.5 Hz, 2H), 6.63 (t, J = 7.5 Hz, 1H) (C_6H_5), 7.23 (s, 1H) (*H*C=C(Ph)), 4.43 (br s, 1H) (Zr-N*H*), 3.82 (br s, 1H) (cage C*H*), 2.49 (m, 2H) (CH_2CH_2NMe), 2.19 (m, 2H) (CH_2CH_2NMe), 2.10 (s, 3H) (NCH_3), 0.33 (s, 9H), 0.21 (s, 9H) (C_5H_3(Si(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 147.4, 137.3, 135.9, 132.4, 132.3, 129.9, 129.3, 126.9, 126.5, 123.1, 113.3 (C_6H_5 + C_5H_3(Si(CH_3)$_3$)$_2$ + vinylic *C*), 68.1 (CH_2CH_2NMe), 50.8 (cage *C*), 38.4 (NCH_3), 32.3 (CH_2CH_2NMe), 1.4, 0.8

($C_5H_3(Si(CH_3)_3)_2$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 1.0 (1B), -2.0 (3B), -6.5 (3B), -12.3 (1B), -17.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2581 (vs), ν_{NH} 3336 (vs). Anal. Calcd for $C_{24}H_{45}B_9N_2Si_2Zr$ (**VIII-2c**): C, 47.54; H, 7.48; N, 4.62. Found: C, 47.13; H, 7.98; N, 4.68.

Preparation of $(\eta^5$-Cp'')$[\eta^1:\sigma:\eta^5$-{MeN[(CH_2)C(=NXy)C(=NXy)](CH_2CH_2)}$C_2B_9H_{10}$]Zr(CNXy) (VIII-2d). This complex was prepared as pale-orange crystals from $(\eta^5$-Cp'')$[\eta^1:\sigma:\eta^5$-{MeN$(CH_2)(CH_2CH_2)$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and 2,6-dimethylphenylisocyanide (0.079 g, 0.60 mmol) in toluene (10 mL), using the same procedure reported for **VIII-2a**: yield 0.15 g (80%). ^1H NMR (benzene-d_6): δ 7.37 (m, 1H), 6.53 (m, 1H), 6.03 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 7.02 (m, 1H), 6.92 (m, 1H), 6.80 (m, 2H), 6.77 (m, 2H), 6.73 (m, 2H), 6.40 (m, 1H) (C_6H_3), 3.87 (br s, 1H) (cage C*H*), 3.31 (m, 2H) (CH_2CH_2NMe), 3.03 (d, J = 15.0 Hz, 1H), 2.64 (d, J = 15.0 Hz, 1H) ($MeNCH_2C_\beta C_a$), 2.89 (m, 2H) (CH_2CH_2NMe), 2.21 (s, 3H) (NCH_3), 2.15 (s, 3H), 2.10 (s, 6H), 2.07 (s, 6H), 1.76 (s, 3H) ($C_6H_3(CH_3)_2NC$), 0.34 (s, 9H), 0.28 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 184.7 (ZrC_a), 172.4, 168.2 (N=*C*), 155.2, 147.2, 138.2, 131.9, 131.4, 131.2, 130.6, 130.3, 129.9, 129.7, 128.9, 126.0, 125.1, 124.8, 124.2, 122.1, 113.2 (C_6H_3 + $C_5H_3(Si(CH_3)_3)_2$), 68.3 ($MeNCH_2C$=N), 60.3 (CH_2CH_2NMe), 59.9 (cage *C*), 47.0 (NCH_3), 38.4 (CH_2CH_2NMe), 21.8, 21.2, 19.3, 18.9, 17.5 ($C_6H_3(CH_3)_2$), 1.9, 0.6 ($C_5H_3(Si(CH_3)_3)_2$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 1.6 (2B), -1.9 (2B), -6.0 (2B), -9.5 (2B), -17.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2520 (vs). Anal. Calcd for $C_{47.5}H_{71}B_9N_4Si_2Zr$ (**VIII-2d** + 0.5 C_7H_8): C, 60.51; H, 7.59; N, 5.94. Found: C, 60.50; H, 7.24; N, 5.44.

Preparation of (η^5-Cp'')[η^1:σ:η^5-{MeN[(CH_2)C(=S)N^{n}Bu](CH_2CH_2)}$C_2B_9H_{10}$]Zr (VIII-2e). This complex was prepared as pale-orange crystals from (η^5-Cp'')[η^1:σ:η^5-{MeN$(CH_2)(CH_2CH_2)$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.20 g, 0.40 mmol) and ^{n}BuNCS (0.046 g, 0.40 mmol) in toluene (10 mL), using the same procedure reported for **VIII-2a**: yield 0.16 g (65%). ^{1}H NMR (benzene-d_6): δ 8.38 (m, 1H), 6.81 (m, 1H), 5.98 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 4.42 (m, 2H) (CH_2CH_2NMe), 3.80 (d, J = 17.1 Hz, 1H), 3.63 (d, J = 17.1 Hz, 1H) ($MeNCH_2C$=S), 3.73 (br s, 1H) (cage C*H*), 2.82 (m, 2H) ($NCH_2CH_2CH_2CH_3$), 1.96 (m, 2H) (CH_2CH_2NMe), 1.61 (m, 2H) ($CH_2CH_2CH_2CH_3$), 1.46 (s, 3H) (NCH_3), 1.31 (m, 2H) ($CH_2CH_2CH_2CH_3$), 0.90 (t, J = 6.9 Hz, 3H) ($CH_2CH_2CH_2CH_3$), 0.18 (s, 9H), 0.16 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 200.1 (*C*=S), 130.8, 141.4, 130.2, 128.7, 126.2 ($C_5H_3(Si(CH_3)_3)_2$), 76.3 ($MeNCH_2C$=S), 65.1 (CH_2CH_2NMe), 55.9 (cage *C*), 53.5 ($NCH_2CH_2CH_2CH_3$), 46.0 (NCH_3), 36.5 (CH_2CH_2NMe), 29.9, 21.4, 14.0 ($CH_2CH_2CH_2CH_3$), 0.51, 0.42 ($C_5H_3(Si(CH_3)_3)_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 5.1 (2B), 0.9 (2B), -1.7 (2B), -8.4 (2B), -16.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2539 (vs). Anal. Calcd for $C_{22}H_{49}B_9N_2Si_2SZr$ (**VIII-2e**): C, 42.73; H, 7.99; N, 4.53. Found: C, 42.73; H, 7.58; N, 4.39.

Preparation of (η^5-Cp'')[η^1:σ:η^5-{MeN[(CH_2)C$(Ph)_2$O](CH_2CH_2)}$C_2B_9H_{10}$]Zr (VIII-2f). This complex was prepared as orange crystals from (η^5-Cp'')[η^1:σ:η^5-{MeN$(CH_2)(CH_2CH_2)$}$C_2B_9H_{10}$]Zr (**VI-1**; 0.10 g, 0.20 mmol) and Ph_2C=O (0.037 g, 0.20 mmol) in toluene (5 mL), using the same procedure reported for **VIII-2a**: yield 0.090 g (66%). ^{1}H NMR (pyridine-d_5): δ 8.69 (m, 1H), 6.83 (m, 1H), 7.84 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 7.85 (d, J = 6.9 Hz, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.39 (m, 4H), 7.29 (t, J = 7.8 Hz, 2H), 7.24 (m, 1H) (C_6H_5), 5.10 (d, J = 13.2 Hz, 1H), 4.74 (d, J = 13.2

Hz, 1H) ((Ph)$_2$C(O)CH_2NMe), 3.97 (br s, 1H) (cage CH), 2.61 (m, 2H) (CH$_2$CH_2NMe), 2.20 (s, 3H) (NCH_3), 1.89 (m, 2H) (CH_2CH$_2$NMe), 0.42 (s, 9H), 0.37 (s, 9H) (C$_5$H$_3$(Si(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 142.1, 137.8, 132.5, 132.0, 130.0, 129.2, 128.9, 128.4, 127.7, 127.2, 126.9, 125.5, 124.8 (C_6H$_5$ + C_5H$_3$(Si(CH$_3$)$_3$)$_2$), 86.7 ((Ph)$_2$$C$(O)CH$_2$N), 65.2 ((Ph)$_2$C(O)$CH_2$N), 60.6 (CH$_2$$CH_2$NMe), 51.3 (cage C), 44.4 (NCH$_3$), 31.5 (CH$_2$CH$_2$NMe), 0.65, 0.38 (C$_5$H$_3$(Si(CH$_3$)$_3$)$_2$). ^{11}B{^{1}H} NMR (pyridine-d_5): 2.9 (1B), -0.5 (1B), -5.9 (2B), -13.3 (2B), -15.2 (2B), -20.6 (1B). IR (KBr, cm^{-1}): ν_{BH} 2542 (vs). Anal. Calcd for C$_{30}$H$_{50}$B$_9$NOSi$_2$Zr (**VIII-2f**): C, 52.57; H, 7.35; N, 2.04. Found: C, 52.81; H, 7.71; N, 1.69.

