Synthesis, Structure, and Reactivity of Group 4 Metal-Carboryne Complexes

REN, Shikuo

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Assessment Committee:

Professor Kevin W. P. Leung, Chair

Professor Hak-Fun Chow, Committee Member

Professor Zuowei Xie, Research Supervisor

Professor Tamotsu Takahashi, External Examiner

(Hokkaido University)

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Abstract

A series of group 4 metal-carboryne complexes were synthesized by the reaction of $Li_2C_2B_{10}H_{10}$ with dichloro group 4 metal complexes. Reaction of (η^2-$C_2B_{10}H_{10}$)$ZrCl_2(THF)_3$ with 2 equiv of [MeC(NCy)$_2$]Li or [^{n}Pr$_2$NC(NPr^i)$_2$]Li also effectively yielded the corresponding group-4-metal-carboryne complexes. On the other hand, treatment of $C_2B_{10}H_{10})ZrCl_2(THF)_3$ with 2 equiv of ^{t}BuOK or [^{t}BuCOCHCO^{t}Bu]Na gave unexpected product [(η^2-$C_2B_{10}H_{10})_2Zr(O^tBu)(THF)$] [$Zr(OBu^t)_3(THF)_3$] or [$\sigma$:$\sigma$:$\sigma$-{^{t}BuC(O)=CHC(^{t}Bu)(O)$C_2B_{10}H_{10}$}]Zr(η^2-^{t}BuCOCHCOBu^t)$(THF)_2$.

Subsequently, the reactivities of group 4 metal-carbroyne complexes toward unsaturated molecules were studied. Polar molecules such as azide, ketone, nitrile, carbodiimide, isocyanate, thioisocyanate, carbon disulfide, and isonitrile were inserted into the M-C bond in metal-carboryne complexes to form mono-, di-, or tri-insertion products. These metal-carboryne complexes, however, showed no reactivity toward internal alkynes and alkenes. Terminal alkynes protonated the carboryne complexes to afford neutral *o*-carborane.

Next, the reactivities of $Cp_2Zr(\mu$-Cl)(μ-$C_2B_{10}H_{10})Li(OEt_2)_2$ toward alkynes, alkenes and pyridines were studied. Various kinds of internal alkynes, and terminal alkenes reacted with this Zr-carboryne precursor to effectively generate the mono-insertion products zirconacyclopentene and zirconacyclopentane, respectively. Interaction of $Cp_2Zr(\mu$-Cl)(μ-$C_2B_{10}H_{10})Li(OEt_2)_2$ and pyridines afforded a new kind of carboranyl zirconocene complexes via C-H activation at α-position of pyridines.

Finally, the reactivities of aforementioned zirconacyclopentene and zirconacyclopentane complexes were studied. A new class of benzocarboranes and dihydrobenzocarboranes were prepared by indirect [2+2+2] cycloaddition of

carboryne with two different alkynes, or with one alkene and one alkyne, mediated by Ni(II) or Fe(III). In the presence of CuCl and HMPA, zirconacyclopentenes or zirconacyclopentanes reacted with *ortho*-dihalobenzene reagents to generate naphthalocarborane or dihydronaphthalocarborane derivatives. A series of carborane fused cyclobutenes and cyclobutane were also prepared from zirconacyclopentenes or zirconacyclopentanes complexes mediated by Cu(II).

摘 要

本论文首先描述了一系列第四族金属-碳硼炔络合物的合成。碳硼烷二锂盐与第四族金属二氯二脒基或胍基络合物反应生成金属有机-碳硼炔络合物。碳硼烷二锂盐与 $ZrCl_4(THF)_2$ 直接反应亦可以生成$(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$。$(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$ 与两当量的 $[MeC(NCy)_2]Li$ 或 $[^nPr_2NC(NPr^i)_2]Li$ 反应，可以有效地制备二脒基或二胍基金属-碳硼炔络合物。然而，当它与两当量的 ^{t}BuOK 或 $[^t$BuCOCHCO^{t}Bu]Na 反应只能生成 $[(\eta^2\text{-}C_2B_{10}H_{10})_2Zr(O^t$Bu)(THF)][Zr(OBu^t)$_3(THF)_3$] 或 [σ:σ:σ-{^{t}BuC(O)=CHC(^{t}Bu)(O)$C_2B_{10}H_{10}$}]Zr(η^2-^{t}BuCOCHCOBu^t)(THF)$_2$。

接下来，我们研究了这一类金属-碳硼炔络合物的反应性。结果发现酮、腈、碳二亚胺、异腈酸酯、硫代异腈酸酯，二硫化碳，以及异腈等极性不饱和有机分子都可以插入金属-碳硼炔中的 M-C 键生成单、双或三插入产物，然而，这类金属-碳硼炔不与中间炔和烯烃反应；末端炔烃会使这些金属碳硼炔质子化形成中性碳硼烷。

然后，我们对 $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ 与炔、烯和吡啶的反应进行了系统研究。结果表明中间炔和末端烯烃与这个锆-碳硼炔前提反应分别生成单插入产物：含一个碳硼烷单元的锆杂环戊烯和锆杂环戊烷络合物；该锆-碳硼炔前提与吡啶反应生成一类新的吡啶 α-氢被活化转移的碳硼烷二茂锆络合物。

最后，本文阐述了这类锆杂环戊烯和锆杂环戊烷的化学性质。在镍（II）或铁（III）的存在下，通过间接的[2+2+2]环加成反应，锆杂环戊烯或环戊烷与炔烃反应生成一系列的苯并或二氢苯并碳硼烷。在 CuCl 和 HMPA 存在下，

锆杂环戊烯或环戊烷与邻-二卤苯反应生成萘并或二氢萘并碳硼烷衍生物。通过与 Cu（II）的转金属反应，锆杂环戊烯或环戊烷可生成一系列碳硼烷的环丁烯或环丁烷衍生物。

Abbreviation

Ar	aryl
br	broad
brs	broad singlet (NMR)
^{n}BuLi	*n*-butyl lithium
^{t}Bu	*tert*-butyl
compd	compound
Cp	cyclopentadienyl
Cp''	1,3-bis(trimethylsilyl)cyclopentadienyl
Cp^{tt}	1,3-bis(*tert*-butyl)cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	doublet (NMR)
DCC	dicyclohexylcarbodiimide
dd	double doublet (NMR)
DMAD	dimethylacetylenedicarboxylate
DME	dimethoxyethane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
Et	ethyl
Et_2O	diethyl ether
Fig.	figure
h	hour
GC-MS	gas chromatography-mass spectrum

IR	infrared spectroscopy
Ln	lanthanide
NMR	nuclear magnetic resonance
m	multiplet (NMR)
M	metal
Me	methyl
MeCN	acetonitrile
HRMS	high resolution mass spectroscopy
Ph	phenyl
^{i}Pr	*iso*-propyl
Py	pyridine
s	singlet (NMR)
t	triplet (NMR)
Tf	trifluoromethanesulfonate
TBAF	tetrabutylammonium fluoride
TBDMS	*tert*-butyldimethylsilyl
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl
xs	excess

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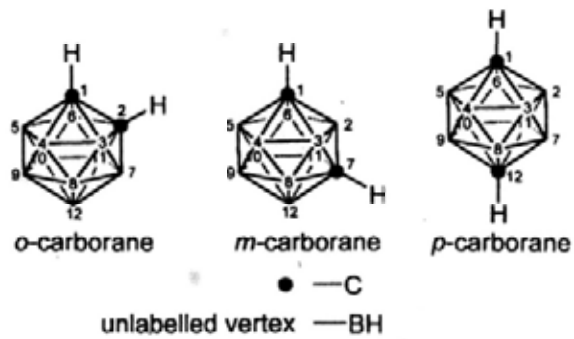
Chapter 1. Introduction

1.1. Carboranes

Carboranes are a class of boron clusters with one or more polyhedral boron vertices replaced by CR unit(s) (R = H, alkyl, aryl, et al). They were known as early as 1960s.[1] These species have been extensively studied and reviewed.[2] Icosahedral carboranes ($C_2B_{10}H_{12}$) contains ten-boron and two-carbon vertices, existing as 1,2 (*ortho* or *o*)-, 1,7 (*meta* or *m*)- and 1,12 (*para* or *p*)-isomers ($C_2B_{10}H_{12}$). Their structures and IUPAC numbering of the three isomers are shown in Chart 1.1.[2] The inter-atomic distances are shown in Table 1.1.[2c] Both C-C (1.62-1.70 Å) and C-B (1.70-1.75 Å) bond distances are much longer than the normal values (*ca.* 1.54 and 1.56 Å, respectively) found in organic compounds.[3] The B-B bond distances (1.70-1.79 Å) are shorter than those (1.82-1.86 Å) found in organic boron compounds.[4]

Chart 1.1. The Numbering Systems of *o*-, *m*- and *p*-$C_2B_{10}H_{12}$.

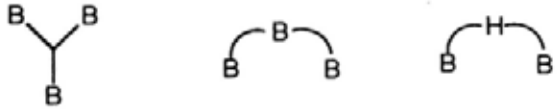


Polyhedral carborane clusters are characterized by delocalized electron-deficient bonding, with too few valence electrons for bonding to be described exclusively in terms of 2-center-2-electron (2c2e) bonds.[5,6] One characteristic of electron-deficient structures is the aggregation of atoms to form 3-center-2-electron (3c2e) bonds, in which three atoms are linked by a single pair of electrons, typically leading to the formation of trigonal faces and hyper-coordination. Three types of three-center-two-electron bonds maybe involved in the carborane molecules shown in Chart 1.2.[2a] The high connectivity of atoms in a cluster compensates for the relatively low electron density in skeletal bonds.[7]

Table 1.1. Bond Distances in *o*-Carboranes.

bond	distance (Å)
C-C	1.62-1.70
C-B	1.70-1.75
B-B	1.70-1.79

Chart 1.2. Typical Three-Center Two-Electron Bonds Observed in Carboranes.



Any of these bonds requires a contribution of one orbital from each of the three atoms to form three molecular orbitals, one of which is bonding, a second is

antibonding, and the third is either antibonding or nonbonding. A pair of electrons may then, of course, occupy the bonding orbital. Figure 1.1 illustrates in idealized form the atomic orbital contributions.[2a]

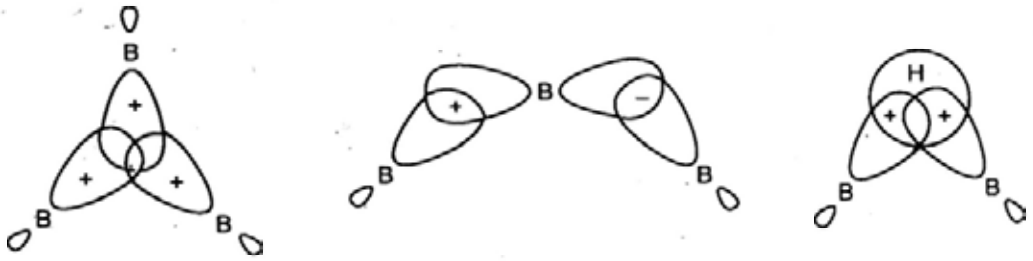


Figure 1.1. Orbital Contributions to Three-Center Bonds.

A large amount of experimental data has been collected and several calculations have been made to describe the charge distributions of the carboranes.[8-10] The results show that the electron densities of the boron atoms are enhanced with the increased remoteness from the cage carbons of the carborane cluster. Thus, the 9-/12-boron atoms and the 9-/10-boron atoms of *o*- and *m*-carborane, respectively, possess higher electron densities than the other carborane-borons which are all neighboring one or two carbon atoms (numbering according to Chart 1.1). This charge distribution makes *o*-carborane the most polar/least lipophilic carborane, and *p*-carborane, with an even charge distribution of the boron atoms, the least polar/most lipophilic carborane. If one compares the electron densities of the carbon atoms of each cluster, the lowest density is found around the carbon atoms of the *o*-carborane and the highest around the carbon atoms of *p*-carborane. From the experimental, the CH-proton acidities of the carboranes are obtained and summarized in Table 1.2.[11]

They are in accordance with the electron densities calculated based on molecular orbital theory.

In drawing these polyhedral structures, it is common not to indicate the atoms at each vertex specifically. If no atom is indicated, it is assumed that the vertex replaced by a black dot contains a carbon atom C, and the other contains a BH group as shown in Chart 1.1. If the vertex contains a BH_2 group, only one of the hydrogens is shown explicitly. If the hydrogen is needed to be shown, using a circle represents boron atom B. Substituents other than H are always shown explicitly. If a vertex contains an atom other than B, BH or C, the heteroatom and its substituent including hydrogens are both shown explicitly. We adopt this notation for the structural formulas shown in this thesis.

Table 1.2 Experimentally Determined Equilibrium Acidity Constants pK_a of the Carboranes.[11]

	pK_a1, Streitwieser's scale	pK_a1, polarographic scale
o-carborane	23.3	19
m-carborane	27.9	24
p-carborane	30.0	26

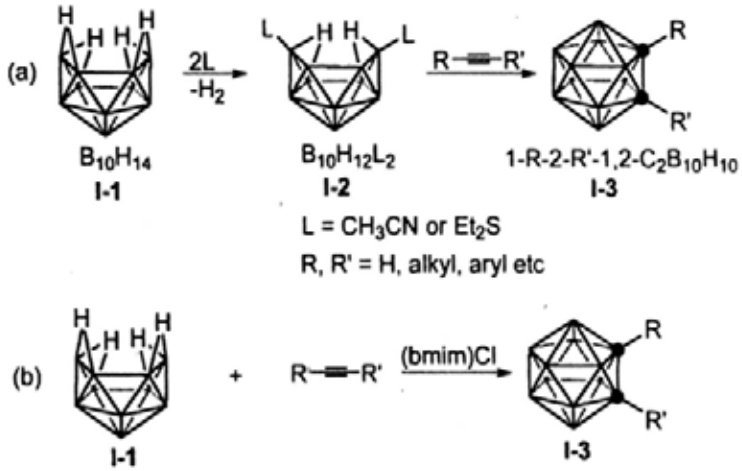
1.1.1. Synthesis

The synthesis of *o*-carborane was first reported in 1963 by two groups of Heying[12] and Fein.[13] *o*-Carboranes are prepared by the reaction of acetylenes, including both

mono and di-substituted alkynes, with $B_{10}H_{12}L_2$ (L = CH_3CN, RSR, R_3N) in acetonitrile or toluene at reflux for several hours. A variation on this method entails the use of dimethylacetylenedicarboxylate (DMAD) to give $1,2\text{-}(CO_2CH_3)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, which can be degraded to the $1,2\text{-}C_2B_{10}H_{12}$.[14]

The functionalization of carboranes is usually accomplished by two methods that have been dominant since the early days of carborane chemistry: (a) mono- or di-functionalized *o*-carborane formation from the insertion of a prefunctionalized alkyne into decaborane (Scheme 1.1); (b) base promoted CH-proton abstraction followed by substitution.

Scheme 1.1. Synthesis of *o*-Carborane Derivatives from Decaborane



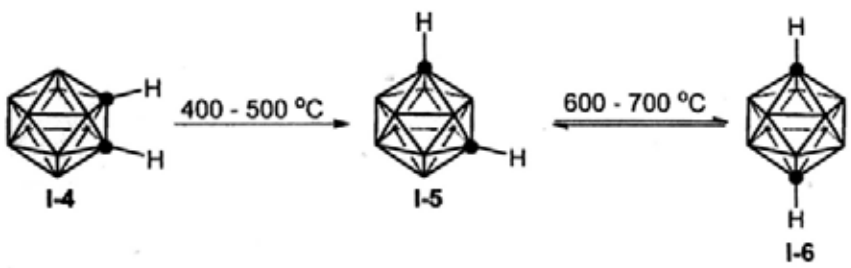
Indeed, the reaction of prefunctionalized alkyne with decaborane can tolerate many functional groups such as carbamates, esters, ethers, halides, nitro-groups etc. However, it is not compatible with alcohols, acids or amines, since nucleophilic

functionalities degrade the $B_{12}H_{12}L_2$ complexes. Acetylenes containing polar, nucleophilic group must therefore be protected prior to the insertion reaction with decaborane. In general, the yields range from 6 to 75% (Scheme 1.1a).[12,13,15] Recently, Sneddon and co-workers reported an improved method for the synthesis of 1,2-disubstituted *o*-carboranes by direct reaction of $B_{10}H_{14}$ or 6-R-$B_{10}H_{13}$ with alkynes in ionic liquid in higher yields (Scheme 1.1b).[16]

Carboranes are chemical building blocks with a unique combination of two carbon and ten boron atoms. The hexacoordinated carbon and boron atoms within the cluster give rise to an icosahedral structure with high chemical, thermal and biological stability.[2] By heating *o*-carborane in inert atmosphere, *m*-carborane is formed between 400 and 500 ℃, which is, in turn transformed into *p*-carborane between 600 and 700℃.

It is found that the rearrangement of *m*-carborane into *p*-carborane and the rearrangement of *p*-carborane into *m*-carborane in the gas phase are reversible processes giving rise to an equilibrium mixture of the *m*- and *p*-isomers in approximately equimolar amounts (Scheme 1.2).[17]

Scheme 1.2. Rearrangement of Carboranes



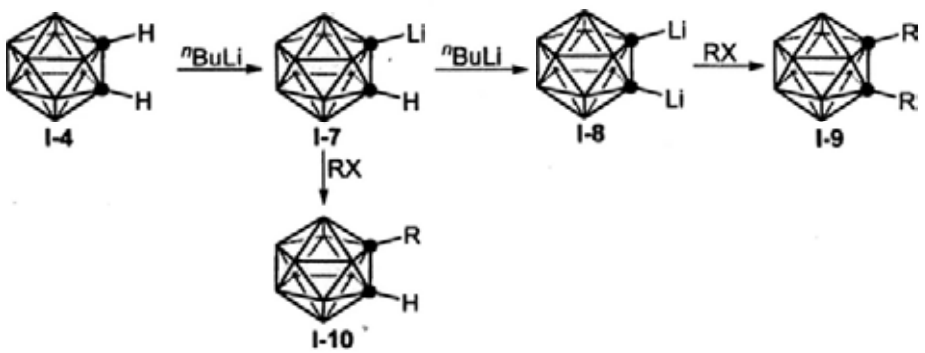
1.1.2. Functionalization of the Cage Carbon Atoms of Carborane

The chemistry of the carboranes has been extensively investigated over the years due to its commercial availability. There are five types of important reactions for *o*-carborane, including (1) deprotonation and introduction of substituents at the cage CH vertices; (2) base-promoted removal of BH vertex from the cage to form the *nido*-species with a five-membered ring face; (3) reduction of the cage by alkali metal Li or Na or K to form *nido*- and *arachno*-species with six or seven-membered ring face; (4) electrophilic substitution at cage BH vertices; and (5) thermal rearrangements to form *m* or *p*-carborane as discussed above.

(1) Base Promoted CH-Proton Abstraction Followed by Electrophilic Substitution

As mentioned above, due to the mildly acidic C-H bonds in *o*-carborane, the easily generated mono- or di-lithio carborane prepared by reaction of *o*-carborane with ^{n}BuLi, can be used in coupling reactions (Schemes 1.14 and 1.15), or more commonly as a nucleophile in substitution reactions as shown in Scheme 1.3.[18]

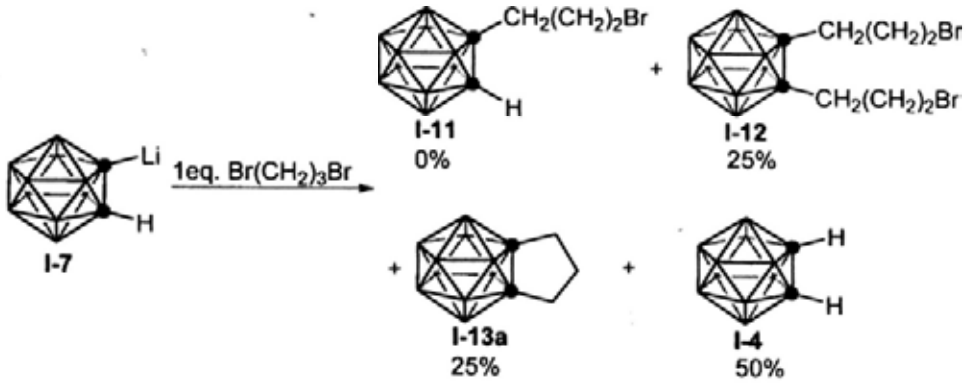
Scheme 1.3. Substitution Reaction on CH Vertices



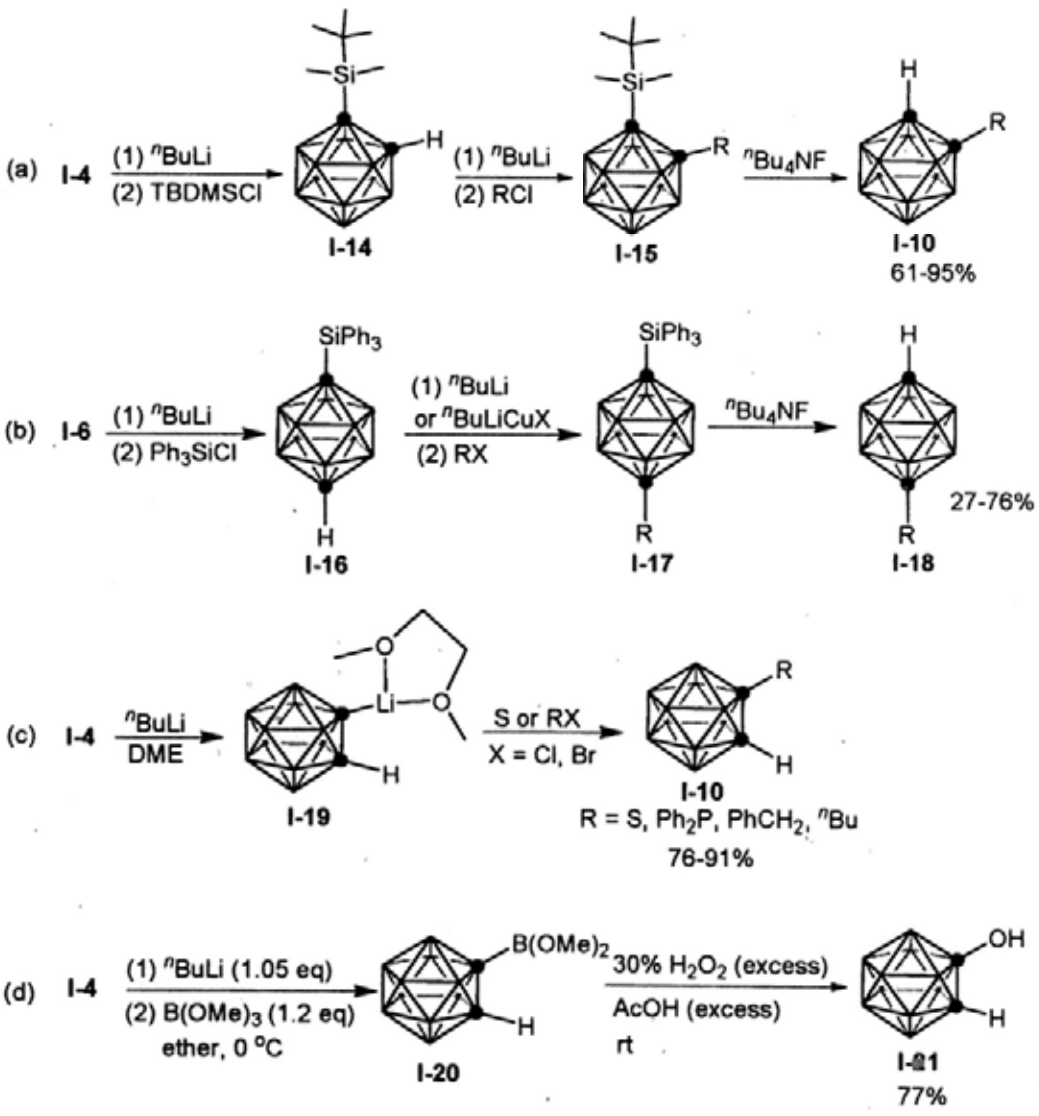
Note that mono-lithio carborane may undergo disproportionation leading to a mixture of products as exemplified in Scheme 1.4.[19] Reaction of mono-lithio *o*-carborane with 1 equiv of 1,3-dibromopropane yields a mixture of three products in a molar ratio of 1:1:2.

To avoid these undesired side-reactions, efficient methods have been developed by the groups of Hawthorne and Kaszynski to block one of the cage carbons using silicon based protective agents such as TBDMSCl (Scheme 1.5a)[20] and triphenylsilyl chloride (Scheme 1.5b).[21] The Teixidor group reported very recently that some mono-substituted *o*-carborane derivatives can be directly prepared in dimethoxyethane (DME) without any protection. It is suggested that DME can effectively stabilize monolithium salt by the formation of a bulky Li(DME) moiety which may block the disproportionation.[19] The reaction of *o*-carborane with 1 equiv of BuLi in dimethoxyethane is presumed to give only 1-Li-1,2-$C_2B_{10}H_{11}$. Upon reaction of this compound with sulfur powder, or suitable X-R compounds, such as $BrCH_2Ph$, $ClPPh_2$, and ^nBuBr, monosubstituted 1-R-1,2-$C_2B_{10}H_{11}$ compounds are obtained in high to excellent yields (Scheme 1.5c).[19] 1-OH-1,2-$C_2B_{10}H_{11}$ can be conveniently prepared in one pot in 77% isolated yield from the reaction of monolithio carborane with $B(OMe)_3$ followed by treatment with excessive 30% H_2O_2 and AcOH (Scheme 1.5d).[22] Due to the steric hindrance very small amount of 1,2-dihydroxycarborane forms. There are some other methods for preparation of C-hydroxycarboranes, but the process is troublesome, or the yield is very low.[23]

Scheme 1.4. Reaction of Mono-Lithio Carborane with 1,3-Dibromopropane

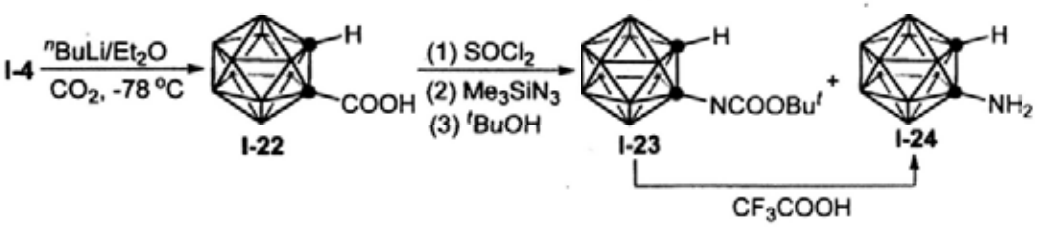


Scheme 1.5. Synthesis of Mono-Substituted Carborane



The monoacid of *o*-carborane is an important reactive synthon in its own right and has been prepared by monolithiation of *o*-carborane in benzene followed by carbonylation with CO_2 with quite variable yields of the desired product, usually contaminated with some diacid.[24] Reaction of the monolithio derivative with CO_2 in diethyl ether or THF generally gives only the diacid and unreacted starting material, probably through a disproportionation reaction. However, by carrying out the lithiation in diethyl ether at -78 °C under high-dilution conditions, the monoacid of *o*-carborane can be obtained in reproducibly high yields (≥90%) even on a 10 g scale. Preparation of the monoacids of *m*- and *p*-carborane by this method is similarly successful and efficient.[25] The 1-NH_2-1,2-carborane is quantitatively prepared from the monoacid of *o*-carborane by further four steps conversion using $SOCl_2$, Me_3SiN_3, ^{t}BuOH and CF_3COOH, successively (Scheme 1.6).[26]

Scheme 1.6. Preparation of Monoacid and Monoamino *o*-Carboranes

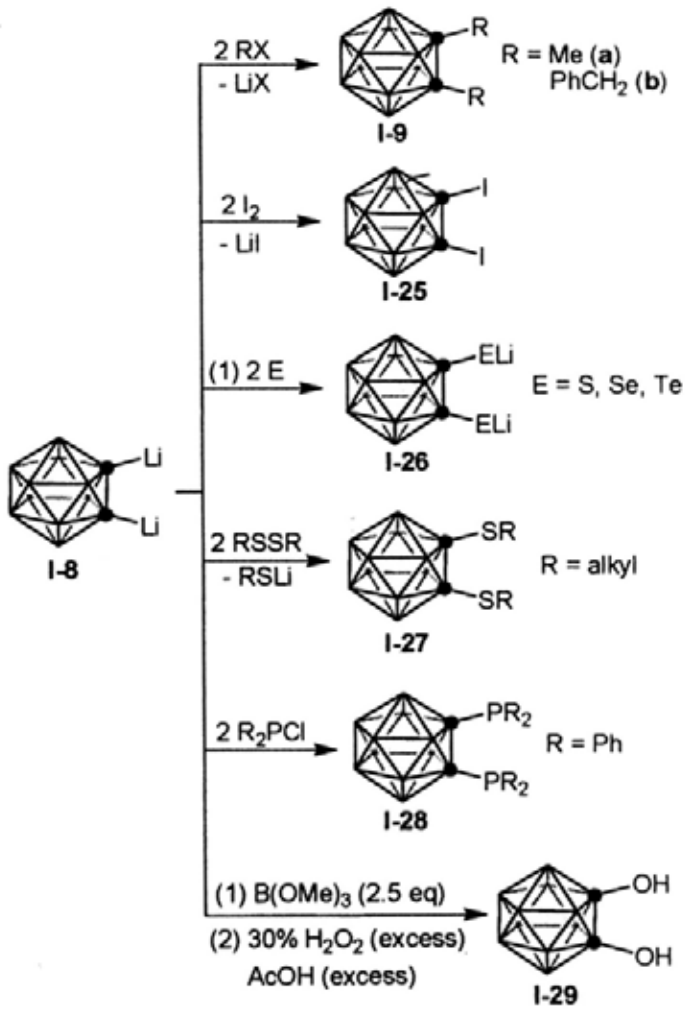


It is very clear that both solvents and reaction temperature are very important for suppressing the disproportionation of monolithio-*o*-carborane.

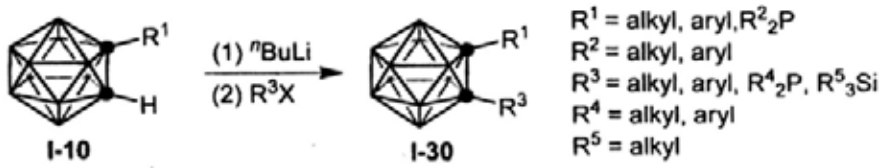
Reaction of dilithio-*o*-carborane with two equiv of electrophiles, such as RX (R = CH_3, $PhCH_2$ or Ph_2P; X = Br or Cl), I_2, sulfur or R'SSR' yields conveniently the

desired corresponding di-substituted carboranes $R_2C_2B_{10}H_{10}$ (R = CH_3,[27a] $PhCH_2$,[27b] I,[27c] SeLi,[27d] TeLi,[27d] SLi,[27e] SR',[27e] or Ph_2P[27f]) (Scheme 1.7). Treatment of dilithio-*o*-carborane with excessive $B(OMe)_3$ followed by oxidation using excessive 30% H_2O_2 and AcOH offers 1,2-dihydroxycarborane in 60% isolated yield.[22] However, the carboranes having two different substituents on the carbon atoms should be prepared from the mono-substituted ones (Scheme 1.8).[27f,28]

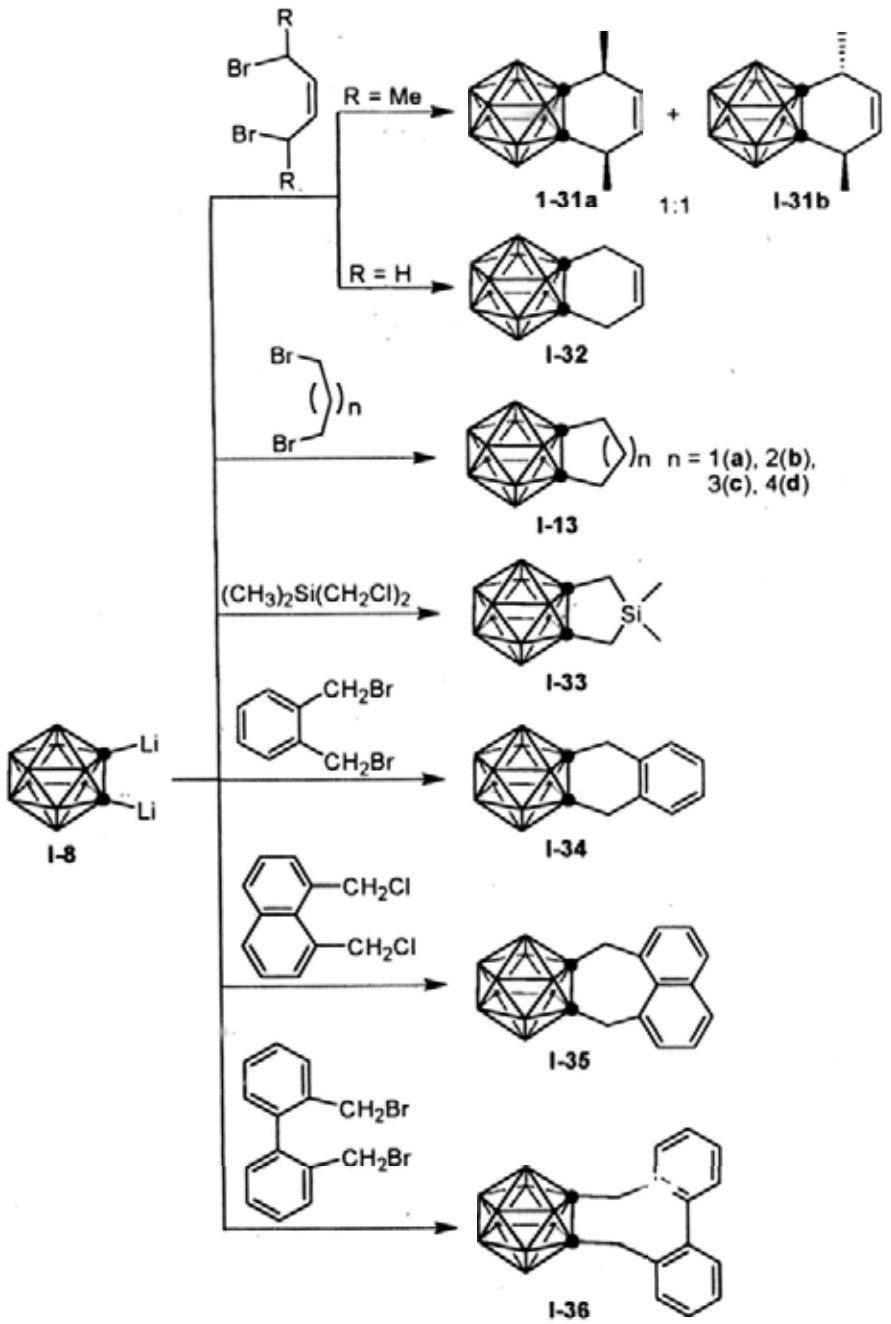
Scheme 1.7. Preparation of Di-Substituted Carboranes



Scheme 1.8. Preparation of Di-Substituted Carborane Bearing Different Substituents



Scheme 1.9. Synthesis of Cage Carbons Bridged *o*-Carboranes

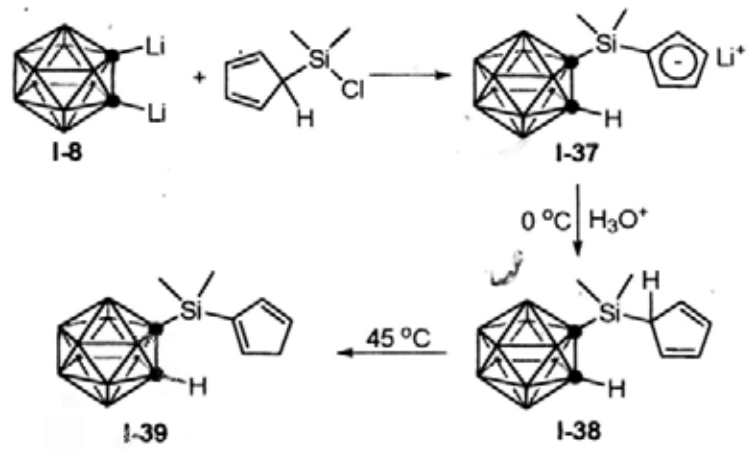


Similarly, the cage carbons bridged *o*-carboranes can be prepared from the reaction of dilithio-*o*-carborane with dihalo compounds. Reaction of dilithio-*o*-carborane with 2,5-dibromo-3-hexene gives two stereo-isomers in 1:1 ratio (Scheme 1.9).[29]

Reaction with 1,4-dibromo-2-butene yields dihydrobenzocarborane **I-32**.[30] Treatment of $Li_2C_2B_{10}H_{10}$ with $(CH_3)_2Si(CH_2Cl)_2$, $BrCH_2(CH_2)_nCH_2Br$ (n = 1, 2, 3, 4), $1,2\text{-}C_6H_4(CH_2Br)_2$, $1,8\text{-}C_{10}H_6(CH_2Cl)_2$, or $1,1'\text{-}(C_6H_4)_2\text{-}2,2'\text{-}(CH_2Br)_2$ gives the corresponding cage carbons linked *o*-carboranes $1,2\text{-}(CH_3)_2Si(CH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$,[18b] $\mu\text{-}1,2\text{-}(CH_2)_{2+n}\text{-}1,2\text{-}C_2B_{10}H_{10}$ (n = 1, 2, 3, 4),[31] $\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}$,[32] $\mu\text{-}1,2\text{-}[1,8\text{-}C_{10}H_6(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}$,[32d] or $\mu\text{-}1,2\text{-}[1,1'\text{-}(C_6H_4)2\text{-}2,2'\text{-}(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}$,[32d] respectively (Scheme 1.9). These cage-carbons linked carborane derivatives are very important starting materials for the syntheses of supercarboranes,[33] and the super-metallacarboranes.[33c-g] The relationships between the bridge length and the cage C–C bond cleavage during reductive processes have also been investigated.[31b,32d]

A compound bearing both cyclopentadienyl and carboranyl moieties ($Me_2Si(C_5H_5)(C_2B_{10}H_{11})$) is prepared by reaction of $Me_2Si(C_5H_5)Cl$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/ether at 0 ℃, in 79% isolated yield after hydrolysis (Scheme 1.10).[34]

Scheme 1.10. Preparation Si-Bridged Carboranyl Cyclopentadiene



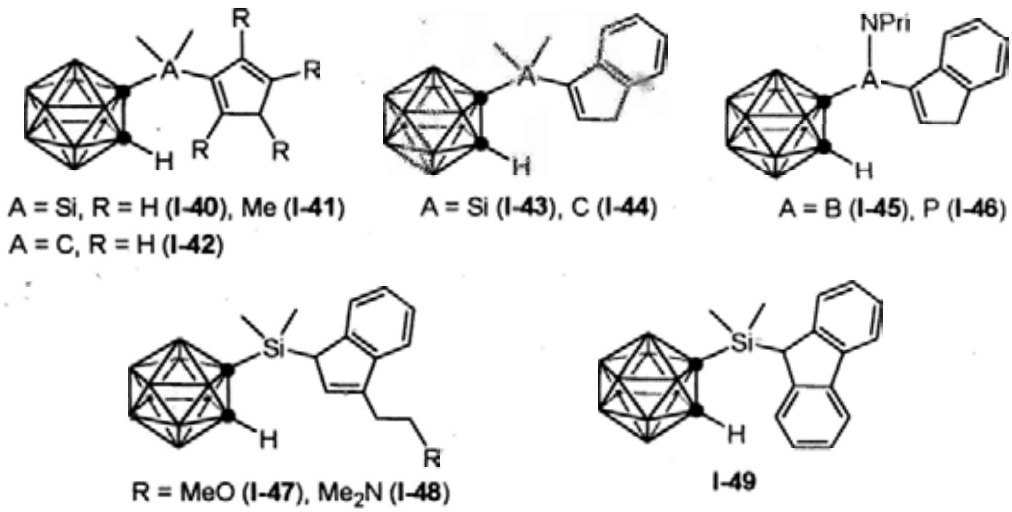


Figure 1.2. Some Typical Cyclopentadienyl-Carboranyl Hybrid Compounds.

A dilithium salt must be used, since one molar equivalent is consumed by the acidic proton of cyclopentadienyl unit in $(C_5H_5)SiMe_2Cl$, and the remaining one is necessary to provide the nucleophile for reaction with the Si-Cl bond to form the target molecule. This reaction can be closely monitored by ^{11}B NMR. Thus,

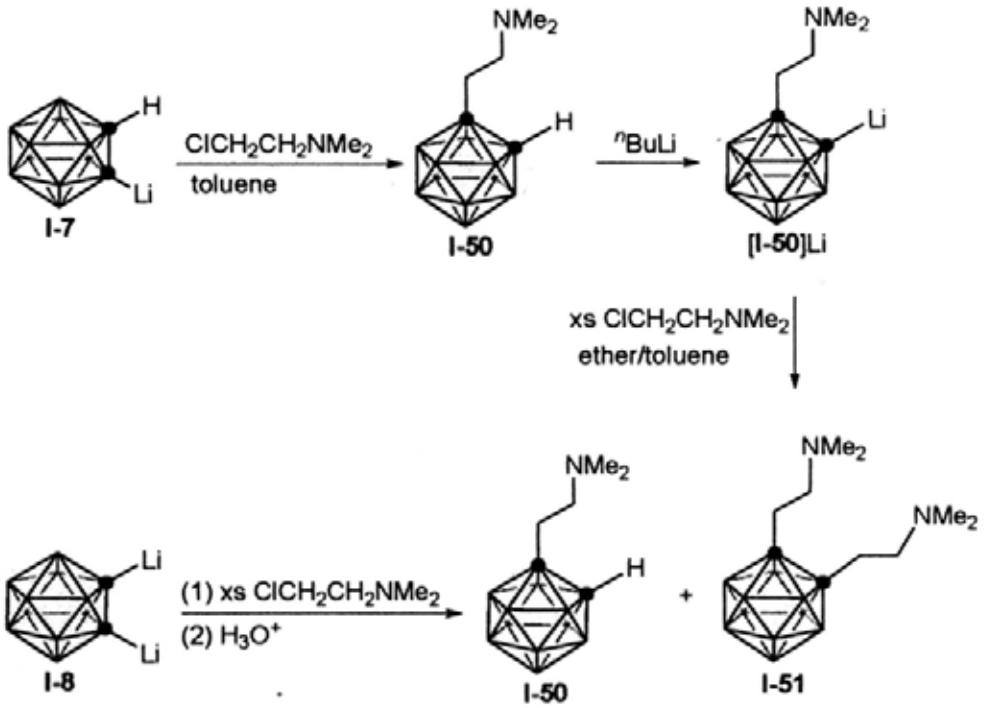
following this motif, a class of cyclopentadienyl-carborane compounds can be prepared[35] via a nucleophilic substitution reaction of $Li_2C_2B_{10}H_{10}$ with different electrophiles, in which both the nature of the electrophilic site and the structure of the cyclopentadienyl ring can be varied. Some examples are listed in Figure 1.2.

The syntheses of amidoalkyl- and ether-*o*-carboranyl species are commonly achieved by the addition of corresponding alkynes to activated boranes $B_{10}H_{12}L_2$.[12,36] This method is not practical for carboranes with more than one methylene unit separating the cage carbon and donor atoms because of rather low yields.[12,36] Later, several routes were developed using lithio-*o*-carboranes as starting materials to prepare Lewis-base functionalized *o*-carboranes.[18,23,37] It is noted that all these compounds bear only one type of donor atom. In view of the great impact of functionalized sidearms on the structures and reactivities of metallocenes,[38] compounds with two different appended functionalities are of particular interest for the studies on sidearm effects.

Treatment of $Li_2C_2B_{10}H_{10}$ with 2.5 equiv. of $Me_2NCH_2CH_2Cl$ in toluene-Et_2O mixture gives, after chromatographic separation, 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**I-50**), 1,2-$(Me_2NCH_2CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (**I-51**) and *o*-$C_2B_{10}H_{10}$ in 25, 51 and 5% isolated yields, respectively (Scheme 1.11).[39] The ^{11}B NMR spectrum shows that the molar ratio of **I-50** : **I-51** (1 : 2) remains unchanged even when a large excess amount of $Me_2NCH_2CH_2Cl$ is added and the peaks attributable to $Li_2C_2B_{10}H_{10}$ don't disappear after prolonged reaction time. This phenomenon is also observed in the

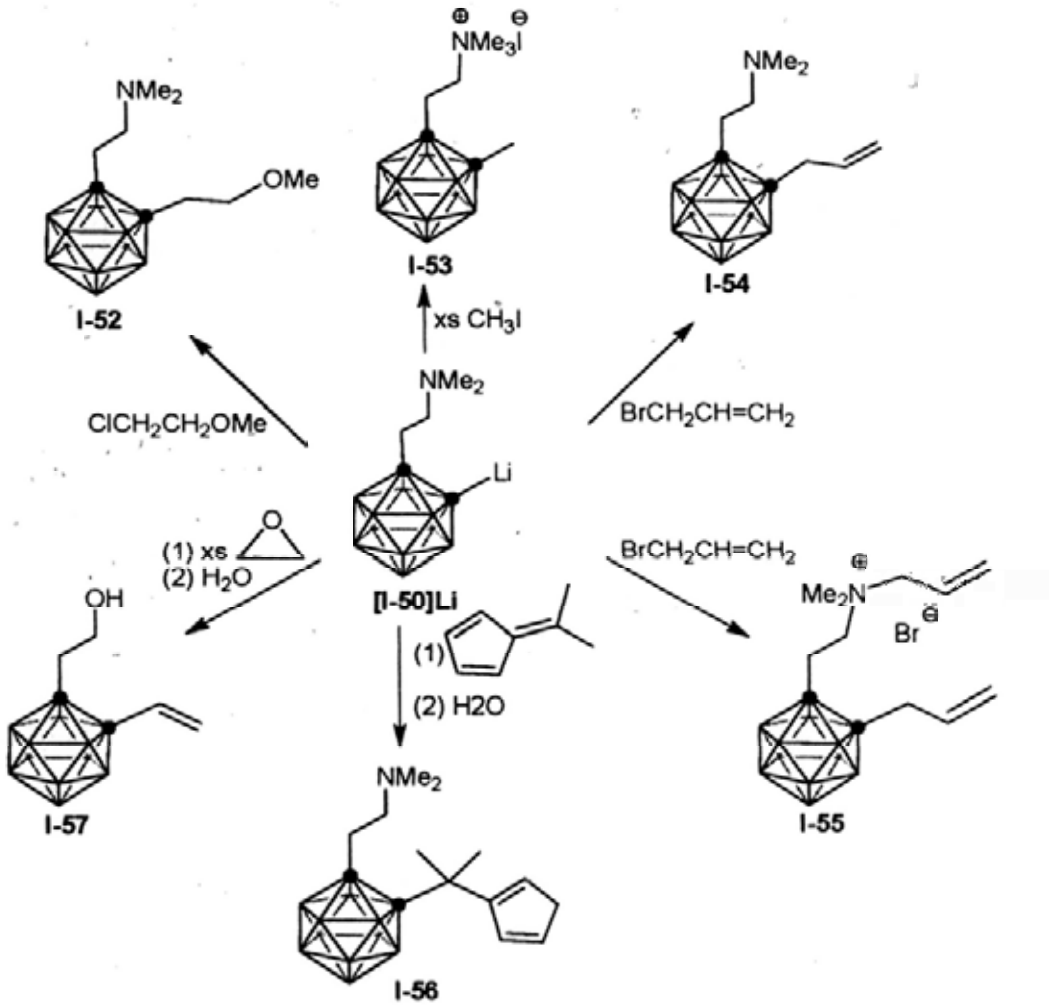
reaction of $Li_2C_2B_{10}H_{10}$ with $MeOCH_2CH_2Cl$.[37b] However, treatment of $LiC_2B_{10}H_{11}$ with 1 equiv of $Me_2NCH_2CH_2Cl$ in toluene at reflux temperature results in the isolation of **I-50** in 92% yield. It is conveniently converted into the lithium salt 1-$Me_2NCH_2CH_2$-2-Li-1,2-$C_2B_{10}H_{10}$ (**[I-50]**Li) by treatment with 1 equiv of *n*-BuLi. Reaction of **[I-50]**Li with excess $Me_2NCH_2CH_2Cl$ at reflux temperature yields **I-51** in 97% yield (Scheme 1.11).[39]

Scheme 1.11. Preparation of Amidoalkyl Carborane Derivatives



[I-50]Li is a very useful synthon for the production of bisfunctional *o*-carboranes. Some typical reactions of this synthon are summarized in Scheme 1.12.[39] Reaction of **[I-50]**Li with $MeOCH_2CH_2Cl$ affords

Scheme 1.12. Reactions of Intermediate [**I-50**]Li

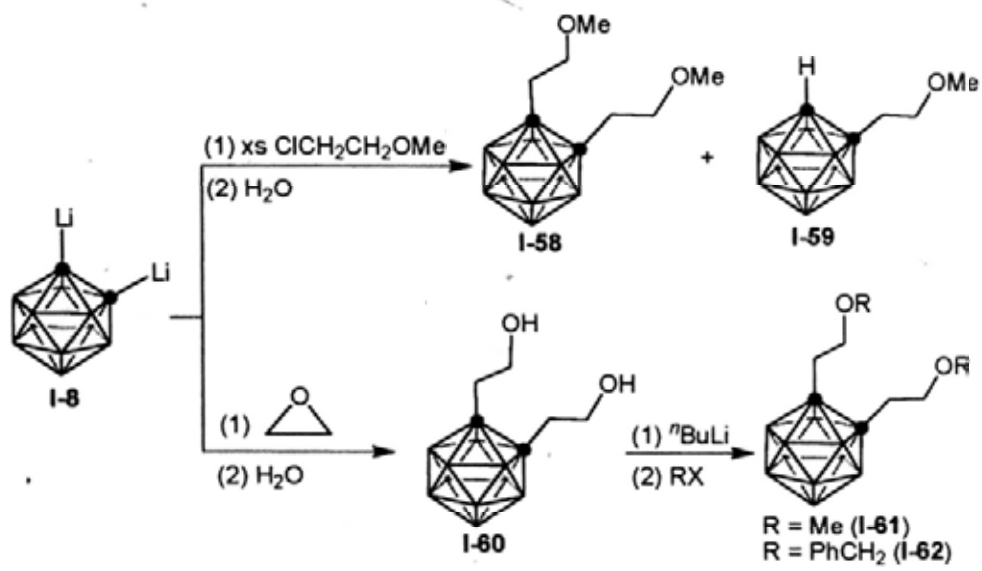


1-$Me_2NCH_2CH_2$-2-$MeOCH_2CH_2$-1,2-$C_2B_{10}H_{10}$ (**I-52**). Treatment of [**I-50**]Li with excess MeI or allyl bromide gives the ionic salts, [1-$Me_3NCH_2CH_2$-2-Me-1,2-$C_2B_{10}H_{10}$][I] (**I-53**) and [1-$Me_2N(CH_2{=}CHCH_2)CH_2CH_2$-2-($CH_2{=}CHCH_2$)-1,2-$C_2B_{10}H_{10}$][Br] (**I-55**), respectively. Interaction of [**I-50**]Li with 1 equiv of allyl bromide affords 1-$Me_2NCH_2CH_2$-2-($CH_2{=}CHCH_2$)-1,2-$C_2B_{10}H_{10}$ (**I-54**). Treatment of [**I-50**]Li with excess dimethylfulvene gives 1-$Me_2NCH_2CH_2$-2-$C_5H_5CMe_2$-1,2-$C_2B_{10}H_{10}$ (**I-56**). Interaction of [**I-50**]Li with excess ethylene oxide generates an unexpected product

1-$HOCH_2CH_2$-2-$(CH_2{=}CH)$-1,2-$C_2B_{10}H_{10}$ (**I-57**).

Similarly, 1,2-$(HOCH_2CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (**I-58**), its derivatives 1,2-$(ROCH_2CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (R = CH_3 (**I-61**), CH_2Ph (**I-62**)), and 1-$(CH_3OCH_2CH_2)$-1,2-$C_2B_{10}H_{11}$ (**I-59**) were prepared as outlined in Scheme 1.13.[37b]

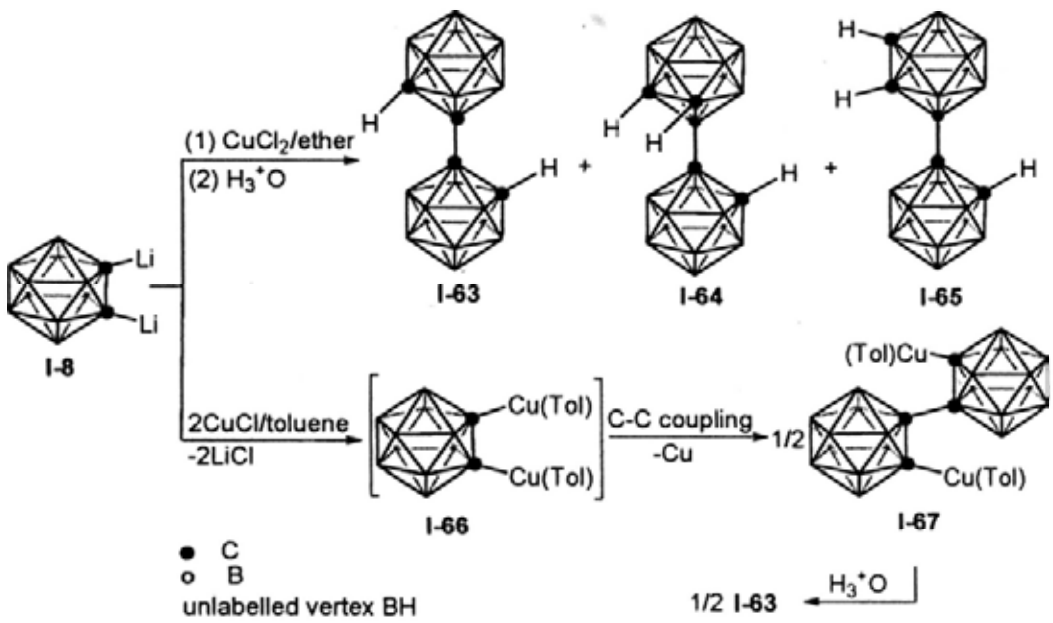
Scheme 1.13. Preparation of 1-$ROCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ and 1,2-$(ROCH_2CH_2)_2$-1,2-$C_2B_{10}H_{10}$



Dilithio-*o*-carborane can undergo coupling reaction to form bis-*o*-carboranes in the presence of Cu(I) or Cu(II).[40] Bis-*o*-carborane is usually prepared by the reaction of $B_{10}H_{12}{\cdot}2L$ (L = SEt_2, CH_3CN) with $HC{\equiv}C\text{-}C{\equiv}CH$.[40a,b] $CuCl_2$-mediated coupling reactions of the monolithium[40c] or dilithium salts of *o*-carborane are also reported to give 1,1′- bis(*o*-carborane), but in low yields, since the C-B and B-B coupling products (**I-64** and **I-65**) are generated in the same reaction.[40d] The separation of

1,1-$(C_2B_{10}H_{11})_2$ from its isomers is a tedious process (Scheme 1.14).

Scheme 1.14. Preparation of Bis-*o*-Carborane

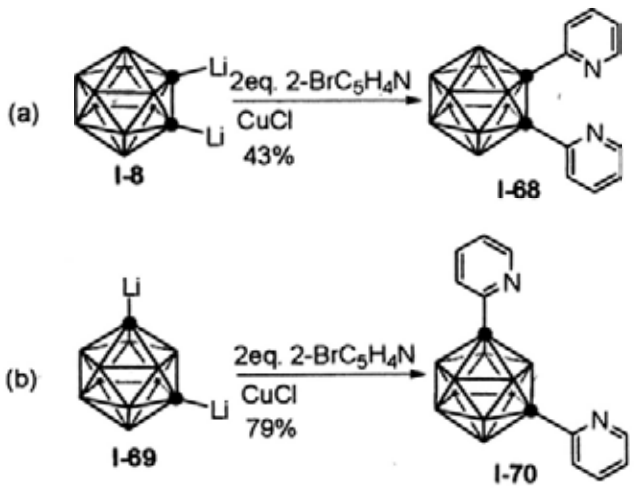


We were interested in the properties of 1,1′-bis(*o*-carborane) as potential multidentate π ligands[33f,33g,41] after reduction.[42] We then revisited the copper-mediated coupling reactions and found that in the presence of CuCl, the dilithium salt of *o*-carborane in toluene can efficiently form two cages C-C coupling product bis-*o*-carborane (**I-63**) in high yield at room temperature.[40e] Donor solvents such as THF, diethyl ether, and DME offer poor yields. On the other hand, the copper salts play a crucial role in the reaction. Both CuCN and CuI are much less active than CuCl, and $CuCl_2$ leads to a mixture of isomers containing C-C, C-B, and B-B coupling products.[40d] The use of cuprous salt is essential to avoid C-B and B-B

couplings. When the monolithium salt $LiC_2B_{10}H_{11}$ is used instead of $Li_2C_2B_{10}H_{10}$, the yield of 1,1'-bis(*o*-carborane) is dramatically decreased to 30% with a recovery of *o*-carborane. The coupling efficiency also drops if <2 equiv of CuCl is used. No coupling product is observed when 1-Li-2-Me- 1,2-$C_2B_{10}H_{10}$ is employed as starting material.[41e]

The cage carbon can be arylated, by reaction of the copper(I)-salt of a carborane with aryl halides in the presence of pyridine, which was developed by Wade and co-workers in the early 1990s.[43] Successive treatment of *o*-carborane with ^{n}BuLi, copper(I) chloride and 2-bromopyridine, in the presence of pyridine, gives 1,2-di-2'-pyridyl-*o*-carborane in 43% yield based on the available 2-bromopyridine, together with unchanged *o*-carborane.[43a] Similarly, successive treatment of *m*-carborane with ^{n}BuLi, copper(I) chloride and 2-bromopyridine in the presence of pyridine gives the dipyridyl product in 79% yield (Scheme 1.15).[43b]

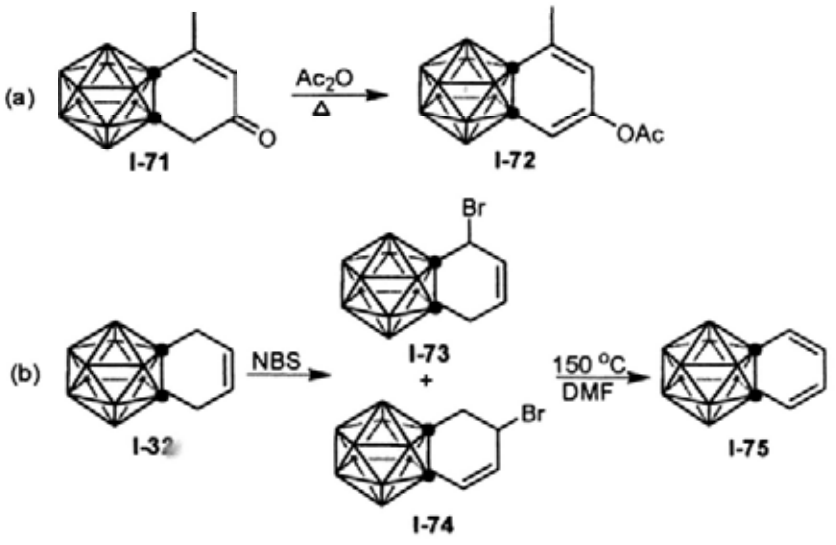
Scheme 1.15. Copper-Mediated Reaction of Carborane with 2-Bromopyridine



Benzocarborane **I-72/I-75** can be prepared by rearrangement of

4,5-(*o*-carborano)-2-cyclohexen-1-one (**I-71**)[44] or by elimination of HBr from 1-bromo-5,6-(*o*-carborano)-2-cyclohexene (**I-73**) and 1-bromo-4,5-(*o*-carborano)-2-cyclohexene (**I-74**)[45] (Scheme 1.16).