Preparation of (η^5-Cp*)[η^1:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$]Zr[N=C(Me)$_2$] (VIII-3a). To a THF (10 mL) suspension of (η^5-Cp*)[η^1:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$]Zr(Me) (**VII-1**; 0.18 g, 0.40 mmol) was added CH$_3$CN (0.016 g, 0.40 mmol). The yellow suspension was stirred at room temperature for 2 days to give a clear yellow solution. After filtration, the yellow filtrate was concentrated to *ca.* 4 mL. Complex **VIII-3a** was isolated as pale-yellow crystals after this solution stood at room temperature for 2 days (0.144 g, 74%). ^{1}H NMR (pyridine-d_5): δ 3.47 (br s, 1H) (cage CH), 3.33 (m, 2H) (CH$_2$CH_2NMe), 3.17 (m, 2H) (CH_2CH$_2$NMe), 2.63 (s, 6H) (N(CH_3)$_2$), 2.00 (s, 3H), 1.98 (s, 3H) (C(CH_3)$_2$), 1.95 (s, 15H) (C$_5$(CH_3)$_5$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 128.9 (N=C(CH$_3$)$_2$), 125.3 (C_5Me$_5$), 71.6 (CH$_2$$CH_2NMe_2$), 51.2 (cage C), 43.8 (N(CH$_3$)$_2$), 36.3 (CH$_2$CH$_2$NMe), 22.4, 20.8 (C(CH$_3$)$_2$), 12.2 (C$_5$(CH$_3$)$_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -10.9 (2B), -14.0 (1B), -15.6 (1B), -19.1 (2B), -21.4 (1B), -32.8 (1B), -36.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2535 (vs). Anal. Calcd for C$_{19}$H$_{41}$B$_9$N$_2$Zr (**VIII-3a**): C, 46.95; H, 8.50; N, 5.76. Found: C, 47.11; H, 8.63; N, 5.73.

Preparation of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr[N=C(Me)($CH_2CH(CH_2)_2$)] (VIII-3b). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.18 g, 0.40 mmol) and cyclopropyl acetonitrile (0.032 g, 0.40 mmol) in THF (10 mL), using the same procedure reported for **VIII-3a**: yield 0.16 g (76%). ^{1}H NMR (pyridine-d_5): δ 2.99 (br s, 1H) (cage C*H*), 2.60 (m, 2H) (CH_2CH_2NMe), 2.31 (s, 3H), 2.08 (s, 3H) (N(CH_3)$_2$), 2.28 (m, 2H) (CH_2CH_2NMe), 2.10 (s, 15H) ($C_5(CH_3)_5$), 1.99 (d, J = 9.6 Hz, 2H) ($CH_2CH(CH_2)_2$), 1.83 (s, 3H) (N=C(CH_3)), 0.56 (m, 1H) ($CH(CH_2)_2$), 0.17 (m, 4H) ($CH(CH_2)_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 129.7 (N=*C*(CH_3)), 122.5 (C_5Me_5), 66.8 (CH_2CH_2NMe), 55.0 (cage *C*), 48.6, 46.8 (N(CH_3)$_2$), 36.9 (CH_2CH_2NMe), 24.3 ($CH_2CH(CH_2)_2$), 13.6 ($C_5(CH_3)_5$), 12.6 ($CH(CH_2)_2$), 6.0, 5.8 ($CH(CH_2)_2$). ^{11}B{^{1}H} NMR (pyridine-d_5): -0.4 (1B), -2.9 (1B), -5.2 (1B), -8.0 (2B), -10.0 (2B), -18.4 (1B), -20.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{22}H_{45}B_9N_2Zr$ (**VIII-3b**): C, 50.22; H, 8.62; N, 5.32. Found: C, 50.42; H, 8.50; N, 6.06.

Preparation of (η^5-Cp*)[η^1:σ:η^5-{MeN(HC=C(Ph)N(H))N(CH_2CH_2)}$C_2B_9H_{10}$]Zr(PhCN)·C_7H_8 (VIII-3c·C_7H_8). To a THF (10 mL) suspension of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.09 g, 0.20 mmol) was added PhCN (0.041 g, 0.40 mmol). The yellow suspension was refluxed for 2 days to give a clear yellow solution. After filtration, the filtrate was concentrated to *ca.* 3 mL. Complex **VIII-3c**·C_7H_8 was isolated as pale-yellow crystals after this solution stood at room

temperature for 3 days (0.10 g, 69%). ^{1}H NMR (pyridine-d_5): δ 7.72 (d, J = 9.0 Hz, 2H), 7.62 (d, J = 9.0 Hz, 2H), 7.48 (m, 4H), 7.34 (t, J = 9.0 Hz, 2H), 7.27 (t, J = 9.0 Hz, 2H), 7.16 (t, J = 9.0 Hz, 3H) (C_6H_5), 5.62 (s, 1H) (*H*C=C(Ph)), 5.00 (br s, 1H) (Zr-N*H*), 3.81 (br s, 1H) (cage C*H*), 2.91 (m, 2H) (CH_2CH_2NMe), 2.75 (s, 3H) (NCH_3), 2.30 (m, 2H) (CH_2CH_2NMe), 2.20 (s, 3H) ($C_6H_5(CH_3)$), 2.12 (s, 15H) ($C_5(CH_3)_5$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 148.1, 133.5, 132.7, 129.9, 129.6, 129.3, 129.0, 126.8, 126.7, 126.1, 121.4 (aryl *C* + C_5Me_5 + vinylic *C*), 113.5 (PhC≡N), 72.2 (ZrN(H)*C*HCPh), 68.2 (CH_2CH_2NMe), 66.1 (cage *C*), 49.4 (NCH_3), 26.2 (CH_2CH_2NMe), 21.7 ($C_6H_5(CH_3)$), 13.9 ($C_5(CH_3)_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 0.5 (1B), -1.2 (1B), -4.3 (2B), -7.6 (2B), -9.4 (1B), -13.7 (1B), -18.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2517 (vs), ν_{NH} 3360 (vs). Anal. Calcd for $C_{31.75}H_{46}B_9N_3Zr$ (**VIII-3c** + 0.25 toluene): C, 57.93; H, 7.04; N, 6.38. Found: C, 57.92; H, 7.37; N, 6.17.

Alternate Method. A THF (10 mL) suspension of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.09 g, 0.20 mmol) was heated to reflux overnight to give a clear orange solution, to which was added PhCN (0.04 g, 0.40 mmol). The reaction mixture was stirred at room temperature for one day. The resulting solution was treated using the same procedure reported above to give **VIII-3c** as pale-yellow crystals (0.11 g, 73%)