Scheme 1.16. Preparation of Benzocarborane

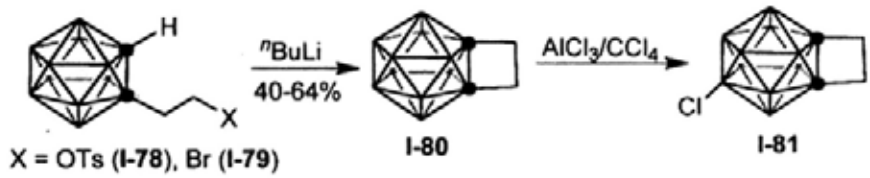


It is reported that naphthalocarborane can be prepared from the cage carbon-linked species μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$ (**I-34**) by sequential bromination and HBr elimination as shown in Scheme 1.17.[46]

Scheme 1.17. Preparation of Naphthalocarborane

Cyclobutyl carborane (or 1,2-ethano-*o*-carborane) as a kind of 1,2-disubstituted carboranes, can be prepared by treatment of XCH_2CH_2 (X = OTS, Br) substituted carborane with ^{n}BuLi in benzene or in gas phase. It reacts with $AlCl_3$ in CCl_4 to form 9-chloro carborane derivative **I-81** (Scheme 1.18).[37c,47]

Scheme 1.18. Preparation of Cyclobutyl Carborane

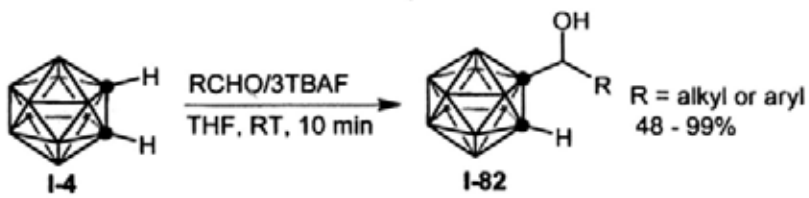


X = OTs (**I-78**), Br (**I-79**) **I-80** **I-81**

Cyclobutenyl carborane (or carborane fused cyclobutene), as an analogue of benzocyclobutene, is usually prepared from the [2+2] coupling reaction of in situ formed carboryne with alkyne.[48]

The selective monoaddition of *o*-carborane anion to aldehydes proceeds very smoothly in the presence of aqueous tetrabutylammonium fluoride (TBAF, 3 equiv) at room temperature, giving the corresponding carbinols (**I-82**) in high yields (Scheme 1.19).[49]

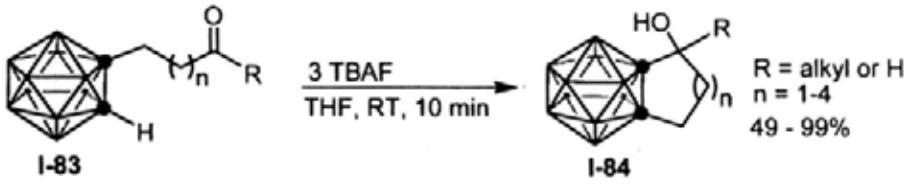
Scheme 1.19. 1,2-Addition of *o*-Carborane to Aldehydes in the Presence of TBAF



I-4 **I-82**

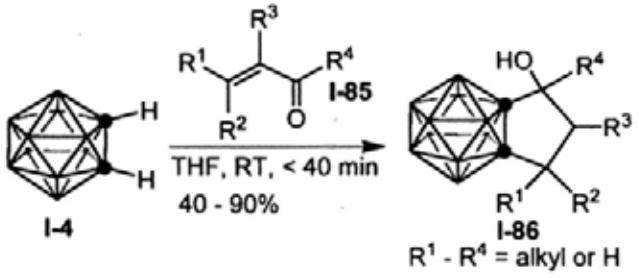
The TBAF-mediated reaction is applied to the intramolecular cycloaddition of *o*-carboranyl aldehydes and ketones (**I-83**) prepared by reaction of $B_{10}H_{12}L_2$ complex with the corresponding alkynes. The corresponding five-, six-, and seven-membered carboracycles (**I-84**) are obtained in good-to-high yields (Scheme 1.20).[49]

Scheme 1.20. Intramolecular Cycloaddition of Carboranyl Aldehydes and Ketones Prompted by TBAF



I-83 I-84

Scheme 1.21. Annulation Reaction of *o*-Carborane with *α,β*-Unsaturated Enals and Enones



I-4 I-86

R^1 - R^4 = alkyl or H

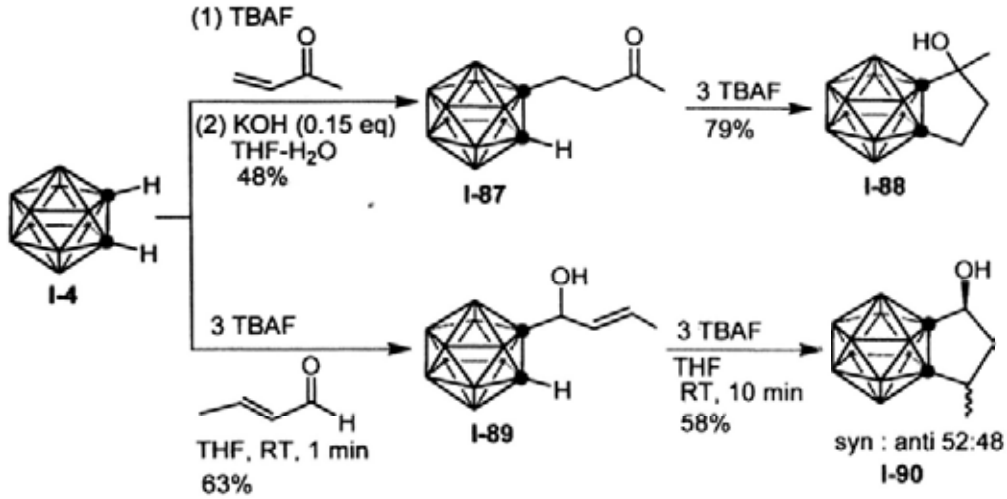
Furthermore, [3 + 2] annulation between *o*-carborane (dianionic C_2 synthons) and *α,β*-unsaturated aldehydes or ketones (dicationic C_3 synthons) proceeds very smoothly in the presence of TBAF to give the corresponding five-membered carbocycles (**I-86**) in good-to-high yields (Scheme 1.21).[49]

Detailed studies show that five-membered carbocycles can be formed step by step

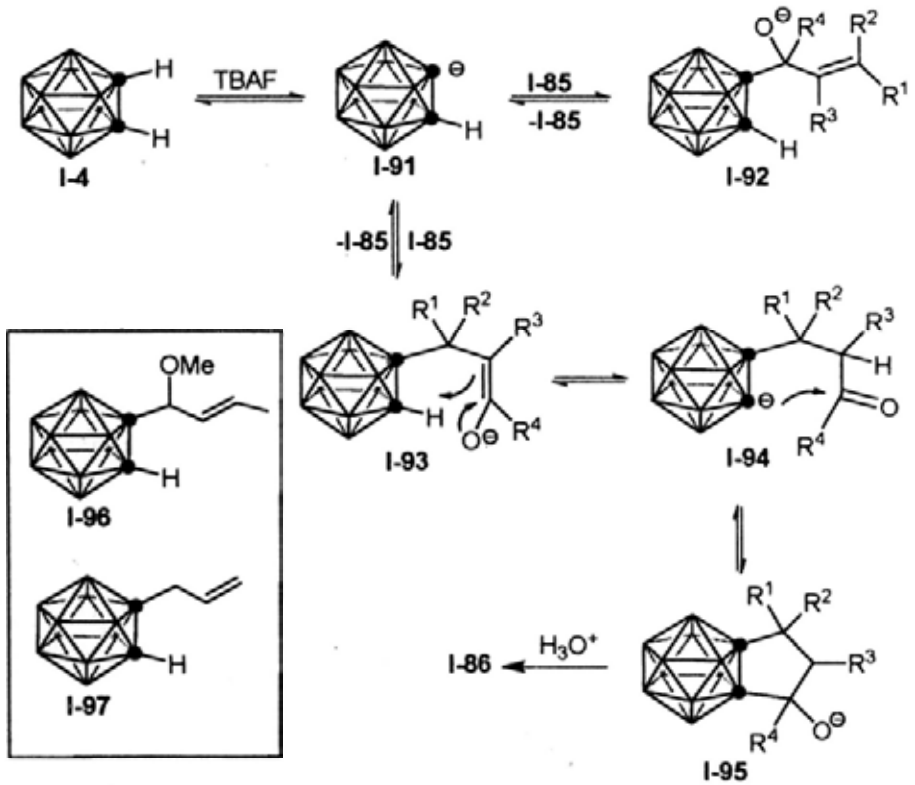
as depicted in Scheme 1.22. These studies reveal that the [3 + 2] annulation would proceed through kinetically controlled 1,2-addition followed by a thermodynamically controlled cyclization process (Scheme 1.23).[49] According to the mechanism for this unprecedented annulation reaction, an anionic intermediate **I-91**, which would produce by the reaction of *o*-carborane with TBAF (or from 1,2-adduct **I-92**), would undergo addition to α,β-unsaturated aldehydes or ketones (**I-85**) either in a 1,2- or in a 1,4-manner to give the 1,2-adduct **I-92** or 1,4-adduct **I-93**, respectively. There would be equilibrium between **I-92** and **I-93**, and the formation of **I-92** should be a kinetically controlled process. The thermodynamically favored **I-93** would undergo proton exchange to afford the *o*-carborane anion **I-94**, which would give **I-86** via an intramolecular ring closure. The methylated 1,2-adduct analogue **I-96** and allylcarborane **I-97** don't undergo the [3 + 2] annulation reaction by treatment with TBAF. These results support that a hydroxyl group at the allylic position is essential for the equilibrium between **I-95** and 1,2-adduct **I-92** and for the annulation reaction.[50]

TBAF promoted C(cage) mono-substitution reaction, intramolecular cycloaddition of *o*-carboranyl aldehydes and ketones and [3 + 2] annulation between *o*-carborane and α,β-unsaturated aldehydes and ketones serve as another useful method for the preparation of carborane derivatives.

Scheme 1.22. Step by Step Annulation Reaction



Scheme 1.23. Possible Mechanism for [3+2] Annulation Reaction

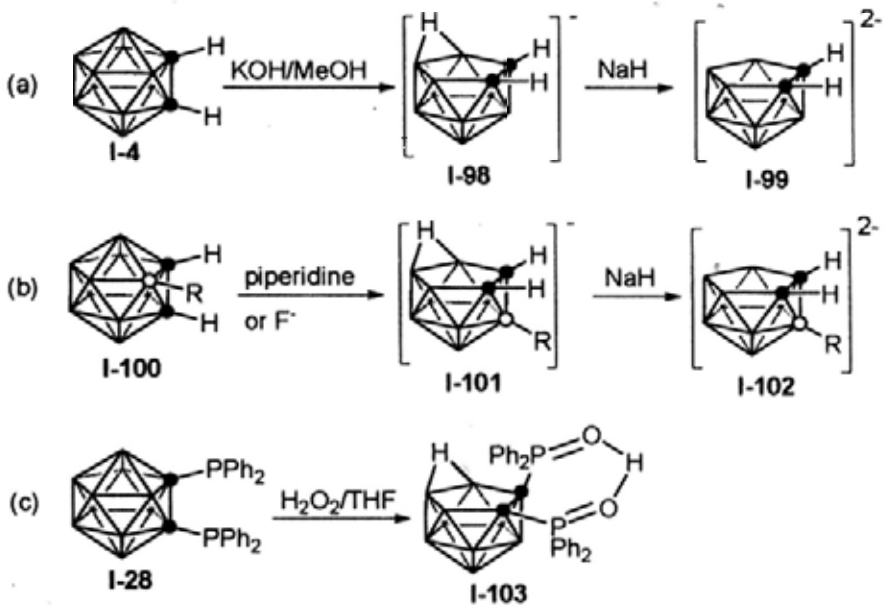


(2) Base-Promoted Removal of BH Vertex

Although carboranes are much thermally stable, they are very highly versatile

molecules. Treatment with suitable base such as KOH, CsF, piperidine and fluorides gives dicarbollide ions *nido*-$C_2B_9H_{11}^{2-}$ which is capable of being bonded to metal ions in η^5-fashion.[51]

Scheme 1.24. Deboration of *o*-Carborane



The two boron atoms closest to the carbon atoms (3- and 6-position) in *o*-carborane are the most electron-poor and are the most readily attacked by a variety of nucleophiles, such as alkoxide anion and fluoride anion. Early pioneering work by Hawthorne and co-workers demonstrates that interaction of *o*-carborane with KOH in methanol generates [*nido*-$C_2B_9H_{12}$]$^-$ anion[52] by removing the vertex B(3) or B(6). Further deprotonation using strong base, such as NaH and ^{n}BuLi, yields the dianion [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ (Scheme 1.24a),[53] which has an open five-membered C_2B_3 ring face and is isolobal and isoelectronic with Cp^-.[54] Its derivatives

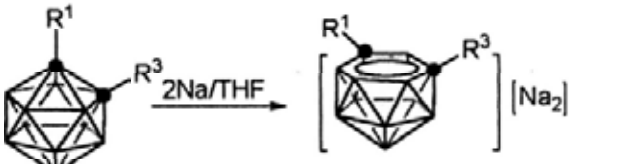
[*nido*-7,8-R'R''-$C_2B_9H_9$]$^{2-}$ are very useful precursors for preparation of many metallacarboranes by salt metathesis[51,54] and B(3)/B(6) substituted carboranes by further capitation reaction.[55] However, the deboration using the potassium hydroxide/methanol or ethanol route is not suitable for carborane derivatives that contain functional groups susceptible to the attack of a strong base or nucleophile.[56]

Other reagents have been found to effect partial deboration, e.g. tertiary amines such as trimethyl amine (requiring sealed tube experiments),[57] hydrazine,[18a,58] ammonia[59] and piperidine.[60] Piperidine is a relatively mild deboration reagent compared to KOH or KOMe, since the latter always results in C(cage)-C(cage) bond breaking and shows no selectivity for BH and BR moiety during deboration, whereas the former has a good selectivity for both of them (Scheme 1.24b). Deboration reagents, such as TBAF, KF and CsF[56,61] are the promising alternative because they are very weak nucleophiles yet effective as well as easy to handle.[62] The facile and mild deboration of a range of *o*-carboranes using ethanolic solution of cesium fluoride, which leaves intact other functional groups, such as esters, has been reported.[61e] There is one report on the deboration of 1,2-$(PPh_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ using H_2O_2 and the chelating influence of the two phosphine ligands (Scheme 1.24c).[63] It is thought that the proton from H_2O_2 induces the conversion of the *closo*-C_2B_{10} to the *nido*-C_2B_9.

(3) Reduction with Group 1 Metals

It is well documented that *o*-$R_2C_2B_{10}H_{10}$ (R = H, alkyl, aryl) can be reduced by group 1 metals to give carbons-apart dianionic species [*nido*-$R_2C_2B_{10}H_{10}$]$^{2-}$ (Scheme 1.25),[64] which are very useful versatile synthons for the production of numerous metallacarboranes of s-, p-, d-, and f-elements.[51,54] In fact Grafstein and Dvorak reported electron addition to the *o*-carborane using sodium in liquid ammonium to form [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ as early as 1963.[17a] The resulting [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ ions may be protonated to yield [$C_2B_{10}H_{13}$]$^-$ [65,66] and oxidized to $C_2B_{10}H_{12}$ isomers with or without polyhedral rearrangement.[65]

Scheme 1.25. Reduction of *closo*-1-R^1-2-R^2-1,2-$C_2B_{10}H_{10}$

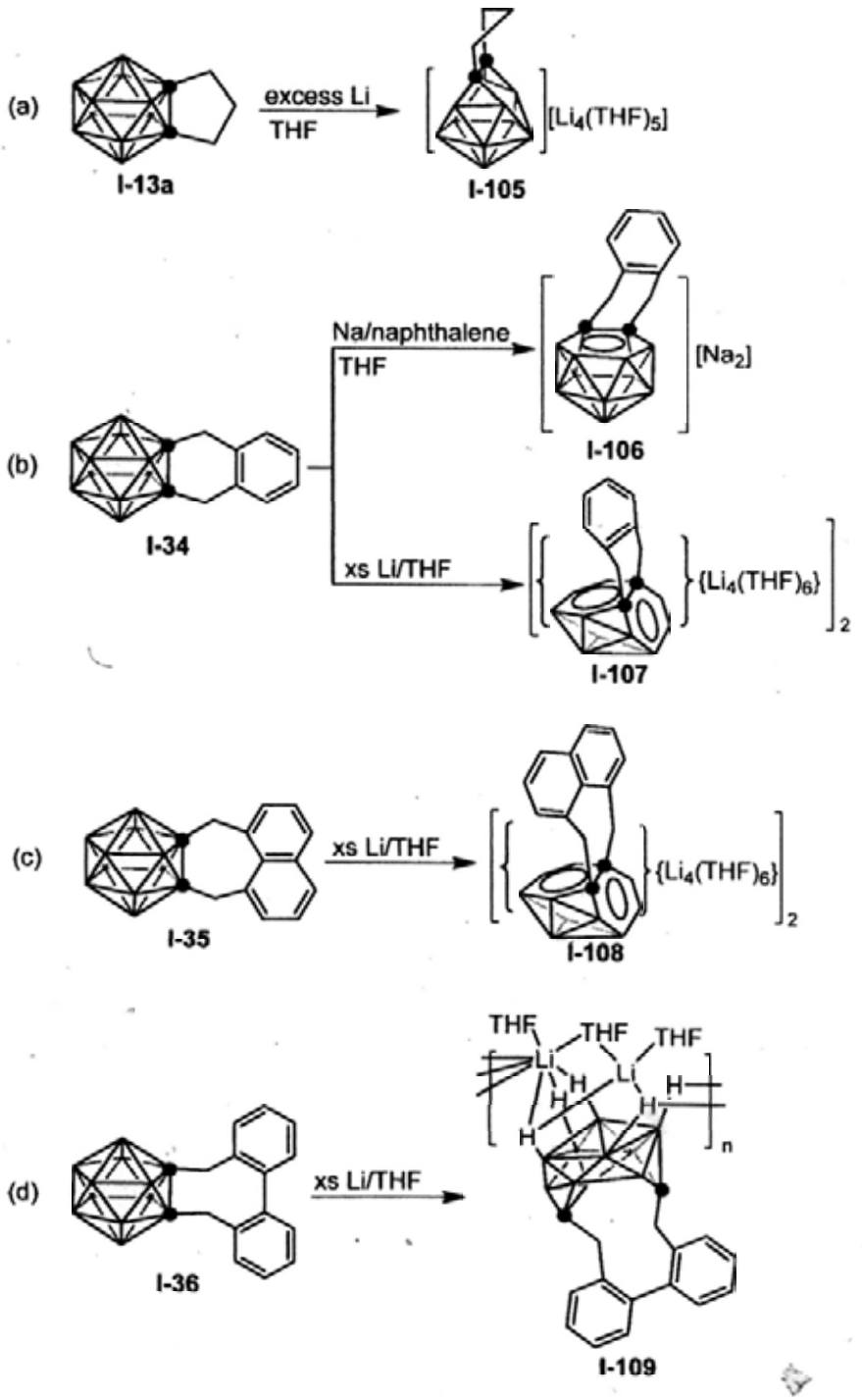


I-30 [*nido*-7-R^1-9-R^3-$C_2B_{10}H_{10}$]Na_2 **I-104**

This reduction process leads to the complete cleavage of the cage C–C bond. Excessive alkali metals cannot directly drive *o*-carborane to *arachno*-carborane since the carbons-apart [*nido*-$R_2C_2B_{10}H_{10}$]$^{2-}$ are much poorer electron acceptors than their neutral counterparts.[10,54b,d,f] Electrochemical data indicate that the arrangement of the cage carbon atoms has large influences on the chemical properties of carborane cage compounds, and carbons-adjacent isomers are generally more reactive than their carbons-apart ones.[67] Thus, carbons-adjacent carborane anions may lead to

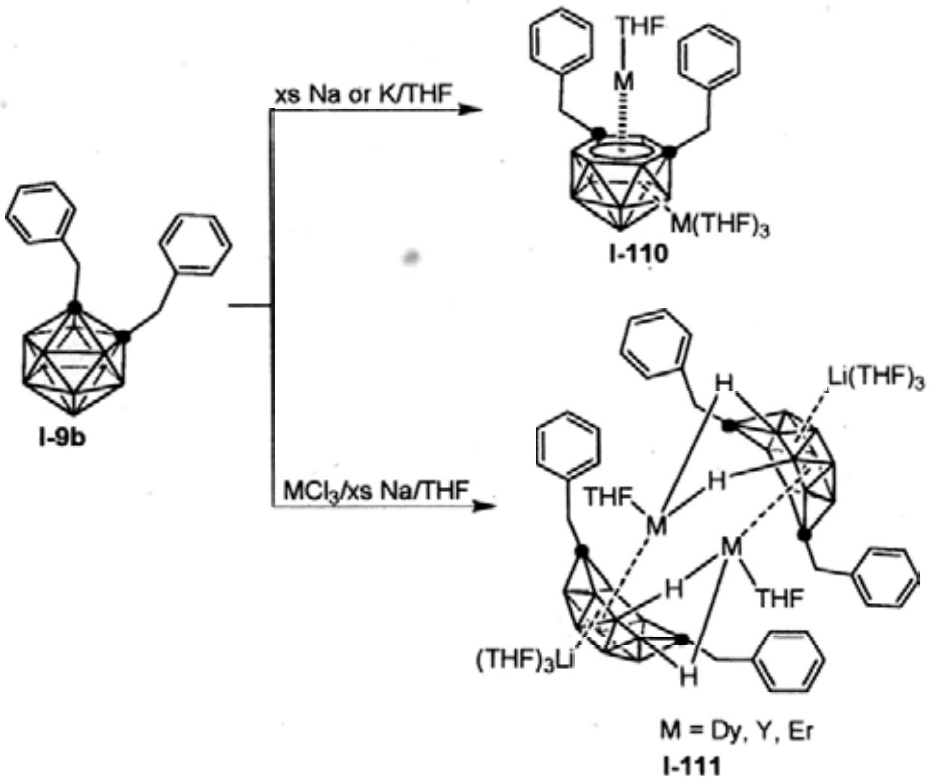
metallacarborane complexes with higher reactivities and thus are amenable to further chemistry.

Scheme 1.26. Reduction of Cage-Carbon Linked *o*-Carboranes



To control the positions of two cage carbon atoms of an *o*-carborane during the reduction processes, the most effective and easiest way is to introduce a proper linkage between the two cage carbon atoms forcing them in place. By varying the bridge length of cage carbons-linked *o*-carboranes, the two cage carbon atoms are locked in place during the reactions, leading to the controlled syntheses of *ortho*-, *meta*- or *para*-isomer of *nido*-carborane dianions (Scheme 1.26).[31b,32d,51d]

Scheme 1.27. Preparation of $[arachno\text{-}R_2C_2B_{10}H_{10}]^{4-}$ in the Presence of Transition Metal Ions



Although *o*-carborane cannot be directly reduced to the *arachno* species, in the

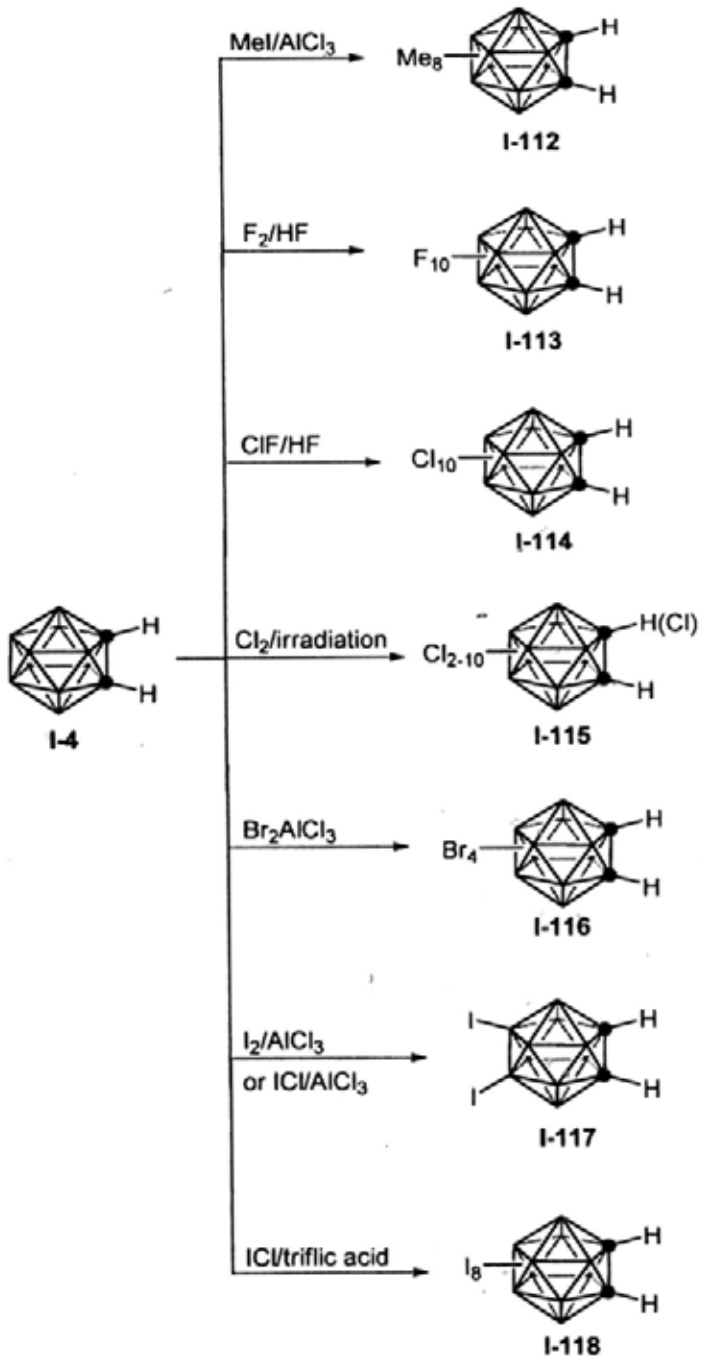
presence of d^0/f^n transition-metal ions, it can undergo four-electron reduction with excess alkali metals to form a [*arachno*-$C_2B_{10}H_{12}]^{4-}$ tetraanion (Scheme 1.27) that is capable of being η^7-bound to metal ions, leading to a new class of 13-vertex *closo*-metallacarboranes.[41a,68]

(4) Electrophilic Substitution Reactions

It is generally accepted that icosahedral carboranes are aromatic molecules and can be viewed as a three-dimentional relative of benzene.[69] They can undergo electrophilic substitution reaction like aromatics.[70] Zakharkin et al.[71a] and Plešek et al.[71b] independently reported that the sequential partial alkylation at cage BH vertices in *o*-carborane follows the decreasing electron density of the boron atoms. In *o*-carborane this sequence correlates with the distance to the cluster carbon atoms. The farthest boron atoms from the carbon atoms and the richest in electron density are B(8,9,10,12); the closest are B(3,6), which are poorer in electron density. Therefore, positions B(8,9,10,12) should be the first to be attacked by electrophiles.[72] The typical examples of electrophilic reaction of *o*-carborane are summarized in Scheme 1.28.

Hawthorne et al. have achieved the maximum methylation via the reaction of *o*-carborane with MeI by direct methylation in the presence of $AlCl_3$ to get 4,5,7,8,9,10,11,12-Me_8-1,2-$C_2B_{10}H_4$.[73] Methylation at B(3,6) is not observed. Further study by the group of Teixidor based on their experimentals and calculations concludes that methyl groups are electron-withdrawing when bonded to boron in

Scheme 1.28. Electrophilic Substitution Reaction of *o*-Carborane

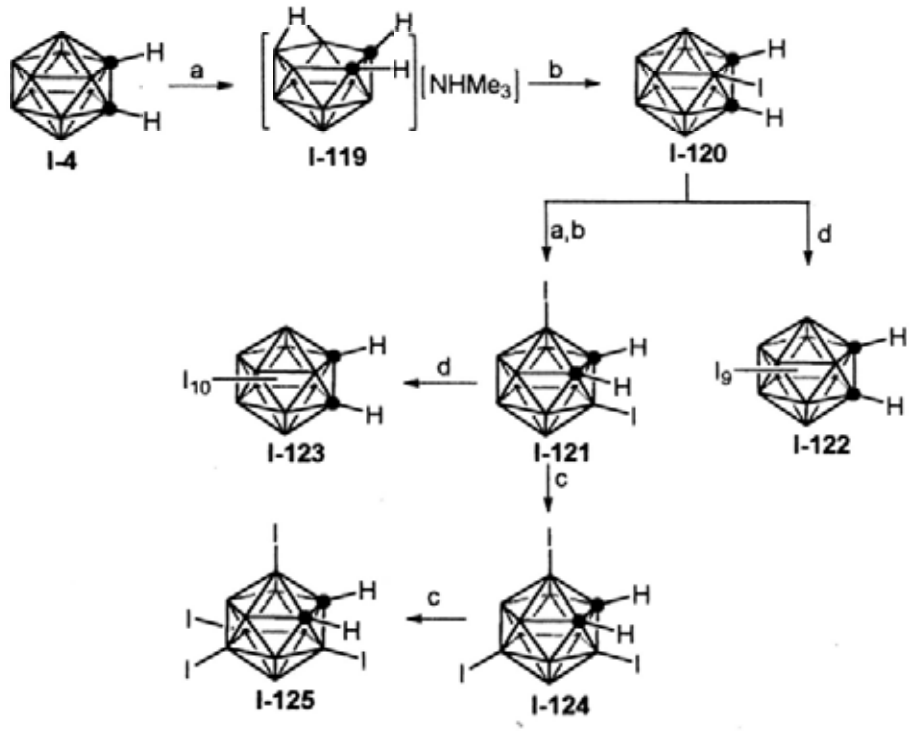


boron clusters.[70] For the particular case of neutral carboranes, methyl substitution produces a build-up of positive charge that prevents permethylation. Reaction of

o-carborane with excessive elemental fluorine in liquid hydrogen fluoride gives perfluorinated compound *o*-$C_2B_{10}F_{10}H_2$ in 30% isolated yield,[74] and the chlorination using chlorine irradiated by ultraviolet results in the stepwise formation of polychlorocarboranes containing two to eleven chlorine atoms per molecule.[75] Decachloro-*o*-carborane can be prepared by reaction of *o*-carborane with excessive ClF in liquid hydrogen fluoride in 64% isolated yield.[74] 1,2-Me_2-1,2-$C_2B_{10}H_{10}$ can be tetrabrominated, but *o*-$C_2B_{10}H_{12}$ can only be tribrominated.[27a,76] Full bromination of *o*-carborane has not been accomplished to date. The electrophilic iodination of *o*-carborane with iodine or ICl in the presence of $AlCl_3$ efficiently gives the 9,12-diiodo-*o*-carborane (**I-117**) in 90% yield,[72b,77] while the reaction of *o*-carborane with ICl in triflic acid affords octaiodo-*o*-carborane (**I-118**) in 67% isolated yield.[78] The 3,6-diiodo-*o*-carborane (**I-121**) can be synthesized by decapitation of *o*-carborane and capitation using BI_3 (Scheme 1.29).[55,79] 3,6,9-Triiodo-*o*-carborane (**I-124**),[55] 3,9,12-triiodo-*o*-carborane,[55] 3,6,9,12-tetraiodo-*o*-carborane (**I-125**),[55] nonaiodo-*o*-carborane (**I-122**)[80] and periodinated 1,2-H_2-1,2-*closo*-$C_2B_{10}I_{10}$ (**I-123**)[81] can be synthesized regioselectively by the combination of electrophilic substitution and neucleophilic deboration for reconstruction of the cage (Scheme 1.29).

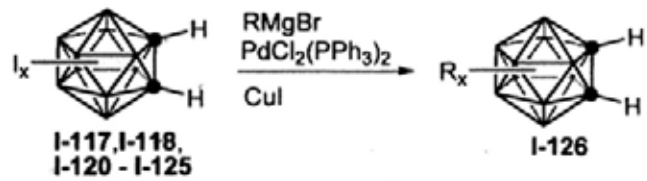
The iodo substituted *o*-carboranes can be conveniently converted to alkyl substituted derivatives by coupling with Grignard reagents in the presence of catalytic palladium reagent and copper(I) iodide (Scheme 1.30).[77b]

Scheme 1.29. Iodination of *o*-Carborane



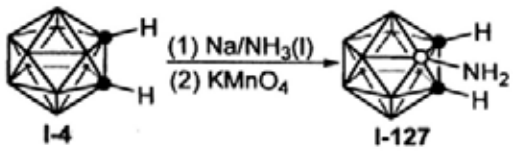
a. KOH/MeOH, Me_3NHCl; b. ^nBuLi, BI_3; c. $I_2/AlCl_3$; d. I_2/triflic acid

Scheme 1.30. Coupling Reaction of Iodo-*o*-Carborane



It is reported that 3-amino-*o*-carborane can be prepared in 84% yield by reduction of *o*-carborane with sodium in liquid ammonium followed by oxidation using $KMnO_4$ (Scheme 1.31).[25]

Scheme 1.31. Preparation of 3-Amino-*o*-Carborane

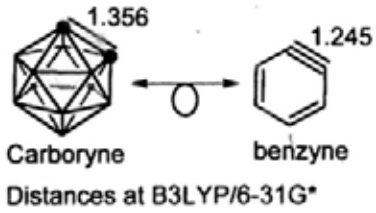


It should be mentioned that the cage CH vertices are not affected in the electrophilic substitution reactions due to the higher electronegativity of carbon than that of boron.

1.2. Carborynes

Carboryne, or 1,2-dehydro-*o*-carborane, is an unstable derivative of *o*-carborane with the formula of $C_2B_{10}H_{10}$. The hydrogen atoms on the cage carbon in the parent *o*-carborane are removed to form this species. Carboryne, can be viewed as a three-dimensional relative of benzyne (Chart 1.3).[48,82]

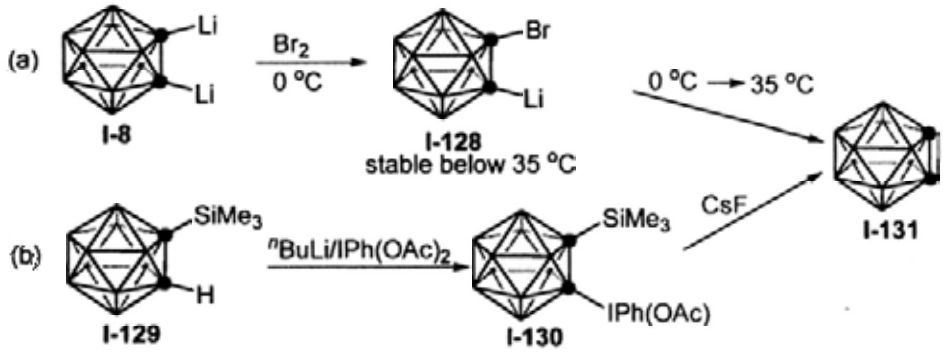
Chart 1.3. Isolobal Relationship of Carboryne and Benzyne.



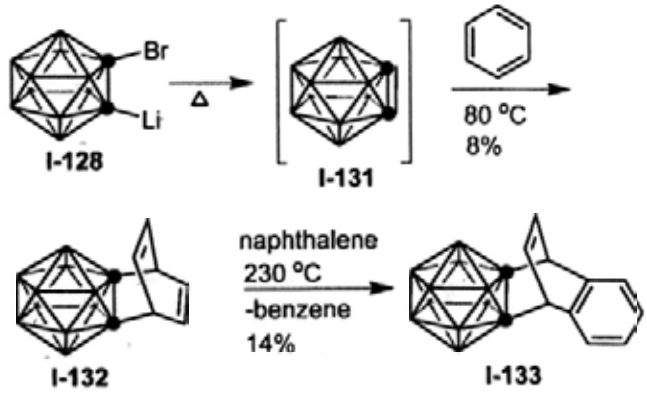
The carboryne was first generated as an active species in 1990 from *o*-carborane.[83] According to the report by the Jones group, the hydrogen atoms connected to carbon

are removed by ^{n}BuLi in THF and the resulting dilithio-*o*-carborane is reacted with bromine at 0℃ to form the bromo monoanion (**I-128**). Heating the reaction mixture to 35 °C releases carboryne (**I-131**) (Scheme 1.32a). At 0 ℃, the in-situ formed bromo monoanion species is stable. Presumably, this carboryne species owes its relative stability to the presence of the negative charge on a carborane carbon (pK_a = 19-23).[11] Later Jones and coworkers found that the adduct of benzene and carboryne can be used as carboryne source though the yield is very low (Scheme 1.33).[84]

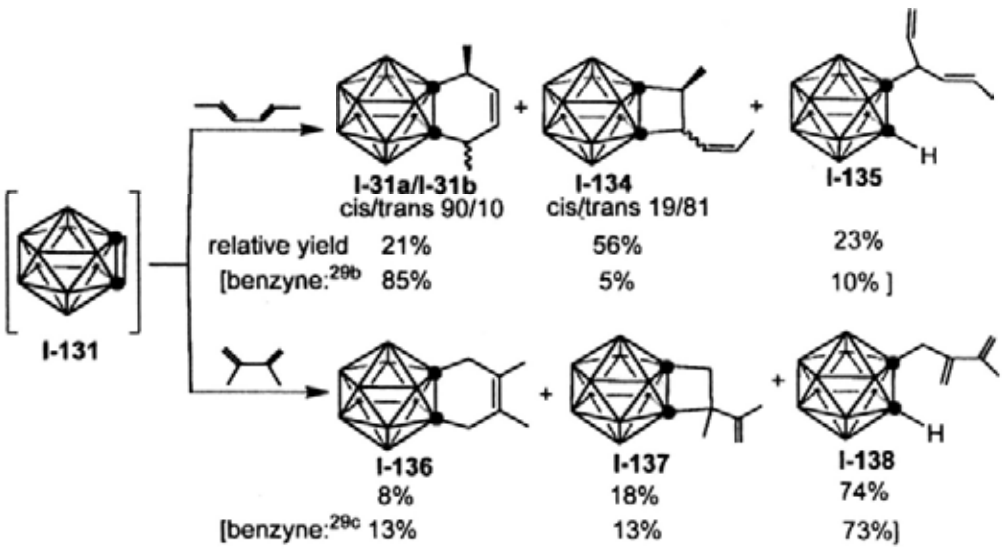
Scheme 1.32. Preparation of Carboryne



Scheme 1.33. Benzene-Carboryne Adduct Functions as a Carboryne Source



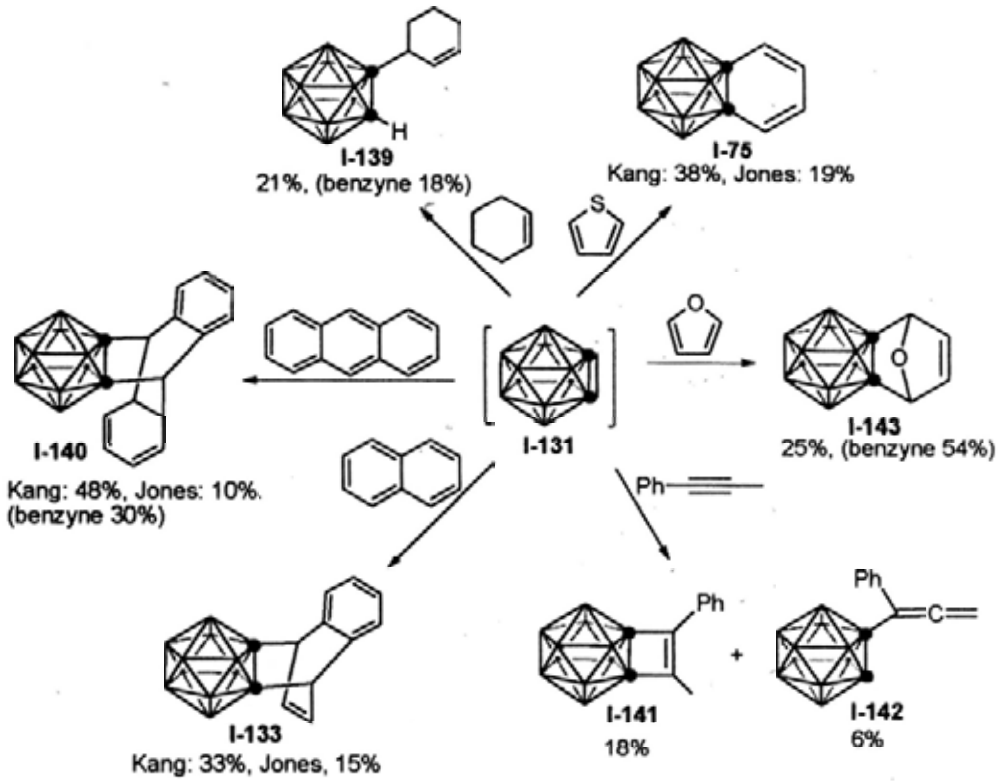
Scheme 1.34. Reaction of Carboryne with Substituted 1,3-Butadiene



The Kang's group reported that carboryne can also be produced from phenyl[*o*-(trimethylsilyl)(carboranyl)]iodonium acetate (**I-130**) in the presence of CsF (Scheme 1.32b).[48] **I-130** is prepared by reaction of [1-$(CH_3)_3$Si-1,2-$C_2B_{10}H_{10}$]Li with $IPh(OAc)_2$ in the yield of 46% and can be view as a precursor of carboryne. Compared with Jones' method, this species produces carboryne intermediate in much milder conditions leading to higher yields of coupling products as shown in Scheme 1.35.

Carboryne has been extensively studied by the groups of both Jones and Kang.[29,48,85] Using dienes as a trapping agent as exemplified in Scheme 1.34,[29] several products form in the types of [2+4] cycloaddition, [2+2] cycloaddition and ene reaction. The data in the bracket are the corresponding yields using benzyne as a starting material.

Scheme 1.35. Reactivity Pattern of Carboryne



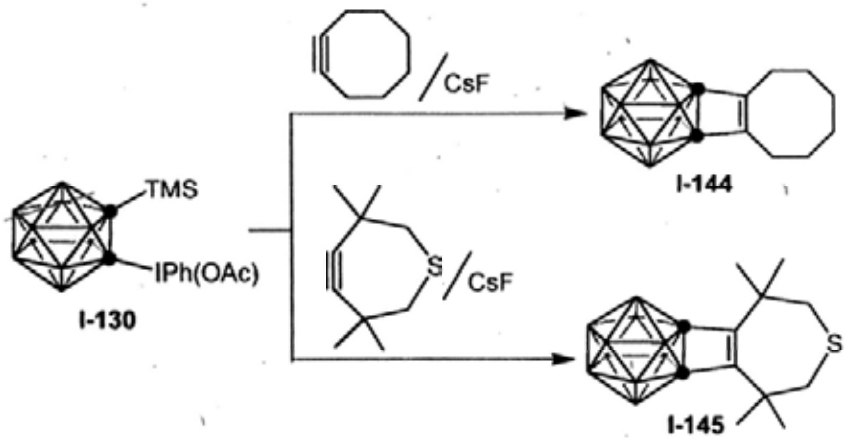
Like benzyne, the in situ generated carboryne can react with alkenes to form alkenyl carborane by ene reaction, with alkynes to form highly constrained cyclobutenyl carborane by [2 + 2] cycloaddition, with anthracene to yield a trypticene-like molecule, and with furan or naphthalene to form [2+4] cycloaddition products (Scheme 1.35).[29,48,85]

Carboryne reacts with thiophenes to form benzocarborane, an analogue of naphthalene, with concomitant loss of sulfur in cycloaddition pattern.[85] It is noteworthy that very few cyclobutenyl carboranes have been reported till now. The other two examples are that reaction of **I-130**, as a precursor of carboryne, with

strained cycloalkynes by [2+2] cycloaddition in the presence of CsF to form the highly constrained cyclobutenyl carboranes in 22-24% yield (Scheme 1.36).[48] It should mentioned that the cyclization of the in situ formed carboryne with some alkynes in the presence of $Ni(PEt_3)_4$, $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ is unsuccessful. Anyway, these studies lead to the syntheses of some important carborane derivatives that cannot be prepared by other means although the yields are generally low.

A theoretical study of carboryne shows that the formation of *o*-carboryne ($1,2\text{-}C_2B_{10}H_{10}$) is energetically comparable to that of benzyne with ca. 99 kcal/mol. The cage C-C bond length of carboryne is calculated to be 1.356 Å, which is significantly shorter than that of 1.625 Å in *o*-carborane, indicating the multiple bond character.[82]

Scheme 1.36. Preparation of Cyclobutenyl Carborane by [2+2] Cycloaddion



However, this bond distance is still significantly longer than that of benzyne (1.245 Å). Maybe these factors lead to the difference that carboryne is more stable and less active than benzyne, although both species have a similar reactivity pattern toward

the same kind of substrates.

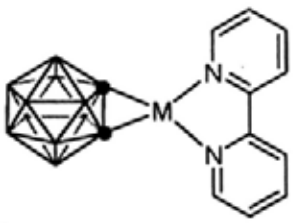
The first metal-carboryne complex $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ is prepared by reaction of $NiCl_2(PPh_3)_2$ with $Li_2C_2B_{10}H_{10}$ (Scheme 1.37).[86] The similar complexes $(\eta^2\text{-}C_2B_{10}H_{10})M(PPh_3)_2$ (M = Pd and Pt) are also prepared using the same method.[87]

Scheme 1.37. Preparation of Late Transition Metal-Carboryne Complexes

I-4 **I-146** **I-147**

M = Ni (**a**), Pd (**b**), Pt (**c**)

The structure of the nickel complex was characterized by X-ray analyses, which shows a four-coordinate square-planar molecular structure. It contains a three-membered ring formed by two Ni-C(cage) bonds and a cage C-C bond. The similar complexes of nickel, palladium and cobalt bearing a bipyridinyl ligand are also known (Figure 1.3) with no structural data.[88]



M = Ni (**I-148**), Pd (**I-149**), Co (**I-150**)

Figure 1.3. Bipyridine Coordinate Late Transition Metal-Carboryne Complexes.

The early transition metal-carboryne complex $[\{\eta^5\text{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$ (**I-152**) was prepared

in 2003 from reaction of [{η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$}$Zr(NMe_2)_2$] (**I-151**) with excess Me_3SiCl followed by treatment with 1 equiv of $Li_2C_2B_{10}H_{10}$ (Scheme 1.38).[89] Its structure is further confirmed by X-ray analyses. Molecular orbital calculations on **I-152** suggest that the bonding interactions between Zr and carboryne moiety are best described as a resonance hybrid of both Zr-C σ and Zr-C π bonding forms, which is similar to that observed in $Cp_2Zr(\eta^2$-$C_6H_4)(PMe_3)$ (Chart 1.4).[90]

Scheme 1.38. The First Zirconocene-Carboryne Complex

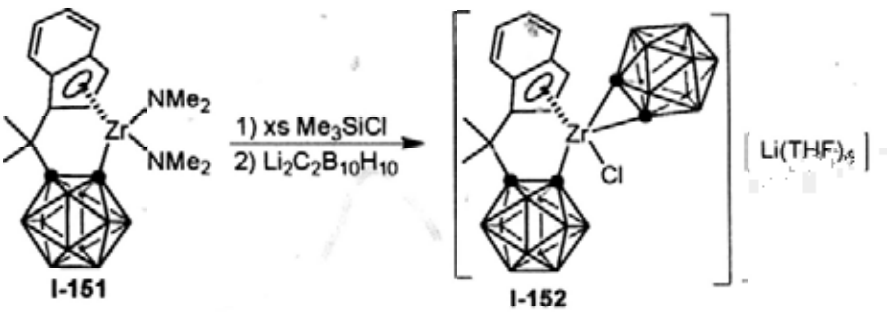
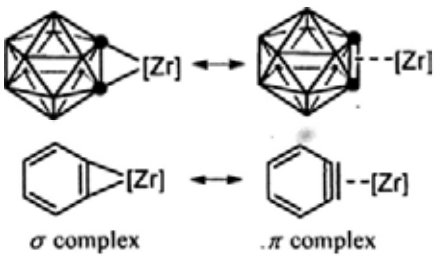


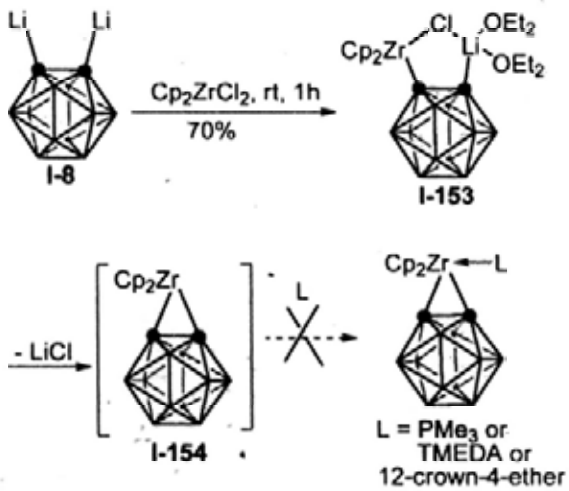
Chart 1.4. Bonding Interactions between Zr and Carboryne or Benzyne



On the other hand, treatment of Cp_2ZrCl_2 with 1 equiv of $Li_2C_2B_{10}H_{10}$ in ether gives $Cp_2Zr(\mu$-$Cl)(\mu$-$C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) in 70% isolated yield, rather than the expected zirconocene-carboryne complex $Cp_2Zr(\eta^2$-$C_2B_{10}H_{10})$ (Scheme 1.39).[91] This product has been structurally characterized by X-ray analyses. The unique

molecule can be viewed as an intermediate to the zirconocene-carboryne complex. Attempts to isolate $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})(L)$, an analogue of $Cp_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$, in the presence of PMe_3, TMEDA, or 12-crown-4-ether via a complete salt metathesis reaction are all unsuccessful.

Scheme 1.39. Preparation of Zirconocene-Carboryne Complex

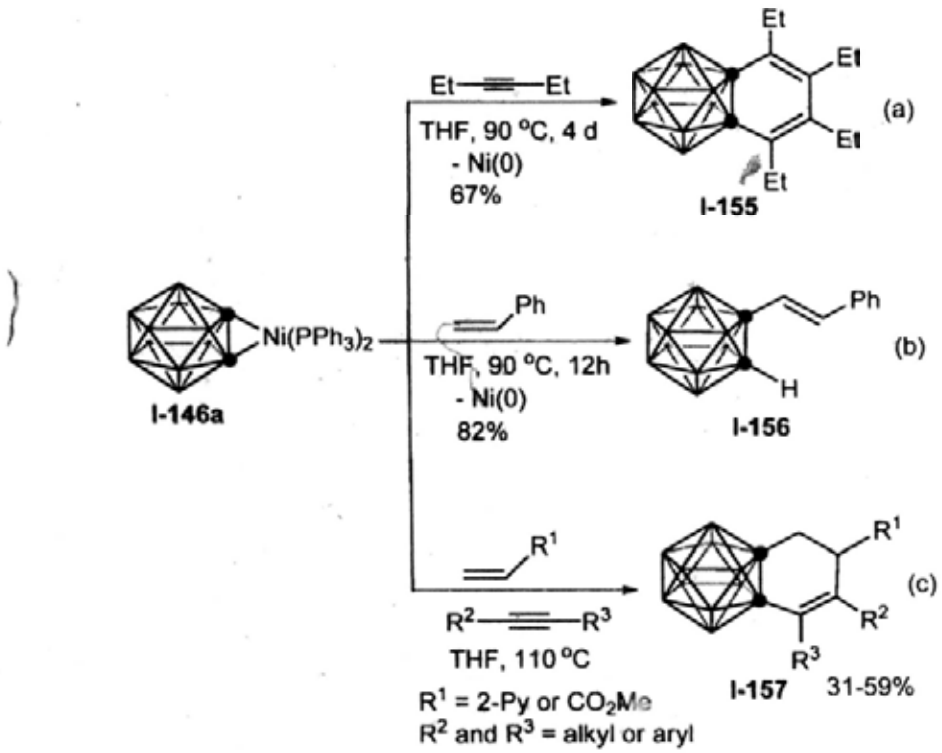


The reaction chemistry of this kind of metal-carboryne complexes has been studied.[86,91,92] Reaction of Ni-carboryne with alkynes offers benzocarboranes in the yield of 33-67% via two-component [2+2+2] cycloaddition (Scheme 1.40a).[86b]

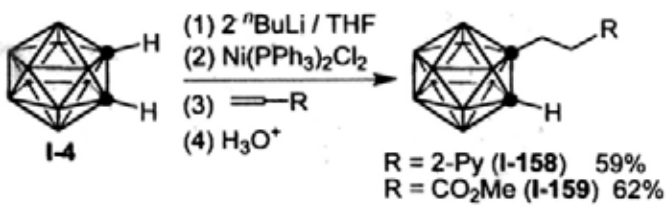
Carboryne $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ can also react with styrene to afford a mono-substituted carborane 1-(trans-$C_6H_5CH{=}CH$)-1,2-$C_2B_{10}H_{11}$ in > 80% isolated yield (Scheme 1.40b).[91a] Thus, many alkenylcarboranes can be prepared by this cross-coupling reaction of Ni-carboryne with alkenes. Only alkylcarboranes are obtained after hydrolysis using methyl acrylate or 2-vinylpyridine as the starting

material (Scheme 1.41). This result implies that the donor atom of the olefin may stabilize the intermediate, preventing the β-H elimination. These intermediates do not show any activity toward olefins, but react readily with alkynes to give three-component [2 + 2 + 2] cycloaddition dihydrobenzocarboranes (Scheme 1.40c).[91b]

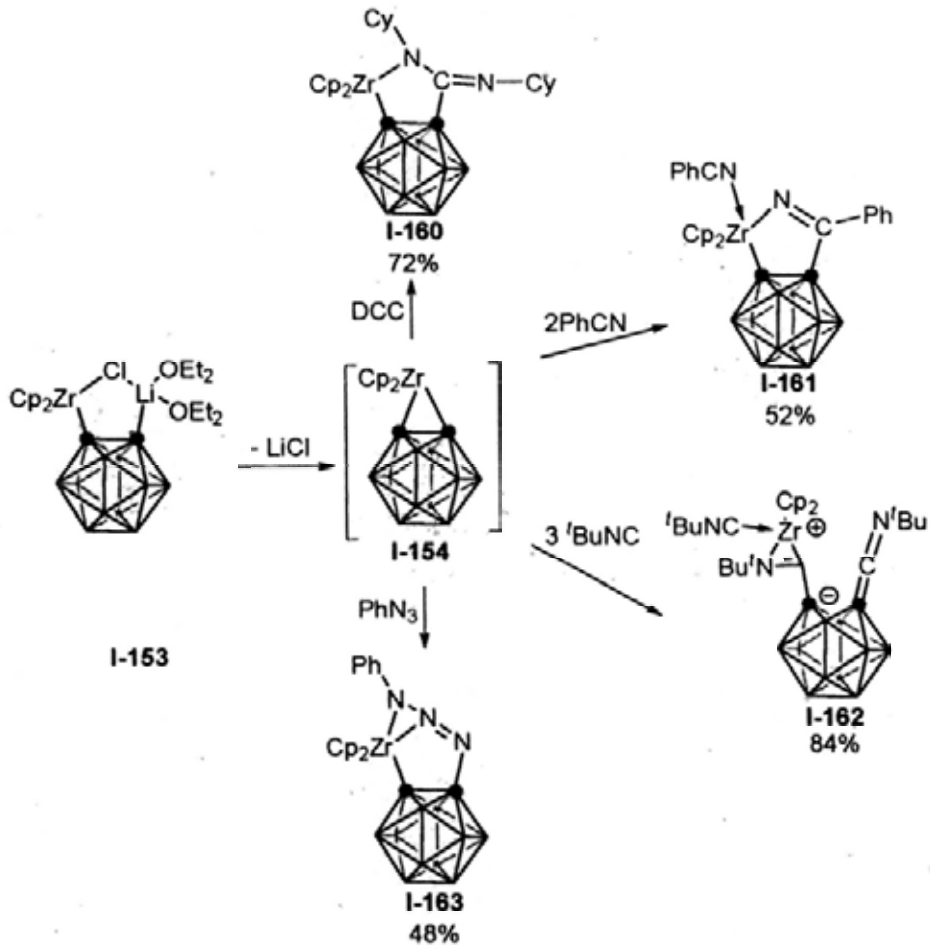
Scheme 1.40. Reactivities of Nickel-Carboryne Complex



Scheme 1.41. Nickel-Mediated Coupling of Carboryne with Activated Alkenes



Scheme 1.42. Reactivity of Zirconocene-Carboryne Complex



Although Ni-carboryne does not react with polar unsaturated molecules, complex **I-153** is very active toward these unsaturated molecules to afford a series of metallacycles.[91] Reactions of **I-153** with DCC (CyNCNCy, Cy = C_6H_{11}), PhCN, ^{t}BuNC and PhN_3 result in the formation of $Cp_2Zr[\sigma,\sigma\text{-CyNC(=NCy)}(C_2B_{10}H_{10})]$ (**I-160**), $Cp_2Zr[\sigma,\sigma\text{-N=C(Ph)}(C_2B_{10}H_{10})](PhCN)$ (**I-161**), $Cp_2Zr[\eta^2\text{-}^t\text{BuNC}(C_2B_{10}H_{10})=CN^t\text{Bu}](CN^t\text{Bu})$ (**I-162**) and $Cp_2Zr[\eta^2,\sigma\text{-(PhNN=N)}(C_2B_{10}H_{10})]$ (**I-163**), respectively, in moderate to high yields (Scheme 1.42).