Preparation of (η^5-Cp*)[η^1:σ:η^5-{MeN[(CH_2)C(=NCy)NCy](CH_2CH_2)}$C_2B_9H_{10}$]Zr (VIII-3d). A THF (15 mL) suspension of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.18 g, 0.40 mmol) was heated to reflux overnight to give a clear orange solution, to which was

added diisopropylcarbodiimide (CyN=C=NCy) (0.082 g, 0.40 mmol). The reaction mixture was stirred at room temperature for 2 days. After filtration, the red filtrate was concentrated to *ca.* 5 mL. Complex **VIII-3d** was isolated as red crystals after this solution stood at room temperature for 3 days (0.18 g, 71%). ^{1}H NMR (pyridine-d_5): δ 3.91 (d, J = 7.5 Hz, 2H) (MeNCH_2C=N), 3.87 (br s, 1H) (cage CH), 2.83 (m, 1H) (ZrNCH(CH$_2$)$_5$), 2.35 (m, 1H) (NCH(CH$_2$)$_5$), 2.67 (m, 2H) (CH$_2$CH_2NMe), 2.49 (s, 3H) (NCH_3), 2.18 (s, 15H) (C$_5$(CH_3)$_5$), 1.95 (m, 2H) (CH_2CH$_2$NMe), 1.86-1.33 (m, 20H) (NCH(CH_2)$_5$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 155.8 (*C*=N), 128.6 ((*C*$_5$(CH$_3$)$_5$)), 68.5 (ZrN*C*H(CH$_2$)$_5$), 68.2 (MeN*C*H$_2$CNCy), 66.1, 64.5 (cage *C*), 62.6 (CH$_2$*C*H$_2$NMe), 57.1 (N*C*H(CH$_2$)$_5$), 45.8 (N*C*H$_3$), 37.2 (*C*H$_2$CH$_2$NMe), 36.0, 35.9, 33.5, 28.0, 26.9, 26.8, 26.2, 25.1 (NCH(*C*H$_2$)$_5$), 14.3 (C$_5$(*C*H$_3$)$_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.2 (1B), -0.4 (1B), -3.7 (2B), -7.5 (2B), -10.1 (1B), -15.3 (1B), -21.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2535 (vs). Anal. Calcd for C$_{29}$H$_{56}$B$_9$N$_3$Zr (**VIII-3d**): C, 54.83; H, 8.88; N, 6.61. Found: C, 55.01; H, 8.42; N, 6.65.

Preparation of (η^5-Cp*)[η^1:σ:η^5-{MeN[(CH$_2$)C(=N^{i}Pr)N^{i}Pr](CH$_2$CH$_2$)}C$_2$B$_9$H$_{10}$]Zr·C$_7$H$_8$ (VIII-3e·C$_7$H$_8$). This complex was prepared as red crystals from (η^5-Cp*)[η^1:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$]Zr(Me) (**VII-1**; 0.089 g, 0.20 mmol) and isopropylcarbodiimide (^{i}PrN=C=N^{i}Pr) (0.031 g, 0.20 mmol) in THF (10 mL), using the same procedure reported for **VIII-3d**: yield 0.10 g (77%). ^{1}H NMR (pyridine-d_5): δ 7.26 (m, 2H), 7.16 (m, 3H) (C$_6$*H*$_5$CH$_3$), 3.85 (br s, 1H) (cage CH), 3.82 (s, 2H) (MeNCH_2C=N^{i}Pr), 3.55 (m, 1H), 3.20 (m, 1H) (NCH(CH$_3$)$_2$), 2.65 (m, 2H) (CH$_2$CH_2NMe), 2.49 (s, 3H) (NCH_3), 2.20 (m, 2H) (CH_2CH$_2$NMe), 2.15 (s, 15H) (C$_5$(CH_3)$_5$), 1.67 (d, J = 6.0 Hz, 3H),

1.52 (d, J = 6.0 Hz, 3H), 1.18 (d, J = 6.0 Hz, 6H) (NCH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 155.5 (C=N), 128.7 ($C_5(CH_3)_5$), 129.8, 129.0, 126.1, 123.0 ($C_6H_5CH_3$), 73.7 (MeNCH_2C=N^{i}Pr), 68.5 (CH_2CH_2NMe), 61.9, 59.8 (N$CH(CH_3)_2$), 53.7 (cage C), 49.5 (NCH_3), 45.8 (CH_2CH_2NMe), 37.1 ($C_6H_5CH_3$), 26.0, 25.7, 24.0, 22.8 (NCH(CH_3)$_2$), 14.2 ($C_5(CH_3)_5$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 2.8 (1B), 1.5 (1B), -1.4 (1B), -2.9 (1B), -5.4 (1B), -8.4 (1B), -10.4 (1B), -14.5 (1B), -19.0 (1B). IR (KBr, cm^{-1}): ν_{BH} 2539 (vs). Anal. Calcd for $C_{30}H_{56}B_9N_3Zr$ (**VIII-3e** + C_7H_8): C, 55.67; H, 8.72; N, 6.49. Found: C, 55.71; H, 9.16; N, 6.57.

Preparation of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(OMe) (VIII-3f). This complex was prepared as yellow crystals from (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.18 g, 0.40 mmol) and MeOH (0.013 g, 0.40 mol) in THF (10 mL), using the same procedure reported for **VIII-3a**: yield 0.14 g (76%). ^1H NMR (pyridine-d_5): δ 3.87 (s, 3H) (OCH_3), 3.10 (br s, 1H) (cage CH), 2.93 (m, 2H) (CH_2CH_2NMe), 2.22 (m, 2H) (CH_2CH_2NMe), 2.44 (s, 3H), 2.29 (s, 3H) (N(CH_3)$_2$), 2.04 (s, 15H) ($C_5(CH_3)_5$), $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 125.1 ($C_5(CH_3)_5$), 68.2 (OCH_3), 66.7 (CH_2CH_2NMe), 59.5, 53.3 (cage C), 46.5, 45.9 (N(CH_3)$_2$), 36.4 (CH_2CH_2NMe), 13.2 ($C_5(CH_3)_5$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 2.5 (1B), 0.9 (1B), -1.5 (2B), -3.5 (1B), -5.8 (1B), -9.3 (1B), -12.5 (1B), -16.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2542 (vs). Anal. Calcd for $C_{17}H_{38}B_9NOZr$ (**VIII-3f**): C, 44.29; H, 8.31; N, 3.04. Found: C, 44.40; H, 8.29; N, 3.44.

Preparation of (η^5-Cp*){η^1:σ:η^5-($Me_2N(CH_2CH_2)$[O(CH_3)CH]$C_2B_9H_9$}Zr (VIII-3g). A Schlenk flask with a Teflon valve was charged with

(η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.22 g, 0.5 mmol), carbon monoxide (1-2 atm) and THF (5 mL). The flask was closed and heated at 60°C for 1 day to give a clear pale-yellow solution. After removal of solvent, the residue was washed with *n*-hexane and extracted with THF (20 mL). After filtration, the yellow filtrate was concentrated to *ca.* 3 mL. Complex **VIII-3g** was isolated as almost colorless crystals after this solution stood at room temperature for 5 days (0.13 g, 56%). ^{1}H NMR (pyridine-d_5): δ 4.17 (q, J = 6.9 Hz, 1H) (OC*H*Me), 3.81 (m, 2H) ($CH_2CH_2NMe_2$), 3.20 (m, 2H) ($CH_2CH_2NMe_2$), 2.89 (s, 15H) ($C_5(CH_3)_5$), 2.88 (s, 6H) ($N(CH_3)_2$), 1.80 (d, J = 6.9 Hz, 3H) ($OCH(CH_3)$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 129.8 ($C_5(CH_3)_5$), 60.0 (*O*CHMe), 52.0, 51.1 (cage *C*), 44.0 ($CH_2CH_2NMe_2$), 43.7 ($N(CH_3)_2$), 35.8 ($CH_2CH_2NMe_2$), 33.8 ($OCH(CH_3)$), 14.6 ($C_5(CH_3)_5$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 14.6 (1B), 0.73 (1B), -2.9 (1B), -5.6 (1B), -8.5 (2B), -12.9 (2B), -20.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2528 (vs). Anal. Calcd for $C_{18}H_{39}B_9NOZr$ (**VIII-3g**): C, 45.71; H, 8.10; N, 2.96. Found: C, 45.64; H, 7.73; N, 2.80.

Preparation of (η^5-Cp*){σ:η^3-[$(CH_3)_2N(CH_2CH_2)$][^{t}BuN(CH_3)CH]$C_2B_9H_9$}Zr(CN^tBu) (VIII-4a). To a toluene (15 mL) suspension of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.22 g, 0.50 mmol) was added *tert*-butylisocyanide (0.12 g, 1.50 mmol) with stirring. The reaction mixture was stirred at room temperature for 2 days to give a clear orange solution. After filtration, the orange filtrate was concentrated to *ca.* 5 mL. Complex **VIII-4a** was isolated as orange crystals after this solution stood at room temperature for 2 days (0.23 g, 74%). ^{1}H NMR (benzene-d_6): δ 3.87 (br s, 1H) (cage C*H*), 3.57 (q, J = 8.1 Hz, 1H) (^{t}BuNC*H*Me), 2.44 (m, 2H) ($CH_2CH_2NMe_2$), 2.13 (m, 2H) ($CH_2CH_2NMe_2$), 2.01 (d, J = 8.1

Hz, 3H) (^{t}BuNCH(CH_3)), 1.86 (s, 3H), 1.82 (s, 3H) (N(CH_3)$_2$), 1.84 (s, 15H) (C$_5$(CH_3)$_5$), 1.27 (s, 9H), 1.03 (s, 9H) (C(CH_3)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 156.6 (^{t}BuN*C*), 121.7 (*C*$_5$Me$_5$), 63.3 (^{t}BuN*C*HMe), 60.6 (CH$_2$*C*H$_2$NMe$_2$), 59.7 ((CH$_3$)$_3$*C*NCHMe), 58.3 ((CH$_3$)$_3$*C*N=C), 53.6, 51.9 (cage *C*), 46.3, 46.0 (N(*C*H$_3$)$_2$), 38.3 (*C*H$_2$CH$_2$NMe$_2$), 32.8, 30.4 ((*C*H$_3$)$_3$C), 28.3 (^{t}BuNCH(*C*H$_3$)), 13.4 (C$_5$(*C*H$_3$)$_5$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 14.0 (1B), -3.7 (1B), -9.5 (1B), -11.0 (2B), -16.3 (2B), -25.1 (1B), -37.0 (1B). ^{11}B NMR (benzene-d_6): δ 14.0 (1B), -3.7 (d, J = 113 Hz, 1B), -9.5 (d, J = 129 Hz,1B), -11.0 (d, J = 137 Hz, 2B), -16.3 (d, J = 113 Hz, 2B), -25.1 (d, J = 139 Hz, 1B), -37.0 (d, J = 131 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2538 (vs). Anal. Calcd for C$_{27}$H$_{56}$B$_9$N$_3$Zr (**VIII-4a**): C, 53.05; H, 9.23; N, 6.87. Found: C, 53.52; H, 9.12; N, 6.75.

Preparation of (η^5-Cp*){σ:η^3-[(CH$_3$)$_2$N(CH$_2$CH$_2$)][^{t}BuN(CH$_3$)CH]C$_2$B$_9$H$_9$}Hf(CN^{t}Bu) (VIII-4b). This complex was prepared as pale-yellow crystals from (η^5-Cp*)[η^1:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$]Hf(Me) (**VIII-1a**; 0.27 g, 0.50 mmol) and *tert*-butylisocyanide (0.12 g, 1.50 mmol) in toluene (15 mL), using the same procedure reported for **VIII-4a**: yield 0.22 g (63%). ^{1}H NMR (benzene-d_6): δ 3.25 (q, J = 9.0 Hz, 1H) (^{t}BuNC*H*(CH$_3$)), 2.62 (d, J = 9.0 Hz, 3H) (^{t}BuNCH*Me*), 2.47 (m, 2H) (CH$_2$C*H*$_2$NMe$_2$), 2.16 (s, 3H), 2.12 (s, 3H) (N(CH_3)$_2$), 1.87 (s, 15H) (C$_5$(CH_3)$_5$), 1.80 (m, 2H) (C*H*$_2$CH$_2$NMe$_2$), 1.19 (s, 9H), 1.04 (s, 9H) (C(CH_3)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 156.5 (^{t}BuN=*C*), 117.7 (*C*$_5$Me$_5$), 62.4 (^{t}BuN*C*HMe), 62.1 ((CH$_3$)$_3$*C*NCHMe), 60.5 (CH$_2$*C*H$_2$NMe$_2$), 60.2 ((CH$_3$)$_3$*C*N=C), 54.0 (cage *C*), 46.5, 46.2 (N(*C*H$_3$)$_2$), 38.4 (*C*H$_2$CH$_2$NMe$_2$), 30.3, 29.2 ((*C*H$_3$)$_3$C), 23.4 (^{t}BuNCH*C*H$_3$), 12.6 (C$_5$(*C*H$_3$)$_5$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 19.5 (1B),

8.6 (1B), -7.3 (2B), -10.4 (2B), -18.4 (2B), -30.0 (1B). ^{11}B NMR (benzene-d_6): δ 19.5 (1B), 8.6 (d, J = 115 Hz, 1B), -7.3 (d, J = 122 Hz, 2B), -10.4 (d, J = 140 Hz, 2B), -18.4 (d, J = 130 Hz, 2B), -30.0 (d, J = 129 Hz, 2B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{27}H_{56}B_9N_3Hf$ (**VIII-4b**): C, 46.42; H, 8.08; N, 6.02. Found: C, 46.68; H, 8.02; N, 5.76.

Preparation of (η^5-Cp'')\{η^1:σ:η^5-(Me$_2$NCH$_2$CH$_2$)[^{t}BuN(CH$_3$)CH]C$_2$B$_9$H$_9$\}Hf (VIII-4c). This complex was prepared as pale-yellow crystalline solids from (η^5-Cp'')[η^1:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$]Hf(Me) (**VIII-1b**; 0.30 g, 0.50 mmol) and *tert*-butylisocyanide (0.12 g, 1.50 mmol) in toluene (15 mL), using the same procedure reported for **VIII-4a**: yield 0.18 g (53%). ^{1}H NMR (pyridine-d_5): δ 7.56 (m, 2H), 6.83 (m, 1H) (C$_5H_3$(Si(CH$_3$)$_3$)$_2$), 5.20 (br s, 1H) (cage C*H*), 3.94 (m, 2H) (CH$_2$C*H*$_2$NMe), 2.96 (q, J = 8.1 Hz, 1H) (^{t}BuNC*H*Me), 2.93 (s, 3H), 2.44 (s, 3H) (N(C*H*$_3$)$_2$), 2.64 (m, 2H) (C*H*$_2$CH$_2$NMe), 2.39 (d, J = 8.1 Hz, 3H) (^{t}BuNCH(C*H*$_3$)), 1.81 (s, 9H) ((C*H*$_3$)$_3$C), 0.46 (s, 9H), 0.41 (s, 9H) (C$_5$H$_3$(Si(C*H*$_3$)$_3$)$_2$). ^{13}C\{^{1}H\} NMR (pyridine-d_5): δ 139.8, 136.7, 131.9, 128.2, 127.5 (*C*$_5$H$_3$(Si(CH$_3$)$_3$)$_2$), 65.5 (CH$_2$*C*H$_2$NMe$_2$), 58.9 (cage *C*), 53.9 (^{t}BuN*C*HMe), 47.8 ((CH$_3$)$_3$*C*NCHCH$_3$), 46.1 (N(*C*H$_3$)$_2$), 36.8 (*C*H$_2$CH$_2$NMe$_2$), 31.0 ((*C*H$_3$)$_3$CNCHCH$_3$), 28.9 ((CH$_3$)$_3$CNCH*C*H$_3$), 1.3, 1.2 (Si(*C*H$_3$)$_3$). ^{11}B\{^{1}H\} NMR (pyridine-d_5): δ 13.5 (1B), -3.5 (1B), -9.9 (2B), -13.4 (1B), -15.6 (1B), -17.2 (1B), -19.1 (1B), -25.9 (1B). ^{11}B NMR (benzene-d_6): δ 13.5 (1B), -3.5 (d, J = 115 Hz, 1B), -9.9 (d, J = 122 Hz, 2B), -13.4 (d, J = 140 Hz, 1B), -15.6 (d, J = 130 Hz, 1B), -17.2 (d, J = 129 Hz, 1B), -19.1 (d, J = 127 Hz, 1B), -25.9 (d, J = 130 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2543 (vs). Anal. Calcd for C$_{23}$H$_{53}$B$_9$N$_2$Si$_2$Hf (**VIII-4c**): C, 40.06; H, 7.75; N, 4.06. Found: C, 39.98; H, 7.62; N, 4.08.