1.3. Research Objectives

Our previous work shows that the structure of Zr-carboryne resembles that of Zr-benzyne. In view of the very rich chemistry of metal-benzyne[90,93] and our preliminary work on metal-carboryne complexes,[86,89,91,92] we plan to explore the chemistry of group 4 metal-carboryne complexes. The main objectives include (1) synthesis and structural characterization of neutral group 4 metal-carboryne complexes, (2) reaction chemistry of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**), and group 4 metal-carboryne complexes, and (3) structure/reactivity relationships of metal-carboryne complexes. These results are described in the following chapters.

Chapter 2. Synthesis and Structure of Group 4 Metal-Carboryne Complexes

2.1. Background

Icosahedral carboranes constitute a class of structurally unique molecules with exceptionally thermal and chemical stabilities and the ability to hold various substituents.[2a,94] These properties have made them as useful basic units for boron neutron capture therapy (BNCT) drugs,[15b,95] supramolecular design,[96] and ligands for transition metals[97] and material science.[98] On the other hand, the sterically demanding carboranes make the transition metal–cage carbon ($M–C_{cage}$) bond inert toward unsaturated organic molecules, which limits the derivatization of these clusters.[40e,51a,99] We thought if a transition metal was bound to both cage carbon atoms of a carborane cage, the resultant three-membered metallacycle (metal-carboryne, carboryne = 1,2-dehydro-1,2-carborane) may be more accessible for unsaturated molecules as the metal would have a larger open coordination sphere. This approach has proved to be very successful. For examples, Ni-carboryne $(Ph_3P)_2Ni(\eta^2\text{-}C_2B_{10}H_{10})$ can undergo [2+2+2] cycloaddition reaction with 2 equiv of alkynes to give benzocarboranes,[86b] react with 1 equiv of alkenes to generate alkenylcarborane coupling products,[92a] and undergo three-component [2+2+2] cyclotrimerization with 1 equiv of alkene and 1 equiv of alkyne to afford dihydrobenzocarboranes.[92b] This Ni-carboryne complex does not show any activity

toward polar unsaturated molecules. On the other hand, the zirconium-carboryne precursor $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) can react with 1 equiv of polar unsaturated molecules to give five-membered zirconacycles,[91] and interact with 1 equiv of alkyne to yield zirconacyclopentene.[100] The latter is an important reagent for the preparation of a variety of carborane derivatives.[100a] These reactions are suggested to proceed via a zirconocene-carboryne ($Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$) intermediate although many attempts to prepare this complex failed.

The first early transition metal-carboryne complex is $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$ (**I-152**),[89] prepared from the reaction of in situ generated $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]ZrCl_2$ (**I-151**) with $Li_2C_2B_{10}H_{10}$. It is inert toward unsaturated organic molecules probably because of the anionic nature of this zirconium-carboryne complex.

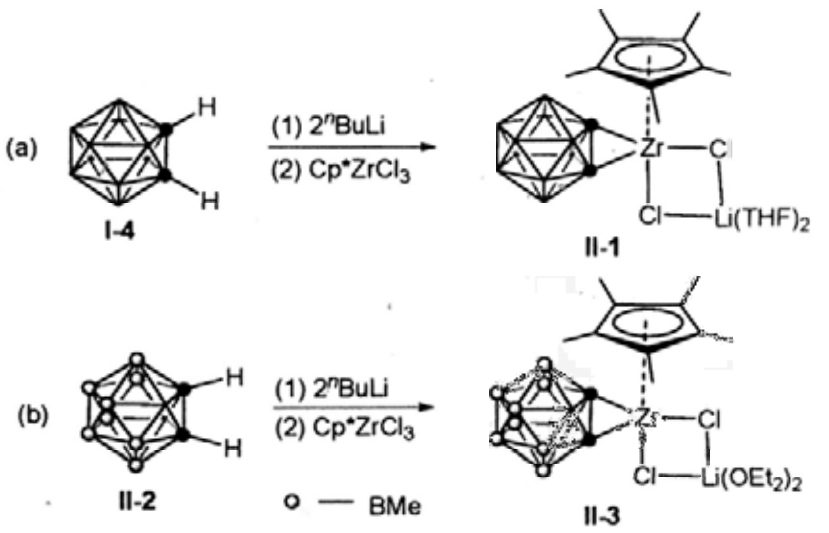
The aforementioned results show that both ligands and electronic configuration of transition metal ions have significant effects on the reactivity of the corresponding metal-carboryne complexes.

Salt metathesis between $Li_2C_2B_{10}H_{10}$ and metal halides is a useful method for the construction of metal-carboryne unit, leading to successful preparation of $(Ph_3P)Ni(\eta^2\text{-}C_2B_{10}H_{10})$[86a,92] and $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$.[89] Reaction of Cp_2ZrCl_2 with $Li_2C_2B_{10}H_{10}$, however, did not result in the formation of expected zirconocene-carboryne complex $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$, rather afforded the ate complex

$Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**).[91] It was believed that the presence of two Cp ligands created a crowded environment around the Zr atom, which may destabilize the Zr-carboryne complex. To overcome this problem, Cp^*ZrCl_3 ($Cp^* = C_5Me_5$) was then chosen as the starting material.

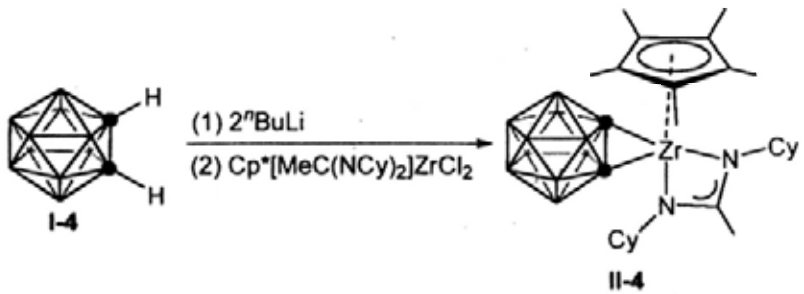
Treatment of Cp^*ZrCl_3 with 1 equiv of $Li_2C_2B_{10}H_{10}$ in Et_2O gave, after recrystallization from THF, $Cp^*(\eta^3\text{-}C_2B_{10}H_{10})Zr(\mu\text{-}Cl)_2Li(THF)_2$ (**II-1**) in 73% isolated yield (Scheme 2.1a). This result suggested the importance of steric effect in the formation of metal-carboryne complex. A more bulky octamethylcarborane might lead to a neutral metal-carboryne. Reaction of Cp^*ZrCl_3 with 1 equiv of $Li_2C_2B_{10}Me_8H_2$ prepared from the reaction of 1,2-$C_2B_{10}Me_8H_4$ (**II-2**) with 2 equiv of ^{n}BuLi in Et_2O, afforded $Cp^*(\eta^3\text{-}C_2B_{10}Me_8H_2)Zr(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**II-3**) in 65% isolated yield (Scheme 2.1b). It showed that increasing the bulkiness of carborane did not block the coordination of Cl^- to the electron-deficient Zr atom.

Scheme 2.1. Reaction of Cp^*ZrCl_3 with 1,2-$Li_2C_2B_{10}H_{10}$



In view of the interactions between the Zr atom and η^3-(o-$C_2B_{10}H_{10}$) moiety (vide infra), the dianionic $[\eta^3$-(o-$C_2B_{10}H_{10})]^{2-}$ ligand formally donates three pairs of electrons to the metal center and is isolobal with Cp^-.[89] Therefore, one can conveniently correlate these zirconium complexes with those having a general formula of Cp_2ZrX_2. Based on this consideration, replacement of a chloro anion in **II-1** and **II-3** by a uninegative amidinate ligand should afford neutral species, as this type of amidinate ligands normally function as bi-dentate π ligands and can donate more electrons to the metal center to meet the electronic requirement. Thus, an equimolar reaction of Cp*[η^2-CyNC(Me)NCy]$ZrCl_2$ (Cy = cyclohexyl) with $Li_2C_2B_{10}H_{10}$ in diethyl ether generated the neutral species Cp*[η^2-CyNC(Me)NCy]Zr(η^3-$C_2B_{10}H_{10}$) (**II-4**) in 51% isolated yield (Scheme 2.2).

Scheme 2.2. Preparation of Neutral [Zr]-Carboryne Complex **II-4**



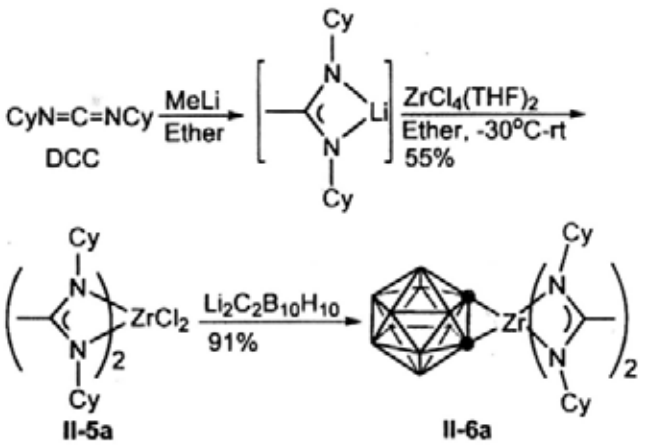
These primary results prompt us to explore the general synthetic methods of metal-carboryne complexes. In this section we will describe the synthesis and structural characterization of a variety of [M]-carboryne (M = Ti, Zr and Hf) complexes bearing different types of ligands.

2.2. Synthesis

Reaction of $(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}CyNC(Me)NCy]Cl_2$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene afforded $(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}CyNC(Me)NCy](\eta^2\text{-}C_2B_{10}H_{10})$ (**II-4**) in 51% yield (Scheme 2.2),[101] which was characterized by ^1H, ^{13}C and ^{11}B NMR spectra.

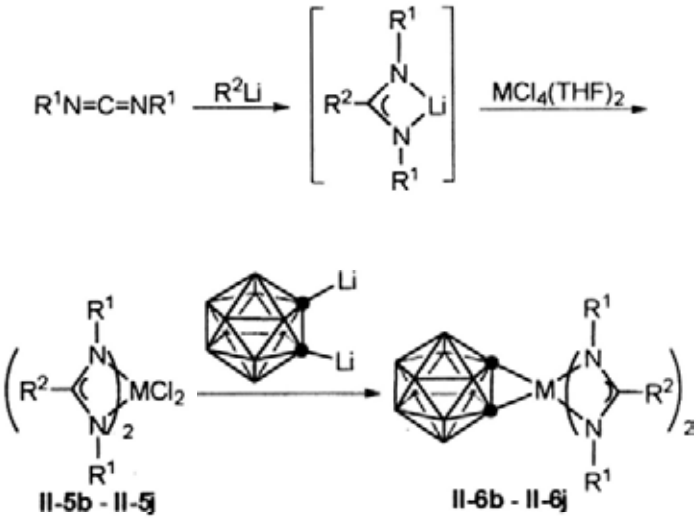
In the neutral Zr-carboryne complex of $(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}CyNC(Me)NCy](\eta^2\text{-}C_2B_{10}H_{10})$ (**II-4**), when the ligand Cp^* ($\eta^5\text{-}C_5Me_5$) was replaced by an acetoamidinato ligand, another type of neutral zirconium-carboryne would be prepared. Treatment of carbodiimide $R^1N{=}C{=}NR^1$ (R^1 = Cy) with MeLi in diethyl ether, followed by reaction with $ZrCl_4(THF)_2$ in diethyl ether for 12 hours, afforded diamidinato zirconium dichloride complex $[\eta^2\text{-}CyNC(Me)NCy]_2ZrCl_2$ (**II-5a**).[102] Complex **II-5a** reacted with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene at room temperature for 24 hours, to give a neutral zirconium-carboryne complex $[\eta^2\text{-}CyNC(Me)NCy]_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ (**II-6a**) as yellow crystals in 91% yield (Scheme 2.3).

Scheme 2.3. Preparation of $[\eta^2\text{-}CyNC(Me)NCy]_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ (**II-6a**)



Subsequently, we synthesized a series of diamidinato and diguanidinato group 4 metal dichloride complexes in 50 – 83% yields using the same method as that for the preparation of **II-5a**,[102] $[\eta^2\text{-}R^1NC(R^2)NR^1]_2MCl_2$ (**II-5b**, R^1 = Cy, R^2 = Ph, M = Zr; **II-5c**, R^1 = Cy, R^2 = ^{n}Bu, M = Zr; **II-5d**, R^1 = Cy, R^2 = Ph, M = Ti; **II-5e**, R^1 = ^{i}Pr, R^2 = Me, M = Zr; **II-5f**, R^1 = ^{i}Pr, R^2 = Ph, M = Zr; **II-5g**, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Zr; **II-5h**, R^1 = ^{i}Pr, R^2 = $(^n\text{Pr})_2$N, M = Zr; **II-5i**, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Ti; **II-5j**, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Hf) (Scheme 2.4). They are soluble in toluene, THF and diethyl ether, but insoluble in hexane.

Scheme 2.4. Preparation of Diamidinato/Diguanidinato Group 4 Metal-Carboryne Complexes (**II-6b – II-6j**)

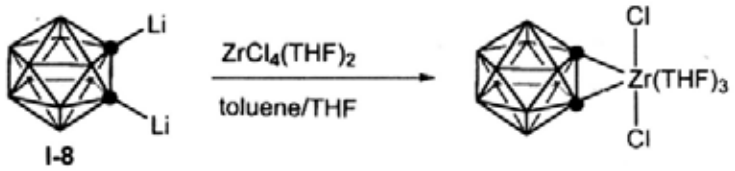


b R^1 = Cy, R^2 = Ph, M = Zr
c R^1 = Cy, R^2 = ^{n}Bu, M = Zr
d R^1 = Cy, R^2 = Ph, M = Ti
e R^1 = ^{i}Pr, R^2 = Me, M = Zr
f R^1 = ^{i}Pr, R^2 = Ph, M = Zr
g R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Zr
h R^1 = ^{i}Pr, R^2 = $(^n\text{Pr})_2$N, M = Zr
i R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Ti
j R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Hf

Using the same method for the preparation of **II-6a**, several diamidinato/diguanidinato group 4 metal-carboryne complexes $[\eta^2\text{-}R^1NC(R^2)NR^1]_2M(\eta^2\text{-}C_2B_{10}H_{10})$ (**II-6b**, R^1 = Cy, R^2 = Ph, M = Zr; **II-6c**, R^1 = Cy, R^2 = ^{n}Bu, M = Zr; **II-6d**, R^1 = Cy, R^2 = Ph, M = Ti; **II-6e**, R^1 = ^{i}Pr, R^2 = Me, M = Zr; **II-6f**, R^1 = ^{i}Pr, R^2 = Ph, M = Zr; **II-6g**, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Zr; **II-6h**, R^1 = ^{i}Pr, R^2 = $(^n\text{Pr})_2$N, M = Zr; **II-6i**, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Ti; **II-6j**, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Hf) were synthesized in high yields (70 – 95%) (Scheme 2.4).

Direct treatment of $ZrCl_4(THF)_2$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ in a mixed solvent of toluene/THF (10/1 in v/v) afforded a dichlorozirconium-carboryne complex $(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$ (**II-6k**) in 88% yield (Scheme 2.5).

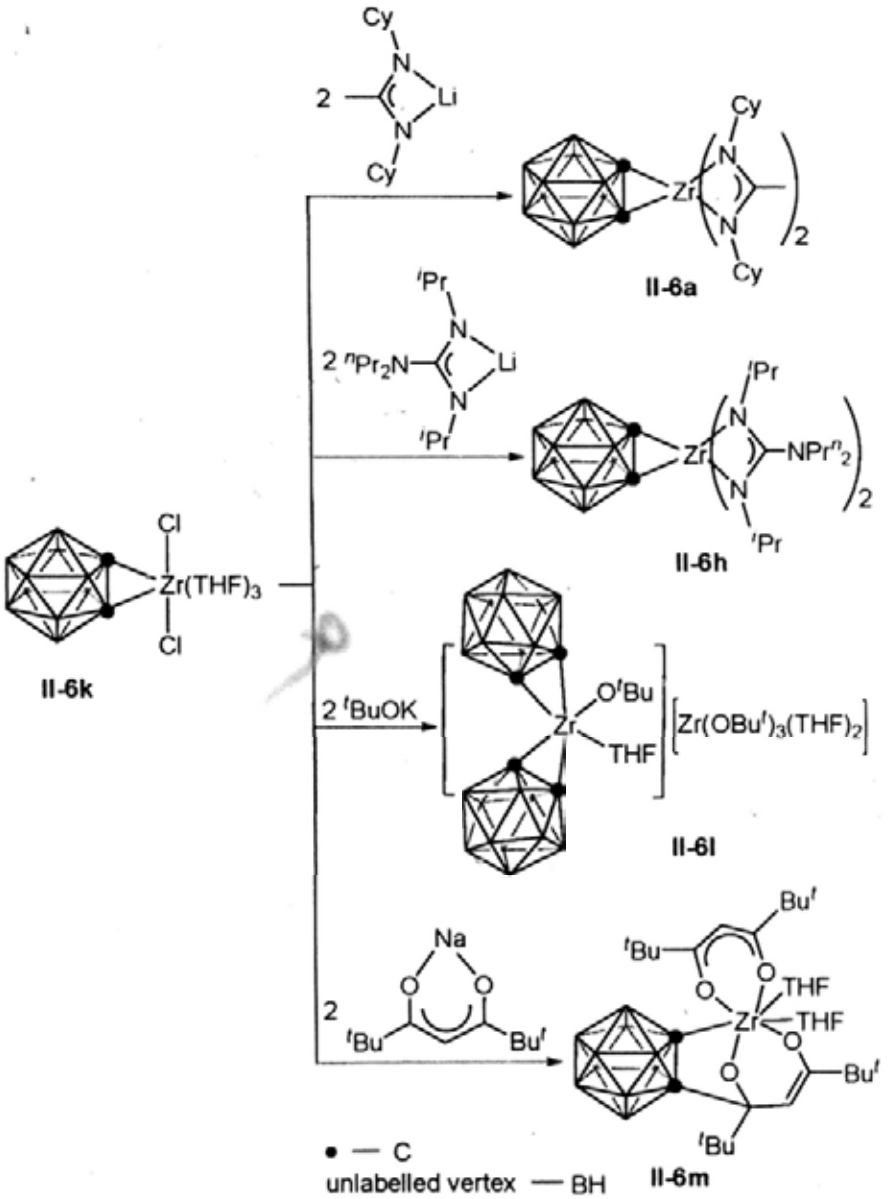
Scheme 2.5. Preparation of $(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$ (**II-6k**)



I-8 **II-6k**

Complex **II-6k** contains two reactive Zr-Cl bonds, and may be a useful starting material for the preparation of a series of organozirconium-carboryne complexes. In fact, reaction of **II-6k** with 2 equiv of $[MeC(NCy)_2]Li$ or $[^nPr_2NC(NPr^i)_2]Li$ produced **II-6a** or $[\eta^2\text{-}^nPr_2NC(NPr^i)_2]_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ (**II-6h**), respectively, in high yields. Treatment of **II-6k** with 2 equiv of ^{t}BuOK in Et_2O led to the isolation of an ionic complex $[(\eta^2\text{-}C_2B_{10}H_{10})_2Zr(O^tBu)(THF)][Zr(OBu^t)_3(THF)_3]$ (**II-6l**) in 64% yield. Reaction of **II-6k** with 2 equiv of $[^tBuCOCHCO^tBu]Na$ in Et_2O gave an

Scheme 2.6. Reaction of Dichlorozirconium-Carboryne (**II-6k**) with Nucleophiles



unexpected product [σ:σ:σ-{^{t}BuC(O)=CHC(^{t}Bu)(O)$C_2B_{10}H_{10}$}]Zr(η^2-^{t}BuCOCHCOBu^t)$(THF)_2$ (**II-6m**) in 57% yield (Scheme 2.6). It is speculated that the expected Zr-carboryne complex (η^2-^{t}BuCOCHCO^{t}Bu)$_2$Zr(η^2-$C_2B_{10}H_{10}$) might serve as an intermediate, followed by a nucleophilic attack at the C=O to form **II-6m**.

Other possibilities cannot be ruled out at this stage. The remaining Zr-C(cage) bond is inert as observed in other metal-carboranyl complexes.[40e,99] On the other hand, no pure product was isolated from the reactions of **II-6k** with 1 equiv of $Li_2C_2B_{10}H_{10}$ or 1 (or 2) equiv of CpNa. These results suggest that a proper combination of the ligands is important for the preparation of neutral Zr-carboryne complexes.

Complexes **II-6a – II-6k** are thermally stable even in refluxing toluene for several days. However, **II-6l,m** are only stable at room temperature. They are all extremely air and moisture-sensitive. Complexes **II-6a – II-6k** have a poor solubility in toluene and diethyl ether, however, **II-6l,m** are easily dissolved in toluene and diethyl ether.

2.3. Structural Characterization

Complexes **II-5b – II-5j** have been fully characterized by various spectroscopic techniques and elemental analyses. The distinctive quaternary carbons of the amidinato ligands were observed in the range of 177.0 to 181.3 ppm in their ^{13}C NMR spectra, which can be well compared to that of **II-5a**[102] and $[Me_3SiNC(C_6H_5)NSiMe_3]_2ZrCl_2$.[103] Influenced by the heteroatom N of the substituent $^nPr_2N$, the quaternary carbon signal of guanidinato ligand in **II-5h** shifts slightly to high-field (173.3 ppm) in its ^{13}C NMR spectrum.

The ^{11}B NMR spectrum of $Li_2C_2B_{10}H_{10}$ exhibited four resonances at 1.7, -1.9, -6.5 and -9.4 ppm with relative intensities 2:2:4:2. Although the same 2:2:4:2 pattern was observed in the ^{11}B NMR spectra of **II-4**, the chemical shifts were observed at -0.8, -2.3, -7.9, -15.0 ppm, respectively, which is very different from that of $Li_2C_2B_{10}H_{10}$,

but is very similar to that of **II-1** and **II-3**.

The same 2:2:4:2 pattern was observed in the ^{11}B NMR spectrum of complex **II-6j**. The relative chemical shifts were found at -0.8, -0.7, -7.5, -15.2 ppm, respectively, similar to those of **II-1** and **II-4** (Table 2.1). The ^{11}B NMR spectra of **II-6a – II-6i** and **II-6k,l** displayed a 4:4:2 pattern in the range of -0.1 to -15.2 ppm whereas that of **II-6m** showed a 2:3:2:3 pattern at -3.3, -6.5, -9.9, -11.9 ppm due to the unsymmetrical structure resulted from the insertion of C=O. It can be seen that the ^{11}B NMR spectroscopy is a very useful technique to follow the above-mentioned reactions. Although, it was not possible to reliably determine J_{BH} values for complexes **II-4** and **II-6a – II-6m** due to overlapping resonances, the J_{BH} values were obtained from ^{1}H-coupled ^{11}B NMR spectrum of **II-4**, which fell in the range 130 – 170 Hz. No significantly reduced J_{BH} values and no very deshielded signal in the ^{11}B NMR spectra were observed in complexes **II-4** and **II-6a – II-6m**,[104] although some B-H···Zr interactions were found in the solid-state structures of **II-4** and **II-6l** (*vide infra*).

The distinctive quaternary carbons of the amidinato/guanidinato ligands and carborane cage carbons were found in the range of 173 to 182 ppm and 95 to 116 ppm, respectively, in the ^{13}C NMR spectra of metal-carboryne complexes (Table 2.2) while the cage carbons of **II-6k** was found at 78.2 ppm. These values for cage carbons can be compared to the 56.0 ppm for *o*-$C_2B_{10}H_{12}$ and 92.1 ppm for $Li_2C_2B_{10}H_{10}$.

The IR spectra (KBr) exhibited one very strong and broad ν_{B-H} stretching band at about 2565 cm^{-1} for **II-4** and **II-6a – II-6m** whereas that of **II-3** showed two ν_{B-H} bands at 2613 and 2453 cm^{-1}, respectively. The latter might indicate some B-H···Zr interactions in **II-3**.[105] The same phenomenon was not observed in **II-1**, **II-4** and **II-6l** presumably due to the overlapping of very strong and broad ν_{B-H} stretching bands resulting from the ten B-H bonds comparing with only two B-H bonds in **II-3**.

Table 2.1. Summary of ^{11}B NMR Data of Complexes **II-4** and **II-6a – II-6f**.

	II-4	**II-6a**	**II-6b**	**II-6c**	**II-6d**	**II-6e**	**II-6f**
^{11}B {H} (δ ppm)	-0.8(2B), -2.3(2B), -7.9(4B), -15.0(2B)	-0.7(4B), 7.1(4B), -14.8(2B)	-1.4(4B), -6.7(4B), -13.8(2B)	-0.1(4B), -6.5(4B), -14.2(2B)	-2.1(4B), -7.2(4B), -14.9(2B)	-1.4(4B), -6.9(4B), -13.8(2B)	-0.7(4B), -6.5(4B), -13.9(2B)
	II-6g	**II-6h**	**II-6i**	**II-6j**	**II-6k**	**II-6l**	**II-6m**
^{11}B {H} (δ ppm)	-0.4(4B), -6.8(4B), -14.4(2B)	-1.2(4B), -7.8(4B), -15.2(2B)	-2.7(4B), -7.5(4B), -15.2(2B)	-0.8(2B), -0.7(2B), -7.5(4B), -15.2(2B)	-1.0(4B), -7.4(4B), -15.4(2B)	-1.9(4B), -8.0(4B), -11.9(2B)	-3.3(2B), -6.5(3B), -9.0(2B), -11.9(3B)

Table 2.2. The Characteristic ^{13}C NMR Chemical Shift (δ ppm) in Group 4 Metal-Carboryne Complexes.

	II-4	**II-6a**	**II-6b**	**II-6c**	**II-6d**	**II-6e**	**II-6f**	**II-6g**	**II-6h**	**II-6i**	**II-6j**	**II-6k**	**II-6l**	**II-6m**
NCN	166.2	177.6	179.3	182.0	177.6	177.3	178.7	181.7	171.6	179.1	181.4			
Cage *C*	98.0	103.9	105.7	104.2	107.0	104.2	104.6	103.8	101.0	105.9	116.0	78.5	93.3	100.8/97.1
CNCH	57.8	57.9	59.1	57.8	61.4	48.9	50.5	48.7	51.3/48.4	51.2	48.5			

The Molecular structures of complexes **II-5b**, **II-5d**, **II-5e**, **II-5f** and **II-5i** were determined by single-crystal X-ray diffraction studies as shown in Figures 2.1 – 2.5. The key structural data were summarized in Table 2.3.

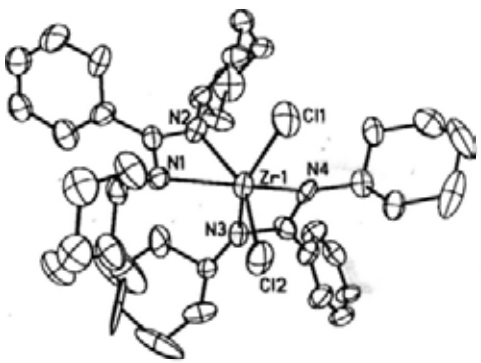


Figure 2.1. Molecular Structure of $[\eta^2\text{-CyNC(Ph)NCy}]_2ZrCl_2$ (**II-5b**).

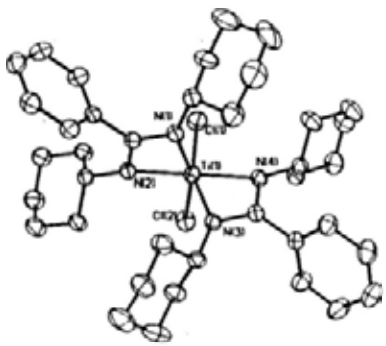


Figure 2.2. Molecular Structure of $[\eta^2\text{-CyNC(Ph)NCy}]_2TiCl_2$ (**II-5d**).

The average Zr-N bond lengths in $[\eta^2\text{-R}^1\text{NC(R}^2\text{)NR}^1]_2ZrCl_2$ (**II-5b**, **II-5e** and **II-5f**) are very close to those found in the benzamidinato complex $[Me_3SiNC(C_6H_5)NSiMe_3]_2ZrCl_2$.[103] Both Ti-Cl and Ti-N bond lengths are obviously shorter than those found in zirconium or hafnium complexes. Both Cl-Zr-Cl angles and Zr-Cl bond lengths in these complexes are slightly smaller than those found in

Cp_2ZrCl_2 (Cl-Zr-Cl 97.1(2)°; Zr-Cl: 2.441(5) Å).[106]

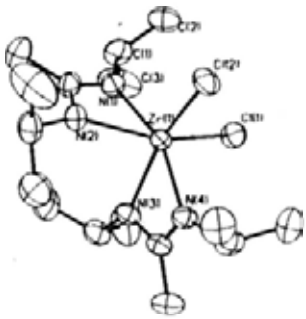
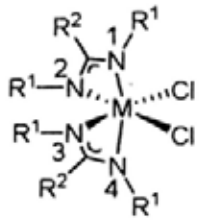


Figure 2.3. Molecular Structure of $[\eta^2$-^{i}PrNC(Me)NPr$^i]_2ZrCl_2$ (**II-5e**).

Table 2.3. Selected Bond Lengths (Å) and Angles (deg.) for **II-5**



compd	M-Cl[a]	M-C[b]	M-N[a]	N-M-N[c]	Cl-M-Cl
II-5a[102]	2.431(3)	--	2.210(7)	59.8(3)	93.1(1)
II-5b	2.430(6)	2.69(2)	2.214(15)	59.9(6)	95.5(3)
II-5d	2.286(1)	2.503(3)	2.075(2)	63.8(1)	95.0(1)
II-5e[d]	2.426(1)	2.640(5)	2.200(4)	60.2(2)	96.5(6)
II-5f	2.416(2)	2.638(6)	2.202(4)	59.9(2)	96.4(1)
II-5i	2.309(1)	2.507(2)	2.067(2)	63.8(1)	93.8(1)
II-5j[107]	2.412(1)	--	2.185(4)	60.6(1)	95.3(1)

[a] the average value of two Zr-Cl bonds. [b] the distance of Zr to the quaternary carbon. [c] the average value of N-Zr-N angles in two amidinato ligands. [d] the average value of two molecules in one unit cell.

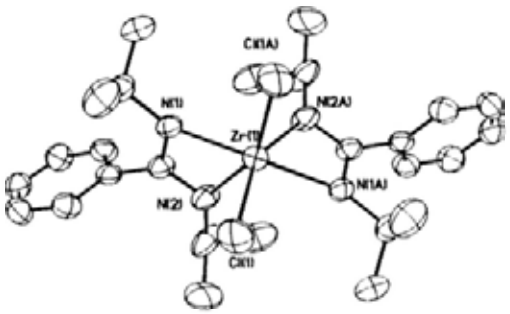


Figure 2.4. Molecular Structure of $[\eta^2$-^{i}PrNC(Ph)NPr$^i]_2ZrCl_2$ (**II-5f**).

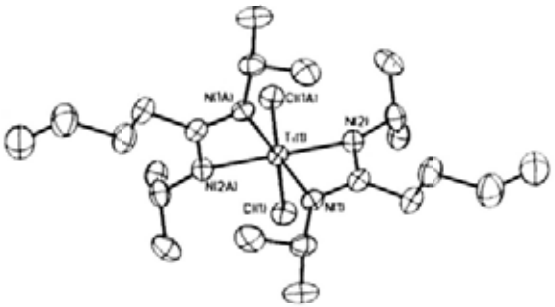


Figure 2.5. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr$^i]_2TiCl_2$ (**II-5i**).

The molecular structures of **II-6a**, **II-6b**, **II-6e**, **II-6g** – **II-6m** were further determined by X-ray analyses, and shown in Figures 2.6 – 2.15. The selected bond distances and angles are summarized in Table 2.4. Complexes **II-6a**, **II-6g** – **II-6j** have a perfect symmetrical geometry (Figures 2.6, 2.9 – 2.12), in which the Zr/Ti/Hf atom is η^2-bound to two amidinate (or guanidinate) ligands and to the carboryne moiety (Zr···B distances > 2.89 Å) (Table 2.4). The average distances of C(cage)-C(cage) in a range of 1.625 to 1.696 Å and Zr-C(cage) in a range of 2.258 to 2.299 Å in complexes **II-6a**, **II-6g**, **II-6h** and **II-6j** are close to those of 2.264(4)/1.662(6) Å found in complex **II-1** and 2.275(6)/1.686(11) Å in complex

II-3,[91] slightly less than those of 1.708(7) and 2.305(6)Å found in **II-4**,[101] respectively, but markedly less than those of 1.763(11)/2.377(7) Å found in $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) viewed as the precursor of $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$.[91] The average distances of Zr-C(cage) are also very close to that of 2.248(5) Å observed in $Cp_2Zr(PMe_3)(1,2\text{-}C_6H_4)$.[90] The average Zr-N distances in a range of 2.187 to 2.208 Å in **II-6a**, **II-6g**, **II-6h** and **II-6j** are very close to those of 2.210(7) and 2.216(3) Å found in complexes **II-5a**,[102b] and **II-4**,[101] respectively. The angles of C(cage)-Zr-C(cage) in a range of 42.1 to 44.7° obviously become smaller than that of Cl-Zr-Cl in a range of 93.1 to 96.5° found in **II-5a**, **II-5b**, **II-5d** – **II-5f**, **II-5h** and **II-5i**, but much lager than that of 35.3° observed in $Cp_2Zr(PMe_3)(1,2\text{-}C_6H_4)$.[90] However, the average N-Zr-N angles in a range of 60.3 to 60.7° in **II-6a**, **II-6g**, **II-6h** and **II-6j** are very close to that of 59.8(3)° found in **II-5a**,[102] but slightly less than that of 62.0(1)° in **II-4**.[101] Furthermore, complex **II-6i** has a dramatically short distance of C(cage)-C(cage) (1.625(9) Å), *av.* Ti-C(cage) (2.137(4) Å), and *av.* Ti-N (2.067(2) Å) compared to other Zr/Hf-carboryne complexes **II-6a**, **II-6g**, **II-6h** and **II-6j**, which results in the larger angle of C(cage)-Ti-C(cage) (44.7(2)°) and *av.* N-Ti-N (63.3(1)°) than those of **II-6a**, **II-6g**, **II-6h** and **II-6j** due to the size effect of the metal center. However, the average Ti-N bond length of 2.067(2) Å and N-Ti-N angle of 63.8(1)° have no significant change compared to those observed in **II-5d** and **II-5i**.

Figure 2.6. Molecular Structure of $[\eta^2$-CyNC(Me)NCy$]_2$Zr(η^2-$C_2B_{10}H_{10}$) (**II-6a**).

Table 2.4. Selected Bond Lengths (Å) and Angles (deg.) for M-Carboryne Complexes.

compd	*av.* M-C_{cage}	C_{cage}-C_{cage}	*av.* M-N/Cl/O	M···B	C_{cage}-M-C_{cage}	*av.* N-M-N
II-6a	2.279(2)	1.672(3)	2.203(2)	2.918(3)	43.0(1)	60.4(1)
II-6b	2.321(4)	1.678(5)	2.251(3)	2.926(5)	42.4(1)	59.1(1)
II-6e	2.324(3)	1.668(6)	2.233(2)	2.896(4)	42.1 (1)	59.8(1)
II-6g	2.271(2)	1.685(4)	2.201(1)	2.900(2)	43.6(1)	60.3(1)
II-6h	2.299(5)	1.682(7)	2.208(5)	2.927(6)	42.9(2)	60.4(2)
II-6i	2.137(4)	1.625(9)	2.067(2)	2.805(5)	44.7(2)	63.3(1)
II-6j	2.258(2)	1.696(6)	2.187(2)	2.895(4)	44.1(2)	60.7(1)
II-1[101]	2.264(4)	1.662(6)	2.488(2)	2.693(5)	43.0(2)	--
II-3[101]	2.275(6)	1.686(11)	2.503(2)	2.618(10)	43.5(3)	--
II-4[101]	2.305(6)	1.708(7)	2.216(3)	2.792(7)	43.5(2)	62.0(1)
II-6k	2.267(4)	1.641(4)	2.464(1)	2.917(4)	42.4(1)	157.7(1)[b]
II-6l	2.345(8)	1.613(11)[a]	1.884(4)	2.625(10)	40.1(3)[a]	--
II-6m	2.391(3)	1.690(3)	2.084(2)	3.427(3)	--	--

[a] average value of two cages. [b] the angle of Cl-Zr-Cl.

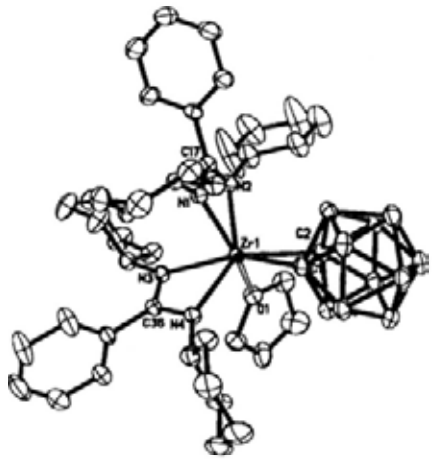


Figure 2.7. Molecular Structure of $[\eta^2$-CyNC(Ph)NCy$]_2$Zr(η^2-$C_2B_{10}H_{10}$)(THF) **(II-6b)**.

In the molecular structures of complexes **II-6a**, **II-6g – 6j**, the Ti/Zr/Hf atom is η^2-bound to two amidinato (or guanidinato) ligands and one carboryne moiety (Zr···B distances > 2.89 Å), resulting in a geometry with approximately C_2 symmetry (Figures 2.6, 2.9 – 2.12).

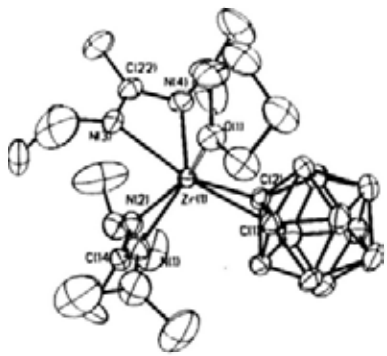


Figure 2.8. Molecular Structure of $[\eta^2$-^{i}PrNC(Me)NPr$^i]_2$Zr(η^2-$C_2B_{10}H_{10}$)(THF) **(II-6e)**.

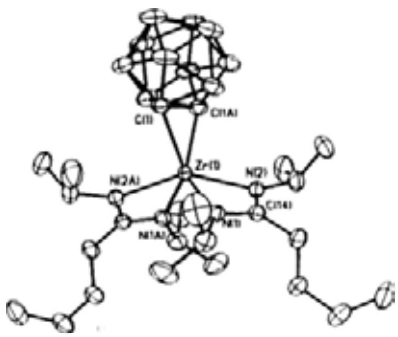


Figure 2.9. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr$^i]_2$Zr(η^2-$C_2B_{10}H_{10}$) (**II-6g**).

On the other hand, an extra THF coordination to the Zr atom is observed in the molecular structures of **II-6b** and **II-6e** (Figures 2.7 and 2.8). As the crystallization conditions for all of **II-6a** – **II-6k** are identical, this difference may be ascribed to electronic effects of electron-withdrawing phenyl group,[108] which makes the Zr atom more acidic in **II-6b**, and the less steric hindrance of methyl and *iso*-propyl in **II-6e**, which allows the coordination of THF to the metal center. The higher coordination number also leads to the longer Zr-C_{cage} and Zr-N distances of 2.321(4)/2.251(3) Å in **II-6b** and 2.324(3)/2.233(2) Å in **II-6e** than those in a range of 2.167 to 2.299 Å/2.067 to 2.208 Å found in **II-6a**, **II-6g** – **II-6j** (Table 2.4).

The molecular structure of **II-6k** (Figure 2.13) is very different from those of **II-6a**, **II-6g** – **II-6j**. The Zr atom adopts a distorted-octahedral geometry with one THF and η^2-carboryne unit at the axial positions. The Zr-C_{cage}/C_{cage}-C_{cage} distances of 2.267(4)/1.641(4) Å are close to those observed in **II-1**, **II-3**, **II-6a**, **II-6g**, **II-6h** and **II-6j**. The Cl(1)-Zr-Cl(2) angle is 157.7(1)°.

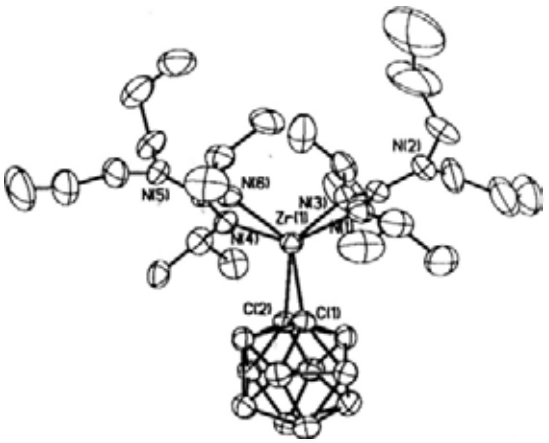


Figure 2.10. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Pr$_2$N)NPr^i$]_2$Zr(η^2-$C_2B_{10}H_{10}$) (**II-6h**).

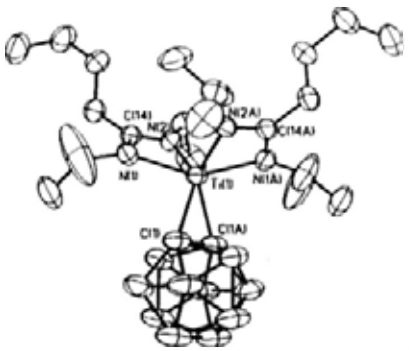


Figure 2.11. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr^i$]_2$Ti(η^2-$C_2B_{10}H_{10}$) (**II-6i**).

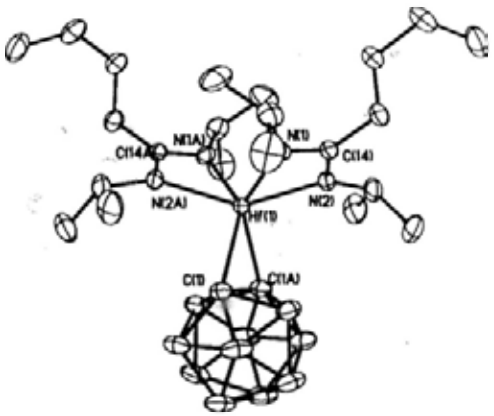


Figure 2.12. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr^i$]_2$Hf(η^2-$C_2B_{10}H_{10}$) (**II-6j**).

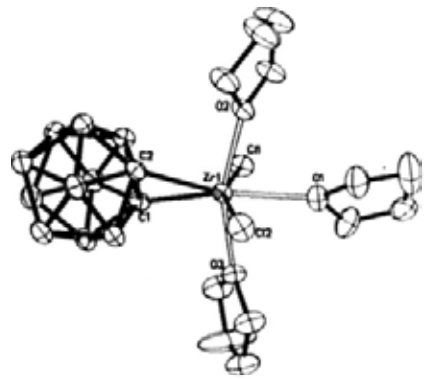


Figure 2.13. Molecular Structure of $(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$ (**II-6k**).

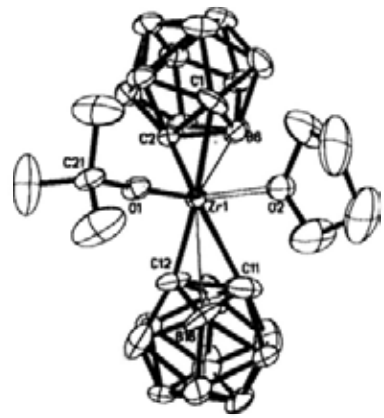


Figure 2.14. Molecular Structure of the Anion $[(\eta^2\text{-}C_2B_{10}H_{10})_2Zr(O^tBu)(THF)]^-$ in **II-6l**.

The solid-state structure of **II-6l** consists of distorted-tetrahedral anions $[(\eta^2\text{-}C_2B_{10}H_{10})_2Zr(OBu^t)(THF)]^-$ and octahedral cations $[Zr(OBu^t)_3(THF)_3]^+$. In the anion, the Zr atom is η^2-bound to two carboryne units and σ-bound to one ^{t}BuO group and coordinated to one THF molecule (Figure 2.14). The very crowded coordination environments result in the longer Zr-C_{cage} distances, shorter C_{cage}-C_{cage} distances and smaller C_{cage}-Zr-C_{cage} angles in comparison with the corresponding

values observed in **II-1**, **II-3**, **II-4**, **II-6a**, **II-6g**, **II-6h** and **II-6j**. The shorest Zr···B distance of 2.625(12) Å in **II-6l** is comparable to those of 2.692(5) Å in **II-1** and 2.618(10) Å in **II-3**, but slightly longer than that of 2.552(10) observed in $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$.[89]

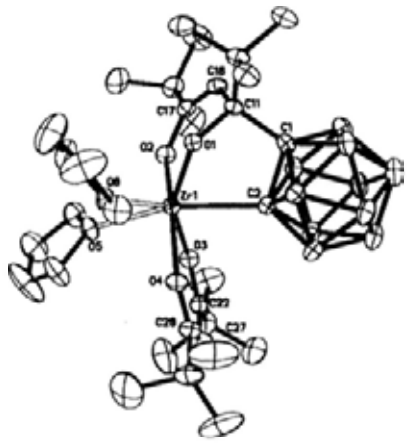


Figure 2.15. Molecular Structure of $[\sigma{:}\sigma{:}\sigma\text{-}\{^tBuC(O)=CHC(^tBu)(O)C_2B_{10}H_{10}\}]$ $Zr(\eta^2\text{-}^tBuCOCHCOBu^t)(THF)_2$ (**II-6m**).

In the molecular structure of **II-6m**, the Zr atom is η^2-bound to one O=C=C=C=O unit, σ-bound to one cage carbon atom and two oxygen atoms and coordinated to two THF molecules in a capped octahedral geometry (Figure 2.15), which is not common in group 4 metal complexes.[109] As expected, the Zr-C_{cage} distance of 2.391(3) Å is significantly larger than the average values observed in **II-1**, **II-3**, **II-4**, **II-6a**, **II-6g**, **II-6h** and **II-6j**. This measured value is close to the 2.377(7) Å in $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**),[91] 2.389(7) Å in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Cp^*ZrCl$[110] and those found in Zr-carboranyl complexes.[51a] It is noted that the C_{cage}-C_{cage} distances observed in Zr-carboryne

complexes **II-6a, II-6g – II-6l and II-6m** (Table 2.4) fall in the range 1.61 – 1.71 Å normally found in Zr-carboranyl complexes.[51a]

The B-H···M interactions in d^0 metal complexes are usually much weaker than those observed in d^n metal complexes because of lacking backbonding.[111] Therefore, it is not too surprised that the B-H···Zr interactions observed in the solid-state structures of **II-1**, **II-3**, **II-4** and **II-6l** are not found in the ^1H and ^{11}B NMR spectra. The short Zr···B distances in the above structures might also partially result from the crystal packing forces.

In view of the above structural data, one can describe the bonding interaction between the Zr atom and the two cage carbon atoms of the neutral *o*-$C_2B_{10}H_{10}$ ligand in terms of the Zr-carboryne form (π complex form) as shown in Chart 1.4. On the other hand, one can formally consider that there are two Zr-C_{cage} bonds (and one weak "agostic-like" B-H···Zr bond in complexes **II-1**, **II-3**, **II-4** and **II-6l**) between the Zr center and dianionic *o*-$C_2B_{10}H_{10}^{2-}$ ligands (σ complex form, Chart 1.4). Accordingly, the formal oxidation states of zirconium would be +2 in π complex form and +4 in σ complex one. It is not surprised that the above two bonding descriptions are both responsible for the Zr and *o*-$C_2B_{10}H_{10}$ interactions. The DFT calculations based on [{η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$}$ZrCl(\eta^3$-$C_2B_{10}H_{10})$][$Li(THF)_4$] also suggest that the bonding interactions between Zr and *o*-$C_2B_{10}H_{10}$ are best described as a resonance hybrid of both the Zr-C σ and Zr-C π bonding forms shown in Chart 1.[89] In other words, the bonding interactions between Zr and *o*-$C_2B_{10}H_{10}$

closely resemble those between Zr and benzyne.[90,93]

2.4. Summary

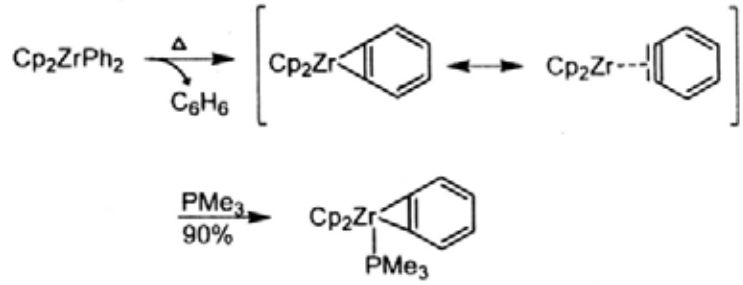
A series of group 4 metal-carboryne complexes have been prepared and fully characterized. Salt metathesis is generally a good method for the synthesis of this type of complexes by reaction of organo-group-4-metal dichloride with $Li_2C_2B_{10}H_{10}$ or treatment of $(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$ (**II-6k**) with anionic ligands (such as $[MeC(NCy)_2]Li$ or $[^nPr_2NC(NPr^i)_2]Li$). However, both steric and electronic factors of the ligands have significant effect on the types of resultant complexes (neutral versus ionic complexes). The bonding interactions between Zr and $o\text{-}C_2B_{10}H_{10}$ are best described as a resonance hybrid of both Zr-C σ and Zr-C π bonding forms. These complexes should have a rich reaction chemistry in view of the chemical properties of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**)[91,100] and $(Ph_3P)_2Ni(\eta^2\text{-}C_2B_{10}H_{10})$.[86b,92]

Chapter 3. Reaction of Group 4 Metal-Carboryne Complexes with Unsaturated Molecules

3.1. Background

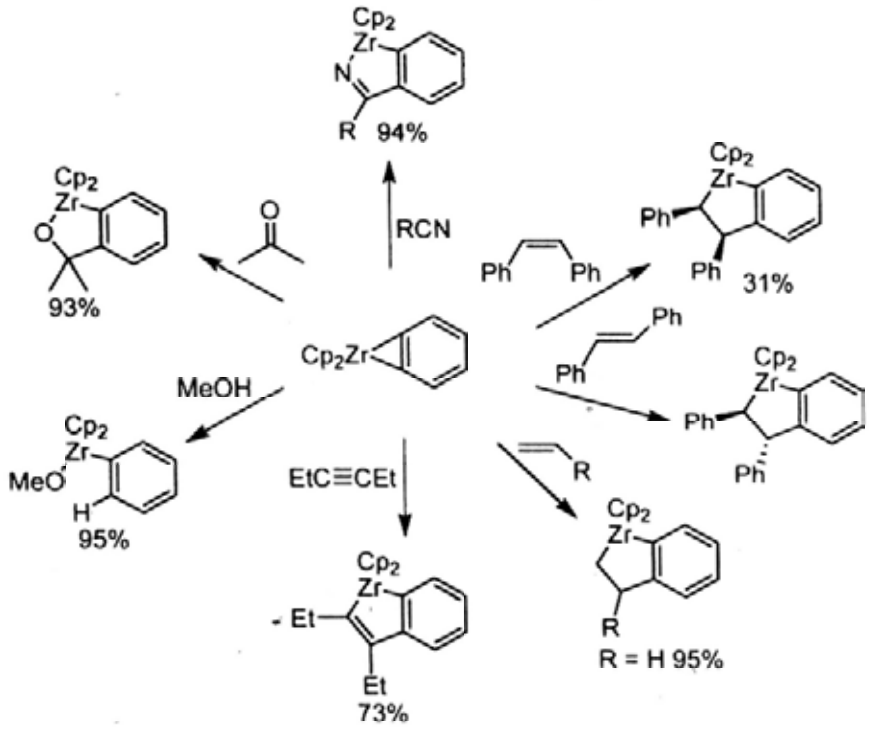
Benzyne and its transition metal complexes have found many applications in organic synthesis, mechanistic studies, and the synthesis of functional materials.[112] The first structurally characterized zirconocene-benzyne complex stabilized by PMe_3, was reported in 1986 by the Buchwald group (Scheme 3.1).[90]

Scheme 3.1. Preparation of Zirconocene-Benzyne Complex



Zirconocene-benzyne complex has very rich reaction chemistry as shown in Scheme 3.2. It reacts with many unsaturated molecules to form the useful organometallic intermediates. For example, reaction of the zirconocene-benzyne with acetone or RCN yields the mono-insertion product $Cp_2Zr[\sigma:\sigma\text{-}(CH_3)_2C(O)C_6H_4]$ or $Cp_2Zr[\sigma:\sigma\text{-}RC(=N)C_6H_4]$ in high yield. Protonation by MeOH forms $Cp_2Zr(C_6H_5)(OCH_3)$ in high yield. Interaction of zirconocene-benzyne with alkyne or alkene affords the mono-insertion product in a general formula of $Cp_2ZrC(R^1)=C(R^2)\text{-}1,2\text{-}C_6H_4$ or $Cp_2ZrCH(R^1)CH(R^2)\text{-}1,2\text{-}C_6H_4$ (Scheme 3.2).[93]

Scheme 3.2. Reactivity of Zirconocene-Benzyne Complex

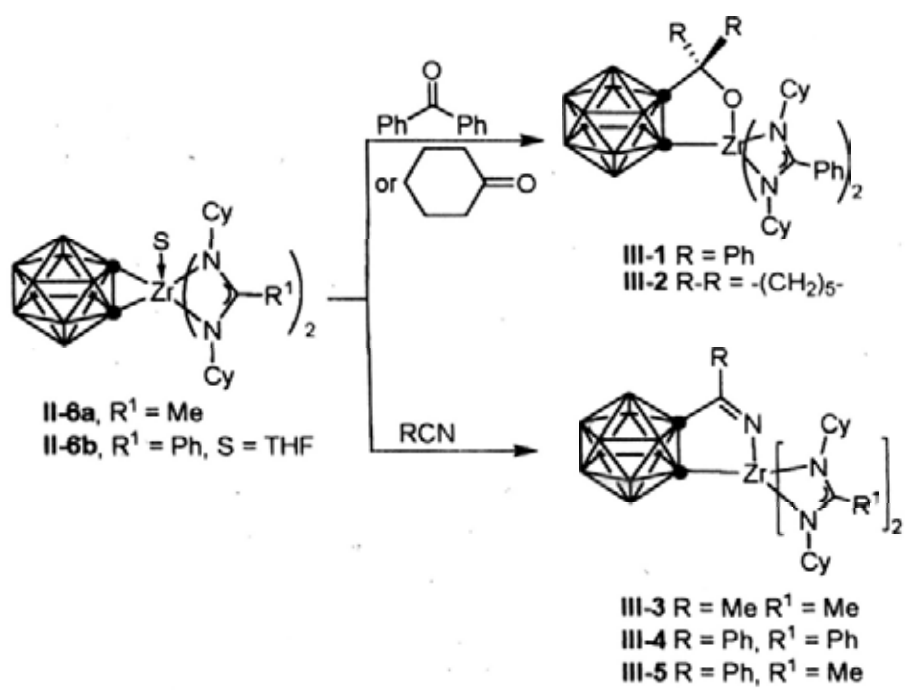


Like benzyne, carboryne can be trapped and stabilized by transition metals. However, the reaction chemistry of group 4 metal-carboryne complexes is largely unknown though some preliminary results were obtained from the reaction of the neutral Zr-carboryne complex Cp*[η^2-CyNC(Me)NCy]Zr(η^3-$C_2B_{10}H_{10}$) (**II-4**)[113] or $Cp_2Zr(\mu\text{-Cl})(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) with polar unsaturated molecules.[91,113] In view of the very rich and exciting chemistry of zirconocene-benzyne complexes,[93] we are interested in exploring the largely undeveloped reaction chemistry of group 4 transition metal-carboryne complexes.

3.2. Mono-Insertion Reaction

Treatment of **II-6b** with 1 equiv of diphenylketone or cyclohexanone in toluene at room temperature yielded the mono-insertion product $[\eta^2$-CyNC(Ph)NCy$]_2$Zr[σ:σ-{$(Ph)_2C(O)C_2B_{10}H_{10}$}] (**III-1**) in 95% or $[\eta^2$-CyNC(Ph)NCy$]_2$Zr[σ:σ-{[-$(CH_2)_5$-]$C(O)C_2B_{10}H_{10}$}] (**III-2**) in 87% isolated yield, respectively (Scheme 3.3).

Scheme 3.3. Reactivities of Group 4 Metal-Carboryne Complexes toward Ketone and Nitrile



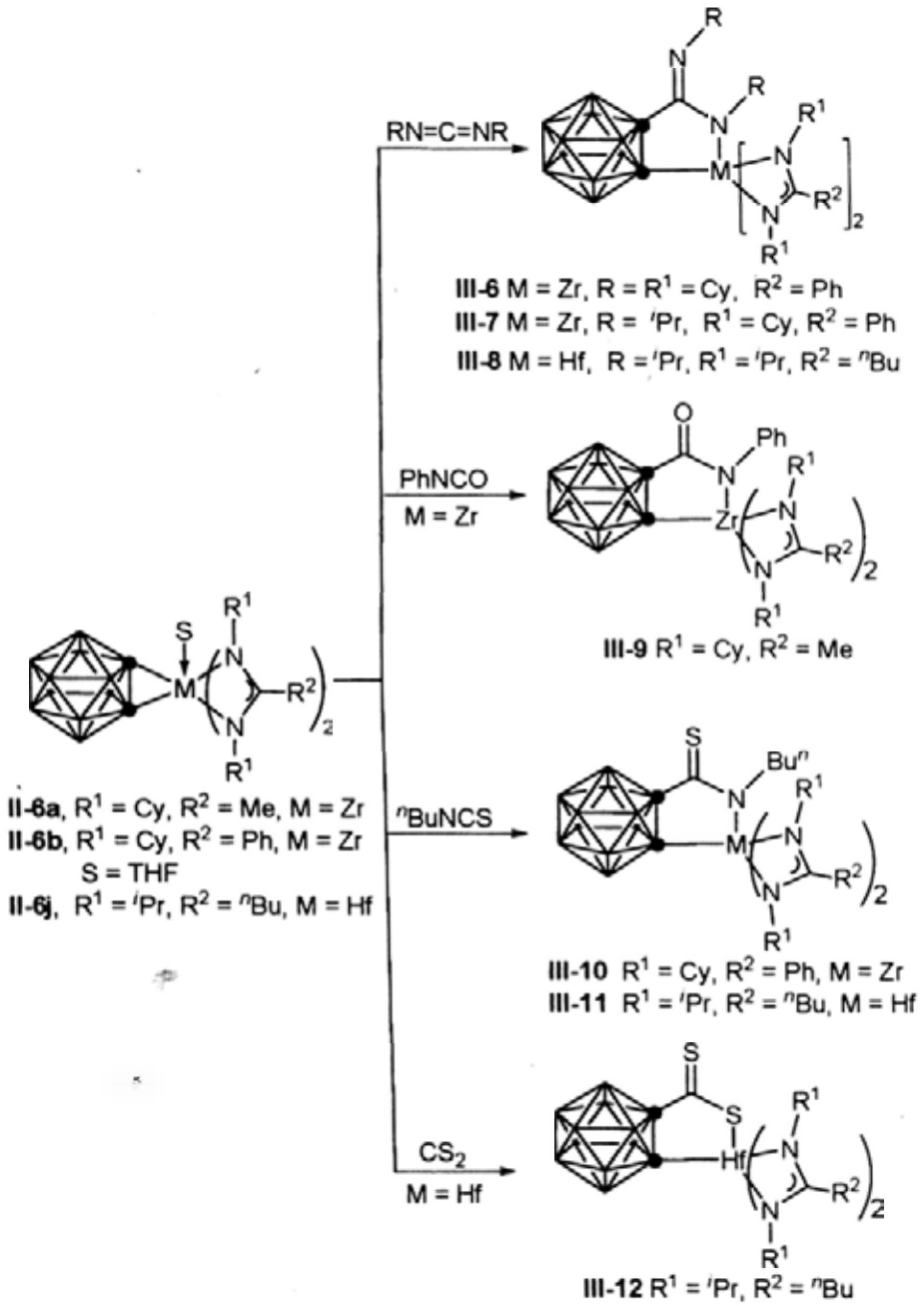
Reaction of **II-6a** with an excess amount of CH_3CN in toluene at room temperature, led to the formation of *o*-carborane and other unidentified species on the basis of ^{11}B NMR spectra analysis. On the other hand, reaction of **II-6a** with equimolar CH_3CN in toluene at 0 °C yielded the mono-insertion product $[\eta^2$-CyNC(Me)NCy$]_2$Zr[σ:σ-

{[N=C(Me)$C_2B_{10}H_{10}$}] (**III-3**) in 37% yield along with the protonated *o*-carborane. This can be ascribed to the acidity of α–proton of CH_3CN. However, reaction of **II-6a** or **II-6b** with 2 equiv of PhCN in toluene at room temperature afforded the mono-insertion product [η^2-CyNC(R)NCy]$_2$Zr[σ:σ-{[N=C(Ph)$C_2B_{10}H_{10}$}] (**III-4**, R = Ph; **III-5**, R = Me) in the yield of 85% for **III-4** and 76% for **III-5** (Scheme 3.3).

Reaction of **II-6b** with 1 equiv of carbodiimide RN=C=NR (R = ^{i}Pr or Cy) in toluene at room temperature afforded the mono-insertion products [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ- {[RNC(=NR)$C_2B_{10}H_{10}$}] (**III-6**, R = ^{i}Pr; **III-7**, R = Cy) in high yields (≥95%). Reaction of **II-6j** with 1 equiv of carbodiimide ^{i}PrNCN^{i}Pr also yielded the mono-insertion product [η^2-^{i}PrNC(^{n}Bu)N^{i}Pr]$_2$Hf[σ:σ-{[^{i}PrNC(=N^{i}Pr)$C_2B_{10}H_{10}$}] (**III-8**) in 91% yield (Scheme 3.4).

Similarly, PhNCO can also insert into one of the metal-carbon(cage) bonds of the metal-carboryne complex. Reaction of **II-6a** with 1 equiv of PhNCO in toluene at room temperature gave the mono-insertion product [η^2-CyNC(Me)NCy]$_2$Zr[σ:σ-{[PhNC(=O)$C_2B_{10}H_{10}$}] (**III-9**) in 93% yield, in which C=N was inserted into the Zr-C(cage) bond (Scheme 3.4). This product is different from that of reaction of $Cp_2Zr(\mu\text{-Cl})(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) with PhNCO, in which a C=O insertion product is formed. Reaction of **II-6b** or **II-6j** with 1 equiv of ^{n}BuNCS in toluene at room temperature yielded the C=N mono-insertion product [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-{[^{n}BuNC(=S)$C_2B_{10}H_{10}$}] (**III-10**) in 76% yield or

Scheme 3.4. Reactivities of Group 4 Metal-Carboryne Complexes toward Carbodiimide, Isocyanate, Thioisoçyanate and Carbon Disulfide



$[\eta^2$-^{i}PrNC(Bu^n)NPr^i]$_2$Hf[σ:σ-{[^{n}BuNC(=S)$C_2B_{10}H_{10}$}] (**III-11**) in 87% yield, respectively (Scheme 3.4). Reaction of **II-6j** with an excessive amount of CS_2 in

refluxing toluene gave the insertion product $[\eta^2$-^{i}PrNC(Bu^n)NPr^i]$_2$Hf[σ:σ-{[SC(=S)$C_2B_{10}H_{10}$}] (**III-12**) in 60% yield whereas no reaction was observed at room temperature based on ^{11}B NMR spectrum (Scheme 3.4). No double-insertion products were observed even under forced reaction conditions.

All products were fully characterized by ^{1}H, ^{13}C and ^{11}B NMR spectra, IR spectroscopy as well as elemental analyses. The ^{11}B NMR spectra showed different patterns from their parent metal-carboryne complexes due to the changes of the molecular symmetry of the insertion products. The characteristic quaternary carbons of the amidinato or guanidinato ligands were shifted to the low-field in a range of 171.8 to 185.2 ppm.

Most of aforementioned complexes (**III-1** – **III-3**, **III-5**, **III-7** – **III-10** and **III-12**) were further confirmed by single crystal X-ray analyses. Their molecular structures were shown in Figures 3.1 – 3.9. The key structural data are summarized in Table 3.1. The metal-C(cage) bond distances (2.340 to 2.413 Å) are elongated compared to those observed in the parent metal-carboryne complexes **II-6a**,**b**,**j**. The C(cage)-C(cage) bond distances in complexes **III-1** – **III-3** and **III-7** are much longer than those observed in the corresponding metal-carboryne complexes (**II-6a** and **II-6b**). However the C(cage)-C(cage) bond distances in complexes **III-9** and **III-12** are smaller than those found in their parent metal-carboryne complexes **II-6a** and **II-6j**, respectively.

Table 3.1. Selected Bond Lengths (Å) and Angles (deg.)

compd	M-C_{cage}	C(1)-C(2)	C(1)-C(5)	X(4)-C(5)	M(3)-X(4)	C(2)-M-X(4)
III-1	2.371(6)	1.710(7)	1.595(7)	1.413(6)	1.954(3)	73.7(2)
III-2	2.402(3)	1.711(5)	1.556(5)	1.421(4)	1.931(2)	74.1(1)
III-3	2.400(3)	1.717(4)	1.549(4)	1.264(3)	2.065(2)	74.0(1)
III-5	2.413(4)	1.679(5)	1.508(6)	1.383(5)	2.089(3)	74.3(1)
III-7	2.396(4)	1.695(6)	1.519(7)	1.389(6)	2.077(4)	72.7(2)
III-8[a]	2.349(4)	1.703(6)	1.534(6)	1.387(6)	2.099(4)	73.9(2)
III-9	2.389(9)	1.658(12)	1.509(11)	1.380(11)	2.208(7)	74.3(3)
III-10	2.383(7)	1.680(10)	1.522(10)	1.330(9)	2.383(7)	74.3(2)
III-12	2.340(5)	1.669(6)	1.514(7)	1.725(6)	2.572(1)	77.4(1)

[a] average value of two molecules in one unit cell.

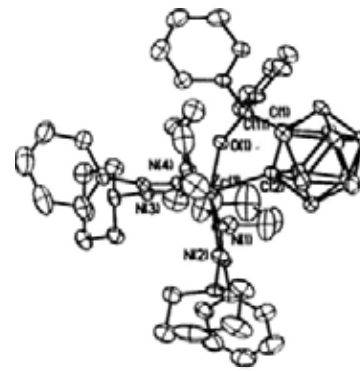


Figure 3.1. Molecular Structure of [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-{(Ph)$_2$C(O)$C_2B_{10}H_{10}$}] (**III-1**).

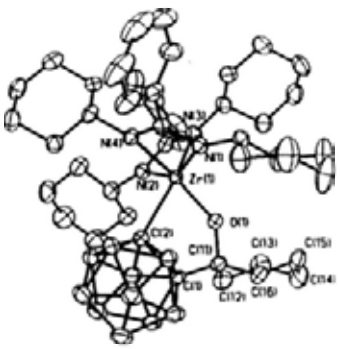


Figure 3.2. Molecular Structure of $[\eta^2$-CyNC(Ph)NCy$]_2$Zr[σ:σ-{[-$(CH_2)_5$-]C(O)$C_2B_{10}H_{10}$}] (**III-2**).

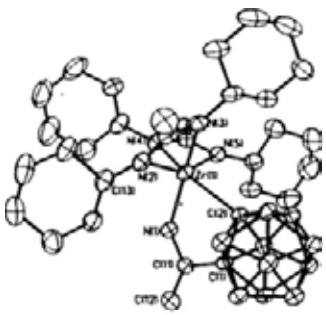


Figure 3.3. Molecular Structure of $[\eta^2$-CyNC(Me)NCy$]_2$Zr[σ:σ-{[N=C(Me)$C_2B_{10}H_{10}$}] (**III-3**).

Figure 3.4. Molecular Structure of $[\eta^2$-CyNC(Me)NCy$]_2$Zr[σ:σ-{[N=C(Ph)$C_2B_{10}H_{10}$}] (**III-5**).

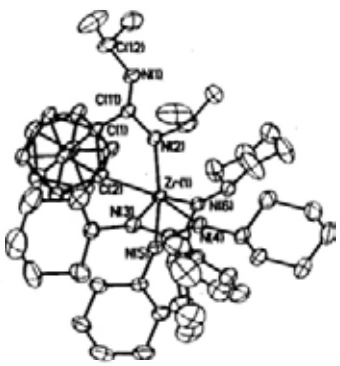


Figure 3.5. Molecular Structure of $[\eta^2$-CyNC(Ph)NCy$]_2$Zr[σ:σ-{[^{t}PrNC(=N^{t}Pr)$C_2B_{10}H_{10}$}] (**III-7**).

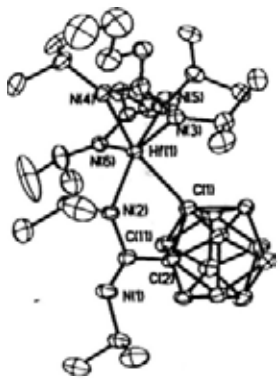


Figure 3.6. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr^i$]_2$Hf[σ:σ-{[^{t}PrNC(=NPr^i)$C_2B_{10}H_{10}$}] (**III-8**).

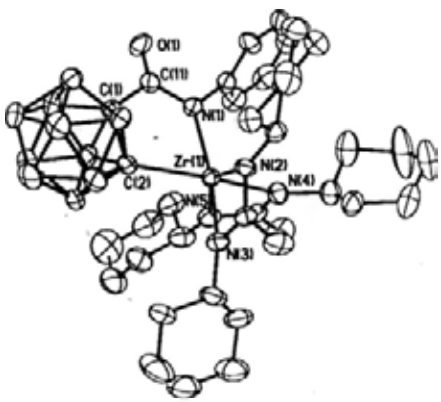


Figure 3.7. Molecular Structure of $[\eta^2$-CyNC(Me)NCy$]_2$Zr[σ:σ-{[PhNC(=O)$C_2B_{10}H_{10}$}] (**III-9**).

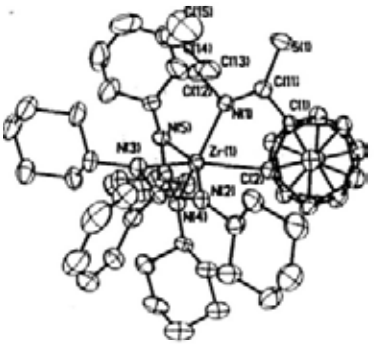


Figure 3.8. Molecular Structure of $[\eta^2$-CyNC(Ph)NCy$]_2$Zr[σ:σ-{[^{n}BuNC(=S)$C_2B_{10}H_{10}$}] **(III-10)**.

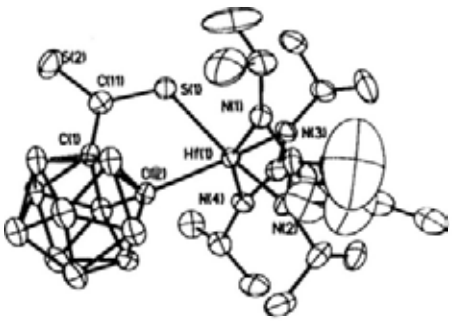


Figure 3.9. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr^i$]_2$Hf[σ:σ-{[SC(=S)$C_2B_{10}H_{10}$}] **(III-12)**.

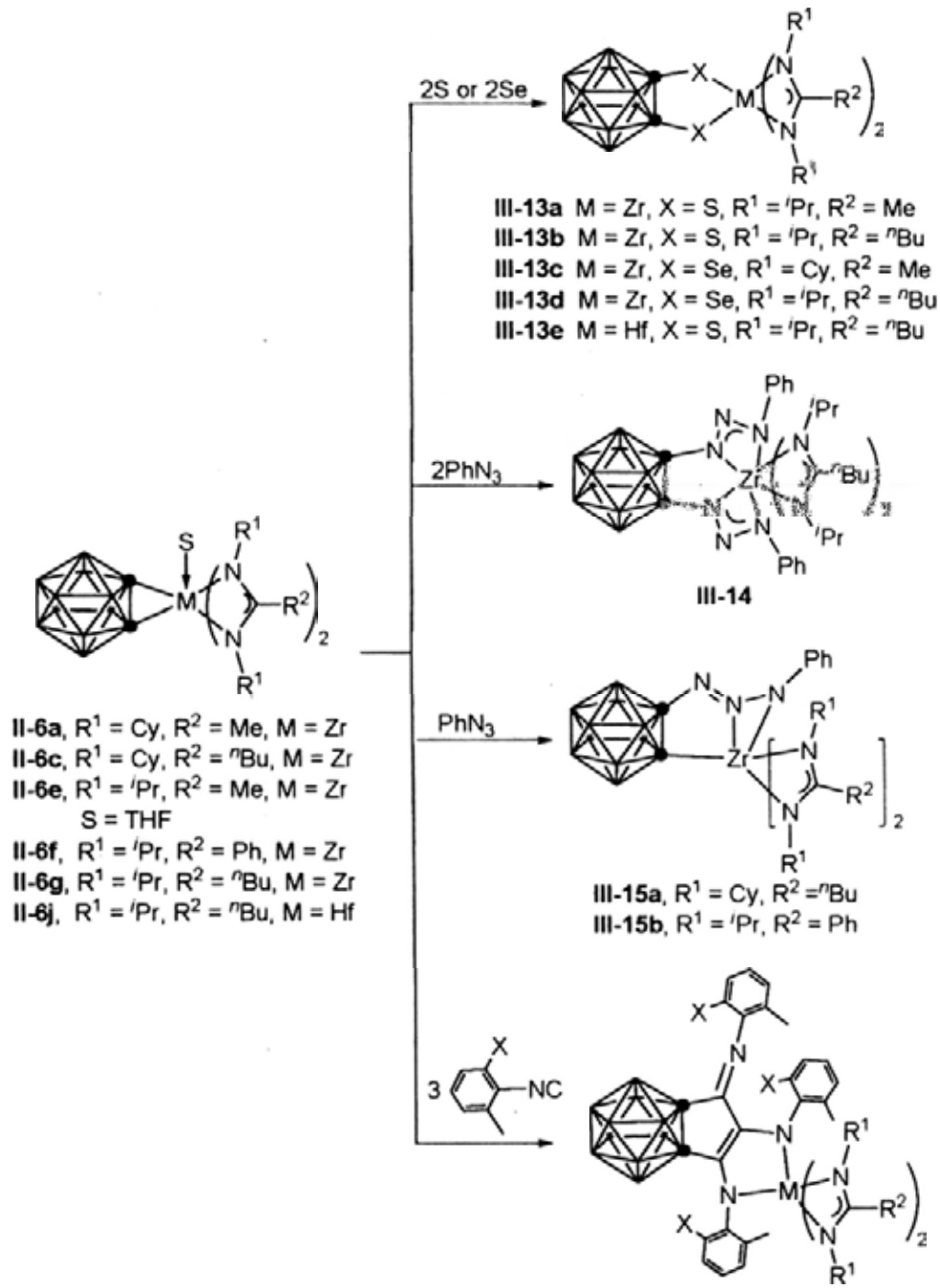
The above results show that the polar unsaturated molecules of ketone, nitrile, carbodiimide, isocyanate, thioisocyanate and carbon disulfide can insert into the group 4 metal-C(cage) bond to form the mono insertion products. No double insertion products are observed probably due to the steric effects.[91]

3.3. Di and Tri-Insertion Reaction

Further study of the reactions of neutral group 4 metal-carboryne complexes revealed that some substrates such as element S, Se, azide and isocyanide can insert

into the metal-C(cage) bond to form di- or tri-insertion products with a general formula of $[\eta^2\text{-}R^1NC(R^2)NR^1]_2M[1,2\text{-}X_2C_2B_{10}H_{10}]$ (**III-13a**, M = Zr, X = S, R^1 = ^{i}Pr, R^2 = Me; **III-13b**, M = Zr, X = S, R^1 = ^{i}Pr, R^2 = ^{n}Bu; **III-13c**, M = Zr, X = Se, R^1 = Cy, R^2 = Me; **III-13d**, M = Zr, X = Se, R^1 = ^{i}Pr, R^2 = ^{n}Bu; **III-13e**, M = Hf, X = S, R^1 = ^{i}Pr, R^2 = ^{n}Bu), $[\eta^2\text{-}^i PrNC(^n Bu)NPr^i]_2Zr[\eta^2\text{:}\eta^2\text{-}$ 1,2-(PhN=N-N)$_2$-1,2-$C_2B_{10}H_{10}$} (**III-14**) and $[\eta^2\text{-}R^1NC(R^2)NR^1]_2M\{[(R^3)NC]_2C(=NR^3)\text{-}1,2\text{-}C_2B_{10}H_{10}\}$ (**III-16a**, M = Zr, R^1 = ^{i}Pr, R^2 = ^{n}Bu, R^3 = 2,6-$Me_2C_6H_3$; **III-16b**, M = Zr, R^1 = ^{i}Pr, R^2 = ^{n}Bu, R^3 = 2-Cl-6-MeC_6H_3; **III-16c**, M = Zr, R^1 = Cy, R^2 = Me, R^3 = 2,6-$Me_2C_6H_3$; **III-16d**, M = Hf, R^1 = ^{i}Pr, R^2 = ^{n}Bu, R^3 = 2,6-$Me_2C_6H_3$; **III-16e**, M = Hf, R^1 = ^{i}Pr, R^2 = ^{n}Bu, R^3 = 2-Cl-6-MeC_6H_3). Reactions of **II-6c** and **II-6f** with excessive PhN_3, gave only mono-insertion products $[\eta^2\text{-}CyNC(^n Bu)NCy]_2Zr[\eta^2\text{:}\sigma\text{-}1\text{-}PhN{=}N\text{-}N\text{-}1,2\text{-}C_2B_{10}H_{10}]$ (**III-15a**) and $[\eta^2\text{-}^i PrNC(Ph)NPr^i]_2Zr[\eta^2\text{:}\sigma\text{-}1\text{-}PhN{=}N\text{-}N\text{-}1,2\text{-}C_2B_{10}H_{10}]$ (**III-15b**) in the yield of 89% and 76%, respectively, which is very similar to that of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**). Surprisingly, a double insertion product **III-14** was isolated in 95% yield from the reaction of **II-6g** with excess PhN_3 under the same reaction conditions. The reasons are not clear, but may be related to the electronic/steric properties of the ligands. These group 4 metal-carboryne complexes do not react with ^{t}BuNC even at refluxing condition.

Scheme 3.5. Di- and Tri-Insertion Reaction of Group 4 Metal-Carboryne Complexes



II-6a, R^1 = Cy, R^2 = Me, M = Zr
II-6c, R^1 = Cy, R^2 = ^{n}Bu, M = Zr
II-6e, R^1 = ^{i}Pr, R^2 = Me, M = Zr
S = THF
II-6f, R^1 = ^{i}Pr, R^2 = Ph, M = Zr
II-6g, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Zr
II-6j, R^1 = ^{i}Pr, R^2 = ^{n}Bu, M = Hf

III-13a M = Zr, X = S, R^1 = ^{i}Pr, R^2 = Me
III-13b M = Zr, X = S, R^1 = ^{i}Pr, R^2 = ^{n}Bu
III-13c M = Zr, X = Se, R^1 = Cy, R^2 = Me
III-13d M = Zr, X = Se, R^1 = ^{i}Pr, R^2 = ^{n}Bu
III-13e M = Hf, X = S, R^1 = ^{i}Pr, R^2 = ^{n}Bu

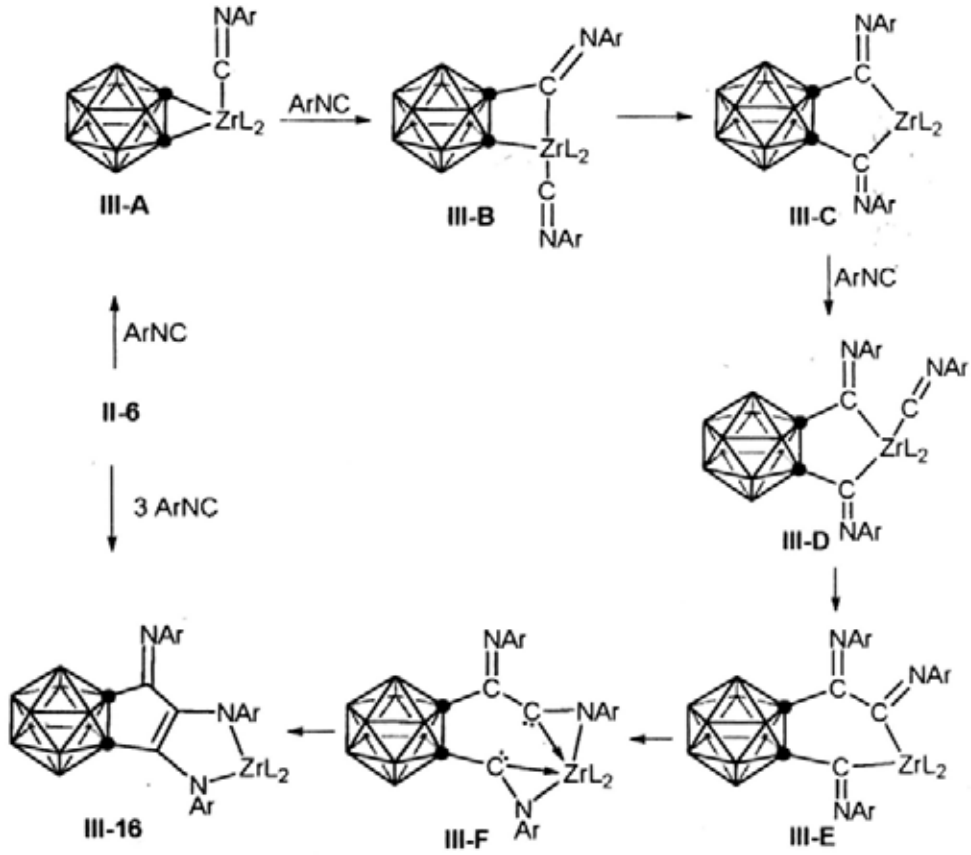
III-14

III-15a, R^1 = Cy, R^2 = ^{n}Bu
III-15b, R^1 = ^{i}Pr, R^2 = Ph

III-16a M = Zr, R^1 = ^{i}Pr, R^2 = ^{n}Bu X= Me
III-16b M = Zr, R^1 = ^{i}Pr, R^2 = ^{n}Bu, X = Cl
III-16c M = Zr, R^1 = Cy, R^2 = Me, X = Me
III-16d M = Hf, R^1 = ^{i}Pr, R^2 = ^{n}Bu, X = Me
III-16e M = Hf, R^1 = ^{i}Pr, R^2 = ^{n}Bu, X = Cl

These complexes do react with ArNC to afford tri-insertion products (**III-16**) (Scheme 3.5). In comparison, treatment of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) with ^{t}BuNC generated $Cp_2Zr[\eta^2\text{-}^t BuNC(C_2B_{10}H_{10})=CN^tBu](CN^tBu)$.[91] These results suggested that steric factors play a crucial role in the reactions.

Scheme 3.6. A Possible Pathway for the Formation of **III-16**



The formation of triple insertion products **III-16a** – **III-16e** may be related to the carbene property of isocyanides. A possible pathway was outlined in Scheme 3.6. The coordination of isocyanide to the metal center forms the intermediate **III-A**,

Insertion of the coordinated isocyanide gives the intermediate **III-B**. Coordination and insertion of the second equivalent of ArNC generate **III-C**, followed by the coordination and insertion of the third equivalent of ArNC to form the intermediate **III-D** and **III-E**. Isomerization of the $Zr(-C=NAr)_2$ unit affords the final product **III-16**. The stronger Zr-N interactions over the Zr-C bonds provide the driving force for the rearrangements (Scheme 3.6).

Complexes **III-13a** – **III-16e** were fully characterized by ^{1}H, ^{13}C and ^{11}B NMR spectra, IR spectroscopy as well as elemental analyses. The characteristic cage carbons were observed in a range of 91.6 to 92.8 ppm for **III-13a**, **III-13b** and **III-13e**, at about 75 ppm for **III-13c** and **III-13d**, in a range of 73.0 to 76.0 ppm for **III-16a** – **III-16e**, and at 95.2 ppm for **III-14** in their ^{13}C NMR spectra. Influenced by the metal center, the cage carbon signals were shifted to the lower field (108.2 to 111.4 ppm) in the mono-insertion products of **III-15a** and **III-15b**. Only one very broad peak at about -7.0 ppm was observed for complexes **III-13a** – **III-13d** in their ^{11}B NMR spectra whereas two peaks at -7.2 and -8.9 ppm with a ratio of 6:4 for the product **III-13e** were found in the ^{11}B NMR spectrum of **III-13e**. Two resonances at about -2.0 and -9.0 ppm with a ratio of 5:5 were observed in the ^{11}B NMR spectra of **III-16a**, **III-16c** and **III-16d** while three peaks at -3.0, -10.0 and -14.0 ppm with a 4:3:3 pattern were found in the ^{11}B NMR spectra of **III-16b** and **III-16e**. The ^{11}B NMR spectra of **III-15a** and **III-15b** exhibited two resonances at -1.0 and -6.0 ppm with a ratio of 2:8 whereas **III-14** showed two peaks at -8.9 and -11.7 ppm with a

ratio of 4:6.

Most of the insertion products (**III-13b**, **III-13d**, **III-13e**, **III-14**, **III-15a**, **III-16a**, **III-16b**, **III-16d** and **III-16e**) were further confirmed by single crystal X-ray analyses. Their molecular structures were shown in Figures 3.10 – 3.18, respectively. The key structural data were summarized in Table 3.2.

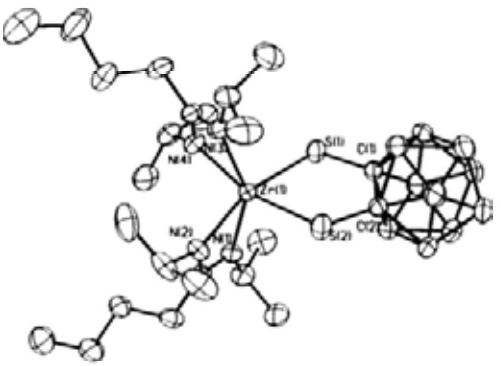


Figure 3.10. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)N^{i}Pr$]_2$Zr[1,2-$S_2C_2B_{10}H_{10}$] (**III-13b**).

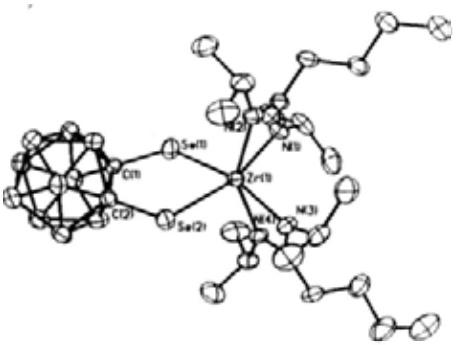
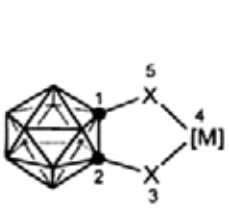


Figure 3.11. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)N^{i}Pr$]_2$Zr[1,2-$Se_2C_2B_{10}H_{10}$] (**III-13d**).

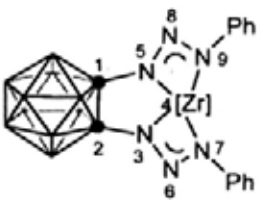
The C(cage)-C(cage) bond distances range from 1.629(7) to 1.728(5) Å. The

largest one (1.728(5)) is found in complex **III-15a** because of the presence of Zr-C(cage) bonding interactions. The distances of C(cage)-S/Se bonds in **III-13b** (1.776(3) Å), **III-13e** (1.774(4) Å) and **III-13d** (1.934(4) Å) are very close to those observed in $[(THF)_3LiS_2C_2B_{10}H_{10}Li(THF)]_2$ (1.772(6) Å),[114] $[Li(THF)_4][Cp''Zr(S_2C_2B_{10}H_{10})_2]$ (1.776(8) Å)[115] and $Cp^*Ir(Se_2C_2B_{10}H_{10})$ (1.941(7) Å).[116]

Table 3.2. Selected Bond Lengths (Å) and Angles (deg.).

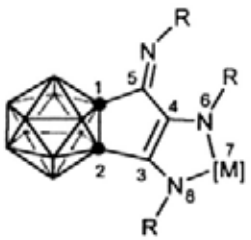


III-13b,d,e



III-14

III-15a



III-16a,b,d,e

compd	C(1)-C(2)	C(2)-X(3)	C(1)-X(5)	X(3)-M	X(5)-M	X(3)-M-X(5)
III-13b	1.692(4)	1.770(3)	1.776(3)	2.550(1)	2.561(1)	83.8(1)
III-13d	1.679(5)	1.934(4)	1.930(4)	2.676(1)	2.688(1)	85.2(1)
III-13e	1.698(5)	1.774(4)	1.773(4)	2.537(1)	2.545(1)	84.8(1)
	C(1)-C(2)	C(2)-N(3)	N(3)-N(6)	N(6)-N(7)	Zr-N[a]	N(3)-Zr-N(5)
III-14	1.657(5)	1.433(4)	1.318(4)	1.296(3)	2.391(3)	66.0(1)
	C(1)-C(2)	Zr-C(2)	C(1)-N(5)	N(4)-N(5)	N(5)-N(6)	Zr-N(4)/Zr-N(6)
III-15a	1.728(5)	2.506(3)	1.449(4)	1.285(4)	1.292(3)	2.137/2.330(3)
	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	C(3)-N(8)	N(8)-M	N(6)-M-N(8)
III-16a	1.642(4)	1.510(4)	1.365(4)	1.365(3)	2.208(2)	77.8(1)
III-16b	1.648(7)	1.513(7)	1.381(7)	1.357(6)	2.244(4)	76.5(2)
III-16d	1.652(8)	1.501(8)	1.370(7)	1.372(7)	2.194(4)	79.0(2)
III-16e	1.629(7)	1.510(7)	1.364(7)	1.378(7)	2.209(4)	78.6(2)

[a] average value of the four Zr-N(3,5,7,9) bonds.

Complexes **III-16a**, **III-16b**, **III-16d** and **III-16e** have a common five-membered ring constructed by two cage carbons and three incoming carbons from isocyanides. The sum of the five interior angles on the five-membered ring is very close to 540°, suggestive of a planar geometry.

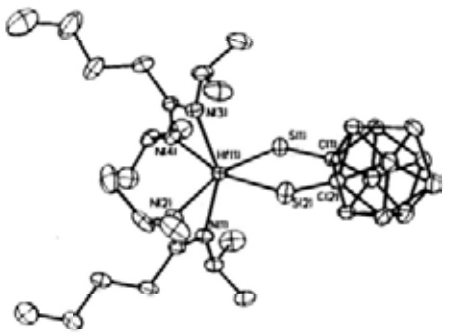


Figure 3.12. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)N^{i}Pr]$_2$Hf[1,2-$S_2C_2B_{10}H_{10}$] (**III-13e**).

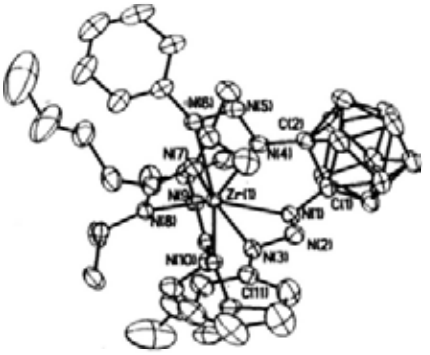


Figure 3.13. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr^i]$_2$Zr[η^2:η^2-1,2-(PhN=N-N)$_2$-1,2-$C_2B_{10}H_{10}$} (**III-14**).

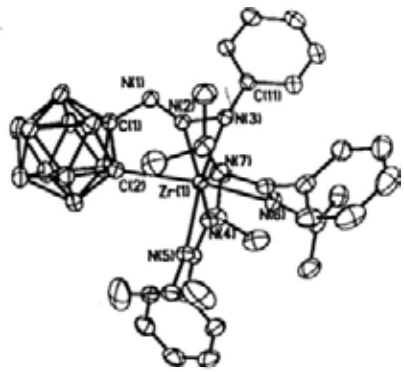


Figure 3.14. Molecular Structure of $[\eta^2$-^{i}PrNC(Ph)NPr$^i]_2$Zr $[\eta^2$:σ-1-PhN=N-N-1,2-$C_2B_{10}H_{10}\}$ **(III-15a)**.

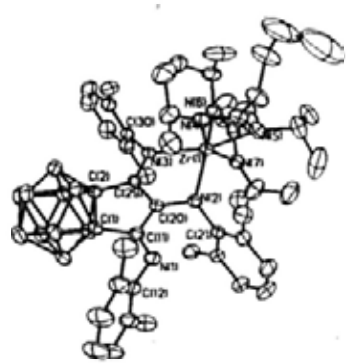


Figure 3.15. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}BuN^{i}Pr]$_2$Zr{[(2,6-$Me_2C_6H_3$)NC]$_2$C[=N-(2,6-$Me_2C_6H_3$)]-1,2-$C_2B_{10}H_{10}\}$ **(III-16a)**.

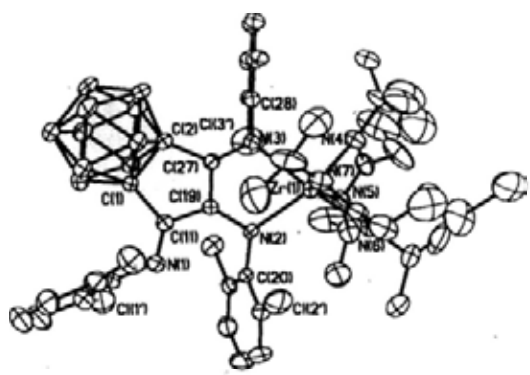


Figure 3.16. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)N^{i}Pr]$_2$Zr {[(2-Cl-6-MeC_6H_3)NC]$_2$C[=N-(2-Cl-6-MeC_6H_3)]-1,2-$C_2B_{10}H_{10}\}$ **(III-16b)**.

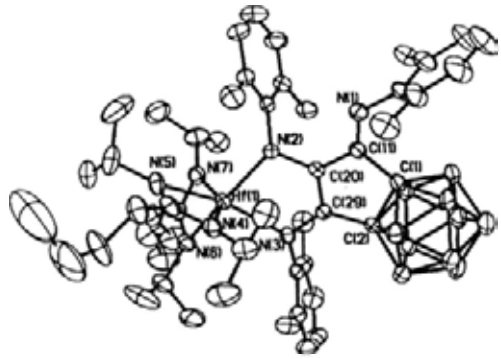


Figure 3.17. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)N^{i}Pr$]_2$Hf {[(2,6-$Me_2C_6H_3$)NC]$_2$C[=N-(2,6-$Me_2C_6H_3$)]-1,2-$C_2B_{10}H_{10}$} (**III-16d**).

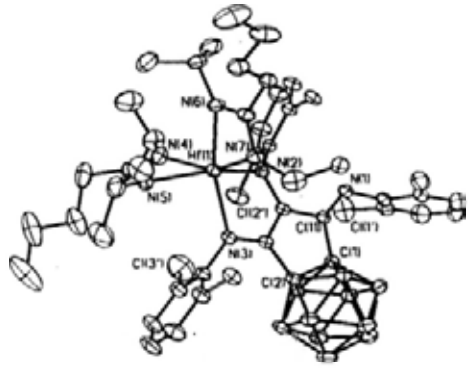
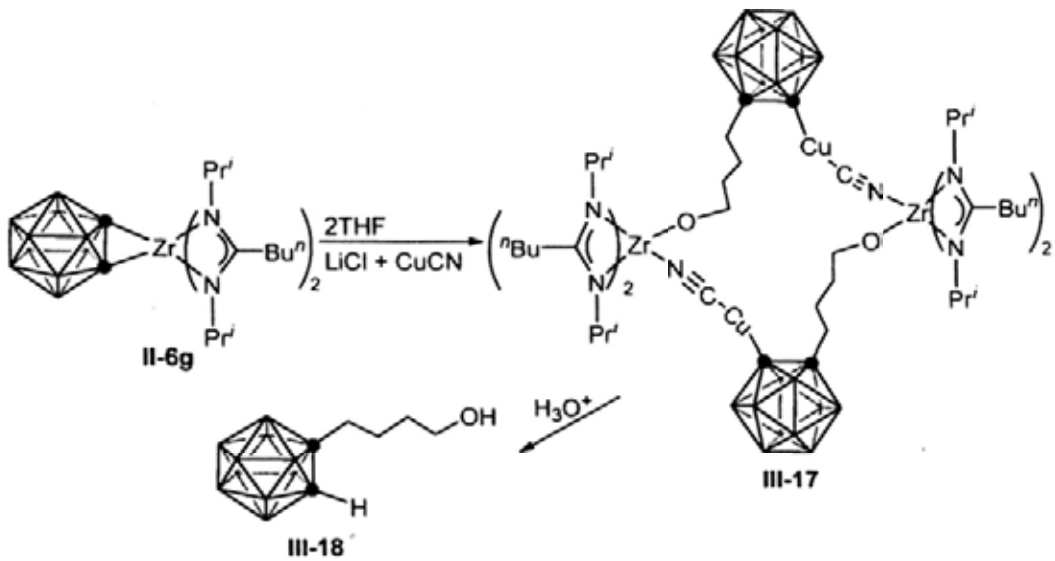


Figure 3.18. Molecular Structure of $[\eta^2$-^{i}PrNC(^{n}Bu)N^{i}Pr$]_2$Hf {[(2-Cl-6-MeC_6H_3)NC]$_2$C[=N-(2-Cl-6-MeC_6H_3)]-1,2-$C_2B_{10}H_{10}$} (**III-16e**).

It is noted that carboryne complexes **II-6a** – **II-6j** do not react with alkenes and internal alkynes even under forced conditions. An unexpected complex {[η^2-^{i}PrNC(^{n}Bu)NPr^i]$_2$Zr}$_2${[1-NCCu-2-O$(CH_2)_4$-1,2-$C_2B_{10}H_{10}$}$_2$ (**III-17**) was isolated in 91% yield when **II-6g** was heated with excess EtC≡CEt in the presence of LiCl/CuCN in THF/toluene at reflux for 3 days (Scheme 3.7).

Scheme 3.7. Formation of **III-17**



This reaction is reproducible without alkyne. It is believed that LiCl can form a complex with CuCN, presumably LiCu(CN)Cl, which has better solubility than LiCl or CuCN in THF/toluene mixture. In the absence of LiCl, no reaction was observed. CuCN is insoluble in THF/toluene. Although the reaction pathway is not clear at this stage, a cooperative effect between metal ions maybe involved. Hydrolysis of **III-17** with 1M HCl gave 1-HO$(CH_2)_4$-1,2-$C_2B_{10}H_{11}$ (**III-18**) in 92% yield (Scheme 3.7).

Complex **III-17** was characterized by various spectroscopic techniques and X-ray analyses. This complex is very sensitive to air and moisture. It has good solubilities in THF, DME and pyridine and but insolubility in toluene, diethyl ether and hexane.

The distinctive quaternary carbons of NCN, CuCN and carborane were observed at 179.4, 122.3, 96.1 and 81.3 ppm, respectively, in the ^{13}C NMR spectrum. Influenced by strong interactions of Zr-N≡C-Cu, the carbon signal of CN was shifted

to high-field compared to those observed in late transition metal complexes {[Ti](C≡CSiMe$_3$)$_2$}Cu[NCAu(PPh$_3$)][BF$_4$] (163.8 ppm),[117a] (CO)$_5$WNCCu(PPh$_3$)$_3$ (160.7 ppm),[117b] (CO)$_5$WCNCu(PPh$_3$)$_3$ (147.8 ppm),[117b] and CuCN(PPh$_3$)$_3$ (152.3 ppm).[117b] The characteristic stretching vibration bands of B-H and C≡N were observed at 2572 cm^{-1} and 2114 cm^{-1} as very strong peaks, respectively, in the solid-state IR spectrum.[117c] The characteristic two cage carbons and one cage CH proton of in **III-18** were observed at 75.4/61.2 and 2.4 ppm in its ^{13}C and ^{1}H NMR spectra, respectively. A 1:1:2:2:2:2 pattern was observed in the ^{11}B NMR spectrum of **III-18**.

The molecular structure of **III-17** is shown in Figure 3.19. It looks like that a molecule of CuCN was inserted into the Zr-C(cage) bond. The bridge is slightly bent with angles of C(1)-Cu(1)-C(37) = 176.0(1)°, Cu(1)-C(37)-N(5) = 175.5(5)° and C(37)-N(5)-Zr(1) = 177.9(3)°. The C(37)-N(5) distance of 1.142(5) Å indicates the presence of a triple bond, which is comparable to that of 1.15(2) Å observed in (CO)$_5$MCNCu(PPh$_3$)$_3$.[117b] The Cu(1)-C(1), Cu(1)-C(37) and Zr-N(5) distances of 1.916(3), 1.858(4) and 2.248(3) Å, respectively, are comparable to the values of Cu-C distance observed in 1,1′:2,2′-[Cu(toluene)]$_2$(1,2-C$_2$B$_{10}$H$_{10}$)$_2$ (1.920(2) Å)[41e] and Zr-N distance in Cp$_2$Zr[σ,σ-N=C(Ph)(C$_2$B$_{10}$H$_{10}$)](PhCN) (2.184(3) Å).[91]

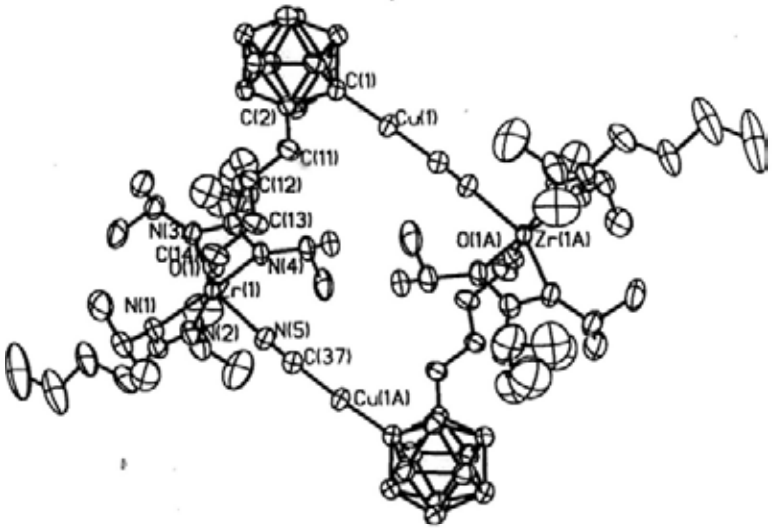
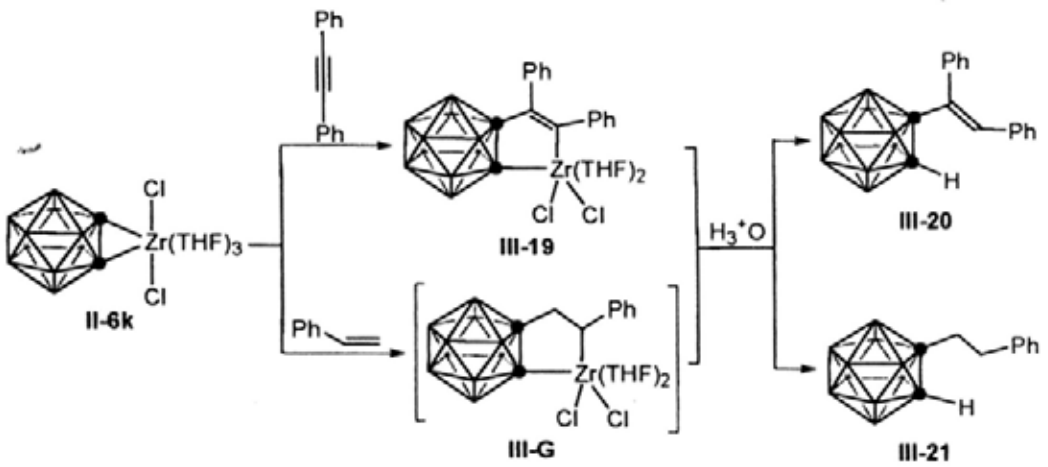


Figure 3.19. Molecular Structure of $\{[\eta^2\text{-}^i\text{PrNC}(^n\text{Bu})\text{NPr}^i]_2\text{Zr}\}_2\{[1\text{-NCCu-2-O}(\text{CH}_2)_4\text{-1,2-}\text{C}_2\text{B}_{10}\text{H}_{10}\}_2$ (**III-17**). (thermal ellipsoids drawn at the 35% probability level). Selected bond distances (Å) and angles (deg): C(1)-C(2), 1.691(4); C(1)-Cu(1), 1.916(3); Cu(1)-C(37), 1.858(4); C(37)-N(5), 1.142(5); C(2)-C(11), 1.522(5); N(5)-Zr(1), 2.248(3); C(1)-Cu(1)-C(37), 176.0(1); Cu(1)-C(37)-N(5), 175.5(5); C(37)-N(5)-Zr(1), 177.9(3).

Dichlorozirconium-carboryne complex **II-6k** has less sterically demanding ligands around the Zr atom. It was found that the reaction of **II-6k** with diphenyl acetylene in toluene at reflux for two days afforded the mono insertion product $1,2\text{-}(\text{THF})_2\text{Cl}_2\text{Zr}[\text{C(Ph)=C(Ph)}]\text{-}1,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}$ (**III-19**) in 37% isolated yield, which was converted to alkenyl carborane $1\text{-(PhCH=CPh)-}1,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{11}$ (**III-20**) after hydrolysis. Similarly, the alkyl substituted carborane $1\text{-}(\text{PhCH}_2\text{CH}_2)\text{-}1,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{11}$ (**III-21**) can be obtained in 20% yield from the reaction of **II-6k** with styrene in toluene at reflux for two days. **III-G** was not isolated in the pure form (Scheme 3.8).

Scheme 3.8. Reactivity of Dichlorozirconium-Carboryne Complex toward Alkyne and Alkene



III-19 was confirmed by ^{1}H, ^{13}C, ^{11}B NMR and IR spectra, elemental analysis and single crystal X-ray analyses. The distinctive vinyl carbons and cage carbons were observed at 208.9/149.4 and 100.6/91.5 ppm in the ^{13}C NMR spectrum of **III-19**. The characteristic stretching vibration of B-H was observed at 2575 cm^{-1} in its IR spectrum. The characteristic vinyl protons and cage C*H* in compound **III-20** were observed at 7.03 and 3.28 ppm, respectively in the ^{1}H NMR spectrum. The vinyl carbons and cage carbons are shifted to a much higher-field at 135.6/134.9 and 78.2/58.0 ppm, respectively. A pattern of 1:1:2:2:2:2 was observed in the ^{11}B NMR spectra of **III-20** and **III-21**. The cage CH proton and carbon of **III-21** were observed at 3.6 and 74.6/61.1 ppm in its ^{1}H and ^{13}C NMR spectra, respectively.

The molecular structure of **III-19** is shown in Figure 3.20. Complex **III-19** adopts a distorted-octahedral coordination environment. The Zr–C(2) distance of 2.361(4) Å is very close to the corresponding values observed in zirconocene-carboranyl

complexes.[33f,33g,51a,118] And the Zr-C(18) distance of 2.231(3) Å is very close to the corresponding values found in zirconacyclopentadienes, such as 2.274(3) Å in $(MeC_5H_4))_2Zr[C(Ph)=C(Ph)-C(Ph)=C(Ph)]$,[119a] 2.230(3) Å in $Cp_2Zr[C(TMS)=C(Ph)-C(Ph)=C(TMS)]$,[119c] 2.281(7) Å in $Cp_2Zr[C(Ph)=C(C_6F_5)-C(C_6F_5)=C(Ph)]$,[119g] 2.243(4) Å in $Cp_2Zr[C(Ph)=C-C=C(Ph)]$,[119g] 2.258(5) Å in $Cp_2Zr[C(Ph)=C(Ph)-C(Ph)=C(Ph)]$,[118k] 2.214(2) Å in $Cp_2Zr([C(Bu^t)]_2\{=C[-(CH_2)_4-]C=\})$,[119l] and 2.208(2) Å in $Cp_2Zr([C(CH_3)]_2\{=C[-(CH_2)_2-]C=\})$.[119l] The C(11)-C(18) distance of 1.327(4) Å and C(2)-C(3) distance of 1.513(5) Å clearly suggest their double and single bond characters. The C(1)-C(2) distance of 1.678(4) Å is a typical value found in *o*-carboranes.[40e,41a,b,54d,f,120] On the other hand, the sum of five interior angles on the five-membered zirconacyclopentene ring is very close to 540°, suggestive of a planar geometry. These structural features resemble those of zirconacyclopentadienes.[119]

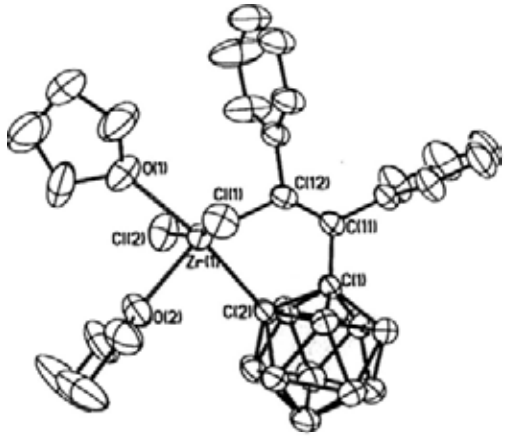


Figure 3.20. Molecular Structure of 1,2-$(THF)_2Cl_2Zr[C(Ph)=C(Ph)]$-1,2-$C_2B_{10}H_{10}$ **(III-19)**.

3.3. Summary

Reactivities of group 4 metal-carboryne complexes toward various kinds of unsaturated molecules have been examined. The results reveal that ketone, nitrile, carbodiimide, isocyanate, thioisocyanate and carbon disulfide can insert into the M-C(cage) (M = Zr or Hf) bond of the M-carboryne complexes with amidinato and guanidinato ligands to give the mono-insertion products, whereas sulfur and selenium can afford the double-insertion products, and aryl isonitrile yields triple-insertion products. On the other hand, metal-carboryne complexes incorporating amidinato and guanidinato ligands show no reactivity toward internal alkyne, alkene and allene. However dichlorozirconium-carboryne complex can react readily with alkyne or alkene to form mono-insertion products probably due to steric reasons.

Chapter 4. Reaction of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ with Alkene, Alkyne and Pyridine

4.1. Background

Zirconacyclopentenes/zirconacyclopentadienes/zirconaindenes are very useful reagents in various organic transformations and their chemistry has been extensively explored.[121] These complexes are commonly prepared by an oxidative coupling of one alkyne and one alkene[122]/two alkynes[123]/one alkyne and one benzyne[93,112e,124] on divalent zirconocene Cp_2Zr(II). In view of the similar reactivity patterns between benzyne and carboryne (1,2-dehydro-1,2-carborane),[29,48,85,86] we initiated a research program to study the chemistry of metal-carboryne complexes[86b,91,92] and to develop a carborane version of zirconacyclopentene/zirconacyclopentadiene reagents. Our previous work on $[\{\eta^5\text{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$[89] shows that the bonding interactions between Zr atom and carboryne resemble those in the zirconocene-benzyne complex $Cp_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$ (Chart 1.4).[90] This result prompts us to prepare the corresponding zirconocene-carboryne $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$. Unexpectedly, only $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) is isolated from the reaction of Cp_2ZrCl_2 with $Li_2C_2B_{10}H_{10}$. Subsequent reactivity studies prove **I-153** to be a precursor of $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$.[91] In this connection, we explored the reactivities of **I-153** toward alkenes, alkynes and pyridines, which will be discussed in this chapter.

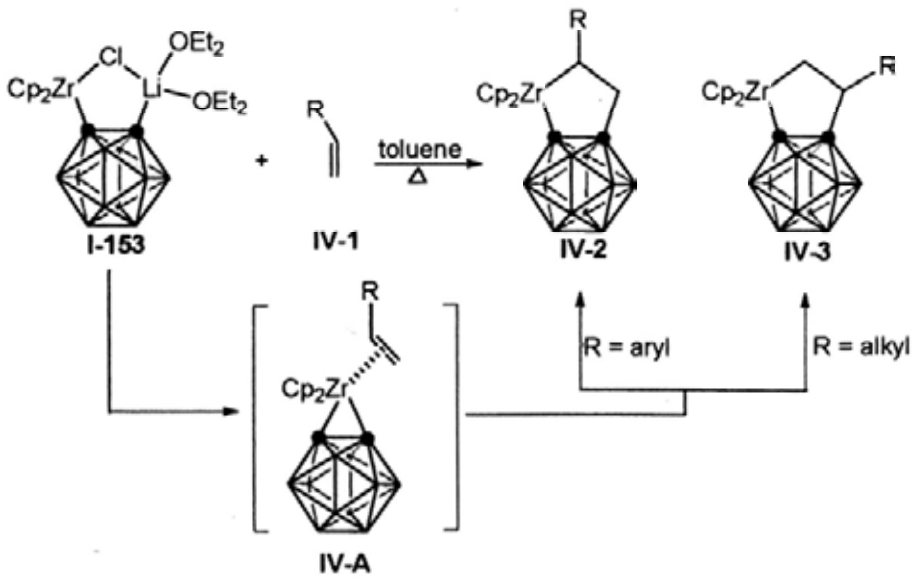
4.2. Reaction with Alkenes

After many attempts we found that the precursor of zirconocene-carboryne complex $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) is active toward mono-substituted alkenes (Scheme 4.1). Treatment of **I-153** with 1.2 – 2.0 equiv of $RC{=}CH_2$ (**IV-1**) in refluxing toluene for two days gave 1,2-$[Cp_2ZrCH(R)\text{-}CH_2]$-1,2-$C_2B_{10}H_{10}$ (R = aryl) (**IV-2a** – **IV-2n**) or 1,2-$[Cp_2ZrCH_2\text{-}CH(R)]$-1,2-$C_2B_{10}H_{10}$ (R = alkyl) (**IV-3a**, **IV-3b**) as yellow or purple crystals in 59–93% isolated yields, respectively (Table 4.1). No double insertion products were observed. An excess amount of alkenes was used to make sure the full consumption of **I-153**, facilitating the isolation of the products. Both solvents and temperatures are crucial to this reaction. Complex **IV-2** or **IV-3** was not observed if the donor solvents such as Et_2O and THF were used instead of toluene, suggesting that the coordination of alkene to the Zr atom is essential for the subsequent insertion. High temperature is required as it can not only promote the dissociation of LiCl from **I-153** forming the Cp_2Zr-carboryne intermediate, but may also facilitate the coupling reaction between carboryne and the coordinated alkene via the intermediate **IV-A** (Scheme 4.1). It is noted that sterically demanding alkenes such as $PhC(Me){=}CH_2$ and cyclohexene did not give the insertion product by reaction with **I-153** even after prolonged heating in toluene due to the steric hindrance. Rather, **I-153** was decomposed to form *o*-carborane and other unidentified species (Scheme 4.2).

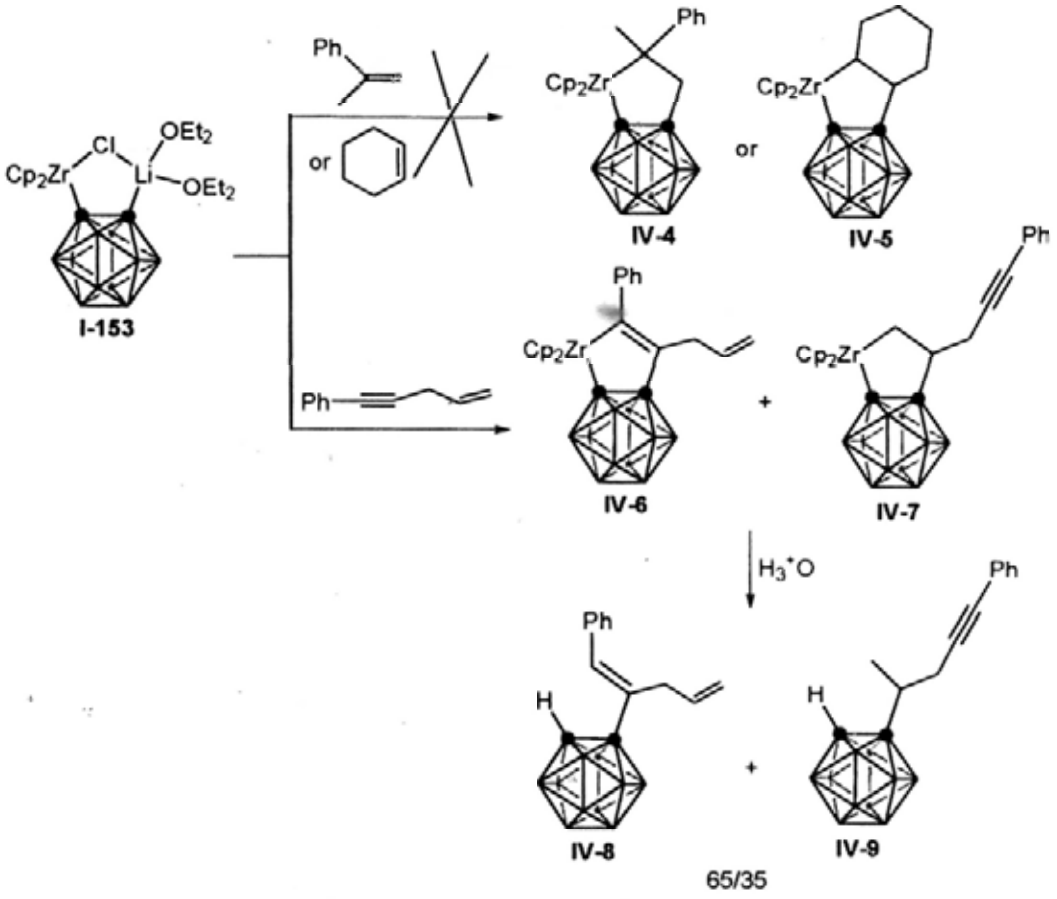
Aryl alkenes could effectively insert into the Zr-C(cage) bond to form the

mono-insertion products **IV-2a–i** (entries 1 – 5, 7 – 10 in Table 4.1). It was found that the bulkiness of substituents on benzene ring has some effects on the insertion of the alkene into the Zr-C(cage) bond. 2-Trifluoromethyl styrene did not react with **I-153** while 3- and 4- trifluoromethyl styrene reacted well with **I-153** to give the mono-insertion products **IV-2f** (91%) and **IV-2g** (73%) in good yields even at room temperature. $TMSCH{=}CH_2$ also generated the mono-insertion product **IV-2j** in good yield (78%). $CH_2{=}CH_2$ and $Ph_2PCH{=}CH_2$ gave the mono-insertion products in much lower yields (45 – 59%). However, $^nBuCH{=}CH_2$ and $Ph_2PCH_2CH{=}CH_2$ afforded another kind of insertion products **IV-3a** and **IV-3b** in 88% and 89% yield, respectively. Obviously, the regio-selectivity of the reactions is controlled by the polarity of the alkene. In general, electron-donating substituents give the complexes **IV-3** whereas electron-withdrawing substituents offer complexes **IV-2**.