Preparation of (η^5-Cp*){σ:η^5-($Me_2NCH_2CH_2$)[$Me_2C_6H_3NCH(Me_2C_6H_3)N=C(CH_3)$]$C_2B_9H_9$}Zr (VIII-4d). To a toluene (10 mL) suspension of (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**VII-1**; 0.22 g, 0.50 mmol) was added 2,6-dimethylphenylisocyanide (0.20 g, 1.50 mmol). The reaction mixture was stirred at room temperature for 2 days to give a red solution. After filtration, the filtrate was concentrated to *ca.* 5 mL. Complex **VIII-4d** was isolated as orange crystalline solids after this solution stood at room temperature for 3 days. (0.25 g, 71 %). ^{1}H NMR (benzene-d_6): δ 6.99 (d, J = 6.9 Hz, 1H), 6.93 (t, J = 7.2 Hz, 2H), 6.87 (d, J = 7.5 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H) ($(CH_3)_2C_6H_3$), 5.38 (br s, 1H) (NC*H*C=N), 2.63 (br s, 1H) (cage C*H*), 2.67 (s, 3H), 2.43 (s, 3H), 2.11 (s, 6H) ($(CH_3)_2C_6H_3$), 2.24 (m, 2H) ($CH_2CH_2NMe_2$), 2.23 (s, 6H) ($N(CH_3)_2$), 1.97 (m, 2H) ($CH_2CH_2NMe_2$), 1.75 (s, 3H) (CH_3C=N), 1.71 (s, 15H) ($C_5(CH_3)_5$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 171.4 (NCHC=N), 136.7, 135.2, 131.9, 131.5, 129.2, 129.1, 127.0, 125.8, 124.5, 123.2, 122.3 ($(CH_3)_2C_6H_3$ + C_5Me_5), 68.2 (NCHC=N), 60.8 ($CH_2CH_2NMe_2$), 53.6 (cage *C*), 45.6 ($N(CH_3)_2$), 36.5 ($CH_2CH_2NMe_2$), 26.2 (CH_3C=N), 20.8, 20.4, 19.7, 19.4 ($(CH_3)_2C_6H_3$), 12.5 ($C_5(CH_3)_5$). ^{11}B{^{1}H} NMR (benzene-d_6): δ 6.9 (1B), -6.4 (4B), -10.7 (3B), -19.4 (1B). ^{11}B NMR (benzene-d_6): δ 6.9 (1B), -6.4 (d, J = 115 Hz, 4B), -10.7 (d, J = 126 Hz,3B), -19.4 (d, J = 121 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2538 (vs). Anal. Calcd for $C_{35}H_{56}B_9N_3Zr$ (**VIII-4d**): C, 59.43; H, 7.98; N, 5.94. Found: C, 59.65; H, 7.53; N, 5.70.

Preparation of (η^5-Cp''){σ:η^5-($Me_2NCH_2CH_2$)[$Me_2C_6H_3NCH(Me_2C_6H_3)N=C(CH_3)$]$C_2B_9H_9$}Hf($CNC_6$

$H_3Me_2)\cdot C_7H_8$ (VIII-4e$\cdot C_7H_8$). This complex was prepared as pale-yellow crystals from (η^5-Cp'')[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Hf(Me) (**VIII-1b**; 0.30 g, 0.50 mmol) and 2,6-dimethylphenylisocyanide (0.20 g, 1.50 mmol) in toluene (10 mL), using the same procedure reported for **VIII-4d**: yield 0.34 g (67%). ^{1}H NMR (pyridine-d_5): δ 7.38 (q, J = 7.5 Hz, 2H), 7.24 (m, 3H), 7.16 (t, J = 7.5 Hz, 3H), 7.00 (m, 4H), 6.85 (q, J = 7.5 Hz, 2H) ($(CH_3)_2C_6H_3$ + $C_6H_5CH_3$), 7.23 (m, 1H), 7.02 (m, 1H), 6.76 (m, 1H) ($C_5H_3(Si(CH_3)_3)_2$), 5.42 (br s, 1H) (NC*H*C=N), 3.78 (br s, 1H) (cage C*H*), 2.86 (s, 3H) (CH_3C=N), 2.71 (s, 3H), 2.58 (s, 3H) ($(CH_3)_2C_6H_3$), 2.61 (s, 6H) ($N(CH_3)_2$), 2.30 (m, 2H) ($CH_2CH_2NMe_2$), 2.20 (s, 3H) ($C_6H_5CH_3$), 2.08 (m, 2H) ($CH_2CH_2NMe_2$), 1.82 (s, 6H), 1.59 (s, 6H) ($(CH_3)_2C_6H_3$), 0.57 (s, 9H), -0.03 (s, 9H) ($C_5H_3(Si(CH_3)_3)_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 172.0 (NCHC=N), 156.0 ($(CH_3)_2C_6H_3$NC), 138.0, 137.8, 137.4, 135.4, 133.1, 132.0, 130.1, 129.7, 129.3, 129.2, 129.0, 128.5, 126.7, 126.1, 125.6, 124.9, 124.5, 123.4, 122.5, 121.6 ($(CH_3)_2C_6H_3$ + $C_6H_5CH_3$ + $C_5H_3(Si(CH_3)_3)_2$), 68.2 (NCHC=N), 59.9 ($CH_2CH_2NMe_2$), 63.3, 53.0 (cage *C*), 45.6 ($N(CH_3)_2$), 36.8 ($CH_2CH_2NMe_2$), 26.1 (CH_3C=N), 23.4 ($C_6H_5CH_3$), 22.5, 21.7, 19.5, 19.0, 19.3 ($(CH_3)_2C_6H_3$), 1.81, 0.21 ($C_5H_3(Si(CH_3)_3)_2$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.5 (1B), -0.4 (2B), -5.5 (3B), -10.0 (2B), -18.2 (1B). ^{11}B NMR (pyridine-d_5): δ 4.5 (1B), -0.4 (d, J = 115 Hz, 2B), -5.5 (d, J = 132 Hz, 3B), -10.0 (d, J = 126 Hz, 2B), -18.2 (d, J = 154 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2532 (vs). Anal. Calcd for $C_{45}H_{71}B_9N_4Si_2Hf$ (**VIII-4e**): C, 54.05; H, 7.16; N, 5.60. Found: C, 54.30; H, 7.47; N, 5.16

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation. An empirical absorption

correction was applied using the SADABS program.[208] 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.[209] For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[210] 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.

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Appendix

Appendix I. Publications Based on the Research Findings

1. Wang, Y.; Liu, D.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 2825.
2. Liu, D.; Wang, Y.; Chan, H.-S.; Tang, Y.; Xie, Z. *Organometallics* **2008**, *27*, 5295.
3. Liu, D.; Dang, L.; Sun, Y.; Chan, H.-S.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2008**, *130*, 16103.
4. Liu, D.; Shen, H.; Wang,Y.; Cai, Y.; Xie, Z. *Asian. J. Chem.* **2011**, *6*, 628.

Appendix II. Crystal Data and Summary of Data Collection and Refinement

	II-2a	**II-2b**	**II-3a**	**II-3b**
formula	$C_{28}H_{35}B_{10}Co$-P	$C_{28}H_{35}B_{10}Ni$-P	$C_{32}H_{37}B_{10}Co$-P	$C_{32}H_{37}B_{10}Ni$-P
cryst size (mm)	0.50 x 0.40 x 0.10	0.50 x 0.30 x 0.20	0.50 x 0.40 x 0.10	0.50 x 0.40 x 0.40
fw	569.6	569.3	619.6	619.4
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	11.562(2)	11.720(2)	12.490(3)	12.322(2)
b, Å	20.123(4)	20.529(4)	13.598(3)	13.403(2)
c, Å	13.887(3)	13.938(3)	19.877(4)	19.755(3)
α, deg	90.00	90.00	90.00	90.00
β, deg	114.60(3)	114.86(3)	90.00(3)	91.25(1)
γ, deg	90.00	90.00	90.00	90.00
V, Å^3	2937.8(10)	3042.7(10)	3375.9(12)	3261.8(7)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.288	1.243	1.219	1.261
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.8 to 51.1	3.8 to 50.8	3.2 to 50.0	3.2 to 50.0
μ, mm^{-1}	0.658	0.709	0.578	0.667
F(000)	1180	1184	1284	1288
no. of obsd reflns	4864	4651	5388	5744
no. of params refnd	361	361	397	397
goodness of fit	1.158	1.148	1.142	1.076
R1	0.046	0.075	0.094	0.036
wR2	0.119	0.189	0.242	0.085