Scheme 4.1. Reaction of **I-153** with Terminal Alkene



Scheme 4.2. Reaction of **I-153** with Multi-Substituted and Alkynyl Alkenes



Reaction of **I-153** with $PhC{\equiv}CCH_2CH{=}CH_2$ gave a mixture of two kinds of insertion products 1,2-$[Cp_2ZrC(Ph){=}CCH_2CH{=}CH_2]$-1,2-$C_2B_{10}H_{10}$ (**IV-6**) and 1,2-$(Cp_2ZrCH_2CHCH_2C{\equiv}CPh)$-1,2-$C_2B_{10}H_{10}$ (**IV-7**) in which alkyne insertion is dominant based on the GC-MS analyses after hydrolysis. In fact, the hydrolysis products 1-$[PhCH{=}CCH_2CH{=}CH_2]$-1,2-$C_2B_{10}H_{11}$ (**IV-8**) and 1-$(CH_3CHCH_2C{\equiv}CPh)$-1,2-$C_2B_{10}H_{11}$ (**IV-9**) were isolated in the yield of 55% and 24%, respectively (Scheme 4.2).

Table 4.1. Reaction of **I-153** with Alkenes.

entry	alkene	R	Product		isolated yield (%)
	IV-1	R	**IV-2**	**IV-3**	
1	**IV-1a**	Ph	**IV-2a**	-	87
2	**IV-1b**	4-$CH_3C_6H_4$	**IV-2b**	-	75
3	**IV-1c**	2-ClC_6H_4	**IV-2c**	-	85
4	**IV-1d**	3-ClC_6H_4	**IV-2d**	-	84
5	**IV-1e**	4-ClC_6H_4	**IV-2e**	-	86
6	**IV-1f**	2-$CF_3C_6H_4$	-	-	none [a]
7	**IV-1g**	3-$CF_3C_6H_4$	**IV-2g**	-	91
8	**IV-1h**	4-$CF_3C_6H_4$	**IV-2h**	-	73
9	**IV-1i**	4-BrC_6H_4	**IV-2i**	-	82
10	**IV-1j**	4-FC_6H_4	**IV-2j**	-	81
11	**IV-1k**	TMS	**IV-2k**	-	78
12	**IV-1l**	Ph_2P	**IV-2l**	-	59
13	**IV-1m**	H	**IV-2m**	-	45
14	**IV-1n**	2-pyridyl	**IV-2n**	-	trace
15	**IV-1o**	^{n}Bu	-	**IV-3a**	88
16	**IV-1p**	Ph_2PCH_2	-	**IV-3b**	59

[a] no insertion product was formed due to the steric effect.

These zirconacyclopentane complexes are sensitive to moisture, and unstable in hot pyridine. Most of them (**IV-2b-e,g,h,j,k,m**, and **IV-3a,b**) are soluble in toluene and polar solvents such as THF, DME and diethyl ether but insoluble in hexane. The complexes **IV-2a,i,l**, and **IV-6/7** are barely soluble in toluene, diethyl ether and hexane but are soluble in polar solvents such as THF and DME.

The above complexes were fully characterized by ^1H, ^{13}C and ^{11}B NMR spectra,

IR and elemental analyses. The characteristic protons and carbons of Cp were observed in the range 5.01 to 6.71 ppm and 107.4 to 117.6 ppm in their ^{1}H and ^{13}C NMR spectra, respectively. Compounds **IV-8** and **IV-9** were characterized by ^{1}H, ^{13}C and ^{11}B NMR spectra as well as HRMS. There are some clear differences in their ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **IV-8** clearly showed one singlet at 7.04 ppm, two multiplets at 5.94 and 5.26 ppm for the four vinyl protons whereas the characteristic methyl protons of **IV-9** were observed at 1.35 ppm in doublet with J = 6.8 Hz. The ^{13}C NMR spectrum of **IV-8** exhibited the distinctive vinyl carbons ranging from 117.9 to 136.4 ppm whereas that of **IV-9** showed two characteristic carbons at 83.8 and 85.8 ppm assignable to C≡C.

Complexes **IV-2a,c,i-l** and **IV-3a,b** were further confirmed by single-crystal X-ray analyses. Figures 4.1 – 4.8 show their molecular structures. Selected bond distances and angles are summarized in Tables 4.2 and 4.3, respectively. Except for **IV-2l** (Figure 4.5) in which an additional coordination bond between the Zr and P atoms with the Zr-P distances of 2.670(1) Å is observed, all other complexes adopt a distorted-tetrahedral coordination environment. As shown in Table 4.2, the Zr–C(1) distance of 2.502(4) Å in **IV-2l** is much longer than those (2.389(3)-2.434(2) Å) observed in its analogues whereas the C(3)-C(4) distance of 1.323(6) Å in **IV-2l** is much shorter than the corresponding values (1.493(8) – 1.552(3) Å) found in its analogues. Such differences result from the additional coordination of the P to the Zr atom. The C(3)-C(4) and C(2)-C(3) distances of ca 1.51 Å clearly suggest their

single bond characters. The C(1)-C(2) distance of ca 1.69 Å is a typical value found in *o*-carboranes.[40d,e,41a,54e,f,120] The Zr-C(1) distances (2.389(3) – 2.502(4) Å) are very close to the corresponding values observed in zirconocene-carboranyl complexes.[33f,g,51a,118] The Zr-C(4) distances fall in a range 2.268(8) – 2.401(2) Å, which are comparable to the corresponding values found in zirconacyclopentenes.[90,124] On the other hand, the sum of five interior angles on the five-membered zirconacyclopentane ring falls in a range 527.6 – 529.4° (Table 4.3), which are obviously less than 540°, suggestive of a non-planar geometry.

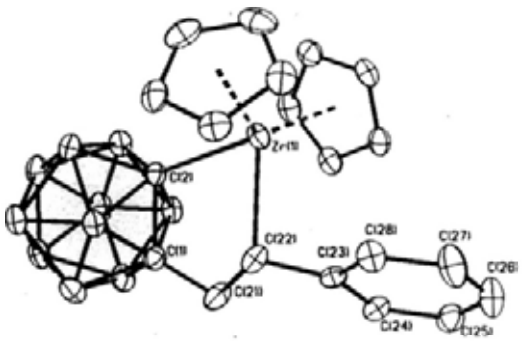


Figure 4.1. Molecular Structure of 1,2-[$Cp_2ZrCH(Ph)$-CH_2]-1,2-$C_2B_{10}H_{10}$ (**IV-2a**).

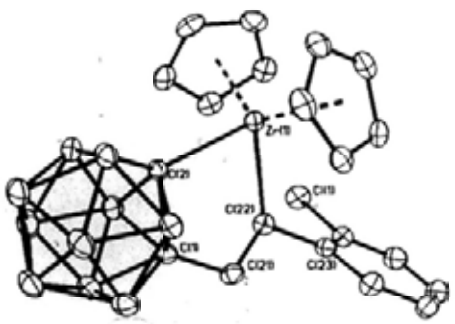
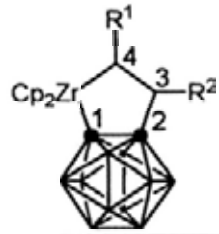


Figure 4.2. Molecular Structure of 1,2-[$Cp_2ZrCH(2$-Cl-$C_6H_4)$-CH_2]-1,2-$C_2B_{10}H_{10}$ (**IV-2c**).

Table 4.2. Selected Bond Lengths (Å).



Compd	*av.* Zr-Cent[a]	*av.* Zr-C (C_5 ring)	Zr-C(1)	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	Zr-C(4)
IV-2a	2.216	2.516(2)	2.434(2)	1.700(3)	1.520(3)	1.520(3)	2.352(2)
IV-2c	2.212	2.513(3)	2.398(3)	1.690(5)	1.523(5)	1.547(5)	2.375(3)
IV-2j	2.209	2.503(5)	2.399(4)	1.683(6)	1.531(7)	1.532(7)	2.367(5)
IV-2k	2.228	2.524(2)	2.406(2)	1.691(3)	1.534(3)	1.552(3)	2.308(2)
IV-2l	2.220	2.501(5)	2.502(4)	1.687(5)	1.521(6)	1.323(6)	2.357(4)
IV-2m	2.212	2.506(3)	2.401(2)	1.689(3)	1.534(4)	1.541(4)	2.401(2)
IV-3a[b]	2.222	2.498(10)	2.391(7)	1.679(10)	1.539(11)	1.493(8)	2.268(8)
IV-3b	2.217	2.513(3)	2.389(3)	1.700(3)	1.546(3)	1.540(4)	2.294(3)

[a] Cent = the centroid of Cp ring. [b] average values of two independent molecules in the unit cell.

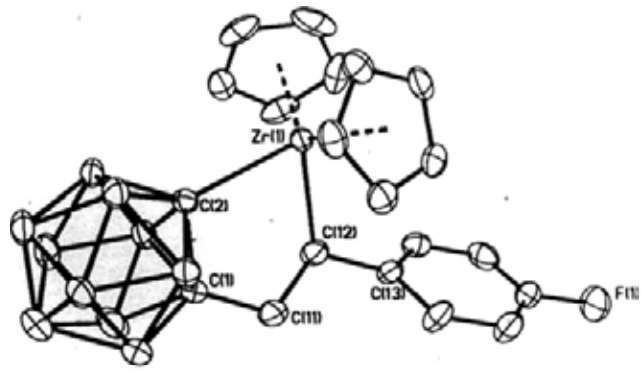
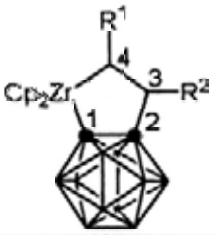


Figure 4.3. Molecular Structure of 1,2-[$Cp_2ZrCH(4\text{-}F\text{-}C_6H_4)\text{-}CH_2$]-1,2-$C_2B_{10}H_{10}$ **(IV-2j)**.

Table 4.3. Selected Bond Angles (deg.).



compd	Cent-Zr-Cent	C(1)-Zr-C(4)	Zr-C(1)-C(2)	C(1)-C(2)-C(3)	C(2)-C(3)-C(4)	C(3)-C(4)-Zr
IV-2a	128.0	74.2(1)	111.2(1)	114.7(2)	112.7(2)	117.4(2)
IV-2c	128.2	78.8(1)	108.3(2)	115.7(3)	115.7(3)	109.5(3)
IV-2j	128.7	77.3(2)	109.4(3)	115.3(4)	114.0(4)	111.6(3)
IV-2k	128.4	78.3(1)	108.4(1)	114.9(2)	114.5(2)	111.8(1)
IV-2l	127.4	69.2(1)	112.6(2)	112.9(3)	115.0(4)	130.0(3)
IV-2m	128.4	77.7(1)	109.3(1)	114.6(2)	114.0(2)	113.8(2)
IV-3a	130.0	76.8(3)	111.0(4)	114.1(6)	115.5(7)	119.3(6)
IV-3b	130.3	76.4(1)	110.5(1)	113.8(2)	111.7(2)	115.6(2)

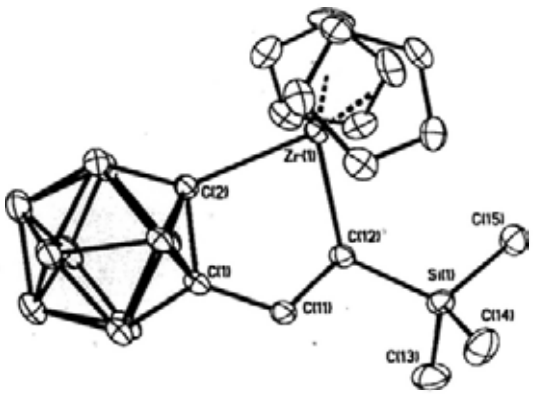


Figure 4.4. Molecular Structure of 1,2-[$Cp_2ZrCH(TMS)$-CH_2]-1,2-$C_2B_{10}H_{10}$ **(IV-2k)**.

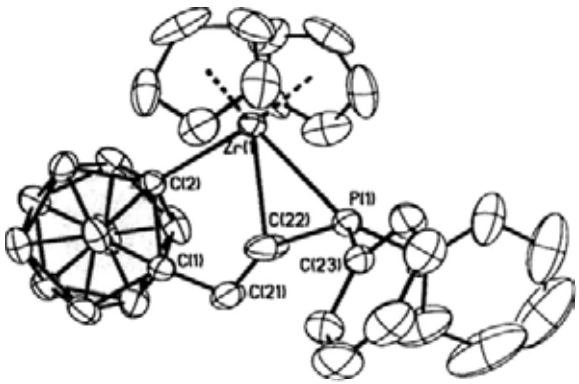


Figure 4.5. Molecular Structure of 1,2-[$Cp_2ZrCH(PPh_2)$-CH_2]-1,2-$C_2B_{10}H_{10}$ **(IV-2l)**.

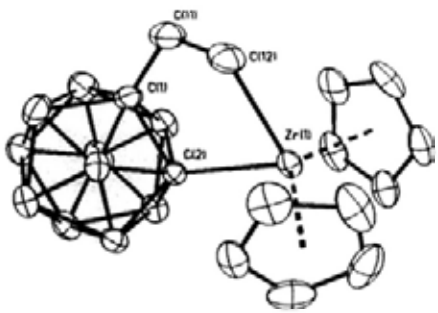


Figure 4.6. Molecular Structure of 1,2-[$Cp_2ZrCH_2CH_2$]-1,2-$C_2B_{10}H_{10}$ **(IV-2m)**.

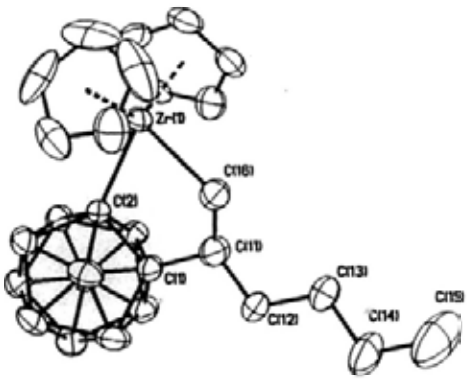


Figure 4.7. Molecular Structure of 1,2-[Cp_2ZrCH_2-$CH(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ **(IV-3a)**.

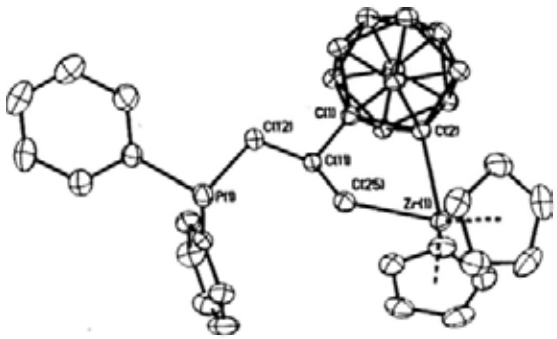


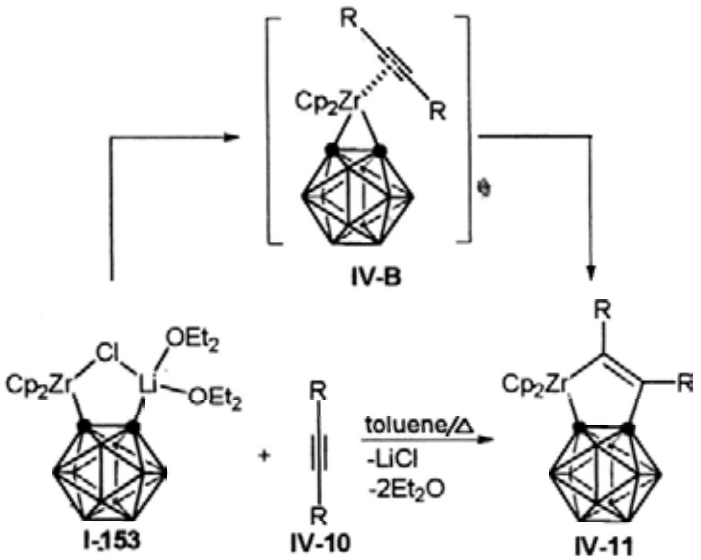
Figure 4.8. Molecular Structure of 1,2-[Cp_2ZrCH_2-$CH(CH_2PPh_2)$]-1,2-$C_2B_{10}H_{10}$ (**IV-3b**).

4.3. Reaction with Alkynes

Reaction with Symmetrical Alkynes. Treatment of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) with 1.5 – 2 equiv of RC≡CR (**IV-10**) in refluxing toluene gave 1,2-[$Cp_2ZrC(R)$=$C(R)$]-1,2-$C_2B_{10}H_{10}$ (**IV-11**) (R = Et (**IV-11a**), ^{n}Pr (**IV-11b**), ^{n}Bu (**IV-11c**), Ph (**IV-11d**)) as yellow crystals in 65% – 93% isolated yields (Scheme 4.3). No double insertion products were observed. An excess amount of alkynes was used to make sure the full consumption of **I-153**, facilitating the isolation of the products. Both solvents and temperatures are crucial to this reaction. Complexes **IV-11a–d** were not observed if the donor solvents such as Et_2O and THF were used instead of toluene, suggesting that the coordination of alkyne to the Zr atom is essential for the subsequent insertion. High temperature is required as it can not only promote the dissociation of LiCl from **I-153** forming the zirconocene-carboryne intermediate, but

may also facilitate the coupling reaction between carboryne and the coordinated alkyne via the intermediate **IV-B** (Scheme 4.3). It is noted that sterically demanding alkyne $Me_3SiC{\equiv}CSiMe_3$ did not react with **I-153** even after prolonged heating in toluene.[125] PhC≡CPh offered a much lower yield (65%) than linear alkynes (80% - 93%). The very bulkyl icosahedral carboranyl moiety may play a role in these insertion reactions because of steric reason.

Scheme 4.3. Reaction of **I-153** with Symmetrical Alkynes



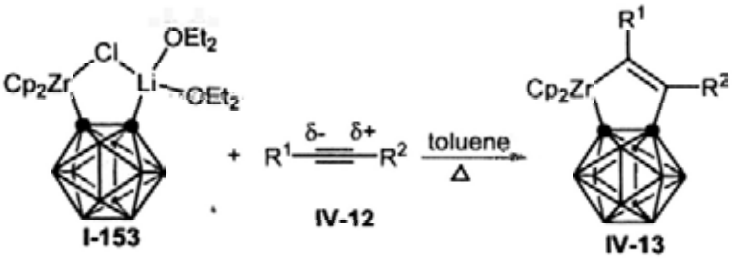
R	Et	^{n}Pr	^{n}Bu	Ph
IV-11	**a**	**b**	**c**	**d**
yield (%)	93	80	81	65

The most characteristic vinyl carbons in the products **IV-11a-d** were observed at about 195 and 144 ppm in their ^{13}C NMR spectra, which are very comparable to the corresponding values of ~194 and ~142 ppm observed in $Cp_2Zr[C(R)=C(R)]_2$.[119]

Two distinct cage carbons were found at ~92 and ~90 ppm, respectively, in the ^{13}C NMR spectra. The unique Cp carbons at ~115 ppm and protons at ~6.6 ppm as a singlet were also observed. The ^{11}B NMR spectra exhibited different patterns, a 1:3:2:2:2 for **IV-11a**, a 1:2:3:4 for **IV-11b** and **IV-11c**, and a 2:3:3:2 for **IV-11d** in the range 0 – 11 ppm.

Reaction with Unsymmetrical Alkynes. In a very similar manner, reaction of **I-153** with 1.5 – 2 equiv of unsymmetrical alkynes **IV-12** in refluxing toluene afforded the mono-insertion products **IV-13a-m** in the yields of 35% – 88%. The results are summarized in Table 4.4. The regioselectivity of these reactions may be best ascribed to the polarity of alkynes as phenyl is often considered as electron-withdrawing group.[108] In case of **IV-12g**, steric factor may also play a role in the regioselectivity (Table 4.4, entry 7). For linear alkynes such as $^{n}PrC{\equiv}CCH_3$, both regioisomers were observed in about 1:1 ratio, resulting in an inseparable mixture. Alkynes containing functional groups, such as **IV-12d,h,l,m** offered relatively low isolated yields due to unknown side reactions, although the conversion of **I-153** is 100%. Terminal alkynes such as PhC≡CH are not compatible with the above reactions as they can protonate **I-153** to generate *o*-carborane.

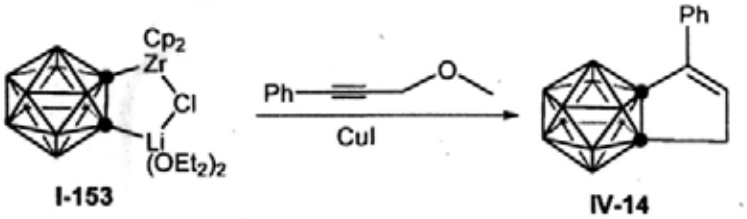
Table 4.4. Reaction of **I-153** with Unsymmetrical Alkynes.



I-153 **IV-12** **IV-13**

entry	alkyne **IV-12**	R^1/R^2	product **IV-13**	isolated yield
1	**IV-12a**	Ph/Me	**IV-13a**	90
2	**IV-12b**	Ph/Et	**IV-13b**	88
3	**IV-12c**	Ph/^{n}Bu	**IV-13c**	76
4	**IV-12d**	Ph/•≡—Ph	**IV-13d**	55
5	**IV-12e**	4-Tolyl/Me	**IV-13e**	68
6	**IV-12f**	TMS/^{n}Bu	**IV-13f**	87
7	**IV-12g**	TMS/Ph	**IV-13g**	50
8	**IV-12h**	 /Et	**IV-13h**	46
9	**IV-12i**	$Ph_2P/^n$Bu	**IV-13i**	76
10	**IV-12j**	Ph/$(CH_2)_3Cl$	**IV-13j**	89
11	**IV-12k**	Ph/$CH_2N(CH_3)_2$	**IV-13k**	78
12	**IV-12l**	Ph/CH_2OCH_3	**IV-13l**	37
13	**IV-12m**	Ph/	**IV-13m**	35

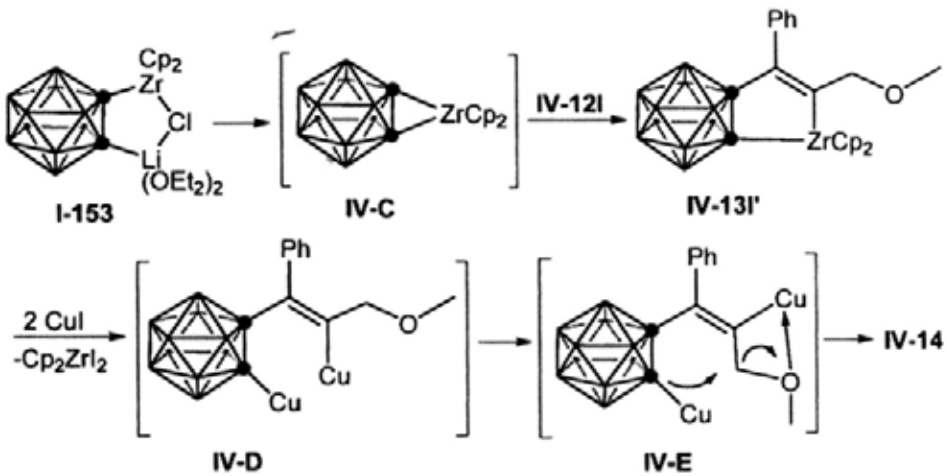
Scheme 4.4. Reaction of **I-153** with $PhC{\equiv}CCH_2OCH_3$ in the Presence of CuI



I-153 **IV-14**

It is noteworthy that treatment of **I-153** with $PhC{\equiv}CCH_2OCH_3$ (**IV-12l**) in the presence of CuI afforded five-membered ring fused carborane 1,2-(1,3-$PhC{=}CHCH_2$)-1,2-$C_2B_{10}H_{10}$ (**IV-14**) in 31% isolated yield as colorless crystals (Scheme 4.4). A possible reaction pathway was depicted in Scheme 4.5. Reaction of **I-153** with **IV-12l** gives **IV-13l'** followed by transmetallation to Cu(I) to afford **IV-D**, Intramolecular nucleophilic substitution reaction leads to the formation of **IV-14**.

Scheme 4.5. A Possible Pathway for the Formation of **IV-14**



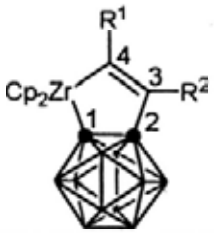
Complexes **IV-11a-d** and **IV-13a-m** are very soluble in donor solvents, but are insoluble in hexane. Complexes **IV-11b,c** and **IV-13f,m** are soluble in hot aromatic solvents, whereas **IV-11a,d** and **IV-13a-e,g-l** are only barely soluble. They are stable in air for a few minutes in the solid-state whereas their solutions are moisture-sensitive.

They were fully characterized by various spectroscopic techniques and elemental

analyses. The Cp protons displayed a singlet at ~6.5 ppm in their ^{1}H NMR spectra. Two characteristic vinyl carbons in the range 140 – 211 ppm and two unique cage carbons at ~90 ppm were observed in their ^{13}C NMR spectra. The ^{13}C NMR spectrum of **IV-14** exhibited two characteristic vinyl carbons and cage carbons at 143.5/134.0 and 85.7/78.6 ppm, respectively. The vinyl proton was found at 6.19 ppm as a triplet with J = 3.0 Hz split by the adjacent CH_2 in the ^{1}H NMR spectrum of **IV-14**. The ^{11}B NMR spectrum of **IV-14** showed a unique pattern of 4:2:2:2 at -6.9, -10.4, -11.9 and -13.8 ppm.

Structure. Molecular structures of **IV-11a,c,d**, **IV-13a,c,d,f-m** and **IV-14** are further confirmed by single-crystal X-ray analyses. Figures 4.9 – 4.23 show the representative structures. Selected bond distances and angles are summarized in Tables 4.5 and 4.6, respectively. Except for **IV-13i** (Figure 4.18) in which an additional coordination bond between the Zr and P atoms with the Zr-P distance of 2.787(3) Å is observed, all other complexes adopt a distorted-tetrahedral coordination environment. As shown in Table 4.5, the Zr–C(1) distance of 2.507(3) Å in **IV-13i** is much longer than those (2.378(4) – 2.406(2) Å) observed in its analogues whereas the Zr-C(4) distance of 2.265(3) Å in **IV-13i** is shorter than the corresponding values (2.277(2) – 2.309(3) Å) found in its analogues. Such differences result from the additional coordination of the P to the Zr atom. The C(3)-C(4) distance of *ca* 1.34 Å and C(2)-C(3) distance of *ca* 1.51 Å clearly suggest their double and single bond characters. The C(1)-C(2) distance of *ca* 1.68 Å is a

Table 4.5. Selected Bond Lengths (Å).



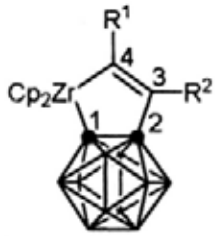
compd	*av.* Zr-Cent[a]	*av.* Zr-C (C_5 ring)	Zr-C(1)	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	Zr-C(4)
IV-11a	2.218	2.516(2)	2.390(2)	1.680(3)	1.510(3)	1.346(3)	2.277(2)
IV-11c	2.214	2.508(3)	2.386(2)	1.688(4)	1.515(4)	1.344(3)	2.289(3)
IV-11d	2.208	2.506(3)	2.391(2)	1.680(3)	1.514(3)	1.342(3)	2.288(2)
IV-13a	2.211	2.512(3)	2.384(3)	1.684(4)	1.509(4)	1.334(4)	2.298(3)
IV-13c	2.213	2.514(4)	2.376(4)	1.695(5)	1.519(6)	1.330(6)	2.296(4)
IV-13d	2.204	2.503(4)	2.385(4)	1.680(5)	1.514(5)	1.349(5)	2.303(4)
IV-13f	2.226	2.524(3)	2.382(2)	1.684(3)	1.531(3)	1.350(3)	2.299(2)
IV-13g	2.232	2.519(3)	2.394(3)	1.678(3)	1.524(4)	1.353(4)	2.309(3)
IV-13h	2.217	2.516(3)	2.406(2)	1.689(3)	1.505(3)	1.341(3)	2.291(2)
IV-13i	2.229	2.526(3)	2.507(3)	1.721(4)	1.505(4)	1.332(4)	2.265(3)
IV-13j	2.209	2.507(4)	2.378(4)	1.684(5)	1.515(5)	1.337(5)	2.299(4)
IV-13k	2.209	2.511(4)	2.382(3)	1.695(5)	1.512(5)	1.338(5)	2.302(4)
IV-13l	2.219	2.515(3)	2.395(3)	1.689(4)	1.513(4)	1.338(4)	2.309(3)
IV-13m	2.211	2.509(4)	2.385(4)	1.684(5)	1.509(5)	1.345(5)	2.297(4)

[a] Cent = the centroid of Cp ring.

typical value found in *o*-carboranes.[40d,e;41a,54c,f;120] The Zr-C(1) distances (2.378(4) – 2.507(3) Å) are very close to the corresponding values observed in zirconocene-carboranyl complexes.[34f,g;51a,118] The Zr-C(4) distances fall in a range 2.265(3) – 2.309(3) Å, which are very close to the corresponding values found in zirconacyclopentadienes.[119] On the other hand, the sum of five interior angles on the five-membered zirconacyclopentene ring is very close to 540°, suggestive of a planar

geometry. These structural features resemble those of zirconacyclopentadienes.[119]

Table 4.6. Selected Bond Angles (deg).



compd	Cent-Zr-Cent	C(1)-Zr-C(4)	Zr-C(1)-C(2)	C(1)-C(2)-C(3)	C(2)-C(3)-C(4)	C(3)-C(4)-Zr
IV-11a	129.9	75.9(1)	109.3(1)	113.6(2)	119.6(2)	121.6(2)
IV-11c	129.6	76.1(1)	109.1(1)	113.8(2)	119.3(2)	121.4(2)
IV-11d	130.3	75.7(1)	109.8(1)	113.0(2)	120.3(2)	121.3(1)
IV-13a	130.2	75.5(1)	109.6(2)	113.6(2)	119.5(2)	121.7(2)
IV-13c	130.6	75.6(2)	109.9(2)	113.0(3)	119.3(4)	122.1(3)
IV-13d	130.2	76.5(1)	109.5(2)	113.3(3)	121.2(3)	119.4(3)
IV-13f	128.8	76.7(1)	109.2(1)	113.4(2)	119.9(2)	119.6(2)
IV-13g	129.2	77.4(1)	108.9(2)	113.2(1)	122.4(2)	117.6(2)
IV-13h	129.3	74.5(1)	110.1(1)	113.2(2)	118.8(2)	123.4(2)
IV-13i	128.1	69.0(1)	111.5(2)	111.3(2)	114.4(3)	132.9(2)
IV-13j	129.9	75.4(1)	110.2(2)	113.1(3)	119.6(3)	121.7(3)
IV-13k	130.3	74.8(1)	110.6(2)	112.7(3)	119.2(3)	122.5(3)
IV-13l	130.7	75.4(1)	109.7(2)	113.5(2)	119.7(3)	121.7(2)
IV-13m	130.6	75.5(1)	109.6(2)	114.1(3)	118.9(3)	122.0(3)

Figure 4.9. Molecular Structure of 1,2-[$Cp_2ZrC(Et)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ **(IV-11a)**.

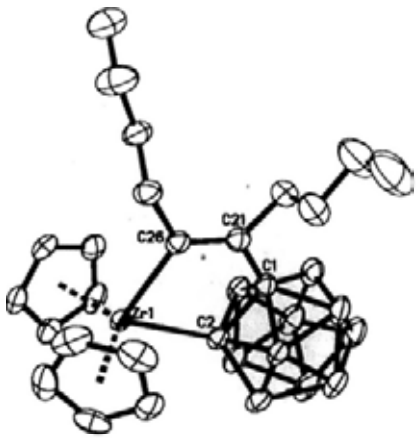


Figure 4.10. Molecular Structure of 1,2-[$Cp_2ZrC(Bu^n)=C(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ **(IV-11c)**.

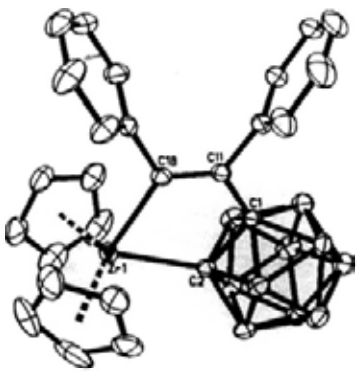


Figure 4.11. Molecular Structure of 1,2-[$Cp_2ZrC(Ph)=C(Ph)$]-1,2-$C_2B_{10}H_{10}$ **(IV-11d)**.

Figure 4.12. Molecular Structure of 1,2-[$Cp_2ZrC(Ph)=C(Me)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13a)**.

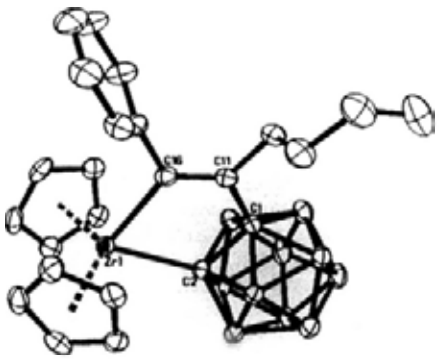


Figure 4.13. Molecular Structure of 1,2-[$Cp_2ZrC(Ph)=C(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13c)**.

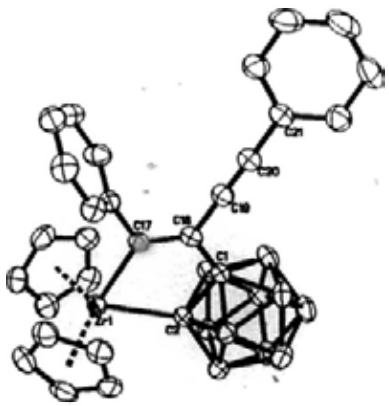


Figure 4.14. Molecular Structure of 1,2-[$Cp_2ZrC(Ph)=C(C\equiv CPh)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13d)**

Figure 4.15. Molecular Structure of 1,2-[$Cp_2ZrC(TMS)=C(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13f)**.

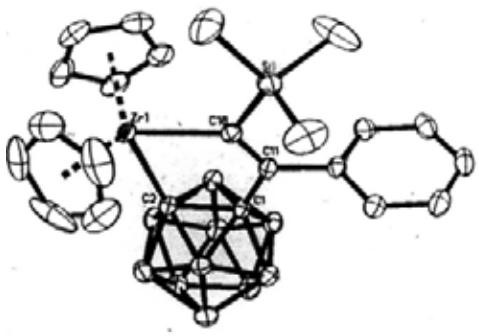


Figure 4.16. Molecular Structure of 1,2-[$Cp_2ZrC(TMS)=C(Ph)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13g)**.

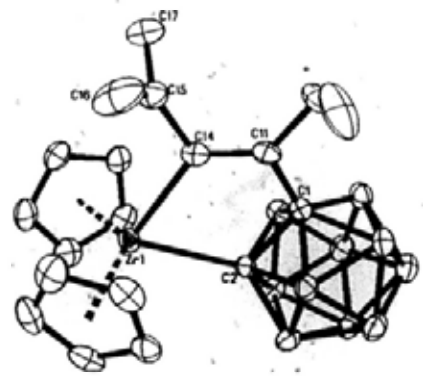


Figure 4.17. Molecular Structure of 1,2-[$Cp_2ZrC((C=CH_2)Me)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13h)**.

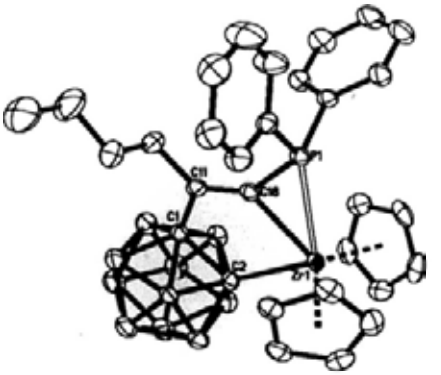


Figure 4.18. Molecular Structure of 1,2-[$Cp_2ZrC(PPh_2)=C(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13i)**.

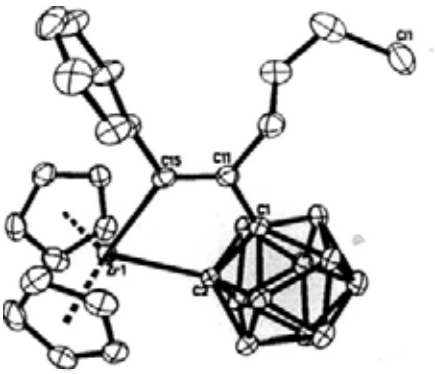


Figure 4.19. Molecular Structure of 1,2-[$Cp_2ZrC(Ph)=C((CH_2)_3Cl)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13j)**.

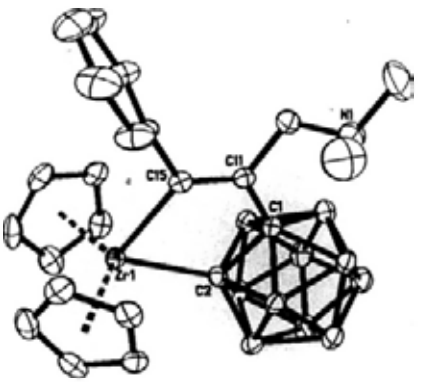


Figure 4.20. Molecular Structure of 1,2-[$Cp_2ZrC(Ph)=C(N(CH_3)_2)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13k)**.

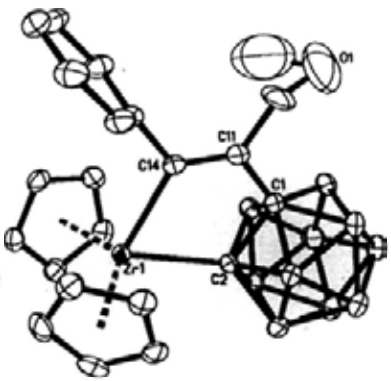


Figure 4.21. Molecular Structure of 1,2-[$Cp_2ZrC(Ph)=C(OCH_3)$]-1,2-$C_2B_{10}H_{10}$ **(IV-13l)**.

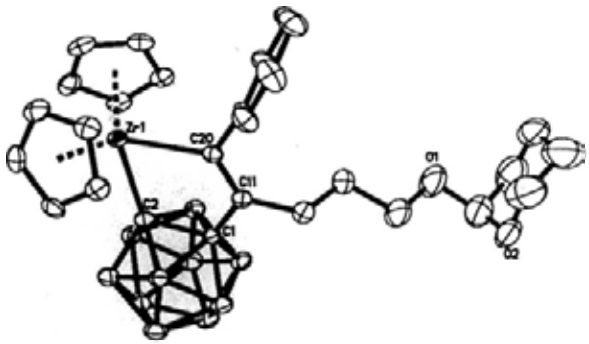


Figure 4.22. Molecular Structure of 1,2-{$Cp_2ZrC(Ph)=C[(CH_2)_3O$ (tetrahydro-2-pyranyl)]}-1,2-$C_2B_{10}H_{10}$ **(IV-13m)**.

In compound **IV-14**, the C(11)-C(18)/C18)-C(19) distances of 1.329(2)/1.500(2) Å suggest double and single bond, respectively. The C(1)-C(2) distance of 1.641(2) Å is a typical value for *o*-carboranes.[40d,e;41a,54c,f;120] Other bonds in the newly-formed five-membered ring are single bond with a typical value of *ca* 1.53 Å. The sum of the interior angles of this five-membered ring is close to 540°, suggestive of the planar geometry of the ring.

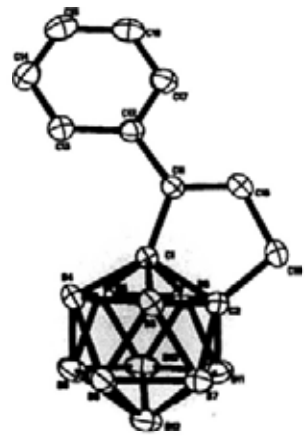


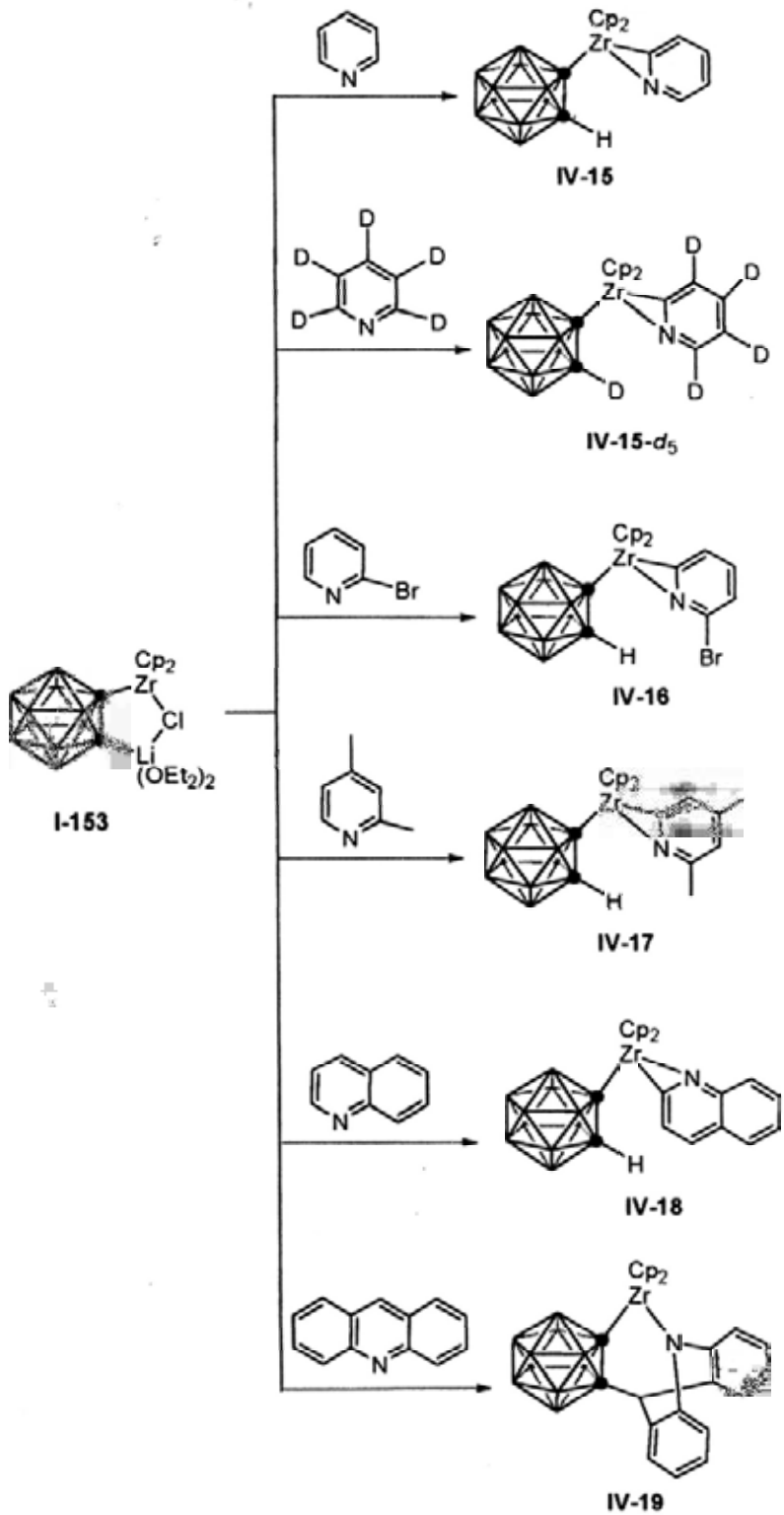
Figure 4.23. Molecular Structure of 1,3-(PhC=CHCH$_2$)-1,2-$C_2B_{10}H_{10}$ (**IV-14**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.641(2), C(1)-C(11) 1.510(2), C(11)-C(18) 1.329(2), C(18)-C(19) 1.500(2), C(2)-C(19) 1.523(2), C(2)-C(1)-C(11) 103.7(1), C(1)-C(11)-C(18) 110.0(1), C(11)-C(18)-C(19) 116.7(1), C(18)-C(19)-C(2) 103.8(1), C(19)-C(2)-C(1) 105.7(1).

4.4. Reaction with Pyridines

We attempted to prepare the pyridine adduct of zirconocene-carboryne complex from the reaction of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) with pyridine, what we isolated is the *α*–CH activation product of pyridine, $Cp_2Zr[\eta^2(C,N)\text{-pyridine}](\sigma\text{-}1\text{-}C_2B_{10}H_{11})$ (**IV-15**). We then extended this reaction to other pyridine derivatives. The results are described in this section.

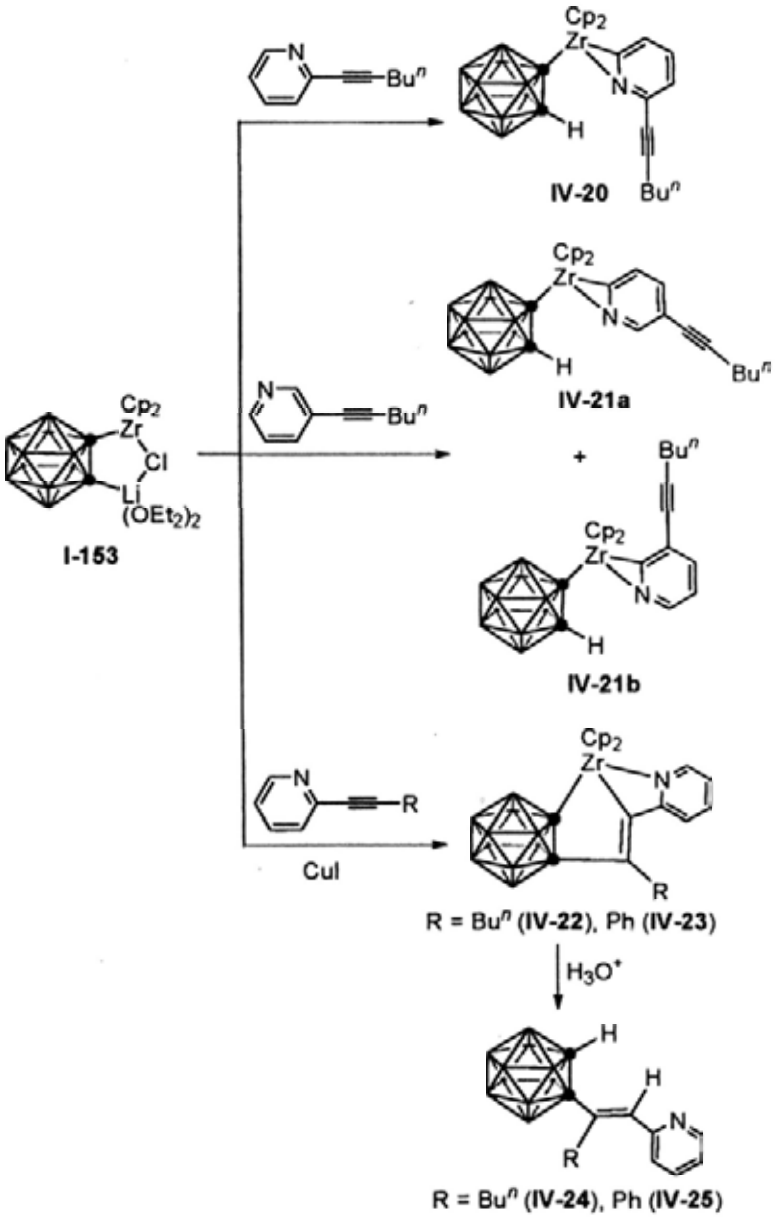
Treatment of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) with excess pyridine in toluene at room temperature gave the C-H activation product $Cp_2Zr[\eta^2(C,N)\text{-pyridine}](\sigma\text{-}1,2\text{-}C_2B_{10}H_{11})$ (**IV-15**) in 90% isolated yield as off-white crystals. Similarly, when 2-bromo-pyridine and 2,4-lutidine were used, the corresponding products $Cp_2Zr(\eta^2\text{-}1,6(N,C)\text{-}(2\text{-bromopyridine})(\sigma\text{-}1,2\text{-}C_2B_{10}H_{11})$ (**IV-16**) and

Scheme 4.6. Reaction of **I-153** with Pyridines



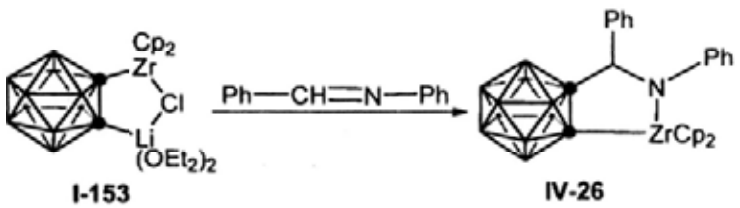
$Cp_2Zr(\eta^2$-1,6(N,C)-(2,4-dimethylpyridine)(σ-1,2-$C_2B_{10}H_{11}$) (**IV-17**) were obtained in 81% and 82% yields, respectively. Under the same reaction conditions, quinoline offered $Cp_2Zr(\eta^2$-1,2(N,C)-quinoline)(σ-1,2-$C_2B_{10}H_{11}$) (**IV-18**) in 85% yield. However, acridine led to the formation of 1,4-addition product $Cp_2Zr\{2$-[9-(η^1-10(N)-dihydroacridine)](σ-1,2-$C_2B_{10}H_{10}$)} (**IV-19**) in 75% yield.

Scheme 4.7. Reaction of **I-153** with Pyridinyl Substituted Alkynes



Unexpectedly, reaction of **I-153** with 2-(1-hexynyl)pyridine gave the C-H activation product $Cp_2Zr\{\eta^2$-1,6(N,C)-[2-(1-^{n}BuC≡C)pyridine]$\}(\sigma$-1,2-$C_2B_{10}H_{11})$ **(IV-20)** in 56% yield rather than the insertion product 1,2-$[Cp_2ZrC$(2-pyridyl)=CBu^n]-1,2-$C_2B_{10}H_{10}$ **(IV-22)**. In the same manner, treatment of **I-153** with 3-(1-hexynyl)pyridine to afford two regio-isomers of $Cp_2Zr\{\eta^2$-1,6(N,C)-[3-(1-^{n}BuC≡C)pyridine]$\}(\sigma$-1,2-$C_2B_{10}H_{11})$ **(IV-21a)** and $Cp_2Zr\{\eta^2$-1,2(N,C)-[3-(1-^{n}BuC≡C)pyridine]$\}(\sigma$-1,2-$C_2B_{10}H_{11})$ **(IV-21b)** in a molar ratio of 42/58 as determined by their ^{1}H NMR spectra. These two products were isolated by fractional crystallization from toluene in 33% yield for **IV-21a** and 35% yield for **IV-21b**, respectively. However, in the presence of CuI, the alkyne insertion product was formed. Reaction of **I-153** with 1.2 equiv of 2-(1-hexynyl)pyridine or 2-(1-phenylacetyl)pyridine in the presence of 2.0 equiv of CuI in toluene at room temperature generated **IV-22** or 1,2-$[Cp_2ZrC$(2-pyridyl)=CPh]-1,2-$C_2B_{10}H_{10}$ **(IV-23)** in 74% or 77% yield, respectively. It is assumed that copper(I) can bind to the nitrogen atom of pyridine, blocking its interactions with the zirconium atom. Thus the alkyne can coordinate to the zirconium atom and subsequently insert into the Zr-C_{cage} bond to form the insertion products **IV-22** and **IV-23**. After hydrolysis of **IV-22** and **IV-23**, the corresponding alkenyl compounds 1-[C(2-pyridyl)=CBu^n]-1,2-$C_2B_{10}H_{11}$ **(IV-24)** and 1-[C(2-pyridyl)=CPh]-1,2-$C_2B_{10}H_{11}$ **(IV-25)** were obtained in 87% and 89% yield, respectively, by flash column chromatography on silica gel using 4/1 hexane/ethyl acetate as eluent.

Scheme 4.8. Reaction of **I-153** with PhCH=NPh

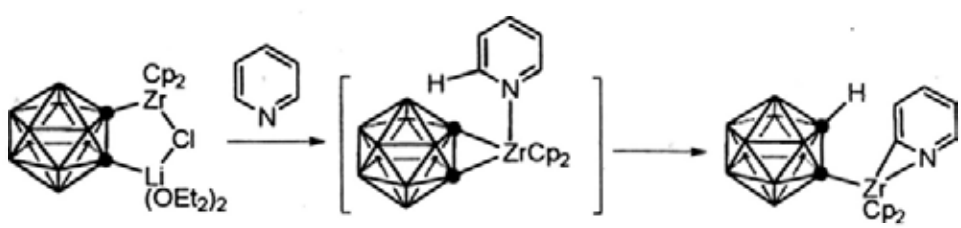


I-153 **IV-26**

To examine the effect of heteroatom in the activation of α-C-H bond in the above reactions, an imine PhCH=NPh was treated with **I-153** under the same conditions. A C=N insertion product 1,2-[$Cp_2ZrN(Ph)CH(Ph)$]-1,2-$C_2B_{10}H_{10}$ (**IV-26**) was isolated in 62% isolated yield (Scheme 4.8). No C-H activation product was observed.

It is suggested that the zirconocene-carboryne may serve as a key intermediate in the above reactions. Coordination to the nitrogen atoms in heterocycles, followed by the proton-transfer yield the final product (Scheme 4.9). This proposed pathway is supported by the following experiments. When pyridine-d_5 was used in the reaction, $Cp_2Zr[\eta^2(C,N)$-pyridine-$d_4](\sigma$-$C_2B_{10}H_{10}D)$ (**IV-15**-d_5) was obtained in 87% isolated yield as off-white crystals (Scheme 4.6).

Scheme 4.9. A Possible Mechanism for α-C-H Activation of Pyridine



I-153 **IV-F** **IV-15**

Complexes **IV-15** – **IV-23** and **IV-26** were fully characterized using various spectroscopic techniques including NMR, IR spectra and elemental analyses. The characteristic cage C-H protons of **IV-15** – **IV-18** and **IV-20** - **IV-23** were observed in a range 3.29 – 4.47 ppm as a broad singlet in their ^{1}H NMR spectra. On the other hand, in the ^{13}C NMR spectra, the α–carbon of pyridine unit was shifted downfield from ca 150 ppm to about 200 ppm in the products. Their ^{11}B NMR spectra showed a pattern of 1:1:2:2:4, which is significantly different from that of their parent complex. In the ^{1}H NMR spectrum of **IV-15**-d_5, only the Cp protons were observed at 5.20 ppm as singlet whereas in its ^{2}H NMR spectrum, the characteristic cage C-D was observed at 3.25 ppm and the corresponding four sp^2 C-D peaks appeared at 6.52, 6.93, 7.18 and 8.45 ppm, respectively. Complexes **IV-15** and **IV-15**-d_5 have the identical ^{11}B NMR spectra.

Table 4.7. Selected Bond Lengths (Å) and Angles (deg.).

compd	*av.* Zr-Cent[a]	*av.* Zr-C (C_5 ring)	Zr-C_{cage}	Zr-$C_{pyridyl}$	Zr-$N_{pyridyl}$	C_{cage}-C_{cage}	$C_{pyridyl}$-$N_{pyridyl}$	Cent-Zr-Cent	$C_{pyridyl}$-Zr-$N_{pyridyl}$
IV-15	2.222	2.520(4)	2.511(4)	2.208(4)	2.273(3)	1.713(7)	1.326(5)	127.1	34.4(1)
IV-17	2.242	2.538(4)	2.512(4)	2.252(5)	2.195(4)	1.738(7)	1.327(6)	130.1	34.7(2)
IV-18	2.230	2.529(4)	2.505(6)	2.271(6)	2.191(4)	1.720(9)	1.292(8)	127.9	33.6(2)
IV-19	2.229	2.528(3)	2.495(3)		2.125(3)	1.723(4)		125.5	88.9(1)[c]
IV-20	2.239	2.532(3)	2.522(3)	2.267(3)	2.200(2)	1.699(4)	1.330(3)	128.1	34.6(1)
IV-21a	2.236	2.531(12)	2.512(16)	2.221(10)	2.306(9)	1.67(2)	1.325(16)	127.4	34.0(4)
IV-23	2.241	2.532(7)	2.529(6)	2.302(6)[b]	2.402(6)	1.711(8)	1.340(8)	128.1	56.9(2)

[a] Cent = the centroid of Cp ring. [b] Zr-C_{vinyl}, [c] C_{cage}-Zr-$N_{pyridyl}$

The molecular structures of complexes of **IV-15**, **IV-17 – IV-20**, **IV-21a**, **IV-23** and **IV-26** were further confirmed by single–crystal analyses and shown in Figures 4.24 – 4.31, respectively. The selected bond lengths and angles were summarized in Table 4.7. The Zr-C_{cage} lengths fall in the range 2.495(3) to 2.529(6) Å which are slightly longer than the corresponding values found in Zr-carboranyl complexes[34f,g,51a,118] The average Zr to the Cp ring distances are about 2.53 Å that is comparable to the corresponding values found in the zirconocene carboranyl complexes such as **IV-11a,c,d**, **IV-13a,c,d,f-m**. The Zr-N(pyridinyl) distances vary from 2.125(3) to 2.402(6) Å. Such a large derivation can be ascribed to the steric effects of the pyridine unit.

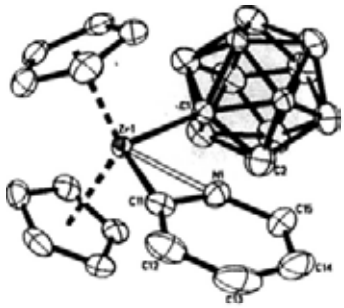


Figure 4.24. Molecular Structure of $Cp_2Zr[\eta^2(C,N)$-pyridine$](\sigma$-1,2-$C_2B_{10}H_{11})$ **(IV-15)**.

Figure 4.25. Molecular Structure of $Cp_2Zr(\eta^2$-1,6(N,C)-(2,4-dimethylpyridine) (σ-1,2-$C_2B_{10}H_{11}$) **(IV-17)**.

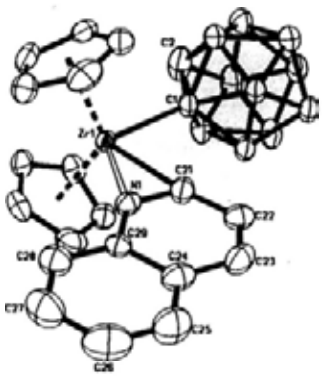


Figure 4.26. Molecular Structure of $Cp_2Zr(\eta^2$-1,2(N,C)-quinoline)(σ-1,2-$C_2B_{10}H_{11}$) **(IV-18)**.

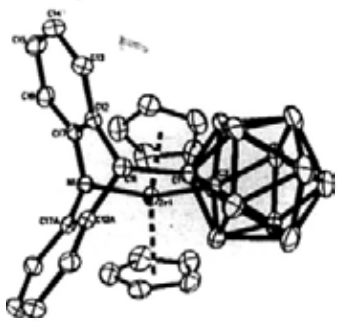


Figure 4.27. Molecular Structure of Cp_2Zr{2-[9-(η^1-10(N)-dihydroacridine)](σ-1,2-$C_2B_{10}H_{10}$)} **(IV-19)**.

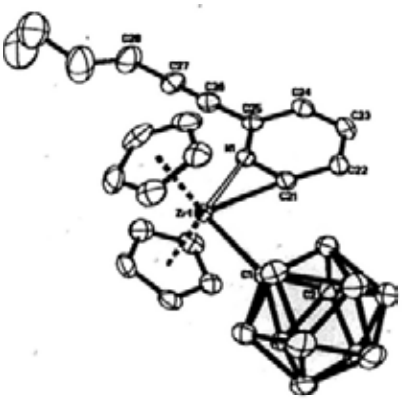


Figure 4.28. Molecular Structure of $Cp_2Zr\{\eta^2$-1,6-[2-(1-^{n}BuC≡C)pyridine]$\}(\sigma$-1,2-$C_2B_{10}H_{11})$ **(IV-20)**.

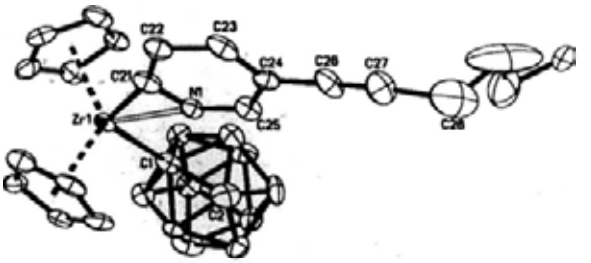


Figure 4.29. Molecular Structure of $Cp_2Zr\{\eta^2$-1,6(N,C)-[3-(1-^{n}BuC≡C)pyridine]$\}(\sigma$-1,2-$C_2B_{10}H_{11})$ **(IV-21a)**.

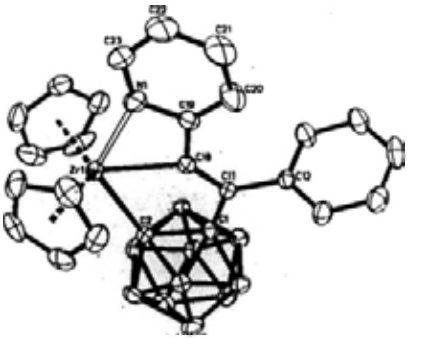


Figure 4.30. Molecular Structure of 1,2-[Cp_2ZrC(2-pyridyl)=CPh]-1,2-$C_2B_{10}H_{10}$ **(IV-23)**.

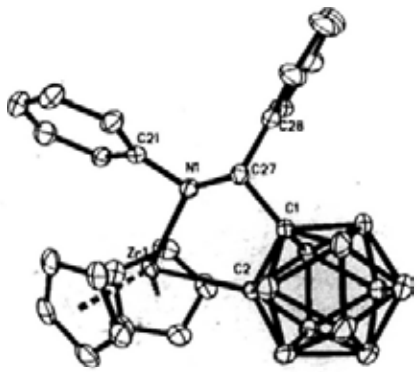


Figure 4.31. Molecular structure of 1,2-[$Cp_2ZrN(Ph)CH(Ph)$]-1,2-$C_2B_{10}H_{10}$ (**IV-26**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.687(4), C(1)-C(27) 1.537(4), C(27)-N(1) 1.455(3), Zr(1)-C(2) 2.443(3), Zr(1)-N(1) 2.154(2), C(2)-Zr(1)-N(1) 71.6(1).

In complex **IV-26** the metal center is η^5-bonded to two Cp rings, and σ-bonded to one cage carbon atom and one nitrogen atom, in a distorted-tetrahedral geometry. The Zr-C(cage)/Zr-N(1) distances of 2.443(3)/2.154(2) Å are comparable to those found in **II-6a,b,e,g,h**, **III-1 – III-3** and **III-5 – III-10**.

4.5. Summary

Reactivities of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**) toward alkenes, alkynes and pyridines have been studied. Terminal alkenes, internal alkynes and imine PhCH=NPh can insert into the Zr-C(cage) bond via the intermediate of zirconocene-carboryne to form zirconacyclopentane, zirconacyclopentene and azazirconacyclopentane complexes incorporating a carboranyl unit in good to high yields. Interaction of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ with pyridine derivatives

affords another kind of zirconocene-carboranyl complexes via α-C-H activation of pyridine unit.

An efficient and practical method was developed to prepare a new class of zirconacyclopentanes/zirconacyclopentenes incorporating a carboranyl unit from the reaction of zirconocene-carboryne precursor **I-153** with alkenes/alkynes. The reaction can tolerate many functional groups such as vinyl, chloro, amido, alkoxyl, tetrahydro-2-pyranyl, diphenylphosphinyl and trifluoromethyl. The resultant zirconacycles are potential intermediates which can be converted to a variety of functionalized carboranes as evidenced by our preliminary results.[100]

Chapter 5. Reactivity of Zirconacyclopentenes Incorporating a Carborane Unit

5.1. Background

Transition metal-mediated C-C coupling reactions, as a powerful strategy constructing useful molecules, have found many applications in organic synthesis, mechanistic studies and the synthesis of functional materials[112,126] It has been documented that zirconacyclopentadienes are suitable starting materials to realize selective cyclotrimerization of three different alkynes to form benzene derivatives.[127] For examples, the one-pot formation of benzene derivatives from three different alkynes in high yields (83-95%) with excellent selectivities is reported through copper-mediated cycloaddition reaction via zirconacyclopentadienes as the intermediates.[127a] The critical limitation of this method is that at least one electron-withdrawing group is required for the third alkyne. Subsequently, a more general method using nickel promoted three-component coupling reactions is developed.[127b] In view of the similarities between zirconacyclopentadiene and zirconacyclopentene bearing a carborane unit, we wondered if the three-component reaction of carboryne with two different alkynes can be achieved using the similar approaches mentioned above. This chapter describes our findings.

5.2. Nickel-Mediated Cycloaddition with Different Alkynes

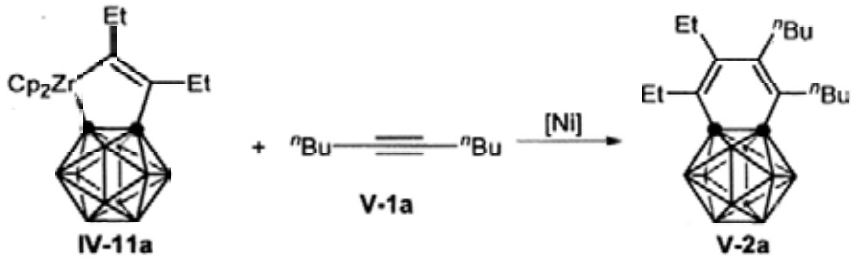
Complex 1,2-[$Cp_2ZrC(Et)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ **(IV-11a)** does not react with alkynes even under forced conditions.[100a] On the other hand, the nickel analogue

1,2-[$(Ph_3P)_2NiC(Et)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ is believed to be active intermediate for the formation of benzocarborane 1,2-[C(Et)=C(Et)-C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ in the reaction of $(Ph_3P)_2Ni(\eta^2$-1,2-$C_2B_{10}H_{10})$ with 2 equiv of EtC≡CEt.[86b] In this connection, it is rational to suggest that transmetallation of **IV-11a** to Ni may lead to an active Ni analogue which could mediate C-C coupling reactions.

We examined the reaction of **VI-11a** with $^nBuC{\equiv}CBu^n$ (**V-1a**) in the presence of Ni(II) species in different solvents. The results were summarized in Table 5.1. Almost no reaction proceeded in the presence of $NiCl_2$. However, addition of 2 equiv of PPh_3 resulted in the formation of the desired benzocarborane 1,2-[C(Et)=C(Et)-C(Bu^n)=C(Bu^n)]-1,2-$C_2B_{10}H_{10}$ (**V-2a**). In general, all $NiCl_2$(phosphines)$_2$ can mediate the C-C coupling reactions. Toluene is much better solvent than THF and DME. Temperature also plays an important role. The best condition is found in entry 7, offering the product **V-2a** in 89% GC yield.

Subsequently, a series of zirconacyclopentenes and alkynes were studied using the above optimum condition. In a typical procedure, a mixture of zirconacyclopentene **(IV-11/13)** (0.20 mmol), alkynes **(V-1)** (0.70 mmol) and $NiCl_2(PMe_3)_2$ (0.21 mmol) in 10 mL of toluene in a closed vessel was heated at 110 °C for 48 h. After removal of the solvent, the products benzocarborane **(V-2)** were isolated by flash column chromatography on silica gel using hexane as eluent. An excess amount of alkynes is necessary in this reaction since some are cyclotrimerized to form substituted benzenes as catalyzed by the formed Ni(0) species.

Table 5.1. Optimization of Reaction Conditions. [a]



entry	T/°C	Solvent	[Ni]	**IV-11a/ V-1a**	time/h	yield/%[b]
1	110	Toluene	$NiCl_2$	1/3.5	72	0
2	110	THF	$NiCl_2$	1/3.5	72	6
3	110	THF	$NiCl_2/2PPh_3$	1/3.5	72	85
4	110	THF	$NiCl_2(PMe_3)_2$	1/3.5	72	42
5	110	DME	$NiCl_2(PMe_3)_2$	1/3.5	72	48
6	90	Toluene	$NiCl_2(PMe_3)_2$	1/3.5	48	37
7	110	Toluene	$NiCl_2(PMe_3)_2$	1/3.5	48	89
8	110	Toluene	$NiCl_2$(dppe)	1/3.5	48	88
9	110	Toluene	$NiCl_2$(dppp)	1/3.5	48	78
10	110	Toluene	$NiCl_2(PPh_3)_2$	1/3.5	48	68
11	110	Toluene	$NiCl_2(PMe_3)_2$	1/3.5	36	82
12	110	Toluene	$NiCl_2(PMe_3)_2$	1/2.0	48	86

[a] Reaction conditions: 0.02 mmol of **IV-11a** and excess alkyne **V-1a** along with 0.02 mmol of [Ni] in 0.6 mL of toluene in a closed vessel. After the reaction was complete, the mixture was treated with H_3O^+ and determined by GC-MS. [b] GC yield.

As shown in Table 5.2, the following general trends can be drawn. Symmetrical alkynes offer very high yields of cycloaddition products **V-2** except for $MeO_2CC{\equiv}CCO_2Me$ (**V-1e**, entry 5). Alkynes containing functional groups such as

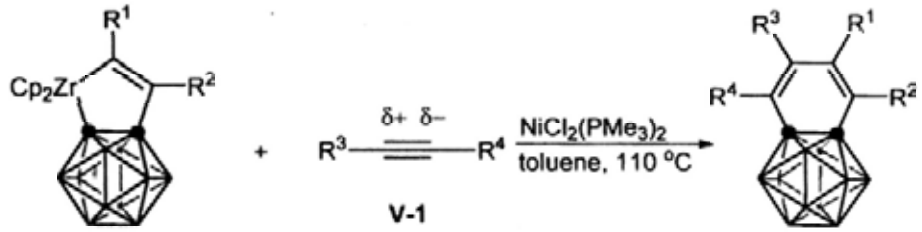
V-1m–p, V-1f give low yields probably due to the coordination of heteroatom to Ni to prevent the coordination of C≡C unit (entries 6, 13–16). Unsymmetrical alkynes produce two isomers and their ratios are largely affected by steric/electronic factors. In general only the major isomers are isolated for polar alkynes which are consistent with the polarity of Ph-C≡C-R (entries 7-9, 14-16, and 22). Very sterically demanding alkynes such as Me_3Si-C≡C-$SiMe_3$ do not react with **IV-11/13**. Terminal alkynes can protonate **IV-11/13** to give 1-[CHR^1=CR^2]-1,2-$C_2B_{10}H_{11}$. The reaction with allene is very complicated.

It is noted that these benzocarboranes can also be prepared in similar yields from one-pot reaction of **I-153** with alkyne, followed by treatment with another type of alkyne in the presence of $NiCl_2(PMe_3)_2$. Thus three-component-coupling of carboryne with two different alkynes can be realized in one pot reactions.

The ^{11}B NMR spectra of benzocarboranes show a 2:5 pattern in a range -6.7 ppm to -13.4 ppm. The characteristic carbons of conjugated diene units and the cage-carbons were all observed at about 130 ppm and 77 ppm, respectively, in their ^{13}C NMR spectra, which are very close to those in the reported benzocarborane derivatives.[86b] The ^{13}C NMR chemical shifts of the cage carbons in benzocarboranes fall in between *o*-carborane[129] and metal–carboryne.[100]

The molecular structures of **V-2j, V-2o, V-2p** and **V-2u** are shown in Figures 5.1 – 5.4. The selected bond lengths and angles are summarized in Table 5.6. It can be seen that these benzocarboranes have a common six-membered ring with the bond

Table 5.2. Synthesis of Substituted Benzocarboranes Mediated by $NiCl_2(PMe_3)_2$.[a]



IV-11/13 V-1 V-2

entry	IV-11/13	R^1/R^2	V-1	R^3/R^4	product V-2	isolated yield/%
1	**IV-11a**	Et/Et	**V-1a**	^{n}Bu/^{n}Bu	**V-2a**	84
2	**IV-11a**	Et/Et	**V-1b**	^{n}Pr/^{n}Pr	**V-2b**	81
3	**IV-11a**	Et/Et	**V-1c**	Et/Et	**V-2c**	78
4	**IV-11a**	Et/Et	**V-1d**	Ph/Ph	**V-2d**	30(70)[b]
5	**IV-11a**	Et/Et	**V-1e**	CO_2Me/CO_2Me	**V-2e**	--[c]
6	**IV-11a**	Et/Et	**V-1f**	^{n}Bu/PPh_2	**V-2f**	--[c]
7	**IV-11a**	Et/Et	**V-1g**	Me/Ph	**V-2g**	76
8	**IV-11a**	Et/Et	**V-1h**	Et/Ph	**V-2h**	81
9	**IV-11a**	Et/Et	**V-1i**	^{n}Bu/Ph	**V-2i**	83
10	**IV-11a**	Et/Et	**V-1j**	^{n}Bu/Bu^t	**V-2j**	71(83/17)[d]
11	**IV-11a**	Et/Et	**V-1k**	Me/Pr^i	**V-2k**	67(81/19)[d]
12	**IV-11a**	Et/Et	**V-1l**	Me/Et	**V-2l**	33(57/43)[d]
13	**IV-11a**	Et/Et	**V-1m**	$CH_3C{\equiv}C(CH_2)_4/Me$	**V-2m**	29(66/34)[d]
14	**IV-11a**	Et/Et	**V-1n**	$(Me)_2NCH_2/Ph$	**V-2n**	21
15	**IV-11a**	Et/Et	**V-1o**	$MeOCH_2/Ph$	**V-2o**	31
16	**IV-11a**	Et/Et	**V-1p**	$(CH{=}CH_2)CH_2/Ph$	**V-2p**	35(74)[e]
17	**IV-11d**	Ph/Ph	**V-1c**	Et/Et	**V-2d**	81
18	**IV-11d**	Ph/Ph	**V-1a**	^{n}Bu/^{n}Bu	**V-2q**	83
19	**IV-13a**	Ph/Me	**V-1a**	^{n}Bu/^{n}Bu	**V-2r**	85
20	**IV-13c**	Ph/^{n}Bu	**V-1a**	^{n}Bu/^{n}Bu	**V-2s**	81

Table 5.2. Continued

21	**IV-13c**	Ph/^{n}Bu	**V-1c**	Et/Et	**V-2t**	80
22	**IV-13c**	Ph/^{n}Bu	**V-1f**	Me/Ph	**V-2u**	36(73)[b]
23	**IV-13j**	Ph/$(CH_2)_3Cl$	**V-1c**	Et/Et	**V-2v**	77

[a] Reaction conditions: 0.20 mmol of **IV-11/13**, 0.70 mmol of alkyne **V-1**, 0.21 mmol of $NiCl_2(PMe_3)_2$ in 10 mL of toluene, 110 ℃, 48h. After removal of the solvent, the product was isolated by flash column chromatography on silica gel using hexane as eluent. [b] The yield in the parentheses was obtained by extending reaction time to 5 days. [c] No product was observed. [d] A mixture of two isomers. They can not be separated by column chromatography. Their molar ratio was measured by GC-MS analyses. After crystallization, only **V-2j** is isolated in 31% yield. [e] The yield in the parentheses was obtained using 2 equiv of $NiCl_2(PMe_3)_2$ and 1.5 equiv of alkyne in the reaction.

lengths of ca 1.65, 1.49, 1.34, 1.47, 1.35, 1.49 Å and the internal bond angels of ca 116, 121, 123, 123, 121, 116°. They have alternative long and short C-C bonds forming a six-membered plane.

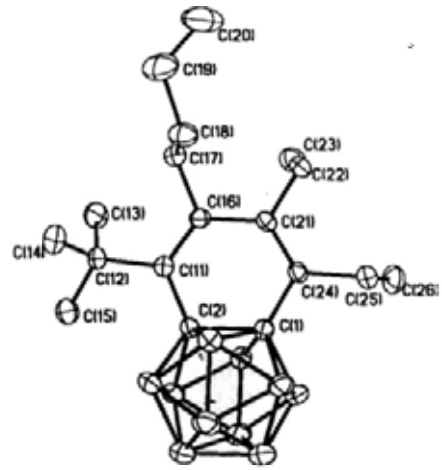


Figure 5.1. Molecular Structure of 1,2-[(^{t}Bu)C=C(^{n}Bu)-C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ **(V-2j)**.

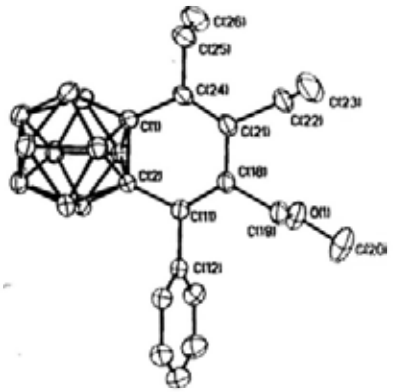


Figure 5.2. Molecular Structure of 1,2-[(Ph)C=C(CH_2OMe)-C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**V-2o**).

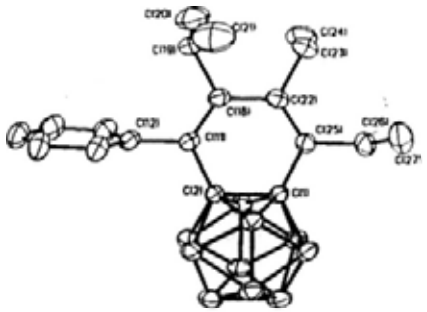


Figure 5.3. Molecular Structure of 1,2-[(Ph)C=C(CH_2-CH=CH_2)-C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**V-2p**).

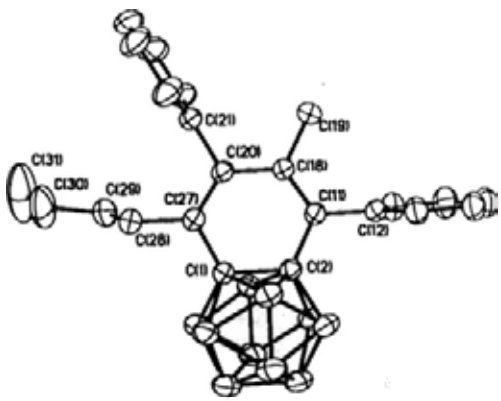
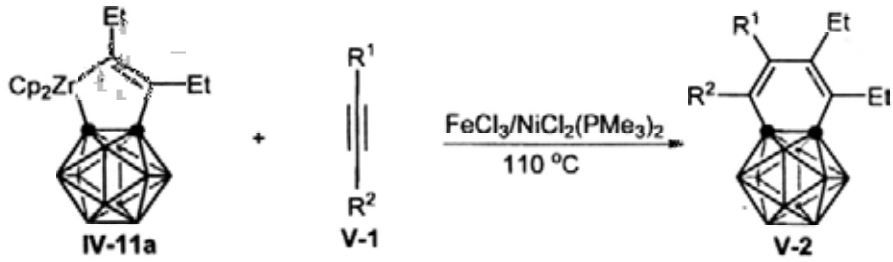


Figure 5.4. Molecular Structure of 1,2-[(Ph)C=C(Me)-C(Ph)=C(Bu^n)]-1,2-$C_2B_{10}H_{10}$ (**V-2u**).

5.3. Nickel/Iron-Mediated Cycloaddition

In the Ni-mediated cycloaddition reactions discussed above, the end product is Ni metal. We thought that Ni(0) should be able to be oxidized to Ni(II) by $FeCl_3$ according to their redox potentials. With this in mind, various reaction conditions were examined and the results were summarized in Table 5.3. It is suggested that the poor solubility of $FeCl_3$ in toluene led to the low yields of benzocarboranes in pure toluene (entries 2-4). Addition of THF can significantly improve the yields in the presence of 15mol% of $NiCl_2(PMe_3)_2$ and 3 equiv of $FeCl_3$ (entries 5 and 6). Almost the same yield is achieved if the amount of $NiCl_2(PMe_3)_2$ is reduced to 10mol% (entry 7). However, the yields is decreased if the amount of $NiCl_2(PMe_3)_2$ is further reduced to 5mol% (entry 8). The best reaction conditions are $FeCl_3$/$NiCl_2(PMe_3)_2$/**IV-11a**/**V-1** = 3/0.1/1/3.5 in a mixed solvent of toluene/THF (2/1 in v/v) at 110 ℃. Under such a condition, both DMAD and PhC≡CTMS give products **V-2e** and **V-2u** in the yields of 41% and 42%, respectively (entries 14 and 17). In sharp contrast, no cycloaddition products are observed if DMAD and PhC≡C(TMS) were used as substrates in the presence of 1 equiv of $NiCl_2(PMe_3)_2$ probably due to the trimerization of alkynes. On the other hand, two isomers are obtained if PhC≡CMe (**V-1g**) or PhC≡CEt (**V-1g**) is used as the reactant (entries 15 and 16). The yield of **V-2d** is largely improved to 87% (entry 12) from 30% (Table 5.2, entry 4) which is obtained using 1 equiv of $NiCl_2(PMe_3)_2$.

Table 5.3. $FeCl_3$ Promoted Ni(II) Catalyzed Cycloaddition Reactions.[a]



entry	V-1/ IV-11a	R^1/R^2	$FeCl_3$/Ni(II) /IV-11a	time/h	toluene/ THF (v/v)	yield (%)[b]
1	3.5	^{n}Bu/^{n}Bu	0/1/1	48	toluene	89
2	3.5	^{n}Bu/^{n}Bu	$FeCl_3$	96	toluene	0
3	3.5	^{n}Bu/^{n}Bu	3/0.15/1	96	toluene	39
4	3.5	^{n}Bu/^{n}Bu	0/0.15/1	96	toluene	12
5	3.5	^{n}Bu/^{n}Bu	3/0.15/1	48	THF	87
6	3.5	^{n}Bu/^{n}Bu	3/0.15/1	48	2	87
7	3.5	^{n}Bu/^{n}Bu	3/0.10/1	48	2	85
8	3.5	^{n}Bu/^{n}Bu	3/0.05/1	48	2	74
9	2	^{n}Bu/^{n}Bu	3/0.10/1	48	2	59
10	3.5	^{n}Bu/^{n}Bu	2/0.10/1	48	2	85
11	3.5	^{n}Bu/^{n}Bu	1/0.10/1	48	2	82
12	3.5	Ph/Ph	3/0.10/1	48	2	87
13	3.5	^{n}Pr/Pr^n	3/0.10/1	48	2	44
14	3.5	MeO_2C/CO_2Me	3/0.10/1	48	2	41
15	3.5	Me/Ph	3/0.10/1	48	2	65(76/24)[c]
16	3.5	Et/Ph	3/0.10/1	48	2	82(73/27)[c]
17	3.5	Ph/TMS	3/0.10/1	48	2	42
18	3.5	Ph/H	3/0.10/1	48	2	-

[a] General reaction conditions: 0.02 mmol of **IV-11a**, **V-1**, $FeCl_3$ and $NiCl_2(PMe_3)_2$ in 1.0 mL of mixed toluene and THF (2/1 in v/v) in a closed vessel. After the reaction was complete, the mixture was treated with H_3O^+ and determined by GC-MS. [b] GC yield. [c] the ratio of two isomers.

5.4. $FeCl_3$-Mediated Cycloaddition with Alkynes

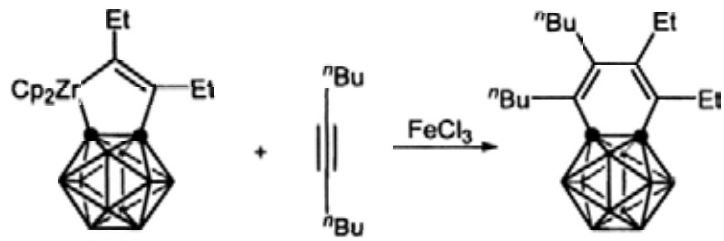
During the course of previous studies we discovered that $FeCl_3$ alone can also mediate the cycloaddition reactions in toluene/THF solvent. The results were summarized in Table 5.4.

No reaction was observed in pure toluene whereas benzocarborane was produced in 24% yield in THF (entries 1 and 2). As shown in Table 5.4, at least 2 equiv of $FeCl_3$ was required for the reaction. The amount of alkynes has little effect on the yields of the products since no trimerization of alkynes is detected. A large excess amount of $FeCl_3$ (3 equiv) does not improve the yield (entry 11). Prolonged heating can slightly improve the yield (entry12). Shortening the reaction time and lowering reaction temperatures dramatically decrease the yields (entries 13 and 14).

Under the above optimized reaction conditions, various alkynes were examined. The results were summarized in Table 5.5. Typical reaction procedures are as follows. In the presence of 2 equiv of $FeCl_3$ in a mixture solvent of toluene and THF with the ratio of 2/1 (v/v), a mixture of zirconacyclopentene and alkyne (1/2, mol/mol) was heated to 110 ℃ for 48 h. The product was determined by GC-MS and isolated by column chromatography on silica gel after standard workup. For the symmetrical alkynes, benzocarboranes were obtained in moderate yields (entries 1-5). It is clear that iron complex is less reactive than the nickel one, leading to lower yields in general. The desired benzocarborane was obtained from DMAD using $FeCl_3$ as mediator (entry 5). Only alkyne cyclotrimerization product was observed if an

equivmolar amount of $NiCl_2(PMe_3)_2$ was used. Reaction with $PhC{\equiv}CCH_2OCH_3$ gave the corresponding benzocarborane in low yield (entry 6). Reaction with unsymmetrical alkynes offered two regioisomers (entries 7-9). Regioselectivity is controlled by the polarity of alkynes and the steric hindrance of the substituent.

Table 5.4. Optimization of $FeCl_3$-Promoted Cycloaddition Reactions. [a]

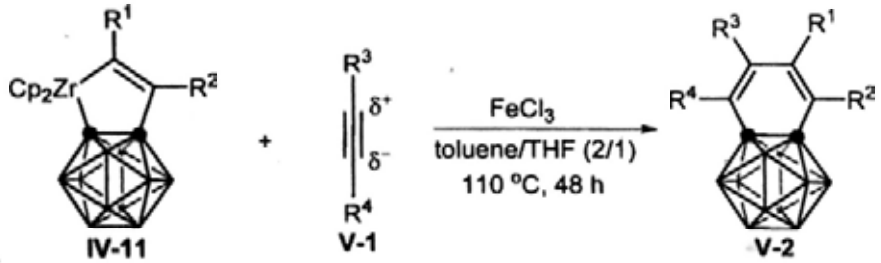


IV-11a **V-1a** **V-2a**

entry	**V-1a/ IV-11a**	$FeCl_3$/ **IV-11a**	time/h	toluene/ THF	temperature/ ℃	yield/%[b]
1	2	2	72	toluene	110	0
2	2	2	48	THF	110	24
3	2	2	48	2	110	78
4	2	2	48	1	110	73
5	2	2	48	10	110	37
6	1.5	2	48	2	110	78
7	3	2	48	2	110	76
8	2	1.5	48	2	110	39
9	2	1	48	2	110	31
10	2	2/3	48	2	110	18
11	2	3	48	2	110	76
12	2	2	72	2	110	80
13	2	2	24	2	110	38
14	2	2	48	2	90	12

[a] Reaction conditions: 0.02 mmol of **IV-11a** and alkyne **V-1a** along with $FeCl_3$ in 0.6 mL of solvent in a closed vessel were heated. After the reaction was complete, the mixture was treated with H_3O^+ and determined by GC-MS. [b] GC yield.

Table 5.5. $FeCl_3$ Promoted Cycloaddition Reactions. [a]



Entry	IV-11	R^1/R^2	V-1	R^3/R^4	product V-2	isolated yield/%[b]
1	**IV-11a**	Et/Et	**V-1a**	^{n}Bu/^{n}Bu	**V-2a**	47(78)
2	**IV-11a**	Et/Et	**V-1b**	^{n}Pr/^{n}Pr	**V-2b**	39(66)
3	**IV-11a**	Et/Et	**V-1c**	Et/Et	**V-2c**	30(60)
4	**IV-11a**	Et/Et	**V-1d**	Ph/Ph	**V-2d**	43(66)
5	**IV-11a**	Et/Et	**V-1e**	CO_2Me/CO_2Me	**V-2e**	20(40)
6	**IV-11a**	Et/Et	**V-1o**	$MeOCH_2$/Ph	**V-2o**	(15)
7	**IV-11a**	Et/Et	**V-1j**	Me/Pr^i	**V-2k**	34(54)[c]
8	**IV-11a**	Et/Et	**V-1k**	Me/Et	**V-2l**	45(74)[c]
9	**IV-11a**	Et/Et	**V-1p**	Ph/Et	**V-2h'**	41(75)[d]
10	**IV-11a**	Et/Et	**V-1q**	^{n}Bu/TMS	**V-2w**	53(74)
11	**IV-11a**	Et/Et	**V-1r**	Ph/TMS	**V-2x**	59(82)
12	**IV-11b**	^{n}Pr/^{n}Pr	**V-1b**	^{n}Pr/^{n}Pr	**V-2y**	44(71)
13	**IV-11a**	Et/Et	**V-1s**	Ph/H	**none**	-[e]
14	**IV-11a**	Et/Et	**V-1f**	Ph_2P/Bu^n	**none**	-[e]

[a] Reaction conditions: 0.20 mmol of **IV-12**, 0.40 mmol **V-1**, and 0.40 mmol of $FeCl_3$ in 10 mL of mixed solvent of toluene/THF (2/1 in v/v) in a closed vessel at 110 ℃ for 48h. After removal of the solvent, the products **V-2** were isolated by flash column chromatography on silica gel. [b] The yields in the parentheses were obtained by GC-MS. [c] Two isomers were obtained in a ratio of 66/34 and 52/48 for entries 7 and 8, respectively. [d] **V-2h'** as major product was observed by GC-MS. [e] No products were obtained.

The molecular structures of **V-2w** and **V-2x** are shown in Figures 5.5 and 5.6, respectively. Selected bond lengths and angles are summarized in Table 5.6, which are similar to those observed in other benzocarboranes.

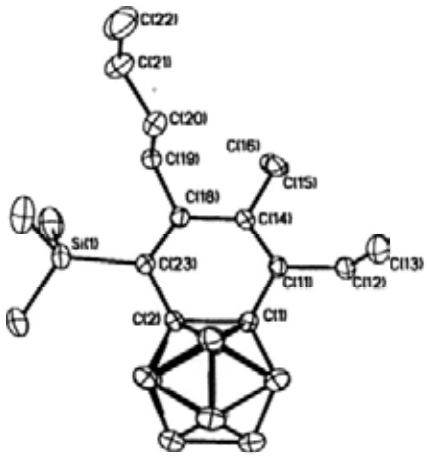


Figure 5.5. Molecular Structure of 1,2-[(TMS)C=C(^{n}Bu)-C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ **(V-2w)**.

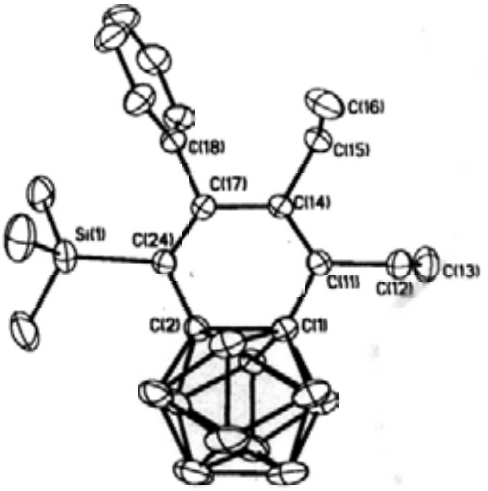


Figure 5.6. Molecular Structure of 1,2-[(TMS)C=C(Ph)-C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ **(V-2x)**.

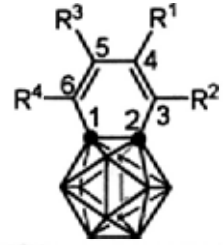
In summary, we have developed an efficient method for preparation of various benzocarborane derivatives with different substituents by [2+2+2] protocol. Both electronic and steric factors play an important role in the formation of the regioselective benzocarboranes.

5.5. Reaction Mechanism

An early attempt to prepare nickelacyclopentene from the reaction of **IV-11a** with $NiCl_2(PMe_3)_2$ failed. We found, however, that a new product 1-[CH(CH=CH_2)=C(Et)]-1,2-$C_2B_{10}H_{11}$ (**V-3**) was formed in this reaction. A possible pathway for the formation of **V-3** was proposed and depicted in Scheme 5.1. After transmetallation, the resultant nickelacyclopentene complex (**V-A**) undergoes β–H elimination to give **V-B** which is isomerized to form the intermediate **V-C**. Reductive elimination affords the product **V-3**. This reaction offers a strong evidence for the transmetallation to Ni(II).

To avoid the β–H elimination and stabilize the intermediate, complex **IV-11d** and $NiCl_2$(dppe) were used as reactant. Nickelacyclopentene complex 1,2-[(dppe)NiC(Ph)=C(Ph)]-1,2-$C_2B_{10}H_{10}$ (**V-4**) was isolated as light brown crystals in 69% yield by reaction of **IV-11d** with $NiCl_2$(dppe) in toluene at reflux for 24 h. (Scheme 5.2).

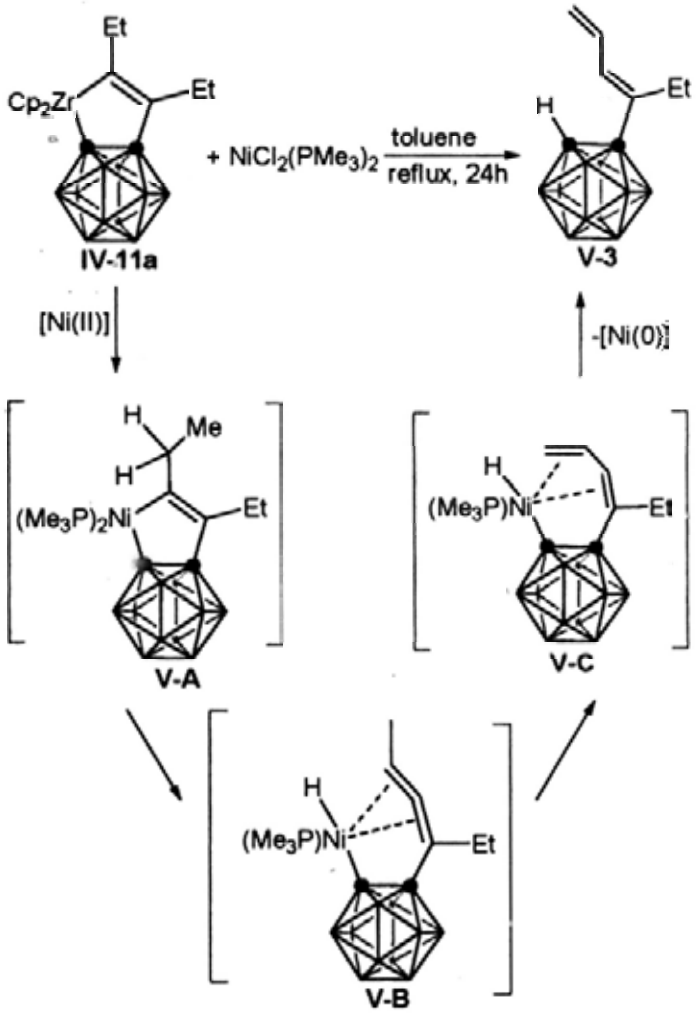
Table 5.6. Selected Bond Lengths (Å) and Angles (deg.)



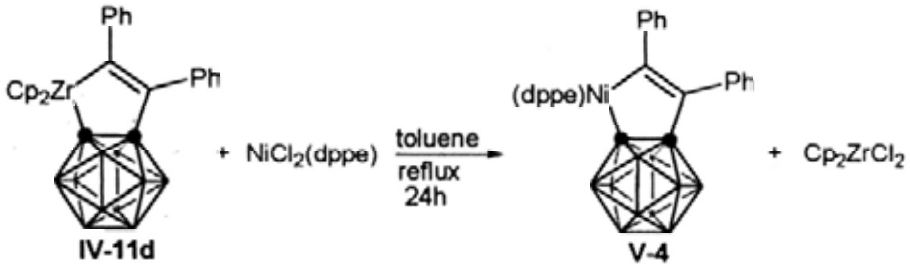
	V-2j	V-2o	V-2p	V-2u	V-2w	V-2x
C(1)-C(2)	1.673(3)	1.646(3)	1.636(2)	1.640(4)	1.659(4)	1.671(3)
C(2)-C(3)	1.485(5)	1.498(3)	1.484(2)	1.488(3)	1.473(4)	1474(3)
C(3)-C(4)	1.341(4)	1.344(3)	1.345(2)	1.344(4)	1.343(6)	1.342(3)
C(4)-C(5)	1.476(3)	1.470(3)	1.473(3)	1.476(4)	1.482(4)	1.487(3)
C(5)-C(6)	1.366(5)	1.348(3)	1.347(3)	1.343(4)	1.359(4)	1.358(3)
C(6)-C(1)	1.520(4)	1.489(2)	1.486(2)	1.494(3)	1.489(6)	1.493(3)
C(1)-C(2)-C(3)	116.6(2)	115.6(2)	116.6(1)	116.3(2)	116.4(3)	116.5(2)
C(2)-C(3)-C(4)	119.4(3)	120.8(2)	120.7(2)	120.4(2)	120.3(3)	120.4(2)
C(3)-C(4)-C(5)	123.6(3)	123.2(2)	122.9(2)	123.8(2)	123.5(3)	122.6(2)
C(4)-C(5)-C(6)	123.9(3)	123.4(2)	123.1(2)	122.8(2)	123.8(3)	125.7(2)
C(5)-C(6)-C(1)	117.2(3)	120.7(2)	121.1(2)	120.8(2)	118.9(3)	117.7(2)
C(6)-C(1)-C(2)	115.7(2)	116.0(2)	115.6(1)	115.9(2)	116.7(3)	116.8(2)

Complex **V-4** was fully characterized by NMR, IR spectra and elemental analysis. The characteristic vinyl carbons and cage carbons were observed at 164.5/147.3 ppm and 90.4/74.7 ppm, respectively, in its ^{13}C NMR spectrum. The characteristic phosphines were observed at -53.9 and 44.6 ppm in its ^{31}P NMR spectrum. Its IR spectrum exhibited the vibration frequencies of B-H and Ni-C=C at 2563 and 1595 cm^{-1}, respectively.

Scheme 5.1. Reaction of **IV-11a** with $NiCl_2(PMe_3)_2$



Scheme 5.2. Formation of Nickelacyclopentene Incorporating a Carboranyl Unit



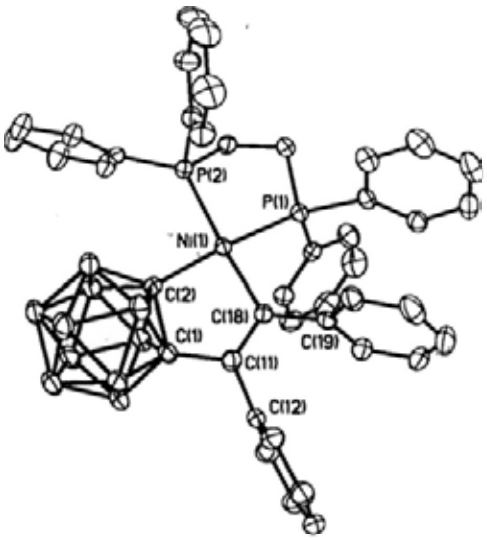


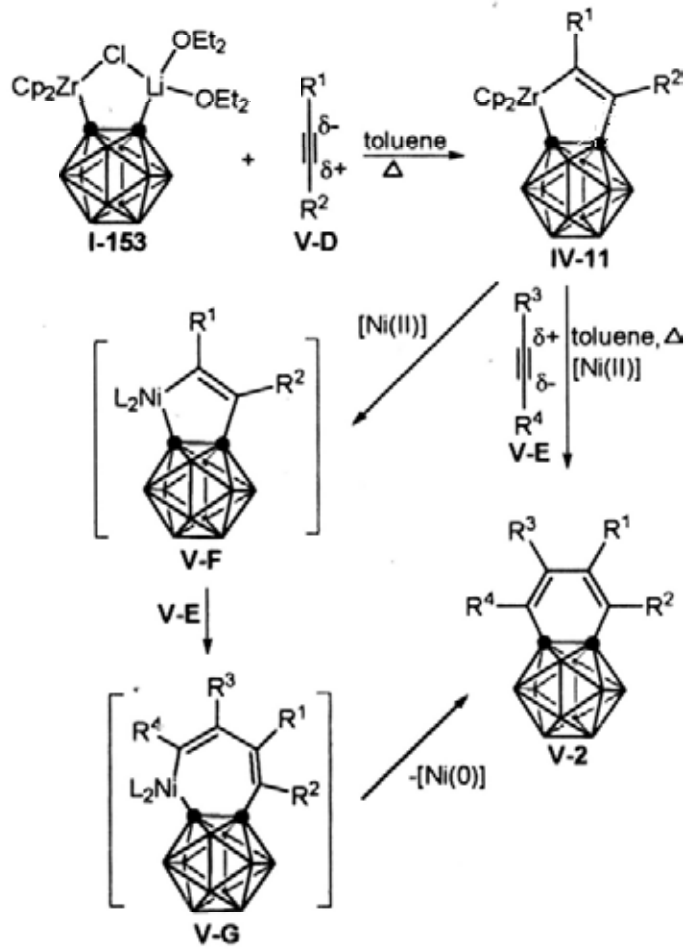
Figure 5.7. Molecular Structure of 1,2-[(dppe)NiC(Ph)=C(Ph)]-1,2-$C_2B_{10}H_{10}$ (**V-4**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.672(5), C(1)-C(11) 1.489(5), C(11)-C(18) 1.347(5), C(2)-Ni(1) 1.950(4), C(18)-Ni(1) 1.963(4), C(2)-Ni(1)-C(18) 86.4(1).

The molecular structure of **V-4** was further confirmed by single-crystal X-ray diffraction. Its molecular structure and essentially planar configuration about Ni atom is illustrated in Figure 5.7, whose structure shows one toluene of solvation. This further supports the previous hypothesis.[86b] The bond distances of Ni-C_{vinyl} and Ni-C_{cage} (1.963(4) Å and 1.950(4) Å) are close to the corresponding values of the Ni-C distances of 1.888(4) Å and 1.875(4) Å in $(Cy_3P)_2Ni(1,2\text{-}C_6H_4)$,[128] and the

1.884(5) Å and 1.966(5) Å in [{[2-CH_2CH(o-C_5H_4N)-1,2-$C_2B_{10}H_{10}$]Ni}$_3$(μ_3-Cl)][Li(DME)$_3$].[92b] Further reaction of **V-4** with "BuC≡CBu" gave the cycloaddition product **V-2q** in high yield (85%).

Based on these experimental results and those of earlier reports,[86b,92b] a possible mechanism is proposed as depicted in Scheme 5.3. Transmetallation of zirconacyclopentene to nickel gives a nickelacyclopentene intermediate (**V-F**), followed by the alkyne insertion to form **V-G**. Reductive elimination affords the final benzocarborane (**V-2**).

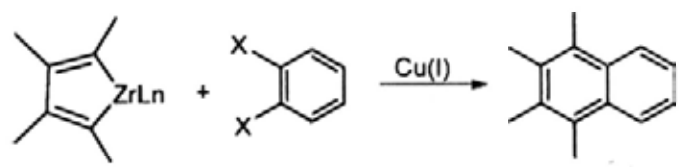
Scheme 5.3. Proposed Mechanism for the Formation of Benzocarborane



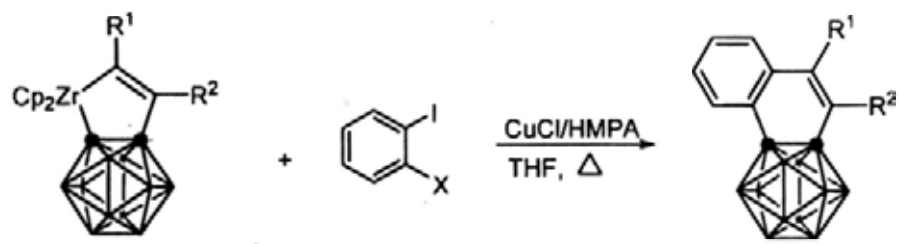
5.6. Copper-Mediated Coupling Reactions

Coupling reactions between sp^2 carbon centers such as alkenyl-aryl coupling reactions have been very attractive for organic synthesis since alkenylmetals can be readily prepared from alkynes.[130] There are several reports on the intermolecular coupling of metallacyclopentadienes with dihalo aromatic compounds to form fused aromatic rings (Scheme 5.4).[131, 132] Zirconacyclopentenes incorporating a carboranyl unit have been easily prepared from reaction of zirconocene-carboryne precursor with alkynes in high yields with high selectivities.[100] In this section we describe a copper-mediated intermolecular coupling of zirconacyclopentenes incorporating a carboranyl unit with dihalo aromatic rings to prepare fused naphthalocarboranyl derivatives.

Scheme 5.4. Preparation of Naphthalene via Metal-Mediated Coupling Reaction



Scheme 5.5. Preparation of Naphthalocarboranes



IV-11a $R^1 = R^2 = Et$
IV-11b $R^1 = R^2 = {}^nPr$
IV-13c $R^1 = Ph$, $R^2 = {}^nBu$

V-5a X = I,
V-5b X = Br,

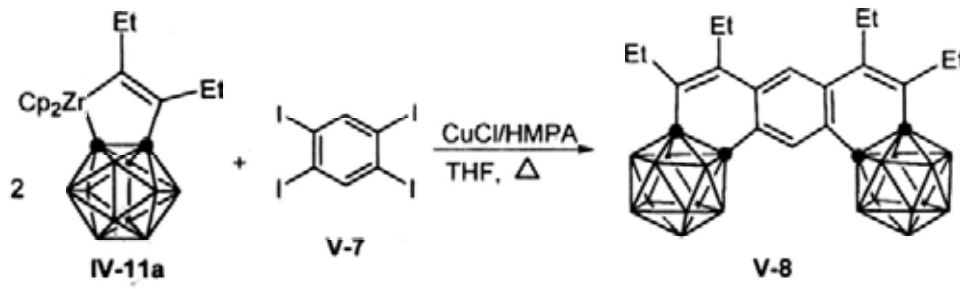
V-6a $R^1 = R^2 = Et$,
V-6b $R^1 = R^2 = {}^nPr$
V-6c $R^1 = Ph$, $R^2 = {}^nBu$

Treatment of **IV-11a,b** or **IV-13c** with one equiv *o*-diiodobenzene (**V-5a**) in the

presence of 2 equiv of CuCl and excessive HMPA in refluxing THF afforded the corresponding naphthalocarboranes $[(R^2)C{=}C(R^1)C_6H_4]$-1,2-$C_2B_{10}H_{10}$ (**V-6a**, R^1 = R^2 = Et; **V-6b**, R^1 = R^2 = ^{n}Pr; **V-6c**, R^1 = ^{n}Bu, R^2 = Ph) as colorless crystals in high yields. Under the same reaction conditions, reaction of **IV-11a** with *o*-bromoiodobenzene also gave the product **V-6a** in 83% yield (Scheme 5.5).

In a similar manner, interaction of **IV-11a** with 1,2,4,5-tetraiodobenzene (**V-7**) yielded two carborane cages fused anthracene $[(Et)C{=}C(Et)C_6H_2(Et)C{=}C(Et)]$-$(1,2\text{-}C_2B_{10}H_{10})_2$ (**V-8**) (Scheme 5.6).

Scheme 5.6. Preparation of Carborane Cage Fused Anthracene



Compounds **V-6a** – **c** and **V-8** were fully characterized by ^{1}H, ^{13}C, ^{11}B NMR spectra and HRMS. The characteristic cage carbons were observed in a range of 71.4 to 75.1 ppm in their ^{13}C NMR spectra. **V-6a** – **c** displayed a pattern of 2:2:6 at about -6.5, 9.0 and 11.4 ppm in their ^{11}B NMR spectra while **V-8** exhibited a 3:2:5 pattern.

Compounds **V-6a** and **V-8** were further confirmed by single-crystal X-ray analyses. Their molecular structures are shown in Figures 5.8 and 5.9. Selected bond lengths and angles are summarized in Table 5.7. They have a common six-membered ring fused with the cage. The sum of the six interior angles is very close to 720°. There are alternative long and short bond lengths of the ring resulted from the conjugated diene unit of C(3)C(4)C(5)C(6).

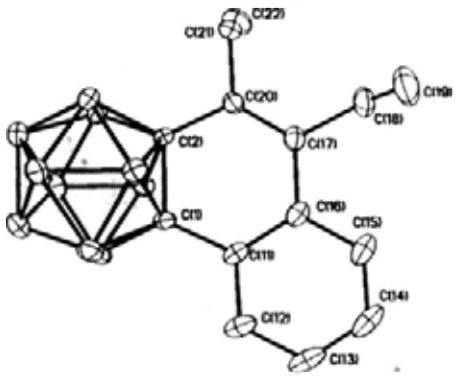


Figure 5.8. Molecular Structure of 1,2-[(Et)C=C(Et)C_6H_4]-1,2-$C_2B_{10}H_{10}$ (**V-6a**).

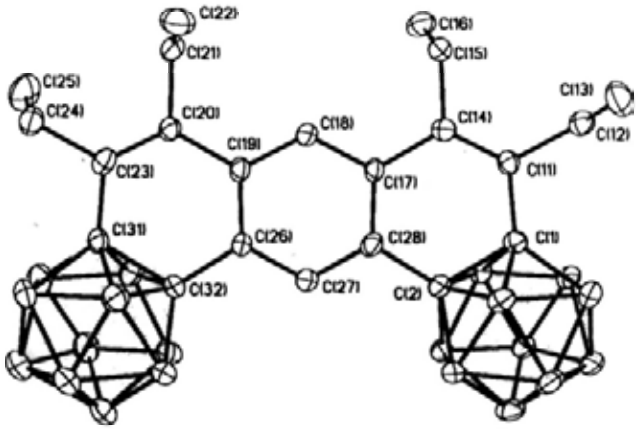
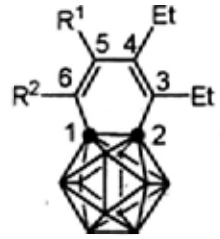


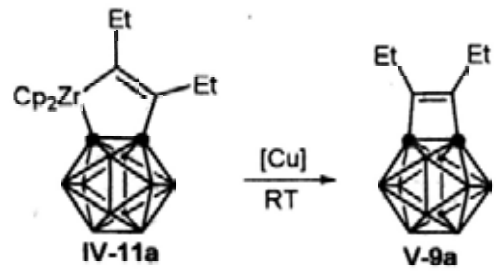
Figure 5.9. Molecular Structure of 1,2-[(Et)C=C(Et)C_6H_2(Et)C=C(Et)]-(1,2-$C_2B_{10}H_{10}$)$_2$ (**V-8**).

Table 5.7. Selected Bond Lengths and Angles for Naphthalocarborane Derivatives **V-7a** and **V-8**.



	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	C(4)-C(5)	C(5)-C(6)	C(6)-C(1)	C(1)-C(2)-C(3)	C(2)-C(3)-C(4)	C(3)-C(4)-C(5)	C(4)-C(5)-C(6)	C(5)-C(6)-C(1)	C(6)-C(1)-C(2)
V-6a	1.639(2)	1.497(2)	1.345(30	1.480(3)	1.399(3)	1.488(3)	116.5(1)	121.3(2)	123.2(2)	122.3(2)	120.5(2)	116.2(2)
V-8	1.639(7) 1.633(7)	1.513(7) 1.511(8)	1.341(7) 1.351(8)	1.482(7) 1.480(7)	1.407(7) 1.420(7)	1.488(7) 1.493(7)	115.3(4) 116.3(4)	122.7(5) 122.0(5)	122.4(5) 122.9(5)	122.4(5) 121.5(5)	120.6(5) 121.2(5)	116.7(4) 116.0(4)

Table 5.8. Selected Conditions for Preparation of **V-11a**.[a]



IV-11a **V-9a**

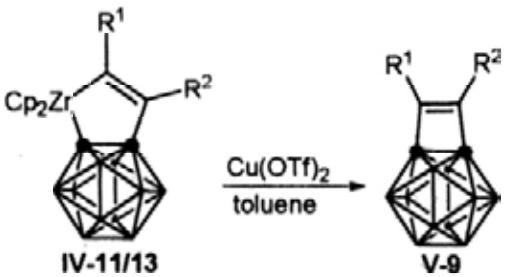
entry	[Cu]	solvent	yield (%)[b]
1	CuCl	toluene	0
2	CuBr	toluene	trace
3	CuI	toluene	0
4	$CuCl_2$	toluene	16
5	$CuSO_4$	toluene	0
6	$Cu(OTf)_2$	toluene	78
7	$Cu(OTf)_2$	THF	52
8	$Cu(OTf)_2$	DME	43
9	$Cu(OTf)_2$	Et_2O	77
10	$Cu(OTf)_2$	hexane	57

[a] Reaction conditions: The mixture of **IV-11a** (8.9 mg, 0.02 mmol) and [Cu] (0.02 mmol) in a solvent (0.6 mL) was stirred at room temperature for 24 hours, then treated with 1 M aqueous HCl and determined by GC-MS. [b] GC yield.

In the preparation of **V-6a**, we found a trace amount of carborane cage fused cyclobutene 1,2-[(Et)C=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**V-9a**) on the basis of GC-MS analyses. Various reaction conditions were then examined to improve the yield. The results were summarized in Table 5.8. It can be seen that Cu(II) salts are generally much

more effective than Cu(I) salts and $Cu(OTf)_2$ is the most active one. Solvents are also crucial for this reaction. Toluene and Et_2O offer the best result. In the following experiments, toluene is used as the solvent and $Cu(OTf)_2$ is employed as the coupling reagent.

Table 5.9. $Cu(OTf)_2$ Mediated Preparation of Carborane Fused Cyclobutenes.[a]



IV-11/13 **V-9**

entry	R^1/R^2	**IV-11/13**	**V-9**	yield (%)
1	Et/Et	**IV-11a**	**V-9a**	63
2	^{n}Pr/^{n}Pr	**IV-11b**	**V-9b**	55
3	^{n}Bu/^{n}Bu	**IV-11c**	**V-11c**	65
4	Ph/Ph	**IV-11d**	**V-9d**	81
5	Ph/Me	**IV-13a**	**V-9e**	65
6	Ph/^{n}Bu	**IV-13c**	**V-9f**	78
7	TMS/^{n}Bu	**IV-13f**	**V-9g**	88
8	TMS/Ph	**IV-13g**	**V-9h**	42(71)[b]
9	Ph/$(CH_2)_3Cl$	**IV-13j**	**V-9i**	89
10	Ph/CH_2OCH_3	**IV-13l**	**V-9j**	24

Reaction condition: a mixture of **IV-11/13** and $Cu(OTf)_2$ in 1:1 molar ratio in toluene was stirred at room temperature for 24 hour. [b] 2 equiv of $Cu(OTf)_2$. The 71% yield was obtained using 1 equiv of $Cu(OTf)_2$ for 10 days.

Many zirconacyclopentene complexes are compatible for this reaction. The results were summarized in table 5.9. Substituents have some effects on the yields. Alkyl (entries 1-6), TMS (entries 7 and 8) and chloro (entry 9) substituents offer good to high yields. MeO substituent gave a low yield of **V-9j** (entry 10). However, under the same reaction conditions, **IV-13g** bearing steric demanding TMS and Ph groups can not yield the expected product **V-9h** whereas it can be obtained in 42% yield using 2 equiv of $Cu(OTf)_2$ or in 71% yield by prolonging the reaction time to 10 days (entry 8). It is noted that the increasing amount of $Cu(OTf)_2$ can enhance the reaction rate and improve the yield, and the prolonged reaction can also increase the yields.

The molecular structure of **V-9d** was determined by X-ray analysis and shown in Figure 5.10. The two single bonds of C(1)-C(11) and C(2)-C(18) are almost equal in length. The distance of C(1)-C(2) gets shorter than that observed in its parent complex. The structural parameters are comparable to those found in 1,2-[(Ph)C=C(Me)]-1,2-$C_2B_{10}H_{10}$.[85c]

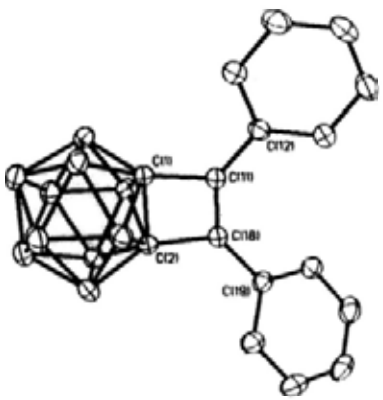


Figure 5.10. Molecular Structure of 1,2-[(Ph)C=C(Ph)]-1,2-$C_2B_{10}H_{10}$ (**V-9d**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.612(2), C(1)-C(11) 1.544(2), C(2)-C(18) 1.539(2), C(11)-C(18) 1.365(2), C(11)-C(1)-C(2) 85.3(1), C(1)-C(11)-C(18) 94.5(1), C(1)-C(2)-C(18) 85.5(1), C(2)-C(18)-C(11) 94.7(1).