	II-4	**II-5a**	**II-5b**	**II-6a**
formula	$C_{32}H_{44}B_{10}N$-NiP	$C_{19}H_{29}B_{10}Co$-N	$C_{19}H_{29}B_{10}NNi$	$C_{37}H_{56}B_{10}$-CoN_2
cryst size (mm)	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.30	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.40
fw	640.5	438.5	438.2	695.9
cryst syst	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
space group	$P(-1)$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
a, Å	10.510(2)	12.585(5)	12.462(3)	10.585(2)
b, Å	13.019(3)	12.826(5)	12.866(3)	20.471(4)
c, Å	13.996(3)	14.284(6)	14.204(3)	19.337(4)
α, deg	101.90(3)	90.00	90.00	90.00
β, deg	106.00(3)	90.00	90	98.77(3)
γ, deg	98.73(3)	90.00	90.00	90.00
V, Å^3	1756.4(6)	2305.6(16)	2277.4(8)	4141.1(14)
Z	2	4	4	4
D_{calcd}, Mg/m^3	1.211	1.263	1.278	1.116
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.0 to 51.0	4.0 to 56.0	4.0 to 51.2	3.0 to 50.6
μ, mm^{-1}	0.622	0.752	0.859	0.442
F(000)	672	908	912	1476
no. of obsd reflns	5630	5763	4056	6512
no. of params refnd	406	280	280	451
goodness of fit	1.086	1.020	1.091	1.131
R1	0.038	0.041	0.040	0.052
wR2	0.105	0.086	0.110	0.134

	II-6b	**II-7**	**II-8**	**III-2**·2THF
formula	$C_{37}H_{56}B_{10}N_2$ -Ni	$C_{30}H_{58}B_{10}Ni$ -$O_{0.5}P$	$C_{54}H_{84}B_{20}$-$Co_2O_2P_2$	$C_{76}H_{152}B_{18}$-Na_6O_{14}
cryst size (mm)	0.50 x 0.40 x 0.30	0.30 x 0.20 x 0.10	0.40 x 0.30 x 0.20	0.60 x 0.45 x 0.35
fw	695.7	624.5	1161.2	1622.5
cryst syst	Monoclinic	Triclinic	Monoclinic	triclinic
space group	$P2_1/n$	$P(-1)$	$P2_1/c$	$P(-1)$
a, Å	10.447(2)	10.233(2)	10.932(1)	11.221(2)
b, Å	20.103(4)	11.973(2)	16.750(2)	14.459(3)
c, Å	19.072(4)	15.377(2)	17.431(2)	33.118(7)
α, deg	90.00	98.02(1)	90	87.40(1)
β, deg	90.86(3)	95.42(1)	103.11(1)	87.56(1)
γ, deg	90.00	110.62(1)	90	67.18(1)
V, Å^3	3957.5(14)	1724.8(5)	3108.4(5)	4945.7(2)
Z	4	2	2	2
D_{calcd}, Mg/m^3	1.168	1.203	1.241	1.090
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.0 to 50.0	2.7 to 50.0	3.4 to 56.0	1.2 to 50.0
μ, mm^{-1}	0.519	0.631	0.625	0.091
F(000)	1480	670	1216	1752
no. of obsd reflns	5968	6038	7716	14893
no. of params refnd	451	385	361	1075
goodness of fit	1.119	0.976	1.034	0.819
R1	0.048	0.057	0.054	0.093
wR2	0.124	0.134	0.129	0.251

	III-4	**III-5a**	**III-5b**	**III-5c**·C_7H_8
formula	$C_{22}H_{50}B_9Cl_2$–	$C_{23}H_{45}B_9Cl$	$C_{29}H_{57}B_9Cl$–	$C_{33}H_{54}B_9NO$
	LiO_6Zr	–NaO_4Zr	NaO_6Zr	–Zr
cryst size (mm)	0.70 x 0.30 x	0.70 x 0.45	0.75 x 0.50	0.60 x 0.35
	0.25	x 0.40	x 0.25	x 0.25
fw	677.0	632.5	748.7	669.3
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	*P*(-1)	$P2_1/n$	*P*(-1)	*C*2/c
a, Å	8.824(1)	16.327 (1)	10.534(1)	34.270(2)
b, Å	13.749(1)	11.679(1)	13.446 (1)	12.187 (1)
c, Å	15.326 (1)	19.050(1)	15.148(1)	23.272(1)
α, deg	74.18(1)	90	105.49 (1)	90
β, deg	89.63(1)	114.66 (1)	105.52 (1)	129.85 (1)
γ, deg	82.88(1)	90	90.74 (1)	90
V, Å^3	1774.3(2)	3301.1(3)	1984.0(2)	7462.1(6)
Z	2	4	2	8
D_{calcd}, Mg/m^3	1.267	1.273	1.253	1.191
radiation (λ), Å	Mo Kα	Mo Kα	Mo Kα	Mo Kα
	(0.71073)	(0.71073)	(0.71073)	(0.71073)
2θ range, deg	3.1 to 50.0	2.7 to 56.0	2.9 to 52.0	3.1 to 50.0
μ, mm^{-1}	0.492	0.454	0.392	0.321
F(000)	704	1312	784	2816
no. of obsd reflns	6227	7974	7354	6583
no. of params refnd	370	352	432	395
goodness of fit	1.071	0.974	1.045	1.022
R1	0.066	0.040	0.042	0.063
wR2	0.200	0.122	0.122	0.190

	IV-1	IV-2	IV-4a	IV-4b
formula	$C_{17}H_{34}B_9N$	$C_{18}H_{35}B_9N_2$ -Zr	$C_{33}H_{59}B_9Cl$-NaO_6Zr	$C_{31}H_{57}B_9Cl$-NaO_6Zr
cryst size (mm)	0.65 x 0.30 x 0.15	0.40 x 0.30 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.10 x 0.05
fw	349.7	468.0	798.8	772.7
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
space group	*P*bca	$P2_1/c$	*P*(-1)	*P*(-1)
a, Å	9.345(1)	14.140(3)	12.265(3)	11.494(2)
b, Å	13.462(2)	10.683(2)	13.110(3)	12.777(3)
c, Å	34.022(5)	16.648(3)	13.761(3)	14.431(3)
α, deg	90	90	78.22(3)	83.71(3)
β, deg	90	111.59(3)	83.36(3)	74.74(3)
γ, deg	90	90	84.01(3)	88.56(3)
V, Å^3	4280.0(1)	2338.4(8)	2144.1(7)	2032.3(7)
Z	8	4	2	2
D_{calcd}, Mg/m^3	1.086	1.329	1.237	1.263
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.4 to 50.0	3.1 to 51.0	3.0 to 51.7	3.2 to 50.0
μ, mm^{-1}	0.055	0.479	0.367	0.385
F(000)	1504	968	836	808
no. of obsd reflns	3366	4214	5695	5236
no. of params refnd	280	271	460	442
goodness of fit	1.023	1.062	1.050	1.131
R1	0.097	0.043	0.063	0.078
wR2	0.262	0.121	0.154	0.221

	IV-4c·0.5C_6-H_6	**IV-4d**·0.5C_6-H_6	**V-4**	**V-5**·THF
formula	$C_{29}H_{43}B_9NO$-Zr	$C_{25}H_{42}B_9O_2$-Zr	$C_{16}H_{37}B_9N_2$-Zr	$C_{26}H_{54}B_9NO_3Zr$
cryst size (mm)	0.40 x 0.30 x 0.20	0.30 x 0.20 x 0.10	0.40 x 0.30 x 0.20	0.10 x 0.08 x 0.05
fw	610.2	563.1	446.0	617.2
cryst syst	monoclinic	triclinic	monoclinic	triclicnic
space group	*C*2/c	*P*(-1)	$P2_1$/n	*P*(-1)
a, Å	27.994(6)	9.879(1)	8.076(1)	11.046(2)
b, Å	14.806(3)	11.449(1)	17.037(1)	17.141(3)
c, Å	17.521(4)	13.980(1)	16.836(1)	18.935(4)
α, deg	90	95.84(1)	90	103.95(3)
β, deg	93.31(3)	108.74(1)	100.33(1)	99.40(3)
γ, deg	90	93.90(1)	90	99.73(3)
V, Å^3	7250.0(3)	1481.0(2)	2278.9(2)	3350.1(12)
Z	8	2	4	4
D_{calcd}, Mg/m^3	1.118	1.263	1.300	1.224
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.9 to 50.0	3.1 to 50.0	3.4 to 52.0	2.2 to 50.8
μ, mm^{-1}	0.325	0.393	0.487	0.356
F(000)	2536	586	928	1304
no. of obsd reflns	5595	5195	4475	8713
no. of params refnd	372	334	253	721
goodness of fit	1.209	1.019	1.106	1.091
R1	0.074	0.068	0.054	0.057
wR2	0.237	0.175	0.143	0.151

	V-6a	**V-6c**	**V-7a**	**V-7b**·THF
formula	$C_{20}H_{40}B_9Cl_2$ -LiO_2Zr	$C_{20}H_{44}B_9Cl_2$ -LiO_4Zr	$C_{32}H_{70}B_9Li$-O_3Si_2Zr	$C_{25}H_{44}B_9NO$ -Zr
cryst size (mm)	0.75 x 0.60 x 0.10	0.50 x 0.30 x 0.20	0.80 x 0.50 x 0.40	0.40 x 0.30 x 0.20
fw	578.9	614.9	754.5	563.1
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*2	*P*(-1)	*P*2/c	$P2_1$/n
a, Å	11.219(3)	8.784(1)	23.139(2)	12.114(2)
b, Å	23.565(6)	11.529(1)	10.897(1)	15.041(3)
c, Å	11.586(3)	15.994(1)	35.411(3)	17.183(3)
α, deg	90	92.13(1)	90	90
β, deg	110.41(1)	101.94(1)	95.62(2)	98.01(3)
γ, deg	90	91.26(1)	90	90
V, Å^3	2870.8(13)	1582.9(2)	8885.6(13)	3100.3(11)
Z	4	2	8	4
D_{calcd}, Mg/m^3	1.339	1.290	1.128	1.206
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	6.4 to 50.0	2.6 to 57.5	1.6 to 50.0	4.3 to 50.0
μ, mm^{-1}	0.586	0.540	0.330	0.374
F(000)	1192	636	3216	1176
no. of obsd reflns	4471	7978	15605	5450
no. of params refnd	317	334	865	334
goodness of fit	1.087	1.056	1.158	1.050
R1	0.079	0.047	0.091	0.069
wR2	0.208	0.124	0.183	0.185

	VI-1	**VI-2a**	**VI-2c**·C_7H_8	**VI-3a**
formula	$C_{17}H_{40}B_9N$-Si_2Zr	$C_{23}H_{50}B_9N$-Si_2Zr	$C_{38}H_{56}B_9N$-Si_2Zr	$C_{26}H_{48}B_9N$-Si_2Zr
cryst size (mm)	0.50 x 0.40 x 0.30	0.60 x 0.35 x 0.25	0.24 x 0.20 x 0.14	0.40 x 0.30 x 0.20
fw	503.2	585.3	771.5	619.3
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P(-1)$	$P(-1)$
a, Å	15.927(3)	19.577(3)	10.175(2)	10.199(2)
b, Å	9.976(2)	9.974(1)	11.110 (2)	11.637(2)
c, Å	17.407(4)	16.926(2)	22.337(4)	15.352(2)
α, deg	90	90	91.67 (1)	80.63(1)
β, deg	101.14(1)	99.29 (1)	91.91 (1)	74.97(1)
γ, deg	90	90	114.03 (1)	76.18(1)
V, Å^3	2713.6(9)	3261.6(7)	2302.5(7)	1698.8(4)
Z	4	4	2	2
D_{calcd}, Mg/m^3	1.232	1.192	1.113	1.211
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.6 to 56.8	4.2 to 56.0	4.0 to 50.0	2.8 to 50.0
μ, mm^{-1}	0.500	0.425	0.316	0.412
F(000)	1048	1232	808	648
no. of obsd reflns	6716	7858	7965	5942
no. of params refnd	271	325	496	352
goodness of fit	1.034	1.067	0.956	1.065
R1	0.051	0.034	0.075	0.037
wR2	0.119	0.088	0.220	0.090

	VI-3b	**VI-3c**	**VI-4a**	**VI-4c**
formula	$C_{28}H_{54}B_9N$-Si_3Zr	$C_{26}H_{58}B_9N$-Si_3Zr	$C_{25}H_{46}B_9N$-Si_2Zr	$C_{22}H_{50}B_9N$-Si_3Zr
cryst size (mm)	0.40 x 0.30 x 0.20	0.50 x 0.30 x 0.20	0.24 x 0.20 x 0.18	0.50 x 0.30 x 0.20
fw	677.5	657.5	605.3	601.4
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	19.530(2)	18.371(2)	10.720(1)	11.055(4)
b, Å	10.208(1)	10.614(1)	17.942(2)	30.190(9)
c, Å	20.640(2)	20.465(2)	16.946(2)	10.338(3)
α, deg	90	90	90	90
β, deg	115.68(1)	115.75(1)	96.34(1)	107.93(6)
γ, deg	90	90	90	90
V, Å^3	3708.2(8)	3594.1(5)	3239.4(7)	3283.0(2)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.214	1.215	1.241	1.217
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.2 to 56.0	2.5 to 50.0	3.3 to 50.0	2.7 to 56.0
μ, mm^{-1}	0.414	0.425	0.430	0.459
F(000)	1424	1392	1264	1264
no. of obsd reflns	8947	6332	5635	7855
no. of params refnd	379	361	344	325
goodness of fit	0.986	1.055	1.005	1.064
R1	0.052	0.045	0.080	0.044
wR2	0.125	0.105	0.175	0.109

	VI-4d·0.5-C_7H_8	**VII-1**	**VII-2**	**VII-3a**
formula	$C_{26.5}H_{54}B_9N$-Si_2Zr	$C_{17}H_{40}B_9N$-Si_2Zr	$C_{16}H_{434}B_9N$-Zr	$C_{22}H_{44}B_9N$-Zr
cryst size (mm)	0.30 x 0.20 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20
fw	631.4	503.2	429.0	511.1
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P(-1)$	$P(-1)$
a, Å	10.909 (1)	15.927(3)	8.477(1)	10.691(1)
b, Å	9.538(1)	9.976(2)	10.231(1)	10.941(1)
c, Å	34.342(3)	17.407(4)	13.944(2)	11.572(1)
α, deg	90	90	107.80(1)	81.20(1)
β, deg	92.43(1)	101.14(1)	92.51(1)	85.30(1)
γ, deg	90	90	108.97(1)	83.53(1)
V, Å^3	3570.1(6)	2713.6(9)	1075.1(2)	1326.3(3)
Z	4	4	2	2
D_{calcd}, Mg/m^3	1.175	1.232	1.325	1.280
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.4 to 50.0	2.6 to 56.8	3.1 to 50.0	3.6 to 50.0
μ, mm^{-1}	0.393	0.500	0.512	0.427
F(000)	1332	1048	444	536
no. of obsd reflns	6279	6716	3769	4660
no. of params refnd	370	271	244	306
goodness of fit	1.067	1.034	1.094	1.080
R1	0.049	0.051	0.031	0.064
wR2	0.121	0.119	0.088	0.167

	VII-3b	**VII-3c**	**VII-4b**·0.5C$_7$H$_8$	**VII-4c**
formula	$C_{24}H_{48}B_9N$-Zr	$C_{26}H_{52}B_9N$-Zr	$C_{30\ 50}H_{52}B_9$-NSiZr	$C_{25}H_{52}B_9N$-SiZr
cryst size (mm)	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.30 x 0.20 x 0.10	0.50 x 0.40 x 0.30
fw	539.1	567.2	649.3	583.3
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P(-1)$	$P(-1)$
a, Å	9.857(1)	15.658(4)	10.999(2)	9.253(1)
b, Å	27.388(4)	9.353(2)	18.648(2)	10.244(1)
c, Å	10.948(2)	21.601(5)	19.836(2)	18.664(2)
α, deg	90	90	115.78(1)	79.92(1)
β, deg	100.66 (1)	95.20(1)	90.66(1)	76.54(1)
γ, deg	90	90	105.15(1)	68.32(1)
V, Å^3	2904.5(6)	3150.5(1)	3499.5(7)	1590.9(3)
Z	4	4	4	2
D_{calcd}, Mg/m^3	1.233	1.196	1.232	1.218
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.0 to 56.0	2.6 to 56.0	2.3 to 50.0	2.2 to 56.0
μ, mm^{-1}	0.393	0.366	0.371	0.400
F(000)	1136	1200	1364	616
no. of obsd reflns	7030	7609	12226	7528
no. of params refnd	316	334	766	334
goodness of fit	1.053	0.992	1.024	1.051
R1	0.051	0.057	0.053	0.045
wR2	0.133	0.131	0.122	0.117