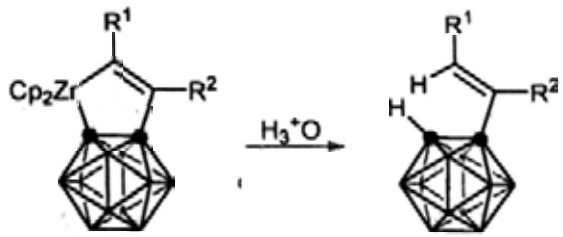
5.7. Hydrolysis and Iodination

Hydrolysis of zirconacyclopentene incorporating a carboranyl unit using 1 M aqueous HCl solution or water (for **IV-13f** and **IV-13g**) generated alkenyl carboranes 1-[CH(R^1)=C(R^2)]-1,2-$C_2B_{10}H_{11}$ (**V-10/V-10'**) in 20-77% yields. The pure products **V-10** were obtained by flash column chromatography on silica gel. In some cases, the minor isomers **V-10'** were also obtained. The ratio of the isomers was determined by GC-MS analyses. The results were summarized in Table 5.10. In the case of PhC≡CCH_2OCH_3, beside the regio-isomers of V-10o and V-10o', a new product 1-[CH_2=C=C(Ph)]-1,2-$C_2B_{10}H_{11}$ (**V-10o-A**) was obtained as colorless crystals in 14% isolated yield (Scheme 5.7). These products were characterized by ^{1}H, ^{13}C and ^{11}B NMR spectra and HRMS analyses.

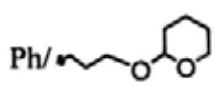
The unique cage C-H and vinyl =C-H protons for most products (entries 1-11, 13, 15, 16) were found in the range 3.19 to 4.25 ppm as a broad singlet and 5.70 to 7.27 ppm as a triplet, respectively, in their ^{1}H NMR spectra. The chemical shifts are affected by the electronic properties of the substituents.

The characteristic of cage and vinyl carbons were observed in the range 58.4 to 79.5 ppm and 120 to 150 ppm, respectively, in their ^{13}C NMR spectra. Their ^{11}B NMR spectra displayed a 1:1:2:4:2 pattern for **V-10a – c,f',g,h',j,m,p**, a 1:1:2:2:2:2 pattern for **V-10d,e,e',f,g',h,h',i,i',k,o** and a 2:4:2:2 pattern for **V-10l,n**.

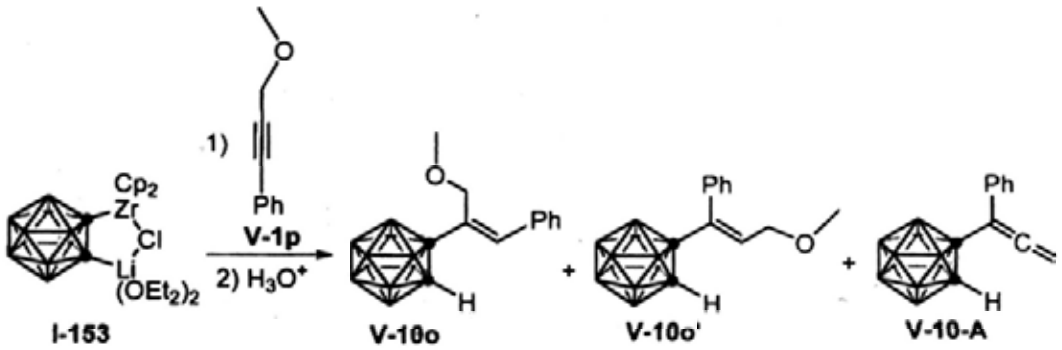
Table 5.10. Hydrolysis of Zirconacyclopentene Complexes.



IV-11/13 **V-10**

entry	R^1/R^2	IV-11/13	product V-10	ratio of V-10/V-10'	isolated yield (%)	
					V-10	V-10'
1	Et/Et	**IV-11a**	**V-10a**	-	75	-
2	^{n}Pr/^{n}Pr	**IV-11b**	**V-10b**	-	77	-
3	^{n}Bu/^{n}Bu	**IV-11c**	**V-10c**	-	76	-
4	Ph/Ph	**IV-11d**	**V-10d**	-	34	-
5	Ph/Me	**IV-13a**	**V-10e**	90/10	58	6
6	Ph/Et	**IV-13b**	**V-10f**	89/11	59	7
7	Ph/^{n}Bu	**IV-13c**	**V-10g**	94/6	65	5
8	Ph/ 	**IV-13d**	**V-10h**	61/39	44	30
9	4-tolyl/Me	**IV-13e**	**V-10i**	81/19	51	8
10	TMS/^{n}Bu	**IV-13f**	**V-10j**	>99	71	0
11	TMS/Ph	**IV-13g**	**V-10k**	>99	33	0
12	 /Et	**IV-13h**	**V-10l**	>99	21	0
13	Ph/$(CH_2)_3Cl$	**IV-13j**	**V-10m**	91/9	73	0
14	Ph/$N(CH_3)_2$	**IV-13k**	**V-10n**	89/11	65	0
15	Ph/CH_2OMe	**IV-13l**	**V-10o**	90/10	25	3
16	Ph/ 	**IV-13m**	**V-10p**	>99	20	0

Scheme 5.7. Reaction of **I-153** with $PhC{\equiv}CCH_2OCH_3$



The unique terminal protons and quaternary carbon of allene in **V-10-A** were found at 5.18 and 208.1ppm in its ^{1}H and ^{13}C NMR spectra, respectively. The structure of **V-10-A** was further confirmed by X-ray analyses as shown in Figure 5.11. The C(11)-C(18) and C(18)-C(19) bond lengths of 1.296(3) Å and 1.305(4) Å are clearly shorter than that of the characteristic C=C double bond (*ca* 1.34 Å). And the C(11)-C(18)-C(19) angle of 179.1(4)° indicates a linear geometry. The sum of angles around C(11) atom are 360°. These data suggest that there is one allene part in this molecule.

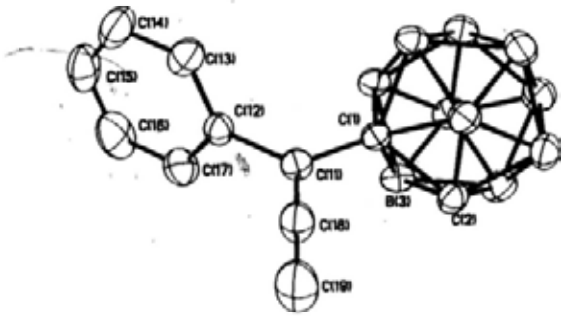
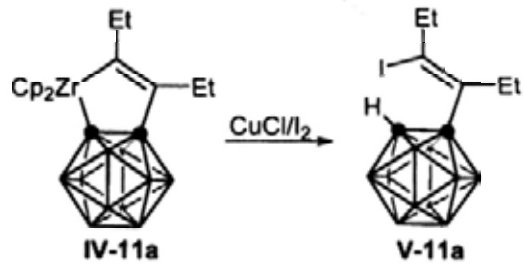


Figure 5.11. Molecular Structure of 1-[CH_2=C=C(Ph)]-(1,2-$C_2B_{10}H_{11}$) (**V-10-A**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.645(3), C(1)-C(11) 1.510(3), C(11)-C(18) 1.296(3), C(18)-C(19) 1.305(4), C(11)-C(12) 1.492(3). C(1)-C(11)-C(12) 117.7(2), C(12)-C(11)-C(18) 122.1(2), C(1)-C(11)-C(18) 120.2(2), C(11)-C(18)-C(19) 179.1(4).

Scheme 5.8. Iodination of **IV-11a**



IV-11a **V-11a**

Interaction of **IV-11a** with excess I_2 (newly sublimed) in the presence of CuCl generated a monosubstituted carborane 1-[CI(Et)=C(Et)]-1,2-$C_2B_{10}H_{11}$ (**V-11a**) in 71% isolated yield (Scheme 5.8). In the absence of CuCl, **V-11a** was isolated in 61% yield. In both cases, the disubstituted species 1-I-2-[CI(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**V-11b**) was not observed. This result is very different from that of zirconacyclopentadienes, in which the diiodo species is the major product in the presence of CuCl.[133] Therefore, it is rational to suggest that after transmetallation, only Cu-C_{vinyl} bond is reactive toward I_2 whereas Cu-C_{cage} bond is inert probably because of steric reasons.[40e,51a,99b] The cage C-H proton in **V-11a** was largely downfield shifted to 5.41 ppm, indicative of an interaction between this acidic proton and iodo group.

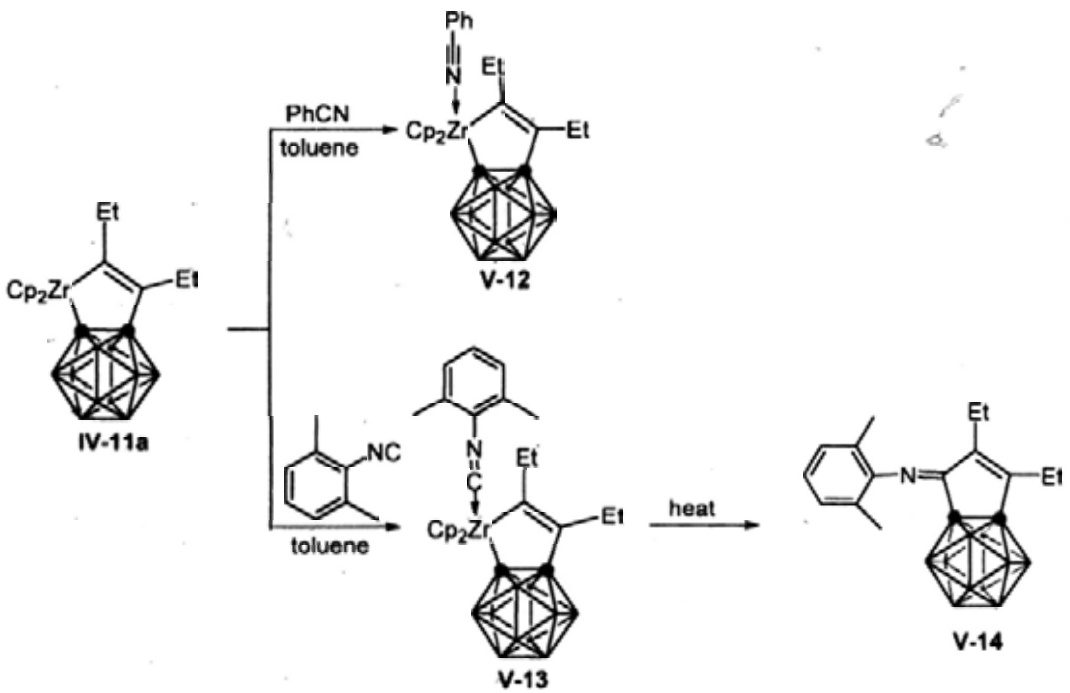
5.8. Reaction with Nitrile and Isonitrile

Interaction of **IV-11a** with PhCN in the presence of CuCl did not yield any insertion product even under forced reaction conditions, but rather gave **V-9a** in low yield. In the absence of CuCl, a PhCN-coordinated complex 1,2-[Cp_2Zr(NCPh)C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**V-12**) was isolated at room temperature, which is stable in refluxing toluene. On the other hand, more reactive 2,6-$(CH_3)_2C_6H_3NC$ can readily insert into the Zr-C_{vinyl} bond to form an insertion

product 1,2-[(2',6'-$Me_2C_6H_3N$=)CC(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**V-14**) in refluxing toluene in the absence of CuCl. At room temperature, the isonitrile-coordinated complex 1,2-[$Cp_2Zr(CNC_6H_3$-2',6'-Me_2)C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**V-13**) was isolated, which was converted to **V-14** upon heating in toluene in the presence of another equiv of isonitrile (Scheme 5.9).[134] In the presence of CuCl, however, both **V-9a** and **V-14** were isolated from the reaction mixture under the same reaction conditions. The reaction pathway may be similar to that proposed for the reaction of zirconacyclopentadiene with isocyanides in the presence of CuCl.[135]

Complexes **V-12** and **V-13** were characterized by ^1H, ^{13}C and ^{11}B NMR spectra, IR spectroscopy and elemental analyses. Compound **V-14** was characterized by ^1H, ^{13}C and ^{11}B NMR spectra and HRMS. Complexes **V-12** and **V-13** were sensitive to air and moisture, and soluble in THF, DME and hot toluene, but less soluble in toluene and diethyl ether, insoluble in hexane.

Scheme 5.9. Reaction of **IV-11a** with Nitrile and Isonitrile



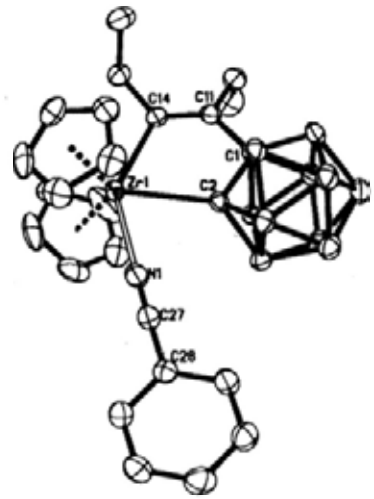


Figure 5.12. Molecular Structure of 1,2-[$Cp_2Zr(NCPh)C(Et)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ (**V-12**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.672(3), C(1)-C(11) 1.505(4), C(11)-C(14) 1.344(4), Zr-C(2) 2.453(2), Zr-C(14) 2.367(3), Zr-N(1) 2.352(2), N(1)-C(27) 1.140(4), C(2)-Zr-C(14) 71.7(1).

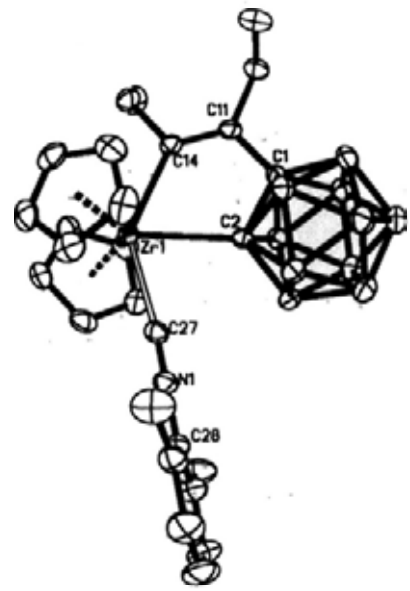


Figure 5.13. Molecular Structure of 1,2-[$Cp_2Zr(CNC_6H_3$-2',6'-$Me_2)C(Et)=C(Et)$] -1,2-$C_2B_{10}H_{10}$ (**V-13**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.672(2), C(1)-C(11) 1.498(2), C(11)-C(14) 1.342(2), Zr-C(2) 2.453(2), Zr-C(14) 2.379(1), Zr-C(27) 2.384(2), C(27)-N(1) 1.147(2), C(2)-Zr-C(14) 71.3(1).

The crystals of **V-12** and **V-13** suitable for X-ray analyses were grown in toluene.

The molecular structures of **V-12** and **V-13** are shown in Figures 5.12 and 5.13. They have a common part **IV-11a** without any significant difference. The most difference of two molecules is the coordination of nitrogen or carbon atom from nitrile or isonitrile to the metal center. In two molecules, the C(27)-N(1) bond length of nitrile or isonitrile is very close to each other with about 1.14 Å, indicative of the character of triple bond.

5.9. Summary

Various kinds of benzocarboranes were prepared by indirect [2+2+2] cycloaddition of carboryne and two different alkynes. In the presence of CuCl and HMPA, zirconacyclpopentene complexes reacted with *ortho*-dihalobenzene reagents to generate naphthalocarborane derivatives. Using 1,2,4,5-tetraiodobenzene, two carborane cage fused anthracene could be prepared. A series of carborane fused cyclobutenes, as an analogue of benzocyclobutadiene, were prepared from zirconacyclopentene complexes by intramolecular coupling reaction after transmetallation of Zr to Cu(II).

Chapter 6. Reactivity of Zirconacyclopentanes Incorporating a Carborane Unit

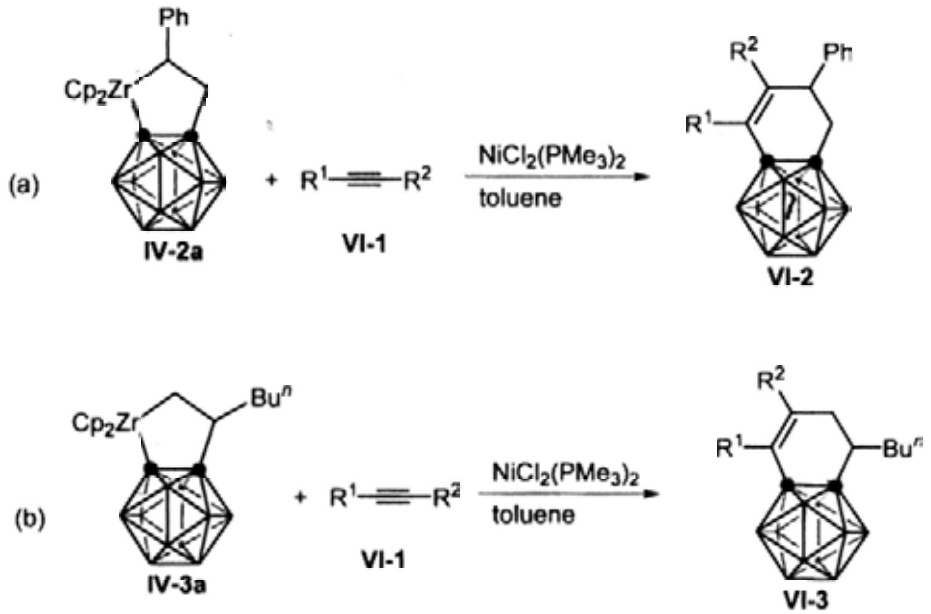
Recently, our group reported three-component [2+2+2] cycloaddition of Ni-carboryne with alkene and alkyne to prepare of dihydrobenzocarborane.[92b] However, only activated alkenes are compatible with this reaction. We learnt from previous work that zirconacyclopentane incorporating a carborane unit does not react with alkenes and alkynes. Transmetallation of Zr to Ni(II), may enhance the reactivities of the resultant nickelacyclopentane.[127b,136] Thus an indirect three component [2+2+2] cycloaddition of carboryne, alkene and alkyne may be achieved. The details are disclosed in this chapter.

6.1. Nickel-Mediated Cycloaddition with Alkynes

Using the optimized condition for the reaction of zirconacyclopentene complexes with alkynes mediated by Ni(II) species, reaction of zirconacyclopentane complexes **IV-2a/3a** with alkynes $R^1C{\equiv}CR^2$ (**VI-1a**, $R^1 = R^2 = Et$; **VI-1b**, $R^1 = R^2 = {}^n Pr$; **VI-1c**, $R^1 = R^2 = {}^n Bu$; **VI-1d**, $R^1 = R^2 = Ph$; **VI-1e**, $R^1 = Ph$, $R^2 = Me$; **VI-1f**, $R^1 = Ph$, $R^2 = Et$; **VI-1g**, $R^1 = Ph$, $R^2 = {}^n Bu$; **VI-1h**, $R^1 = Ph$, $R^2 = CH_2OMe$) in the presence of $NiCl_2(PMe_3)_2$ yielded dihydrobenzocarboranes 1,2-$[(R^1)C{=}C(R^2)CH(Ph)CH_2]$-1,2-$C_2B_{10}H_{10}$ (**VI-2a**, $R^1 = R^2 = Et$; **VI-2b**, $R^1 = R^2 = {}^n Bu$; **VI-2c**, $R^1 = Ph$, $R^2 = {}^n Bu$), 1,2-$[(R^1)C{=}C(R^2)CH_2CH({}^n Bu)]$-1,2-$C_2B_{10}H_{10}$ (**VI-3a**, $R^1 = R^2 = Et$; **VI-3b**, $R^1 = R^2 = {}^n Pr$; **VI-3c**, $R^1 = R^2 = {}^n Bu$; **VI-3d**, $R^1 = R^2 = Ph$; **VI-3e**, $R^1 = Ph$, $R^2 = Me$; **VI-3f**, $R^1 = Ph$, $R^2 = {}^n Bu$; **VI-3g**, $R^1 = Ph$, $R^2 = CH_2OCH_3$), and 1,2-$[(R^2)C{=}C(R^1)CH_2CH({}^n Bu)]$-1,2-$C_2B_{10}H_{10}$ (**VI-3e'**, $R^1 = Me$, $R^2 = Ph$; **VI-3f'**, $R^1 = {}^n Bu$, $R^2 = Ph$; **VI-3g'**, $R^1 = CH_2OCH_3$, $R^2 = Ph$) (Scheme 6.1). The results were summarized in Table 6.1. In general, the yields of **VI-2** ($\leq 32\%$) are

much lower than those of **VI-3** probably due to the steric effects (entries 1-7). Both electronic and steric factors affect the ratio of two isomers formed in the reaction of those unsymmetrical alkynes (entries 8-10).

Scheme 6.1. Preparation of Dihydrobenzocarborane Derivatives



As the alkynes are much more reactive than alkenes, one-pot tandem reaction can be realized by reaction of **I-153** with excess alkene, followed by the addition of alkyne and $NiCl_2(PMe_3)_2$ (Scheme 6.2). This provides a very convenient and efficient method to prepare dihydrobenzocarborane.

Scheme 6.2. One-Pot Preparation of Dihydrobenzocarborane Derivatives

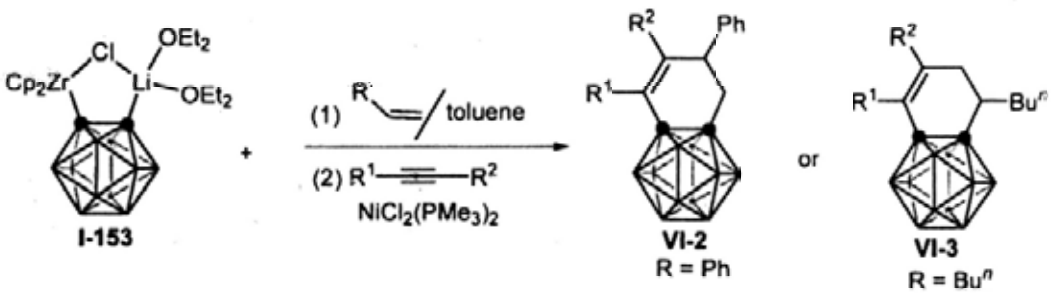


Table 6.1. Synthesis of Dihydrobenzocarboranes. [a]

entry	IV-2a/3a	VI-1	product	
		R^1/R^2	VI-2/3	yield/%
1	**IV-2a**	Et/Et	**VI-2a**	29
2	**IV-2a**	^{n}Bu/^{n}Bu	**VI-2b**	32
3	**IV-2a**	Ph/Et	**VI-2c**	13[b]
4	**IV-3a**	Et/Et	**VI-3a**	66
5	**IV-3a**	^{n}Pr/^{n}Pr	**VI-3b**	63
6	**IV-3a**	^{n}Bu/^{n}Bu	**VI-3c**	70
7	**IV-3a**	Ph/Ph	**VI-3d**	75
8	**IV-3a**	Ph/Me	**VI-3e/VI-3e'**	70(50/50)[c]
9	**IV-3a**	Ph/^{n}Bu	**VI-3f/VI-3f'**	68 (65/35)[c]
10	**IV-3a**	Ph/CH_2OMe	**VI-3g/VI-3g'**	46 (71/29)[c]

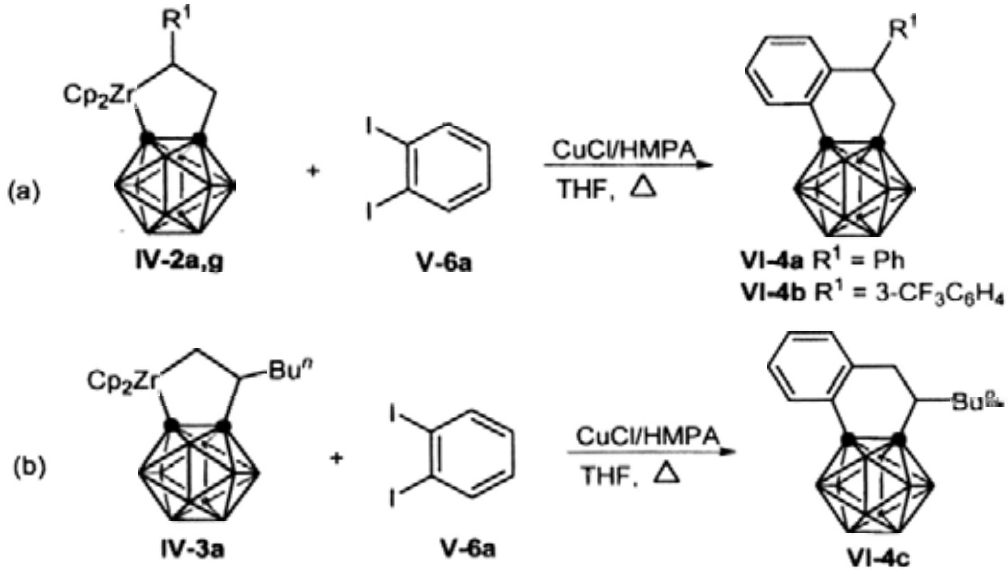
[a] Reaction conditions: 0.20 mmol of **IV-2a/3a**, 0.60 mmol of alkyne **VI-1**, 0.21 mmol of $NiCl_2(PMe_3)_2$ in 8 mL of toluene, 110 ℃, 48h. After removal of the solvent, the product was isolated by flash column chromatography on silica gel using hexane as eluent. [b] GC yield. [c] The ratio of two isomers in the parentheses determined by GC-MS.

6.2. Copper-Mediated Coupling Reaction

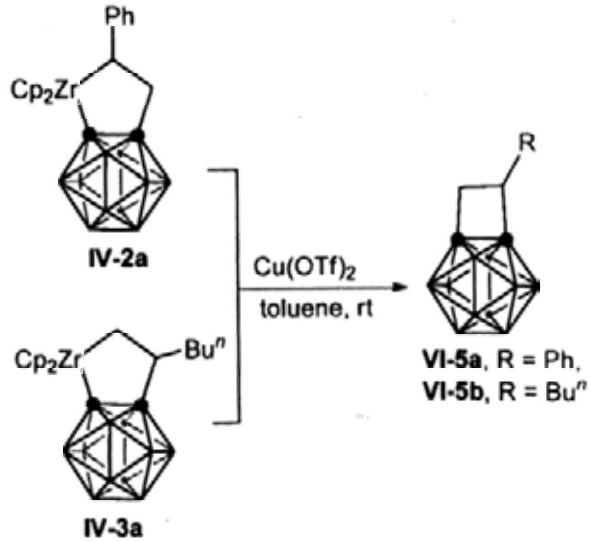
Similar to zirconacyclopentene complexes, in the presence of CuCl/HMPA, zirconacyclopentane complexes (**IV-2a**, **IV-2g** and **IV-3a**) can react with diiodobenzene to give the corresponding dihydronaphthalocarborane derivatives 1,2-[(R^2)CH-CH$(R^1)C_6H_4$]-1,2-$C_2B_{10}H_{10}$ (**VI-4a**, R^1 = Ph, R^2 = H; **VI-4b**, R^1 = 3-$CF_3C_6H_4$, R^2 = H; **VI-4c**, R^1 = H, R^2 = Bu^n) but in low yields (≤ 30%) (Scheme 6.3).

In the presence of 1 equiv of $Cu(OTf)_2$, zirconacyclopentane complexes (**IV-2a** and **IV-3a**) can be converted to the corresponding cyclobutane derivatives 1,2-$[(R)CHCH_2]$-1,2-$C_2B_{10}H_{10}$ (**VI-5a**, R = Ph; **VI-5b**, R = Bu^n) in low yields (< 44%) (Scheme 6.4).

Scheme 6.3. Preparation of Dihydronaphthalocarborane



Scheme 6.4. Preparation of Carborane Cage Fused Cyclobutane



Compounds **VI-4a–c** and **VI-5a,b** were characterized by ^{1}H, ^{13}C and ^{11}B NMR spectra as well as HRMS. The unique cage carbons of carborane were observed in the range 70 to 78 ppm for **VI-4a–c**, while the cage carbons of carborane in **VI-5a,b** were observed at about 74 and 82 ppm in their ^{13}C NMR spectra. **VI-4a** and **VI-4b** showed a pattern of 1:1:4:2:2 in the range -3.4 to 11.7 ppm while **VI-4c** exhibited a 1:2:1:1:1:4 pattern at -3.7, -4.9, -8.6, -9.6, -10.2, -11.7 ppm in their ^{11}B NMR spectra. A pattern of 3:7 for **VI-5a** at -5.0 and -10.5 ppm and a 1:2:7 pattern for **VI-5b** at -4.5, -5.2 and -10.8 ppm were observed in their ^{11}B NMR spectra.

The molecular structures of compounds **VI-4a**, **VI-4c** and **VI-5a** were further confirmed by single crystal X-ray analyses and shown in Figures 6.1 – 6.3.

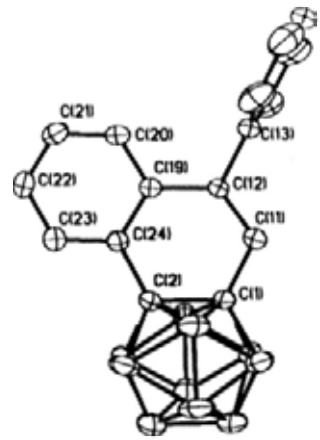


Figure 6.1. Molecular Structure of 1,2-[CH_2-CH(Ph)C_6H_4]-1,2-$C_2B_{10}H_{10}$ (**VI-4a**). Selected bond lengths (Å) and angles (deg) (average of two independent molecules in the unit cell): C(1)-C(2) 1.632(6), C(1)-C(11) 1.522(5), C(11)-C(12) 1.459(6), C(12)-C(19) 1.521(7), C(19)-C(24) 1.402(6), C(2)-C(24) 1.504(6), C(11)-C(1)-C(2) 116.8(3), C(1)-C(11)-C(12) 117.2(4), C(11)-C(12)-C(19) 118.7(5), C(12)-C(19)-C(24) 121.4(5), C(19)-C(24)-C(2) 121.1(4), C(24)-C(2)-C(1) 116.7(3).

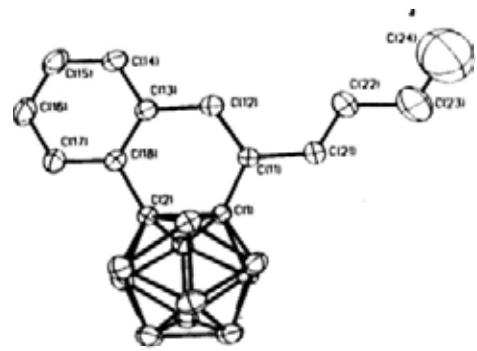


Figure 6.2. Molecular Structure of 1,2-[^{n}BuCH-$CH_2C_6H_4$]-1,2-$C_2B_{10}H_{10}$ (**VI-4c**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.653(3), C(1)-C(11) 1.537(3), C(11)-C(12) 1.531(4), C(12)-C(13) 1.506(4), C(13)-C(18) 1.393(4), C(2)-C(18) 1.496(3), C(11)-C(1)-C(2) 116.9(2), C(1)-C(11)-C(12) 111.6(2), C(11)-C(12)-C(13) 115.3(2), C(12)-C(13)-C(18) 122.2(2), C(13)-C(18)-C(2) 120.4(2), C(18)-C(2)-C(1) 116.6(2).

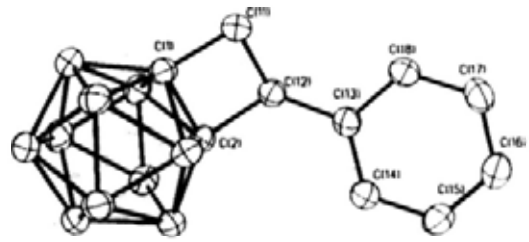


Figure 6.3. Molecular Structure of 1,2-[CH_2-CH(Ph)]-1,2-$C_2B_{10}H_{10}$ (**VI-5a**). Selected bond lengths (Å) and angles (deg): C(1)-C(2) 1.618(2), C(1)-C(11) 1.532(2), C(2)-C(12) 1.568(2), C(11)-C(12) 1.582(2), C(11)-C(1)-C(2) 90.0(1), C(1)-C(11)-C(12) 91.3(1), C(1)-C(2)-C(12) 88.6(1), C(2)-C(12)-C(11) 90.0(1).

6.3. Summary

Dihydrobenzocarborane derivatives can be efficiently prepared from the reaction of zirconacyclopentane with alkynes mediated by $NiCl_2(PM_3)_2$ involving transmetallation, insertion of alkyne and reductive elimination processes. $FeCl_3$ can not mediate such reactions. Dihydronaphthalocarborane and carborane fused cyclobutane can also be prepared but in low yields.

Chapter 7. Conclusions

In this thesis, we describe (1) the synthesis, structural characterization and reactivity of neutral group 4 metal-carboryne complexes, (2) reaction chemistry of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$, a precursor of zirconocene-carboryne, and (3) reaction chemistry of zirconacyclopentenes and zirconacyclopentanes incorporating a carboranyl unit.

A series of group 4 metal-carboryne complexes is prepared by treatment of $Li_2C_2B_{10}H_{10}$ with $(L)_2ZrCl_2$ (L = monoanionic ligands). They are fully characterized by various spectroscopic techniques including ^1H, ^{13}C, ^{11}B NMR and IR spectroscopy as well as elemental analyses. Most are further confirmed by X-ray analyses. In general, salt metathesis is a good method for the synthesis of this type of complexes by reaction of organo-group-4-metal dichloride with $Li_2C_2B_{10}H_{10}$ or treatment of $(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$ with anionic ligands. However, both steric and electronic factors of the ligands have significant effect on the types of resultant complexes (neutral versus ionic complexes). The bonding interactions between Zr and $o\text{-}C_2B_{10}H_{10}$ are best described as a resonance hybrid of both Zr-C σ and Zr-C π bonding forms.

Group 4 metal-carboryne complexes can react with unsaturated molecules to give various kinds of insertion products. The results reveal that ketone, nitrile carbodiimide, isocyanate, thioisocyanate and carbon disulfide give the mono-insertion products, whereas sulfur and selenium afford the double-insertion products. Aryl isonitrile yields triple-insertion products. The metal-carboryne complexes bearing amidinato or guanidinato ligands show no reactivity toward internal alkynes, alkenes and allenes.

On the other hand, $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ reacts readily with alkene, alkyne and pyridines. Terminal alkenes, various internal alkynes and imine PhCH=NPh can insert into the Zr-C(cage) bond of zirconocene-carboryne complexes to form zirconacyclopentane, zirconacyclopentene and azazirconacyclopentane complexes incorporating a carboranyl unit in good to high yield. Interaction of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ and pyridines affords a new kind of carboranyl zirconocene complexes via C-H activation of pyridine.

A new class of benzocarboranes is prepared by indirect [2+2+2] cycloaddition of carboryne and two different alkynes via zirconacyclopentene intermediate. Such a cycloaddition can be promoted by 1 equiv of $NiCl_2(PhMe_3)_2$ or excess $FeCl_3$ or a catalytic amount of $NiCl_2(PMe_3)_2$ in the presence of 2 equiv of $FeCl_3$. These approaches significantly widen the reaction scope of [2+2+2] cycloaddition reaction of carboryne with alkynes.

In the presence of CuCl and HMPA, zirconacyclopentene complexes react with *ortho*-dihalobenzene reagents to generate naphthalocarborane derivatives. Using 1,2,4,5-tetraiodobenzene as starting material, two carborane cage fused anthracene can be prepared. A series of carborane fused cyclobutenes, as an analogue of benzocyclobutene, is also prepared from zirconacyclopentene complexes, via intramolecular coupling reaction after transmetallation of Zr to Cu(II).

The reactivity of zirconacyclopentane incorporating a carborane unit toward alkynes and *o*-diiodobenzene in the presence of Ni(II) or Cu(II) is investigated. Several dihydrobenzocarborane derivatives are efficiently prepared from the reaction of zirconacyclopentane with alkynes mediated by Ni(II), which involves transmetallation, insertion of alkyne and reductive elimination processes.

Similarly, dihydronaphthalocarborane and carborane cage fused cyclobutane are

also prepared from zirconacyclopentane via ineraction with *ortho*-diiodobenzene promoted by Cu(I) and intramolecular coupling reaction mediated by Cu(II), respectively.

The results obtained from this work can not only enhance our basic understanding of chemical properties of metal-carboryne complexes, but also offer new methodologies for the preparation of carborane derivatives which can not be synthesized by conventional methods.

Chapter 8. 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. $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$,[91] PhN_3,[137] $Cp^*Zr[CyNC(Me)NCy]Cl_2$,[138] the alkynes of $PhC{\equiv}CC{\equiv}CPh$,[139a] $PhCCCH_3$,[139b] (4-methylphenyl)propyne,[139b] $TMSC{\equiv}CBu^n$,[139c] $TMSC{\equiv}CPh$,[139d] $Ph_2PC{\equiv}CBu^n$,[139e] $PhC{\equiv}C(CH_2)_3Cl$,[139f] $PhC{\equiv}CCH_2N(CH_3)_2$,[139g] $PhC{\equiv}CCH_2OMe$,[139h] $PhC{\equiv}C(CH_2)_3O$(tetrahydro-2-pyranyl),[139i,j] $PhC{\equiv}CCH_2CH{=}CH_2$,[139k] and $^nBuC{\equiv}C^tBu$[139l] were prepared according to the literature. All alkynes were freshly distilled from CaH_2 prior to use. MeLi (1.6 M in diethyl ether), ^{n}BuLi (1.6 M in hexane), PhLi (1.8 M in dibutyl ether), 1,3-diisopropylcarbodiimide and 1,3-dicyclohexylcarbodiimide (DCC) were purchased from Aldrich and used without further purification. Other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified. Infrared spectra (IR) were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. The ^1H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300, 75, 96 and 121 MHz, or on a Varian Inova 400 spectrometer at 400, 100, 128 and 162 MHz, respectively. All chemical shifts were reported in δ units with references to the residual protons and carbons of the deuterated solvents for proton and carbon chemical shifts, 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 phosphorous chemical shifts. Mass spectra were recorded on Thermo Finnigan MAT 95 XL spectrometry. Elemental analyses were performed by Shanghai Institute of

Organic Chemistry, CAS, China.

Preparation of $Cp^*[\eta^2$-CyNC(Me)NCy]$Zr(\eta^3$-$C_2B_{10}H_{10})$ (II-4). To a stirring solution of *o*-$C_2B_{10}H_{12}$ (144 mg, 1.00 mmol) in tolune/diethyl ether (30 mL, 10/1 in v/v) at 0°C was slowly added ^{n}BuLi (1.3 mL, 2.08 mmol, 1.6 M in hexane), and the mixture was stirred at room temperature for 1 h. The resulting $Li_2C_2B_{10}H_{10}$ suspension was then cooled to -30°C, to which was added $Cp^*Zr[CyNC(Me)NCy]Cl_2$ (495 mg, 1.00 mmol). The reaction mixture was then stirred for 12 h at room temperature, giving a pale orange suspension. After filtration, the yellow filtrate cake was extracted with hot toluene to give a yellow solution of **II-4** which was concentrated to about 10 mL. Complex **II-4** was isolated as orange crystals after this solution stood at room temperature overnight (295 mg, 51%). ^{1}H NMR (benzene-d_6): δ 2.97 (m, 2H, Cy), 2.14 (m, 2H, Cy), 1.79 (s, 15H, $C_5(CH_3)_5$), 1.61 (m, 6H, Cy), 1.46 (s, 3H, CH_3), 1.22 (m, 12H, Cy). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 166.2 (NCN), 124.9 ($C_5(CH_3)_5$), 98.0 (cage *C*), 57.8 (NCH), 35.3, 34.5, 26.0, 25.7, 13.1, 12.3 (CH_2 and CH_3). ^{11}B NMR (benzene-d_6): δ -0.8 (d, J = 162 Hz, 2B), -2.3 (d, J = 170 Hz, 2B), -7.9 (d, J = 130 Hz, 4B), -15.0 (d, J = 140 Hz, 2B). IR (KBr, cm^{-1}): ν 2582 (BH). Anal. Calcd for $C_{26}H_{50}B_{10}N_2Zr$ (**II-4**): C, 52.93; H, 8.54; N, 4.75. Found: C, 52.86; H, 8.66; N, 4.59.

Preparation of $[CyNC(CH_3)NCy]_2ZrCl_2$ (II-5a).[102] A 100 mL Schlenk flask was charged with 1,3-dicyclohexylcarbodiimide (DCC) (0.82 g, 4.00 mmol), diethyl ether (30 mL), and a stir bar. To this solution was added MeLi (2.5 mL, 4.20 mmol, 1.6 M in diethyl ether) dropwise via syringe at room temperature. The solution was stirred for 30 min and then added dropwise via pipette to a white suspension of $ZrCl_4(THF)_2$ (0.75 g, 2.00 mmol) in diethyl ether (10 mL). An immediate color change to light yellow was observed. The resulting solution was then stirred overnight and filtered to

remove LiCl. Evaporation of the solvent yielded a light yellow solid. Recrystallization from hexane/diethyl ether (3/1 in v/v) at -30 °C afforded **II-5a** as a light yellow microcrystalline solid (0.66 g, 1.10 mmol, yield 55%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.01-3.26 (m, 4H, C*H*), 1.73-2.10 (m, 24H, CH_2), 1.52 (s, 6H, CH_3), 1.50-1.60 (m, 4H), 1.16-1.21 (m, 12H) (CH_2 of C_6H_{11}). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 178.2 (NCN), 57.4 (NCH), 35.0, 26.2, 25.8 (CH_2), 10.7 (CH_3). These data are in well agreement with those reported in the literature.[102]

Preparation of [CyNC(Ph)NCy]$_2$ZrCl$_2$ (II-5b). This complex was prepared as light yellow crystals from DCC (0.82 g, 4.00 mmol), PhLi (2.2 mL, 1.8M in diethyl ether) and $ZrCl_4(THF)_2$ (0.75 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.73 g (50%). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.07-7.25 (m, 10H, phenyl *H*), 3.05-3.12 (m, 4H, NC*H*), 2.30-2.41 (m, 8H), 2.07-2.18 (m, 8H), 1.73-1.77 (m, 8H), 1.47-1.50 (m, 4H), 1.16-1.25 (m, 4H), 0.94-1.16 (m, 8H) (C_6H_{11}). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 180.0 (NCN), 131.3, 129.5, 129.0, 126.1 (phenyl *C*), 58.4 (NCH), 35.4, 25.9, 25.7 (C_6H_{11}). IR (KBr, cm^{-1}): ν 2919, 2851, 1629, 1428, 1354, 1206, 1092,1058, 984, 897, 769, 702, 662, 528, 494, 440. Anal. Calcd for $C_{38}H_{54}Cl_2N_4Zr$ **(II-5b)**: C, 62.61; H, 7.47; N, 7.69. Found: C, 62.12; H, 7.08; N, 7.88.

Preparation of [CyNC(^{n}Bu)NCy]$_2$ZrCl$_2$ (II-5c). This complex was prepared as light yellow crystals from DCC (0.82 g, 4.00 mmol), ^{n}BuLi (2.5 mL, 1.6M in hexane) and $ZrCl_4(THF)_2$ (0.75 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 1.03 g (75%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.25 (m, 4H, NC*H*), 2.22 (m, 12H), 1.94 (m, 8H), 1.78 (m, 8H), 1.54 (brs, 4H), 1.45 (m, 4H), 1.29 (m, 12H) (CH_2), 0.80 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 181.3 (NCN), 57.3, 35.3, 29.3, 26.3, 25.8, 24.4, 23.0, 13.7 (C_6H_{11} and C_4H_9). IR (KBr, cm^{-1}): ν

2927, 1636, 1459, 1086, 1018. Anal. Calcd for $C_{34}H_{62}Cl_2N_4Zr$ (**II-5c**): C, 59.27; H, 9.07; N, 8.13. Found: C, 59.30; H, 9.04; N, 8.01.

Preparation of [CyNC(Ph)NCy]$_2$TiCl$_2$ (II-5d). This complex was prepared as purple crystals from DCC (0.82 g, 4.00 mmol), PhLi (2.2 mL, 1.8M in diethyl ether) and $TiCl_4(THF)_2$ (0.67 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.69 g (50%). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.41 (m, 4H), 7.05 (m, 6H) (phenyl *H*), 3.29 (m, 4H, NC*H*), 2.86 (m, 4H), 2.10 (m, 12H), 1.73 (m, 8H), 1.41 (m, 4H), 1.25 (m, 4H), 1.14 (m, 4H), 0.99 (m, 8H) (C_6H_{11}). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 177.0 (NCN), 130.5, 129.7, 129.3, 128.9, 126.8, 125.6 (phenyl *C*), 62.3, 60.5 (NCH), 35.3, 34.4, 33.3 (C_6H_{11}). IR (KBr, cm^{-1}): ν 2926, 1627, 1438, 1378, 1219, 1075, 778, 698, 512, 462. These data are in agreement with the literature.[140]

Preparation of [^{i}PrNC(CH$_3$)NPr^i]$_2$ZrCl$_2$ (II-5e). This complex was prepared as light yellow crystals from ^{i}PrNCNPr^i (0.50 g, 4.00 mmol), MeLi (2.5 mL, 1.6M in diethyl ether) and $ZrCl_4(THF)_2$ (0.75 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.55 g (66%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.31 (m, 4H, NC*H*), 1.37 (s, 6H, C*H*$_3$), 1.29 (d, J = 6.6 Hz, 24H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 178.3 (*C*NC), 48.6 (NCH), 24.5, 10.5 (*C*H$_3$). IR (KBr, cm^{-1}): ν 2912, 2972, 1643, 1434, 1340, 1206, 1132, 1018, 810, 615, 554, 420. Anal. Calcd for $C_{16}H_{34}C_{12}N_4Zr$ (**II-5e**): C, 43.22; H, 7.71; N, 12.60, Found: C, 42.70; H, 7.86; N, 12.59.

Preparation of [^{i}PrNC(Ph)NPr^i]$_2$ZrCl$_2$ (II-5f). This complex was prepared as yellow crystals from ^{i}PrNCNPr^i (0.50 g, 4.00 mmol), PhLi (2.2 mL, 1.8M in diethyl ether) and $ZrCl_4(THF)_2$ (0.75 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.57 g (50%). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.16 (m, 10H, Phenyl

H), 3.40 (m, 4H, NC*H*), 1.47 (d, J = 6.6 Hz, 24H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 178.3 (*C*NC), 131.1, 129.4, 129.0, 126.1 (phenyl *C*), 49.9 (NCH), 24.8 (*C*H$_3$). IR (KBr, cm^{-1}): ν 2959, 1629, 1448, 1414, 1340, 1219,1139, 1011, 769, 702, 487, 427. Anal. Calcd for $C_{26}H_{38}Cl_2N_4Zr$ **(II-5f)**: C, 54.91; H, 6.83; N, 9.85. Found: C, 54.79, H, 6.83, N, 9.75.

Preparation of [^{i}PrNC(^{n}Bu)NPr^i]$_2$ZrCl$_2$ (II-5g). This complex was prepared as yellow crystals from ^{i}PrNCNPr^i (0.50 g, 4.00 mmol), ^{n}BuLi (2.5 mL, 1.6M in hexane) and $ZrCl_4(THF)_2$ (0.75 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.73 g (69%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.53 (m, 4H, NC*H*), 2.03 (t, J = 7.8 Hz, 4H, CH_2), 1.39 (d, J = 6.3 Hz, 24H, CH_3), 1.16 (m, 4H, CH_2), 1.35 (m, 4H, CH_2), 0.76 (t, J = 7.2 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 181.2 (NCN), 48.4 (NCH), 29.1, 24.9, 24.5, 23.1, 13.7. IR (KBr, cm^{-1}): ν 2968, 2930, 2872, 1644, 1466, 1426, 1349, 1210, 1134, 1089, 1057, 841. Anal. Calcd for $C_{22}H_{46}Cl_2N_4Zr$ **(II-5g)**: C, 49.97; H, 8.77; N, 10.60. Found: C, 49.78; H, 8.72; N, 10.57.

Preparation of [^{i}PrNC(N(^{n}Pr)$_2$)NPr^i]$_2$ZrCl$_2$ (II-5h). This complex was prepared as yellow crystals from ^{i}PrNCNPr^i (0.50 g, 4.00 mmol), (^{n}Pr$_2$)NLi prepared from ^{n}BuLi (2.5 mL, 1.6M in hexane) and ^{n}Pr$_2$NH (0.41g, 4.00 mmol) and $ZrCl_4(THF)_2$ (0.75 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.78 g (65%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.66 (m, 4H, NC*H*), 2.75 (t, J = 7.2 Hz, 8H, CH_2), 1.52 (d, J = 6.3 Hz, 24H, CH_3), 1.30 (m, 8H, CH_2), 0.70 (t, J = 7.2 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 173.3 (NCN), 51.0 (NCH), 47.8 (NCH$_2$), 24.7, 21.8, 11.3 (^{i}Pr and ^{n}Pr). IR (KBr, cm^{-1}): ν 2968, 2930, 2873, 1605, 1487, 1414, 1313, 1213, 1181, 1132, 1074, 795, 748. Anal. Calcd for $C_{26}H_{56}Cl_2N_6Zr$ **(II-5h)**: C, 50.79; H, 9.18; N, 13.67. Found: C, 50.41; H, 8.68; N, 13.70.

Preparation of [^{i}PrNC(^{n}Bu)NPr^i]$_2$TiCl$_2$ (II-5i). This complex was prepared as purple crystals from ^{i}PrNCNPr^i (0.50 g, 4.00 mmol), ^{n}BuLi (2.5 mL, 1.6M in hexane) and $TiCl_4(THF)_2$ (0.75 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.81 g (83%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.66 (brs, 4H, NC*H*), 2.02 (t, J = 7.5 Hz, 4H, CH_2), 1.52 (brs, 24H, CH_3), 1.41 (m, 4H, CH_2), 1.16 (m, 4H, CH_2), 0.77 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 178.6 (*N*C*N*CH), 51.2 (NCH), 28.6, 24.3, 23.2, 13.7 (^{i}propyl and ^{n}butyl *C*). IR (KBr, cm^{-1}): ν 2964, 2924, 2867, 1643, 1498, 1459, 1412, 1381, 1346, 1203, 1131, 838, 554, 485. Anal. Calcd for $C_{22}H_{46}Cl_2N_4Ti$ (**II-5i**): C, 54.44; H, 9.55; N, 11.54. Found: C, 54.01; H, 9.06; N, 11.44.

Preparation of [^{i}PrNC(^{n}Bu)NPr^i]$_2$HfCl$_2$ (II-5j). This complex was prepared as colorless crystals from ^{i}PrNCNPr^i (0.50 g, 4.00 mmol), ^{n}BuLi (2.5 mL, 1.6M in hexane) and $HfCl_4(THF)_2$ (0.93 g, 2.00 mmol) using the same procedures as above for **II-5a**: yield 0.80 g (65%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.74 (m, 4H, NC*H*), 2.08 (t, J = 8.1 Hz, 4H, CH_2), 1.40 (d, J = 6.3 Hz, 24H, CH_3), 1.35 (m, 4H, CH_2), 1.17 (m, 4H, CH_2), 0.79 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 180.6 (*N*C*N*), 48.1 (NCH), 29.0, 24.9, 23.2, 13.7 (*iso*-propyl and *norm*-butyl *C*). IR (KBr, cm^{-1}): ν 2966, 2926, 2870, 1643, 1487, 1465, 1429, 1381, 1347, 1219, 1188, 1138, 840. Anal. Calcd for $C_{22}H_{46}Cl_2N_4Hf$ (**II-5j**): C, 42.89; H, 7.53; N, 9.09. Found: C, 43.04; H, 7.38; N, 8.63.

Preparation of (η^2-C$_2$B$_{10}$H$_{10}$)ZrCl$_2$(THF)$_3$ (II-6k). To a white suspension of $ZrCl_4(THF)_2$ (3.78 g, 10.00 mmol) in toluene/THF (30 mL, 10/1 in v/v) was slowly added a toluene (30 mL) solution of $Li_2C_2B_{10}H_{10}$ at 0 °C [prepared from the reaction of *o*-$C_2B_{10}H_{12}$ (1.44 g, 10.00 mmol) with ^{n}BuLi (12.5 mL, 20.00 mmol, 1.6 M in hexane) at room temperature in diethyl ether (30 mL)]. The reaction mixture was

then stirred at room temperature for 3 days. After filtration, the precipitate was washed with hot toluene (3 x 10 mL). The combined solutions were concentrated to about 30 mL. Complex **II-6k** was obtained as colorless crystals after this solution stood at room temperature overnight (4.60 g, 88%). ^{1}H NMR (benzene-d_6): δ 3.57 (brs, 12H, CH_2), 1.37 (brs, 12H, CH_2). ^{13}C{^{1}H} NMR (benzene-d_6): δ 78.2 (cage *C*), 68.2 (OCH_2), 25.6 (CH_2). ^{11}B{^{1}H} NMR (benzene-d_6): δ -1.0 (4B), -7.4 (4B), -15.4 (2B). IR (KBr, cm^{-1}): ν 2569 (BH). Anal. Calcd for $C_{14}H_{34}Cl_2O_3B_{10}Zr$ (**II-6k**): C, 32.30; H, 6.58. Found: C, 31.90; H, 6.53.

Preparation of [η^2-CyNC(CH$_3$)NCy]$_2$Zr(η^2-C$_2$B$_{10}$H$_{10}$) (II-6a). To a stirring solution of *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) in diethyl ether (30 mL) at 0°C was slowly added ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane), and the mixture was stirred at room temperature for 1 h. After removal of the solvent in vacuum, the residue was suspended in toluene (30 mL), to which was slowly added a toluene solution (20 mL) of [η^2-CyNC(CH$_3$)NCy]$_2$ZrCl$_2$ (2.90 g, 5.00 mmol) at 0°C. The reaction mixture was then stirred at room temperature for 24 h. After filtration, the precipitate was washed with hot toluene (3 x 5 mL). Removal of the solvent gave a crude product. Recrystallization from diethyl ether/hexane (30 mL, 10/1 in v/v) at room temperature afforded **II-6a** as yellow crystals (3.08 g, 91%). ^{1}H NMR (benzene-d_6): δ 3.00 (m, 4H, NC*H*), 1.71 (m, 28H, CH_2), 1.52 (s, 6H, CH_3), 1.17 (m, 12H, CH_2). ^{13}C{^{1}H} NMR (benzene-d_6): δ.177.6 (NCN), 103.9 (cage *C*), 57.9 (NCH), 34.8, 26.0, 25.6, 12.3 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (benzene-d_6): δ -0.7 (4B), -7.1 (4B), -14.8 (2B). IR (KBr, cm^{-1}): ν 2569 (BH). Anal. Calcd for $C_{30}H_{60}B_{10}N_4Zr$ (**II-6a**): C, 53.29; H, 8.94; N, 8.29. Found: C, 53.65; H, 9.18; N, 7.92.

Complex **II-6a** was also prepared by reaction of complex **II-6k** (260 mg, 0.50 mmol) with 2 equiv of [CyNC(CH$_3$)NCy]Li, prepared in situ from CyN=C=NCy

(206 mg, 1.00 mmol) and MeLi (0.6 mL, 1.00 mmol, 1.6 M in hexane) in toluene (10 mL), at room temperature followed by the same procedure reported above: yield 280 mg (83%).

Preparation of $[\eta^2$-CyNC(Ph)NCy$]_2$Zr(η^2-$C_2B_{10}H_{10}$)(THF) (II-6b). This complex was prepared as yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and $[\eta^2$-CyNC(Ph)NCy$]_2ZrCl_2$ (3.64 g, 5.00 mmol) in toluene (50 mL) using the same procedure reported for **II-6a**: yield 3.71 g (85%). ^{1}H NMR (benzene-d_6): δ 7.11 (m, 10H, C_6H_5), 3.68 (m, 4H, THF), 3.10 (m, 4H, NC*H*), 2.10 (m, 8H), 1.90 (m, 8H), 1.60 (m, 8H) (C_6H_{11}), 1.53 (m, 4H, THF), 1.36 (m, 4H), 1.08 (m, 4H), 0.94 (m, 8H) (C_6H_{11}). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 179.3 (NCN), 132.3, 129.5, 129.0, 128.7, 126.5, 126.0 (C_6H_5), 105.7 (cage *C*), 73.8 (THF), 59.1, 35.1, 25.9, 25.4, 25.3 (C_6H_{11} + THF). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -1.4 (4B), -6.7 (4B), -13.8 (2B). IR (KBr, cm^{-1}): ν 2562 (BH). Anal. Calcd for $C_{44}H_{72}B_{10}N_4OZr$ (**II-6b**): C, 60.58; H, 8.32; N, 6.42. Found: C, 60.33; H, 8.67; N, 6.29.

Preparation of $[\eta^2$-CyNC(Bu^n)NCy$]_2$Zr(η^2-$C_2B_{10}H_{10}$) (II-6c). This complex was prepared as yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and $[\eta^2$-CyNC(Bu^n)NCy$]_2ZrCl_2$ (3.45 g, 5.00 mmol) in toluene (50 mL) using the same procedure reported for **II-6a**: yield 3.31 g (87%). ^{1}H NMR (benzene-d_6): δ 3.27 (m, 4H, NC*H*), 2.18 (m, 4H, CH_2), 1.81 (m, 24H, CH_2), 1.53 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.26 (m, 16H, CH_2), 0.80 (t, J = 7.2 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 182.0 (NCN), 104.2 (cage *C*), 57.8 (NCH), 35.3, 35.0, 29.4, 26.3, 26.2, 25.4, 23.2, 13.6 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -0.1 (4B), -6.5 (4B), -14.2 (2B). IR (KBr, cm^{-1}): ν 2564 (BH). Anal. Calcd for $C_{36}H_{72}B_{10}N_4Zr$ (**II-6c**): C, 56.87; H,

9.54; N, 7.37. Found: C, 56.74; H, 9.06; N, 7.28.

Preparation of [η^2-CyNC(Ph)NCy]$_2$Ti(η^2-$C_2B_{10}H_{10}$) (II-6d). This complex was prepared as purple crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and [η^2-CyNC(Ph)NCy]$_2$TiCl$_2$ (3.43 g, 5.00 mmol) in toluene (40 mL) using the same procedure reported for **II-6a**: yield 2.73 g (72%). ^{1}H NMR (benzene-d_6): 7.28 (m, 2H), 7.08 (m, 8H), 3.48 (m, 4H, NC*H*), 2.04 (m, 4H), 1.90 (m, 4H), 1.59 (m, 16H), 1.37 (m, 4H), 0.99 (m, 12H) (Cy). ^{13}C{^{1}H} NMR (benzene-d_6): δ 177.6 (NCN), 132.0, 129.9, 128.9, 127.3, 127.0 (phenyl *C*), 107.0 (cage *C*), 61.4 (NCH), 34.8, 34.7, 26.2, 25.5 (CH_2). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.4 (4B), -7.2 (4B), -14.9 (2B). IR (KBr, cm^{-1}): ν 2568 (BH). Anal. Calcd for $C_{40}H_{64}N_4B_{10}Ti$ (**II-6d**): C, 63.47; H, 8.52; N, 7.40. Found: C, 63.50; H, 8.60; N, 7.19.