	VII-4d·THF	**VII-5a**·THF	**VII-5b**	**VIII-1a**
formula	$C_{31}H_{55}B_9N_2OZr$	$C_{26}H_{51}B_9NOZr$	$C_{21}H_{44}B_9NSiZr$	$C_{17}H_{38}B_{19}HfN$
cryst size (mm)	0.40 x 0.30 x0.20	0.24 x 0.20 x 0.14	0.50 x 0.30 x 0.20	0.30 x 0.20 x 0.10
fw	660.3	582.2	527.2	532.3
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P(-1)$	$P(-1)$	$P2_1/n$
a, Å	16.055(2)	10.474(1)	10.813(2)	10.416(1)
b, Å	16.613(2)	12.430(1)	10.847(2)	16.566(2)
c, Å	13.776(2)	13.074(1)	13.229(2)	13.738(2)
α, deg	90	108.23(1)	80.23(1)	90
β, deg	102.91(3)	92.02(2)	76.02(3)	108.80(1)
γ, deg	90	92.74(2)	68.68(1)	90
V, Å^3	3581.4(8)	1612.4(3)	1396.9(4)	2244.1(5)
Z	4	2	2	4
D_{calcd}, Mg/m^3	1.225	1.199	1.253	1.575
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.6 to 50.0	3.5 to 52.8	3.2 to 50.0	1.2 to 50.0
μ, mm^{-1}	0.334	0.361	0.448	4.652
F(000)	1392	614	552	1056
no. of obsd reflns	6309	6486	7662	3949
no. of params refnd	406	343	298	253
goodness of fit	1.039	1.098	1.069	1.053
R1	0.071	0.038	0.046	0.028
wR2	0.187	0.103	0.113	0.064

	VIII-1b	**VIII-2a**	**VIII-2b**	**VIII-2d**·0.5 C_7-H_8
formula	$C_{18}H_{44}B_9Hf$-NSi_2	$C_{30}H_{62}B_9N_3$-Si_2Zr	$C_{19}H_{43}B_9N_2$-Si_2Zr	$C_{47.5}H_{71}B_9$-N_4Si_2Zr
cryst size (mm)	0.50 x 0.30 x 0.10	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.30 x 0.30 x 0.20
fw	606.5	709.5	544.2	942.8
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P(-1)$	$P2_1/c$	$P2_1/c$
a, Å	9.260(1)	10.192(1)	12.351(1)	18.941(2)
b, Å	18.210(2)	14.349(2)	12.621(2)	13.833(2)
c, Å	16.745(2)	14.758(2)	19.039(2)	19.840(2)
α, deg	90	78.74(1)	90	90
β, deg	94.19(1)	70.80(1)	90.35(1)	90.99(3)
γ, deg	90	78.79(1)	90	90(1)
V, Å^3	2816.1(7)	1979.1(5)	2928.4(6)	5197.4(9)
Z	4	2	4	4
D_{calcd}, Mg/m^3	1.431	1.191	1.234	1.205
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.3 to 56.6	2.9 to 50.0	3.3 to 56.0	2.1 to 50.0
μ, mm^{-1}	3.797	0.363	0.469	0.294
F(000)	1216	752	1136	1988
no. of obsd reflns	6988	6923	7071	9156
no. of params refnd	280	406	298	577
goodness of fit	1.055	1.086	1.004	1.005
R1	0.028	0.029	0.045	0.053
wR2	0.064	0.079	0.101	0.126

	VIII-2e	**VIII-2f**	**VIII-3a**	**VIII-3b**
formula	$C_{22}H_{49}B_9N_2$-SSi_2Zr	$C_{30}H_{50}B_9NO$-Si_2Zr	$C_{19}H_{41}B_9N_2$-Zr	$C_{22}H_{45}B_9N_2$-Zr
cryst size (mm)	0.50 x 0.40 x 0.30	0.50 x 0.30 x 0.20	0.30 x 0.20 x 0.10	0.30 x 0.20 x 0.20
fw	618.4	685.4	486.1	526.1
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P(-1)$	$P2_1/c$	$P(-1)$	$P2_1/n$
a, Å	10.331(2)	17.021(2)	10.675(1)	9.267(1)
b, Å	11.207(3)	10.842(1)	10.742(1)	20.067(3)
c, Å	15.486(3)	20.468(2)	11.168(1)	14.946(2)
α, deg	77.34(1)	90	82.81(1)	90
β, deg	77.47(1)	105.76 (1)	88.37(1)	91.66(1)
γ, deg	73.99(1)	90	85.34(1)	90
V, Å^3	1658.0(6)	3635.0(7)	1266.1(2)	2778.2(6)
Z	2	4	2	4
D_{calcd}, Mg/m^3	1.239	1.252	1.275	1.258
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.7 to 56.0	2.5 to 50.0	3.6 to 50.0	3.4 to 50.0
μ, mm^{-1}	0.483	0.394	0.444	0.410
F(000)	648	1432	508	1104
no. of obsd reflns	7871	6392	4440	4881
no. of params refnd	334	397	280	307
goodness of fit	1.0331	1.090	1.074	1.030
R1	0.048	0.030	0.034	0.047
wR2	0.120	0.075	0.085	0.110

	VIII-3c	**VIII-3e**	**VIII-3f**	**VIII-3g**
formula	$C_{34.50}H_{48.50}$-B_9N_3Zr	$C_{28}H_{52}B_9N_3$-Zr	$C_{17}H_{38}B_9NO$-Zr	$C_{18}H_{38}B_9NO$-Zr
cryst size (mm)	0.50 x 0.40 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	693.8	619.2	561.0	473.0
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P(-1)$	$P2_1/n$	$P2_1/n$
a, Å	23.424(1)	10.005(1)	8.997(1)	11.677(1)
b, Å	10.112(1)	10.819(1)	15.332(2)	14.923(2)
c, Å	17.713(5)	15.641(2)	17.599(2)	13.883(2)
α, deg	90	81.01(1)	90	90
β, deg	112.01(1)	85.10(1)	101.04(1)	91.80(1)
γ, deg	90	79.53(1)	90	90(1)
V, Å^3	3889.9(9)	1641.4(4)	2382.8(5)	2418.0(5)
Z	4	2	4	4
D_{calcd}, Mg/m^3	1.185	1.253	1.285	1.299
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	1.8 to 50.2	4.0 to 56.0	3.6 to 50.0	4.0 to 56.0
μ, mm^{-1}	0.310	0.359	0.470	0.465
F(000)	1446	652	960	984
no. of obsd reflns	6773	7802	4193	5825
no. of params refnd	544	370	262	271
goodness of fit	1.311	1.055	1.036	1.063
R1	0.093	0.050	0.028	0.039
wR2	0.211	0.127	0.076	0.103

	III-3a	**VIII-4a**	**VIII-4c**	**VIII-4e**·C_7H_8
formula	$C_{22}H_{50}B_9Cl_2$– NaO_6Zr	$C_{27}H_{56}B_9N_3Zr$	$C_{27}H_{56}B_9Hf$-N_3	$C_{52}H_{79}B_9HfN_4Si_2$
cryst size (mm)	0.65 x 0.45 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.40 x 0.30	0.40 x 0.30 x 0.20
fw	693.0	611.3	698.5	1092.2
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	*P*na2$_1$	*P*2$_1$/c	*P*2$_1$/c	*P*2$_1$2$_1$2$_1$
a, Å	30.143(3)	18.959 (2)	19.002(1)	30.7471)
b, Å	12.916(2)	11.635(1)	11.589 (1)	19.801(2)
c, Å	18.608(2)	16.648(1)	16.570(1)	27.218(2)
α, deg	90	90	90	90
β, deg	90	110.06 (1)	109.96 (1)	90
γ, deg	90	90	90	90
V, Å^3	7244.4(2)	3449.4(5)	3429.6(2)	5791.7(9)
Z	8	4	4	4
D_{calcd}, Mg/m^3	1.271	1.177	1.353	1.253
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.7 to 50.0	2.3 to 56.0	2.3 to 56.0	3.1 to 56.0
μ, mm^{-1}	0.495	0.340	3.063	1.879
F(000)	2880	1296	1424	2256
no. of obsd reflns	9492	8341	8170	14012
no. of params refnd	735	361	362	613
goodness of fit	1.106	0.940	1.154	0.987
R1	0.082	0.061	0.021	0.039
wR2	0.199	0.140	0.053	0.081

Appendix III. X-ray crystallographic data in CIF (electronic form)