Preparation of [η^2-^{i}PrNC(Me)NPr^i]$_2$Zr(η^2-$C_2B_{10}H_{10}$)(THF) (II-6e). This complex was prepared as yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and [η^2-^{i}PrNC(Me)NPr^i]$_2$ZrCl$_2$ (2.22 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **II-6a**: yield 2.06 g (70%). ^{1}H NMR (benzene-d_6): δ 3.68 (m, 4H, THF), 3.49 (m, 4H, NC*H*), 1.46 (s, 6H, CH_3), 1.37 (m, 4H, THF), 1.13 (d, *J* = 6.3 Hz, 12H, CH_3), 1.00 (d, J = 6.6 Hz, 12H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 177.3 (NCN), 104.2 (cage *C*), 71.6 (THF), 48.9 (NCH), 25.1, 24.5, 24.2, 12.9 (^{i}Pr + THF). ^{11}B{^{1}H} NMR (benzene-d_6): δ -1.4 (4B), -6.9 (4B), -13.8 (2B). IR (KBr, cm^{-1}): ν 2556 (BH). Anal. Calcd for $C_{18}H_{52}N_4B_{10}Zr$ (**II-6e** – THF): C, 41.91; H, 8.60; N, 10.86. Found: C, 42.21; H, 8.82; N, 10.67.

Preparation of [η^2-^{i}PrNC(Ph)NPr^i]$_2$Zr(η^2-$C_2B_{10}H_{10}$)(THF) (II-6f). This complex was prepared as yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from

o-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and [η^2-^{i}PrNC(Me)NPr^i]$_2$ZrCl$_2$ (2.85 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **II-6a**: yield 3.24 g (91%). ^{1}H NMR (benzene-d_6): δ 7.29 (m, 2H), 7.17 (m, 8H) (phenyl *H*), 4.06 (m, 4H, THF), 3.56 (m, 4H, NC*H*), 1.54 (m, 4H, THF), 1.23 (d, J = 6.6 Hz, 12H, CH_3), 1.22 (d, J = 6.3 Hz, 12H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 178.7 (NCN), 133.0, 129.3, 129.1, 128.7, 126.2, 125.8 (phenyl *C*), 104.6 (cage *C*), 72.7 (THF), 50.5 (NCH), 25.2, 24.8 (^{i}Pr + THF). ^{11}B{^{1}H} NMR (benzene-d_6): δ -0.7 (4B), -6.5 (4B), -13.9 (2B). IR (KBr, cm^{-1}): ν 2567 (BH). Anal. Calcd for $C_{32}H_{56}N_4OB_{10}Zr$ (**II-6f**): C, 53.97; H, 7.93; N, 7.87. Found: C, 53.66; H, 7.93; N, 7.62.

Preparation of [η^2-^{i}PrNC(Bu^n)NPr^i]$_2$Zr(η^2-$C_2B_{10}H_{10}$) (II-6g). This complex was prepared as light yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and [η^2-^{i}PrNC(Bu^n)NPr^i]$_2$ZrCl$_2$ (2.64 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **II-6a**: yield 2.79 g (93%). ^{1}H NMR (benzene-d_6): 3.47 (m, 4H, NC*H*), 2.01 (t, J = 8.1 Hz, CH_2), 1.32 (m, 4H, CH_2), 1.19 (d, J = 6.6 Hz, 12H, CH_3), 1.13 (d, J = 6.3 Hz, 12H, CH_3), 1.11 (m, 4H, CH_2), 0.77 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 181.7 (NCN), 103.8 (cage *C*), 48.7 (NCH), 29.1, 26.2, 25.2, 24.9, 23.3, 13.6 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -0.4 (4B), -6.8 (4B), -14.4 (2B). IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{24}H_{56}N_4B_{10}Zr$ (**II-6g**): C, 48.04; H, 9.41; N, 9.34. Found: C, 47.73; H, 9.00; N, 9.28.

Preparation of [η^2-^{i}PrNC(NPr$^n_2$)NPr^i]$_2$Zr(η^2-$C_2B_{10}H_{10}$) (II-6h). ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane) was slowly added to a solution of ^{n}Pr$_2$NH (1.01 g, 10.00 mmol) in diethyl ether (20 mL) at 0 °C, and the mixture was stirred at room temperature for 2 h. To this solution was slowly added a diethyl ether (15 mL)

solution of ^{i}PrN=C=NPr^{i} (1.26 g, 10.00 mmol) at 0 °C. The mixture was then stirred at room temperature for 2 h. The resulting solution was slowly added to a suspension of **II-6k** (2.60 g, 5.00 mmol) in toluene (20 mL) at 0°C, and the mixture was stirred at room temperature overnight. After filtration, removal of the solvents gave a white solid. Recrystallization from diethyl ether/hexane (2/1) afforded **II-6h** as colorless crystals (2.78 g, 81%). ^{1}H NMR (benzene-d_6): δ 3.56 (m, 4H, NC*H*(CH$_3$)$_2$), 2.71 (t, J = 7.6 Hz, 8H, N(C*H*$_2$CH$_2$CH$_3$)$_2$), 1.33 (d, J = 6.4 Hz, 12H, C*H*$_3$), 1.28 (d, J = 6.4 Hz, 12H, C*H*$_3$), 1.25 (m, 8H, C*H*$_2$), 0.66 (t, J = 7.2 Hz, 12H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 171.6 (*N*CN), 101.0 (cage *C*), 51.3, 48.2, (*N*CH$_2$CH$_2$CH$_3$ and *N*CH(CH$_3$)$_2$), 24.9, 24.1, 21.3, 11.4 (propyl *C*). ^{11}B{^{1}H} NMR (benzene-d_6): δ -1.2 (4B), -7.8 (4B), -15.2 (2B). IR (KBr, cm^{-1}): ν 2565 (BH). Anal. Calcd for C$_{28}$H$_{66}$B$_{10}$N$_6$Zr (**II-6h**): C, 49.01; H, 9.69; N, 12.25. Found: C, 48.66; H, 9.21; N, 12.37.

Complex **II-6h** was also prepared as colorless crystals from Li$_2$C$_2$B$_{10}$H$_{10}$ [prepared in situ from *o*-C$_2$B$_{10}$H$_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and [η^2-^{i}PrNC(NPr$^{n}_2$)NPr^{i}]$_2$ZrCl$_2$ (3.64 g, 5.00 mmol) in toluene (50 mL) using the same procedure reported for **II-6a**: yield 3.71 g (87%).

Preparation of [η^2-^{i}PrNC(Bu^{n})NPr^{i}]$_2$Ti(η^2-C$_2$B$_{10}$H$_{10}$) (II-6i). This complex was prepared as purple crystals from Li$_2$C$_2$B$_{10}$H$_{10}$ [prepared in situ from *o*-C$_2$B$_{10}$H$_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and [η^2-^{i}PrNC(Bu^{n})NPr^{i}]$_2$TiCl$_2$ (2.43 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **II-6a**: yield 2.64 g (95%). ^{1}H NMR (benzene-d_6): 3.77 (m, 4H, NC*H*), 2.09 (m, C*H*$_2$), 1.39 (m, 4H, C*H*$_2$), 1.20 (d, J = 6.6 Hz, 12H, C*H*$_3$), 1.16 (d, J = 6.6 Hz, 12H, C*H*$_3$), 1.13 (m, 4H, C*H*$_2$), 0.79 (t, J = 7.2 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 179.1 (*N*CN), 105.9 (cage *C*), 51.2 (*N*CH), 28.7, 27.4, 24.8,

24.5, 23.4, 13.6 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -2.7 (4B), -7.5 (4B), -15.2 (2B). IR (KBr, cm^{-1}): ν 2559 (BH). Anal. Calcd for $C_{24}H_{56}N_4B_{10}Ti$ (**II-6i**): C, 51.78; H, 10.14; N, 10.06. Found: C, 52.24; H, 10.64; N, 10.06.

Preparation of $[\eta^2$-^{i}PrNC(Bu^n)NPr$^i]_2Hf(\eta^2$-$C_2B_{10}H_{10})$ (II-6j). This complex was prepared as colorless crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and ^{n}BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)], and $[\eta^2$-^{i}PrNC(Bu^n)NPr$^i]_2HfCl_2$ (3.08 g, 5.00 mmol) in toluene (40 mL) using the same procedure reported for **II-6a**: yield 2.85 g (83%). ^1H NMR (benzene-d_6): 3.67 (m, 4H, NC*H*), 2.05 (t, J = 7.8 Hz, CH_2), 1.34 (m, 4H, CH_2), 1.20 (d, J = 6.3 Hz, 12H, CH_3), 1.16 (d, J = 6.3 Hz, 12H, CH_3), 1.11 (m, 4H, CH_2), 0.78 (t, J = 7.2 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 181.4 (NCN), 116.0 (cage *C*), 48.5 (NCH), 29.1, 26.6, 25.1, 24.8, 23.3, 13.6 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -0.8 (2B), -0.7 (2B), -7.5 (4B), -15.2 (2B). IR (KBr, cm^{-1}): ν 2559 (BH). Anal. Calcd for $C_{24}H_{56}N_4B_{10}Hf$ (**II-6j**): C, 41.94; H, 8.21; N, 8.15. Found: C, 41.87; H, 8.30; N, 7.98.

Preparation of $[(\eta^2$-$C_2B_{10}H_{10})_2Zr(^t$BuO)(THF)$][Zr(OBu^t)_3(THF)_3]$ (II-6l). To a suspension of **II-6k** (520 mg, 1.00 mmol) in diethyl ether (30 mL) was added ^{t}BuOK (224 mg, 2.00 mmol) at 0°C, and the mixture was stirred at room temperature for 24 h. After filtration and removal of solvent, the residue was crystallized from diethyl ether/hexane (20 mL, 3/1 in v/v) to give **II-6l** as colorless crystals (335 mg, 64%). ^1H NMR (benzene-d_6): δ 3.72 (brs, 16H, THF), 1.67 (brs, 16H, THF), 1.35 (s, 9H, Bu^t), 1.14 (s, 27H, Bu^t). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 93.3 (cage *C*), 77.1 (THF), 73.3 ($OC(CH_3)_3$), 32.8 ($C(CH_3)_3$), 32.0 (THF), 25.6 ($C(CH_3)_3$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -1.9 (4B), -8.0 (4B), -11.9 (2B). IR (KBr, cm^{-1}): ν 2556 (BH). Anal. Calcd for $C_{34}H_{84}B_{20}O_{7.5}Zr_2$ (**II-6l** – 0.5THF): C, 40.37; H, 8.37. Found: C, 40.36; H, 8.39.

Preparation of [σ:σ:σ-{^{t}BuC(O)=CHC(^{t}Bu)(O)$C_2B_{10}H_{10}$}]Zr(η^2-^{t}BuCOCHCOBu^t)(THF)$_2$ (II-6m). This complex was prepared as colorless crystals from **II-6k** (520 mg, 1.00 mmol) and (^{t}BuCOCHCO^{t}Bu)Na, prepared from the reaction of ^{t}BuCOCH$_2$CO^{t}Bu (370 mg, 2.00 mmol) with NaH (48 mg, 2.00 mmol) in diethyl ether (15 mL) at room temperature, using the same procedure reported for **II-6l**: yield 424 mg (57%). ^{1}H NMR (benzene-d_6): δ 5.95 (s, 1H, C*H*), 5.36 (s, 1H, C*H*), 3.72 (m, 8H, THF), 1.51 (s, 3H. Bu^t), 1.45 (s, 3H, Bu^t), 1.32 (m, 8H, THF), 1.24 (s, 9H, Bu^t), 1.07 (s, 18H, Bu^t), 1.05 (s, 3H, Bu^t). ^{13}C{^{1}H} NMR (benzene-d_6): δ 203.1 (*C*=O), 165.1 (*C*=O), 103.7 (O-*C*(^{t}Bu)=CH), 100.8 , 97.1 (cage *C*), 95.8 (*C*H=C(^{t}Bu)OZr), 92.6 (ZrO-*C*(^{t}Bu)($C_2B_{10}H_{10}$)), 70.8 (THF), 42.0, 41.0, 36.7, 31.8, 28.5, 27.9, 25.6, 25.2, 24.5 (THF, Bu^t). ^{11}B{^{1}H} NMR (benzene-d_6): δ -3.3 (2B), -6.5 (3B), -9.90 (2B), -11.9 (3B). IR (KBr, cm^{-1}): ν 2567 (BH). Anal. Calcd for $C_{28}H_{56}B_{10}O_5Zr$ (**II-6m** – THF): C, 50.04; H, 8.40. Found: C, 50.35; H, 8.24.

Preparation of [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-{(Ph)$_2$C(O)$C_2B_{10}H_{10}$}] (III-1). To a stirring suspension of **II-6b** (174 mg, 0.20 mmol) in toluene (10 mL) at room temperature was added benzophenone (36 mg, 0.20 mmol), and the mixture was stirred at room temperature for 48 h. A clear colorless solution formed. After removal of the solvent in vacuum to 3 mL, the residue was stood overnight to yield **III-1** as colorless crystals (200 mg, 95%). ^{1}H NMR (pyridine-d_5): δ 8.31 (m, 4H), 7.65 (m, 6H), 7.55 (m, 2H), 7.49 (m, 4H), 7.42 (m, 2H), 7.31 (m, 2H) (phenyl *H*), 3.63 (THF), 2.13 (m, 3H), 1.97 (m, 6H), 1.85 (m, 3H), 1.61 (m, 12H), 1.38 (m, 4H), 1.15 (m, 6H), 1.05 (m, 6H), 0.96 (m, 4H) (Cy). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 182.5 (NCN), 129.3, 128.7, 128.3, 128.0, 127.2, 126.9, 126.8, 126.6, 125.9, 125.1, 122.3 (phenyl *C*), 107.7, 100.3 (cage *C*), 91.6 (*C*-O), 67.1 (THF), 57.8 (NCH), 34.9, 25.1, 25.0, 24.8 (CH_2). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -2.1 (4B), -7.5 (6B). IR (KBr, cm^{-1}): ν 2563

(BH). Anal. Calcd for $C_{61}H_{90}B_{10}N_4O_3Zr$ (**III-1**): C, 64.79; H, 7.59; N, 5.70. Found: C, 64.95; H, 7.12; N, 5.69.

Preparation of $[\eta^2$-CyNC(Ph)NCy$]_2$Zr[σ:σ-{[-$(CH_2)_5$-]C(O)$C_2B_{10}H_{10}$}] (III-2). To a stirring suspension of **II-6b** (174 mg, 0.20 mmol) in toluene (10 mL) at room temperature was added cyclohexanone (20 mg, 0.20 mmol), and the mixture was stirred at room temperature for 48 h. A clear colorless solution formed. After removal of the solvent in vacuum to 3 mL, the residue was stood overnight to yield **III-2** as colorless crystals (156 mg, 87%). ^{1}H NMR (pyridine-d_5): δ 7.56 (m, 4H), 7.50 (m, 4H), 7.42 (m, 2H) (phenyl *H*), 3.36 (m, 2H, NC*H*), 2.99 (m, 2H, NC*H*), 2.42 (m, 2H, CH_2), 1.99 (m, 4H, CH_2), 1.72 (m, 24H, CH_2), 1.46 (m, 6H, CH_2), 1.06 (m, 14H, CH_2). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 181.2 (NCN), 132.1, 129.2, 128.3, 128.0, 127.4, 126.9, 125.9, 122.3 (phenyl *C*), 106.1, 100.7 (cage *C*), 84.9 (*C*-O), 57.1 (NCH), 39.5, 34.9, 34.4, 25.3, 25.0, 22.6, 13.1 (CH_2). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -5.5 (6B), -10.0 (4B). IR (KBr, cm^{-1}): ν 2570 (BH). Anal. Calcd for $C_{46}H_{74}B_{10}N_4OZr$ (**III-2**): C, 61.50; H, 8.30; N, 6.24. Found: C, 60.98; H, 8.36; N, 6.03.

Preparation of $[\eta^2$-CyNC(Me)NCy$]_2$Zr[σ:σ-{[N=C(Me)$C_2B_{10}H_{10}$}] (III-3). This complex was prepared as yellow crystals from **II-6a** (270 mg, 0.40 mmol) and acetonitrile (16 mg, 0.40 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 117 mg (37%). ^{1}H NMR (benzene-d_6): complicated due to the decomposition of the product in solution. ^{13}C{^{1}H} NMR (benzene-d_6): δ 179.6, 172.6 (NCN), 96.2, 85.0 (cage *C*), 65.9 (NCH), 57.1, 56.8, 54.6, 36.3, 35.8, 35.1, 26.6, 26.4, 26.0, 15.5, 13.6, 10.4 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (benzene-d_6): most decomposed to *o*-carborane. IR (KBr, cm^{-1}): ν 2577 (BH). Anal. Calcd for $C_{36}H_{73}B_{10}N_5OZr$ (**III-3** + Et_2O): C, 54.64; H, 9.30; N, 8.85. Found: C, 54.23; H, 9.26; N, 8.61.

Preparation of [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-{[N=C(Ph)$C_2B_{10}H_{10}$}] (III-4). This complex was prepared as yellow crystals from **II-6b** (261 mg, 0.30 mmol) and benzonitrile (62 mg, 0.60 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 230 mg (85%). ^{1}H NMR (benzene-d_6): δ 8.35 (m, 2H), 7.31 (m, 4H), 7.10 (m, 8H), 6.67 (t, J = 8.0 Hz, 1H) (phenyl *H*), 3.31 (m, 4H, NC*H*), 2.01 (m, 8H, CH_2), 1.75 (m, 8H), 1.59 (m, 8H), 1.37 (m, 4H), 1.00 (m, 12H). (CH_2). ^{13}C{^{1}H} NMR (benzene-d_6): δ 181.2 (N*C*N), 135.3, 133.1, 132.4, 132.0, 131.1, 129.9, 129.4, 129.0, 128.6, 126.9 (phenyl *C*), 105.2, 100.1 (cage *C*), 58.2 (N*C*H), 35.6, 26.0, 25.7 (*C*H$_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.3 (3B), -5.8 (3B), -8.8 (4B). IR (KBr, cm^{-1}): ν 2572 (BH). Anal. Calcd for $C_{47}H_{69}B_{10}N_5Zr$ (**III-4**): C, 62.49; H, 7.70; N, 7.75. Found: C, 62.88; H, 7.46; N, 7.40.

Preparation of [η^2-CyNC(Me)NCy]$_2$Zr[σ:σ-{[N=C(Ph)$C_2B_{10}H_{10}$}] (III-5). This complex was prepared as yellow crystals from **II-6a** (270 mg, 0.40 mmol) and benzonitrile (51 mg, 0.50 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 237 mg (76%). ^{1}H NMR (benzene-d_6): δ 8.21 (m, 2H), 7.02 (m, 3H) (phenyl *H*), 3.31 (m, 4H, NC*H*), 1.87 (m, 8H, CH_2), 1.69 (s, 6H, CH_3), 1.65 (m, 8H), 1.55 (m, 8H), 1.29 (m, 8H), 1.12 (m, 6H) (CH_2). ^{13}C{^{1}H} NMR (benzene-d_6): δ 179.4 (N*C*N), 172.3 (CN), 135.4, 131.0, 129.8, 128.1 (phenyl *C*), 104.1, 99.2 (cage *C*), 56.9 (N*C*H), 35.1, 26.0, 13.8 (*C*H$_2$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -1.5 (3B), -5.0 (3B), -8.9 (4B). IR (KBr, cm^{-1}): ν 2585 (BH). Anal. Calcd for $C_{37}H_{65}B_{10}N_5Zr$ (**III-5**): C, 57.03; H, 8.41; N, 8.99. Found: C, 56.91; H, 8.20; N, 9.01.

Preparation of [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-{[CyNC(=NCy)$C_2B_{10}H_{10}$}] (III-6). This complex was prepared as a colorless solid from **II-6b** (174 mg, 0.20 mmol) and N,N'-dicyclohexylcarbodiimide (42 mg, 0.20 mmol) in toluene (10 mL) using the

same procedure reported for **III-1**: yield 195 mg (97%). ^{1}H NMR (pyridine-d_5): δ 7.89 (m, 2H), 7.73 (m, 2H), 7.61 (m, 6H) (phenyl *H*), 4.54 (m, 2H, NC*H*), 4.25 (m, 2H, NC*H*), 3.79 (m, 2H, NC*H*), 3.38 (m, 6H), 3.03 (m, 2H), 2.81 (m, 2H), 2.55 (m, 2H), 2.21 (m, 2H), 2.07 (m, 8H), 1.76 (m, 18H), 1.58 (m, 14H), 1.11 (m, 8H), 0.48 (m, 2H) (CH_2). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 182.1, 177.6 (NCN), 149.9, 132.9, 131.6, 129.4, 128.9, 128.7, 128.6, 128.2, 128.0, 126.1, 126.0, 122.3 (phenyl *C*), 100.1, 81.6 (cage *C*), 59.2, 58.1, 57.5, 57.4, 55.4, 53.9 (NCH), 37.4, 35.7, 35.5, 35.1, 34.4, 33.7, 33.0, 32.6, 30.2, 26.8, 26.4, 26.0, 25.7, 25.6, 25.5, 25.4, 25.3, 25.1, 24.9, 24.7, 23.7 (CH_2). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -1.7 (3B), -6.5 (7B). IR (KBr, cm^{-1}): ν 2569 (BH). Anal. Calcd for $C_{53}H_{86}B_{10}N_6Zr$ (**III-6**): C, 63.18; H, 8.61; N, 8.35. Found: C, 63.23; H, 8.67; N, 7.91.

Preparation of [η^2-CyNC(Ph)NCy]$_2$Zr[σ:σ-{[^{i}PrNC(=N^{i}Pr)C$_2$B$_{10}$H$_{10}$}] (III-7). This complex was prepared as colorless crystals from **II-6b** (174 mg, 0.20 mmol) and N,N'-diisopropylcarbodiimide (25 mg, 0.20 mmol) in toluene (10 mL) using the same procedure reported for **III-1**: yield 176 mg (95%). ^{1}H NMR (pyridine-d_5): δ 7.73 (m, 2H), 7.67 (m, 4H), 7.52 (m, 4H) (phenyl *H*), 4.82 (m, 2H, NC*H*), 3.77 (m, 2H, THF), 3.35 (m, 2H, NC*H*), 2.99 (m, 2H, NC*H*), 2.45 (m, 2H), 2.15 (m, 2H), 2.05 (m, 8H), 1.95 (d, J = 6.0 Hz, 3H, CH_3), 1.88 (d, J = 6.0 Hz, 3H, CH_3), 1.79 (m, 12H, CH_2), 1.63 (m, 2H, THF), 1.45 (m, 6H, CH_2), 1.23 (d, J = 6.0 Hz, 3H, CH_3), 1.20 (d, J = 6.0 Hz, 3H, CH_3), 1.09 (m, 4H, CH_2), 0.96 (m, 6H, CH_2). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 181.8, 180.0, 178.9 (NCN), 149.8, 132.7, 131.8, 129.4, 129.3, 128.8, 128.5, 128.3, 126.5, 126.2, 125.9, 125.7, 122.9, 122.7, (phenyl *C*), 99.8, 80.7 (cage *C*), 59.1, 58.0, 57.3, (NCH), 46.3, 44.6, 36.7, 35.0, 34.8, 34.7, 34.4, 25.9, 25.3, 25.1, 24.9, 24.8, 24.3, 22.6, 21.6 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -2.1 (3B), -6.7 (7B). IR (KBr, cm^{-1}): ν 2582 (BH). Anal. Calcd for $C_{49}H_{82}B_{10}N_6O_{0.5}Zr$ (**III-7** +

0.5 THF): C, 61.14; H, 8.59; N, 8.73. Found: C, 61.28; H, 8.92; N, 8.38.

Preparation of [η^2-^{i}PrNC(^{n}Bu)NPr^i]$_2$Hf[σ:σ-{[^{i}PrNC(=NPr^i)C$_2$B$_{10}$H$_{10}$}] (III-8). This complex was prepared as a colorless solid from **II-6j** (206mg, 0.30 mmol) and N,N'-diisopropylcarbodiimide (76 mg, 0.60 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 223 mg (91%). ^{1}H NMR (benzene-d_6): δ 4.91 (m, 1H), 4.39 (m, 1H), 4.22 (m, 1H) 3.69 (m, 2H), 3.54 (m, 1H) (NC*H*), 2.09 (m, 4H), 1.83 (d, J = 8.4 Hz, 3H, CH_3), 1.58 (d, J = 8.4 Hz, 6H, CH_3), 1.40 (d, J = 8.4 Hz, 3H, CH_3), 1.35 (d, J = 8.4 Hz, 3H, CH_3), 1.31 (m, 8H), 1.25 (m, 9H) (CH_2 and CH_3), 1.17 (d, J = 8.4 Hz, 3H, CH_3), 1.06 (d, J = 8.4 Hz, 3H, CH_3), 0.90 (d, J = 8.4 Hz, 3H, CH_3), 0.86 (d, J = 8.4 Hz, 3H, CH_3), 0.83 (m, 6H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 183.8, 181.6, 151.6 (NCN), 106.7, 81.6 (cage *C*), 49.0, 48.2, 47.7, 47.3, 46.7 (NCH), 29.2, 29.0, 28.7, 27.2, 27.1, 25.9, 25.4, 25.3, 25.0, 24.7, 24.6, 24.3, 23.6, 23.5, 23.4, 21.9, 13.6 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.09 (3B), -7.0 (3B), -10.0 (3B), -11.5 (1B). IR (KBr, cm^{-1}): ν 2580, 2550 (BH). Anal. Calcd for C$_{31}$H$_{70}$B$_{10}$N$_6$Hf (**III-8**): C, 45.77; H, 8.67; N, 10.33. Found: C, 45.77; H, 8.57; N, 10.16.

Preparation of [η^2-CyNC(Me)NCy]$_2$Zr[σ:σ-{[PhN(CO)C$_2$B$_{10}$H$_{10}$}] (III-9). This complex was prepared as colorless crystals from **II-6a** (135 mg, 0.20 mmol) and PhNCO (24 mg, 0.20 mmol) in toluene (10 mL) using the same procedure reported for **III-1**: yield 148 mg (93%). ^{1}H NMR (pyridine-d_5): δ 7.43 (m, 2H), 7.33 (m, 2H), 7.25 (m, 1H) (phenyl *H*), 4.10 (m, 2H, NC*H*), 3.59 (m, 2H, THF), 2.91 (m, 2H, NC*H*), 2.30 (s, 3H), 2.27 (s, 3H) (CH_3), 1.99 (m, 2H), 1.76 (m, 18H), 1.59 (m, 4H), 1.43 (m, 2H), 1.27 (m, 14H), 0.92 (m, 2H) (CH_2). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 183.5, 180.6, 171.8 (NCN and *C*O), 143.7, 128.0, 127.4, 125.7 (phenyl *C*), 88.6, 81.6 (cage *C*), 57.9, 56.0 (NCH), 35.5, 34.0, 32.8, 31.0, 25.7, 24.9, 15.1, 13.5 (*C*H$_2$ and

CH_3). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ -2.7 (4B), -6.9 (6B). IR (KBr, cm^{-1}): ν 2596, 2564 (BH). Anal. Calcd for $C_{37}H_{65}B_{10}N_5OZr$ (**III-9**): C, 55.81; H, 8.23; N, 8.80. Found: C, 55.79; H, 8.29; N, 8.43.

Preparation of $[\eta^2$-CyNC(Ph)NCy$]_2$Zr[σ:σ-{[^{n}BuNC(=S)$C_2B_{10}H_{10}$}] (III-10). This complex was prepared as yellow crystals from **II-6b** (174 mg, 0.20 mmol) and ^{n}BuNCS (46 mg, 0.40 mmol) in toluene (10 mL) using the same procedure reported for **III-1** but recrystallization from a mixed solvent of hexane and ether in 1/2 (v/v): yield 144 mg (79%). ^1H NMR (benzene-d_6): δ 7.77 (d, J = 7.5 Hz, 1H), 7.30 (m, 1H), 7.12 (m, 7H) (phenyl *H*), 4.83 (m, 1H), 4.24 (m, 1H), 4.01 (m, 1H), 3.30 (m, 1H) (NC*H*), 2.91 (m, 1H), 2.64 (m, 1H), 2.06 (m, 2H), 1.86 (m, 8H), 1.69 (m, 18H), 1.44 (m, 6H) (CH_2), 1.04 (t, J = 7.2 Hz, 3H, CH_3), 1.01 (m, 4H), 0.90 (m, 6H) (CH_2). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 204.4, 186.1, 180.2 (NCN and *C*S), 133.0, 130.9, 130.2, 130.1, 129.8, 128.9, 126.5, 126.4, 126.3 (phenyl *C*), 95.4, 92.3 (cage *C*), 60.3, 59.1, 58.2, 58.1, 50.4 (NCH and NCH_2), 44.3, 38.0, 36.9, 36.1, 35.8, 35.4, 35.3, 34.1, 33.8, 31.7, 31.5, 26.7, 26.5, 26.2, 25.8, 25.5, 25.3, 25.2, 21.4, 19.6, 14.5, 13.1 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -2.5 (4B), -6.8 (6B). IR (KBr, cm^{-1}): ν 2563 (BH). Anal. Calcd for $C_{45}H_{73}B_{10}N_5SZr$ (**III-10**): C, 59.04; H, 8.04; N, 7.65. Found: C, 59.07; H, 7.98; N, 7.82.

Preparation of $[\eta^2$-^{i}PrNC(Bu^n)NPr$^i]_2$Hf[σ:σ-{[^{n}BuNC(=S)$C_2B_{10}H_{10}$}] (III-11). This complex was prepared as a light yellow solid from **II-6j** (206 mg, 0.30 mmol) and ^{n}BuNCS (69 mg, 0.60 mmol) in toluene (10 mL) using the same procedure reported for **III-1**: yield 209 mg (87%). ^1H NMR (benzene-d_6): δ 4.65 (m, 2H, NC*H*), 3.58 (q, J = 6.0, 4H, CH_2), 2.10 (q, J = 7.2, 4H, CH_2), 1.61 (m, 2H, C*H*), 1.41 (m, 6H), 1.18 (m, 19H), 0.98 (m, 6H), 0.87 (m, 12H) (CH_2 and CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 205.3, 187.8, 183.0 (NCN and *C*S), 102.7, 91.5 (cage *C*), 51.0, 49.5,

48.2, 47.9, 47.6 (NCH and NCH_2), 30.6, 29.7, 29.5, 28.2, 27.2, 26.8, 26.6, 25.1, 25.0, 24.5, 24.3, 24.0, 23.6, 23.4, 23.3, 21.2, 14.3, 13.6, 13.5 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -3.3 (3B), -7.0 (4B), -8.7 (2B), -12.8 (1B). IR (KBr, cm^{-1}): ν 2594, 2564 (BH). Anal. Calcd for $C_{45}H_{73}B_{10}N_5SZr$ (**III-11**): C, 59.04; H, 8.04; N, 7.65. Found: C, 59.07; H, 7.98; N, 7.82.

Preparation of $[\eta^2$-^{i}PrNC(Bu^n)NPr$^i]_2$Hf[σ:σ-{[SC(=S)$C_2B_{10}H_{10}$}] (III-12). This complex was prepared as light purple crystals from **II-6j** (206 mg, 0.30 mmol) and CS_2 (76 mg, 1.00 mmol) in toluene (20 mL) in a closed flask at 110 ℃ for 3 days. Workup was using the same procedure reported for **III-1**: yield 137 mg (60%). ^1H NMR (benzene-d_6): δ 2.07 (m, 4H, CH_2), 1.33 (m, 4H, CH_2), 1.22 (q, J = 6.4, 12H, CH_3), 1.16 (m, 6H, CH_2), 1.04 (brs, 10H, CH_2), 0.79 (t, J = 7.2, 6H, CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 185.2 (CS), 110.5, 99.5 (cage C), 48.6 (NCH), 28.9, 28.1, 25.0, 24.7, 23.4, 13.5 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -1.2 (1B), -3.4 (2B), -6.7 (4B), -8.7 (3B). IR (KBr, cm^{-1}): ν 2564 (BH). Anal. Calcd for $C_{25}H_{56}B_{10}N_4S_2Hf$ (**III-12**): C, 39.33; H, 7.39; N, 7.34. Found: C, 39.53; H, 7.40; N, 6.87.

Preparation of $[\eta^2$-^{i}PrNC(Me)NPr$^i]_2$Zr[1,2-$S_2C_2B_{10}H_{10}$] (III-13a). This complex was prepared as a light yellow solid from **II-6e** (1.2 g, 2.00 mmol) and sulfur (132 mg, 4.10 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 940 mg (81%). ^1H NMR (benzene-d_6): δ 3.30 (m, 4H, NCH), 1.37 (s, 6H, CH_3), 1.12 (d, J = 6.0, Hz, 24H, CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 180.8 (NCN), 92.8 (cage C), 49.0 (NCH), 24.7, 12.2 (CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -7.7 (10B). IR (KBr, cm^{-1}): ν 2573 (BH). Anal. Calcd for $C_{18}H_{14}B_{10}N_4S_2Zr$ (**III-13a**): C, 37.27; H, 7.65; N, 9.66. Found: C, 37.56; H, 7.92; N, 9.40.

Preparation of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr$^i]_2$Zr[1,2-$S_2C_2B_{10}H_{10}$] (III-13b). This complex was prepared as a light yellow solid from **II-6g** (120 mg, 0.20 mmol) and

sulfur (13 mg, 0.40 mmol) in toluene (10 mL) using the same procedure reported for **III-1**: yield 117 mg (88%). ^{1}H NMR (benzene-d_6): δ 3.44 (m, 4H, NC*H*), 2.01 (t, J = 7.8 Hz, 4H, CH_2), 1.25 (m, 4H), 1.19 (d, J = 6.6 Hz, 24H, CH_3), 1.13 (m, 4H, CH_2), 0.75 (t, J = 6.9 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 183.1 (*N*CN), 91.6 (cage *C*), 48.5 (*N*CH), 29.0, 26.5, 25.2, 23.2, 13.6 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -7.3 (10B). IR (KBr, cm^{-1}): ν 2646, 2566 (BH). Anal. Calcd for $C_{24}H_{56}B_{10}N_4S_2Zr$ (**III-13b**): C, 43.40; H, 8.50; N, 8.44. Found: C, 43.15; H, 8.24; N, 8.48.

Preparation of [η^2-^{i}PrNC(^{n}Bu)NPr^i]$_2$Hf[1,2-$S_2C_2B_{10}H_{10}$] (III-13c). This complex was prepared as a light yellow solid from **II-6j** (206 mg, 0.30 mmol) and sulfur (22 mg, 0.70 mmol) in toluene (15 mL) using the same procedure reported for **III-1**: yield 214 mg (95%). ^{1}H NMR (benzene-d_6): δ 3.61 (m, 4H, NC*H*), 2.01 (t, J = 8.1 Hz, 4H, CH_2), 1.20 (m, 4H), 1.18 (d, J = 6.3 Hz, 24H, CH_3), 1.11 (m, 4H, CH_2), 0.75 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 183.8 (*N*CN), 92.6 (cage *C*), 49.6 ((NCN)*C*H$_2$), 48.8 (*N*CH), 29.2, 25.3, 23.2, 13.6 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -7.2 (6B), -8.9 (4B). IR (KBr, cm^{-1}): ν 2573 (BH). Anal. Calcd for $C_{24}H_{56}B_{10}N_4S_2Hf$ (**III-13c**): C, 38.36; H, 7.51; N, 7.46. Found: C, 38.41; H, 7.59; N, 7.25.

Preparation of [η^2-CyNC(Me)NCy]$_2$Zr[1,2-$Se_2C_2B_{10}H_{10}$] (III-13d). This complex was prepared as a yellow solid from **II-6a** (202 mg, 0.30 mmol) and selenium (48 mg, 0.60 mmol) in toluene (15 mL) using the same procedure reported for **III-1**: yield 198 mg (79%). ^{1}H NMR (benzene-d_6): δ 3.02 (m, 4H, NC*H*), 1.72 (m, 20H, CH_2), 1.53 (m, 4H, CH_2), 1.47 (s, 6H, CH_3), 1.43 (m, 2H), 1.13 (m, 14H) (CH_2). ^{13}C{^{1}H} NMR (benzene-d_6): δ 180.1 (*N*CN), 75.0 (cage *C*), 57.8 (*N*CH), 35.4, 25.9, 25.7, 12.3 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -6.5 (10B). IR (KBr, cm^{-1}):

ν 2567 (BH). Anal. Calcd for $C_{30}H_{60}B_{10}N_4Se_2Zr$ (**III-13d**): C, 43.20; H, 7.25; N, 6.72. Found: C, 43.18; H, 7.24; N, 6.42.

Preparation of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr$^i]_2$Zr[1,2-$Se_2C_2B_{10}H_{10}$] (III-13e). This complex was prepared as a yellow solid from **II-6g** (180 mg, 0.30 mmol) and selenium (48 mg, 0.60 mmol) in toluene (15 mL) using the same procedure reported for **III-1**: yield 184 mg (81%). ^{1}H NMR (benzene-d_6): δ 3.45 (m, 4H, NC*H*), 1.98 (t, J = 7.8 Hz, 4H, CH_2), 1.20 (m, 4H), 1.18 (d, J = 6.6 Hz, 24H, CH_3), 1.11 (m, 4H, CH_2), 0.75 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 183.5 (NCN), 74.9 (cage *C*), 48.8 (NCH), 29.0, 26.1, 25.4, 23.1, 13.6 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -6.1 (10B). IR (KBr, cm^{-1}): ν 2591, 2563 (BH). Anal. Calcd for $C_{24}H_{56}B_{10}N_4Se_2Zr$ (**III-13e**): C, 38.36; H, 7.51; N, 7.46. Found: C, 38.41; H, 7.59; N, 7.25.

Preparation of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr$^i]_2$Zr[η^2:η^2-1,2-(PhN=N-N)$_2$-1,2-$C_2B_{10}H_{10}$] (III-14). This complex was prepared as yellow crystals from **II-6g** (300 mg, 0.50 mmol) and PhN_3 (119 mg, 1.00 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 400 mg (95%). ^{1}H NMR (benzene-d_6): δ 7.63 (d, J = 7.6 Hz, 4H), 7.17 (dd, J = 7.6 and 8.2 Hz, 4H), 6.97 (dd, J = 7.6 Hz, 2H) (phenyl H), 3.79 (m, 2H), 3.70 (m, 1H), 3.34 (m, 1H) (NC*H*), 2.15 (m, 4H), 1.48 (m, 2H), 1.40 (d, J = 6.4 Hz, 6H), 1.27 (m, 2H, CH_2), 1.16 (m, 2H, CH_2), 1.13 (d, J = 6.8 Hz, 6H), 1.09 (d, J = 6.8 Hz, 6H), 1.06 (m, 2H, CH_2), 0.78 (m, 12H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 183.6, 179.2 (NCN), 148.0, 129.0, 126.5, 120.3 (phenyl *C*), 95.2 (cage *C*), 49.5, 48.1 (NCH), 29.6, 28.8, 27.0, 25.9, 24.0, 23.7, 23.5, 23.4, 22.4, 13.7, 13.6 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -8.9 (4B), -11.7 (6B). IR (KBr, cm^{-1}): ν 2594 (BH). Anal. Calcd for $C_{36}H_{66}B_{10}N_{10}Zr$ (**III-14**): C, 51.58; H, 7.94; N, 16.71. Found: C, 51.43; H, 8.06; N, 16.32.

Preparation of $[\eta^2$-CyNC(^{n}Bu)NCy$]_2$Zr$[\eta^2$:σ-1-PhN=N-N-1,2-$C_2B_{10}H_{10}\}$ (III-15a). This complex was prepared as yellow crystals from **II-6c** (380 mg, 0.50 mmol) and PhN_3 (179 mg, 1.50 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 320 mg (76%). ^{1}H NMR (benzene-d_6): δ 8.13 (d, J = 7.6 Hz, 2H), 7.19 (dd, J = 7.6 and 8.0 Hz, 2H), 6.92 (dd, J = 7.6 Hz,1H) (phenyl H), 3.44 (m, 4H, NC*H*), 2.68 (m, 1H), 2.26 (m, 4H), 2.10 (m, 1H), 1.84 (m, 16H), 1.60(m, 10H), 1.40 (m, 4H), 1.28 (m, 10H), 1.18 (m, 6H), 1.04 (m, 2H, CH_2), 0.85 (t, J = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 181.1, 180.0 (NCN), 143.6, 129.2, 127.5, 122.9 (phenyl *C*), 111.2, 108.2 (cage *C*), 58.3, 57.4, 57.2, 56.8 (NCH), 37.5, 36.8, 36.5, 35.9, 35.3, 34.9, 33.7, 33.6, 29.9, 28.9, 26.8, 26.6, 26.2, 26.1, 26.0, 25.9, 25.7, 25.4, 25.3, 23.6, 23.2 (*C*H_2 and *C*H_3). ^{11}B{^{1}H} NMR (benzene-d_6): δ -0.9 (2B), -6.0 (8B). IR (KBr, cm^{-1}): ν 2580 (BH). Anal. Calcd for $C_{42}H_{77}B_{10}N_7Zr$ (**III-15a**): C, 57.36; H, 8.83; N, 11.15. Found: C, 57.61; H, 8.79; N, 11.32.

Preparation of $[\eta^2$-^{i}PrNC(Ph)NPr$^i]_2$Zr$[\eta^2$:σ-1-PhN=N-N-1,2-$C_2B_{10}H_{10}\}$ (III-15b). This complex was prepared as yellow crystals from **II-6f** (357 mg, 0.50 mmol) and PhN_3 (179 mg, 1.50 mmol) in toluene (20 mL) using the same procedure reported for **III-1**: yield 338 mg (89%). ^{1}H NMR (benzene-d_6): δ 8.26 (d, J = 8.1 Hz, 1H), 7.66 (brs, 1H), 7.38 (m, 15H) (phenyl H), 3.56 (m, 1H), 3.45 (m, 1H), 3.29 (m, 2H), (NC*H*), 2.11 (s, CH_3 of toluene), 1.41 (m, 3H), 1.29 (m, 3H), 1.13 (d, J = 5.4 Hz, 12H, CH_3), 0.66 (m, 6H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 179.6, 177.9 (NCN), 143.4, 137.8, 132.5, 131.4, 129.5, 129.3, 129.2, 128.5, 127.5, 126.2, 125.6, 122.6 (phenyl *C*), 111.4, 108.5 (cage *C*), 49.8 (NCH), 26.1, 25.4, 25.0, 23.0, 21.4 (*C*H_3). ^{11}B{^{1}H} NMR (benzene-d_6): δ -1.0 (2B), -6.2 (8B). IR (KBr, cm^{-1}): ν 2555 (BH). Anal. Calcd for $C_{41}H_{61}B_{10}N_7Zr$ (**III-15b** + toluene): C, 57.85; H, 7.22; N, 11.52. Found: C, 57.98; H, 7.27; N, 11.40.

Preparation of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr$^i]_2$Zr{[N(2,6-Me$_2$C$_6$H$_3$)C]$_2$C(=N(2,6-Me$_2$C$_6$H$_3$)-1,2-C$_2$B$_{10}$H$_{10}$} (III-16a). This complex was prepared as brown crystals from **II-6g** (180 mg, 0.30 mmol) and 2,6-dimethylphenylisonitrile (131 mg, 1.00 mmol) in toluene (20 mL) using the same procedure reported for **III-1** but reacting for 3 days: yield 281 mg (94%). ^{1}H NMR (benzene-d_6): δ 6.94 (m, 5H), 6.85 (m, 4H) (phenyl H), 3.71 (m, 4H, NC*H*), 2.59 (s, 6H, C*H*$_3$), 2.54 (s, 6H, C*H*$_3$), 2.13 (m, 4H, C*H*$_2$), 2.10 (s, 6H, C*H*$_3$), 1.35 (m, 4H, C*H*$_2$), 1.18 (m, 4H), 1.11 (d, J = 6.8 Hz, 12H, C*H*$_3$), 0.95 (d, J = 6.8 Hz, 12H, C*H*$_3$), 0.80 (t, J = 7.2 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 182.3 (NCN), 147.9, 147.2, 146.6 (*C*=N and C=*C*-N), 140.5, 135.3, 134.4, 128.5, 127.3, 127.1, 125.9, 124.7, 124.2, 122.9 (phenyl *C*), 75.3, 73.5, (cage *C*), 48.2 (NC*H*), 34.9, 29.4, 29.1, 27.2, 25.6, 24.8, 24.4, 23.6, 22.2, 21.9, 19.0, 13.7 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -1.5 (5B), -9.4(5B). IR (KBr, cm^{-1}): ν 2623, 2571 (BH). Anal. Calcd for $C_{51}H_{83}B_{10}N_7Zr$ (**III-16a**): C, 61.65; H, 8.42; N, 9.87. Found: C, 61.26; H, 8.61; N, 9.41.

Preparation of $[\eta^2$-^{i}PrNC(^{n}Bu)NPr$^i]_2$Zr{[N(2-Cl-6-MeC$_6$H$_3$)C]$_2$C(=N(2-Cl-6-MeC$_6$H$_3$)-1,2-C$_2$B$_{10}$H$_{10}$} (III-16b). This complex was prepared as brown crystals from **II-6g** (180 mg, 0.30 mmol) and 2-chloro-6-methylphenylisonitrile (151 mg, 1.00 mmol) in toluene (20 mL) using the same procedure reported for **III-16a**: yield 171 mg (81%). ^{1}H NMR (benzene-d_6): δ 7.16 (m, 2H), 6.98 (m, 1H), 6.85 (m, 2H), 6.72(m, 1H), 6.65 (m, 2H), 6.49 (m, 1H) (phenyl H), 3.88 (m, 1H), 3.59 (m, 1H), 3.50 (m, 2H) (NC*H*), 2.56 (m, 6H, C*H*$_3$), 2.15 (m, 2H, C*H*$_2$), 2.10 (s, 3H, C*H*$_3$), 1.98 (m, 2H, C*H*$_2$), 1.18 (m, 26H), 0.81 (m, 12H) (C*H*$_2$ and C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 183.3, 183.1, 183.0, 182.3, 182.2, 181.5 (N*C*N), 149.2, 149.0, 148.5, 146.4, 145.8, 145.6, 145.5, 145.2, 145.0, (*C*=N and C=*C*-N), 141.9, 141.6, 141.3, 139.0, 138.9, 138.8, 138.4, 137.0, 136.7, 135.3, 134.2, 133.3, 133.2, 133.0, 132.8,

132.7, 131.2, 130.5, 130.3, 129.7, 129.5, 128.8, 128.6, 127.1, 126.9, 126.7, 126.5, 126.3, 125.5, 125.2, 125.0, 124.6, 124.4, 123.4 (phenyl *C*), 74.8, 73.3 (cage *C*), 67.8 (THF), 65.9 (diethyl ether), 48.8, 48.6, 48.5, 48.3, 48.2 (NCH), 29.5, 29.4, 29.1, 28.5, 25.8 (THF), 25.0, 24.8, 24.7, 24.6, 24.3, 24.2, 23.6, 23.0, 22.2, 22.0, 21.7, 21.6, 21.5, 19.1, 19.0, 15.6 (diethyl ether), 14.3, 13.7 (*CH*$_2$ and *CH*$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -3.0 (4B), -10.1 (3B), -14.0 (3B). IR (KBr, cm^{-1}): ν 2623, 2565 (BH). Anal. Calcd for $C_{48}H_{74}B_{10}Cl_3N_7Zr$ (**III-16b**): C, 54.66; H, 7.07; N, 9.29. Found: C, 54.83; H, 7.18; N, 8.98.

Preparation of [η^2-CyNC(Me)NCy]$_2$Zr{[N(2,6-Me$_2$C$_6$H$_3$)C]$_2$C(=N(2,6-Me$_2$C$_6$H$_3$)-1,2-C$_2$B$_{10}$H$_{10}$} (III-16c). This complex was prepared as brown crystals from **II-6a** (203 mg, 0.30 mmol) and 2,6-dimethylphenylisonitrile (131 mg, 1.00 mmol) in toluene (20 mL) using the same procedure reported for **III-16a**: yield 263 mg (82%). ^{1}H NMR (benzene-d_6): δ 6.96 (m, 2H), 6.93 (m, 3H), 6.82 (m, 4H) (phenyl H), 3.05 (m, 4H, NC*H*), 2.65 (s, 6H, C*H*$_3$), 2.50 (s, 6H, C*H*$_3$), 2.12 (s, 6H, C*H*$_3$), 1.66 (m, 8H, C*H*$_2$), 1.58 (s, 6H, C*H*$_3$), 1.49 (m, 12H), 1.33 (m, 4H), 1.11 (m, 16H) (C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 177.9 (NCN), 147.9, 147.6, 147.0, 146.7 (*C*=N and C=*C*-N), 140.6, 135.3, 133.9, 128.4, 127.3, 127.0, 125.7, 123.9, 122.9 (phenyl *C*), 75.3, 73.6 (cage *C*), 57.7 (NCH), 34.0, 33.2, 26.4, 26.3, 25.8, 25.5, 22.2, 21.1, 18.9, 15.3 (*CH*$_2$ and *CH*$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.3 (5B), -9.5 (5B). IR (KBr, cm^{-1}): ν 2622, 2575 (BH). Anal. Calcd for $C_{57}H_{87}B_{10}N_7Zr$ (**III-16c**): C, 64.00; H, 8.20; N, 9.17. Found: C, 63.96; H, 8.28; N, 8.84.

Preparation of [η^2-^{i}PrNC(^{n}Bu)NPr^i]$_2$Hf{[N(2,6-Me$_2$C$_6$H$_3$)C]$_2$C(=N(2,6-Me$_2$C$_6$H$_3$)-1,2-C$_2$B$_{10}$H$_{10}$} (III-16d). This complex was prepared as brown crystals from **II-6j** (228 mg, 0.30 mmol) and 2,6-dimethylphenylisonitrile (131 mg, 1.00 mmol) in toluene (20 mL) using the same procedure reported for **III-16a**: yield 301

mg (93%). ^{1}H NMR (benzene-d_6): δ 6.96 (m, 4H), 6.87 (m, 5H), (phenyl H), 3.81 (m, 4H, NC*H*), 2.60 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 2.12 (s, 6H, CH_3), 2.10 (t, J = 8.0 Hz, CH_2), 1.30 (m, 4H), 1.12 (m, 4H) (CH_2), 1.10 (d, J = 5.4 Hz, 12H, CH_3), 0.92 (d, J = 6.6 Hz, 12H, CH_3), 0.80 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 182.1 (NCN), 148.1, 148.0, 147.1, 146.6, (*C*=N and C=*C*-N), 140.2, 136.0, 135.3, 128.5, 127.3, 127.2, 125.9, 125.5, 124.0, 122.9 (phenyl *C*), 76.0, 73.2 (cage *C*), 47.9 (NCH), 34.9, 29.7, 29.3, 27.2, 25.6, 24.8, 24.4, 23.6, 22.2, 22.0, 20.9, 19.1, 13.7 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.0 (5B), -9.2 (5B). IR (KBr, cm^{-1}): ν 2627, 2572 (BH). Anal. Calcd for $C_{51}H_{83}B_{10}N_7Hf$ (**III-16d**): C, 56.67; H, 7.74; N, 9.07. Found: C, 56.65; H, 7.80; N, 8.84.

Preparation of [η^2-^{i}PrNC(^{n}Bu)NPr^i]$_2$Hf{[N(2-Cl-6-MeC$_6$H$_3$)C]$_2$C(=N(2-Cl-6-MeC$_6$H$_3$)-1,2-C$_2$B$_{10}$H$_{10}$} (III-16e). This complex was prepared as brown crystals from **II-6j** (228 mg, 0.30 mmol) and 2-chloro-6-methylphenylisonitrile (151 mg, 1.00 mmol) in toluene (20 mL) using the same procedure reported for **III-16a**: yield 191 mg (85%). ^{1}H NMR (benzene-d_6): δ 7.13 (m, 1H), 7.08 (m, 2H), 6.92 (m, 2H), 6.66 (m, 1H), 6.65 (m, 2H), 6.50 (m, 1H) (phenyl H), 3.63 (m, 4H, NC*H*), 2.59 (m, 6H, CH_3), 2.10 (s, 3H, CH_3), 1.99 (m, 2H, CH_2), 1.18 (m, 28H), 0.81 (m, 12H) (CH_2 and CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 183.0, 182.9, 182.7, 182.6, 182.1, 182.0, 181.5 (NCN), 149.9, 149.8, 149.4, 146.7, 146.6, 146.5, 146.2, 145.8, 145.7, 145.5, 145.1, 145.0 (*C*=N and C=*C*-N), 141.7, 141.2, 139.9, 139.0, 137.8, 137.7, 136.3, 135.1, 133.9, 133.7, 132.4, 130.5, 130.4, 129.7, 129.5, 129.3, 128.9, 128.8, 128.7, 128.5, 127.6, 127.0, 126.8, 126.5, 126.3, 126.1, 125.9, 125.6, 125.2, 125.1, 124.8, 124.6, 124.5, 124.4, 123.4 (phenyl *C*), 75.4, 73.0 (cage *C*), 48.1, 48.0, 47.8 (NCH), 29.8, 29.4, 29.3, 25.0, 24.7, 24.3, 23.6, 23.5, 21.9, 21.7, 21.6, 21.5, 21.4, 21.3, 19.2, 19.0, 13.6 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (benzene-d_6): δ -3.0 (4B), -10.5 (3B), -14.0

(3B). IR (KBr, cm^{-1}): ν 2627, 2567 (BH). Anal. Calcd for $C_{52}H_{82}B_{10}Cl_3N_7OHf$ (**III-16e** + THF): C, 51.44; H, 6.81; N, 8.07. Found: C, 51.55; H, 6.96; N, 8.57.

Preparation of $\{[\eta^2$-^{i}PrNC(^{n}Bu)NPr^i]$_2$Zr$\}_2\{$[1-NCCu-2-O(CH$_2$)$_4$-1,2-C$_2$B$_{10}$H$_{10}\}_2$ (III-17). This complex was prepared as light brown crystals from **II-6g** (300 mg, 0.50 mmol), LiCl (22 mg, 0.50 mmol)and CuCN (45 mg, 0.50 mmol) in toluene (20 mL)/THF (1 mL) using the same procedure reported for **III-1**: yield 347 mg (91%). ^{1}H NMR (pyridine-d_5): δ 4.12 (brs, 2H, OCH_2), 3.71 (m, 8H, NCH), 2.67 (m, 6H, CH_2), 2.40 (m, 12H, CH_2), 1.61 (m, 10H), 1.42 (m, 6H, CH_2), 1.28 (d, J = Hz, 48H, CH3), 1.23 (m, 4H, CH_2), 0.93 (t, J = 7.2 Hz, 12H). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 179.4 (NCN), 122.3 (NCCu), 96.1, 81.3 (cage C), 80.1 (OCH$_2$), 47.1, 47.0 (NCH), 41.2, 33.8, 31.0, 28.8, 27.4, 25.5, 24.6, 24.1, 22.6, 22.5, 22.1, 13.1 (CH_2 and CH_3). ^{11}B{^{1}H} NMR (pyridine-d_5): δ -3.1 (2B), -7.1 (8B). IR (KBr, cm^{-1}): ν 2572 (BH), 2114 (CN). Anal. Calcd for $C_{58}H_{128}B_{20}Cu_2N_{10}O_2Zr_2$ (**III-17**): C, 45.73; H, 8.47; N, 9.19. Found: C, 46.13; H, 8.33; N, 8.85.

Preparation of 1-HO(CH$_2$)$_4$(1,2-C$_2$B$_{10}$H$_{10}$) (III-18). Complex **III-17** (152 mg, 0.10 mmol) was treated with 1N aqueous HCl (5 mL), and the resulting solution was extracted with diethyl ether three times (3 × 5 mL), the organic phase was combined and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was subjected to flash column chromatography using 3:2 hexane/diethyl ether as eluent to yield the product **III-18** as a colorless oil (20 mg, 92%). ^{1}H NMR (benzene-d_6): δ 3.10 (t, J = 6.0 Hz, 2H, CH_2), 2.41 (brs, 1H, cage CH), 1.56 (m, 2H), 1.08 (m, 2H), 0.96 (m, 2H) (CH_2), 065 (brs, 1H, OH). ^{13}C{^{1}H} NMR (benzene-d_6): δ 75.4, 61.2 (cage C), 61.6 (OCH_2), 37.7, 30.1, 25.7 (CH_2). ^{11}B{^{1}H} NMR (benzene-d_6): δ -2.6 (1B), -6.0 (1B), -9.6 (2B), -11.8 (2B), -12.9 (2B), -13.5 (2B). IR (KBr, cm^{-1}): ν 2591 (BH). HRMS: m/z calcd for $[C_6H_{20}{}^{11}B_{16}{}^{10}B_4O - H]^+$: 215.2434.

Found: 215.2428.

Preparation of 1,2-[(THF)$_2$Cl$_2$ZrC(Ph)=C(Ph)]-1,2-$C_2B_{10}H_{10}$ (III-19). To a suspension of (η^2-$C_2B_{10}H_{10}$)$ZrCl_2(THF)_3$ (**II-6k**, 260 mg, 0.50 mmol) in toluene (20 mL) was added diphenylacetylene (178 mg, 1.00 mmol) at room temperature. The mixture was heated to reflux for 48 h. The hot brown reaction mixture was filtrated and washed with 5 mL of hot toluene. After removal of the solvent in vacuum, recrystallization from toluene (5 mL) gave **III-19** as brown crystals in 37% yield (116 mg, 0.18 mmol). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.18 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.92 (m, 4H), 6.81 (dd, J = 7.6 Hz, 1H), 6.67 (dd, J = 7.6 Hz, 1H), (phenyl *H*), 3.73 (s, 8H), 1.11 (s, 8H), (THF). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 208.9, 149.4 (olefinic *C*), 139.4, 138.1, 130.3, 129.2, 128.3, 127.5, 127.2, 126.0, (phenyl C), 100.6, 91.5 (cage *C*), 76.6, 25.3, (THF). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ -1.1 (1B), -4.8 (3B), -7.8 (3B), -10.5 (3B). IR (KBr, cm^{-1}): ν 2970, 2883, 2575, 1478, 1449, 1262, 1058, 997, 912, 825, 701, 560, 494. Anal. Calcd for $C_{24}H_{36}B_{10}Cl_2O_2Zr$ (**III-19**): C, 45.99; H, 5.79. Found: C, 46.07; H, 5.61.

Preparation of 1-[HC(Ph)=C(Ph)]-1,2-$C_2B_{10}H_{11}$ (III-20). A diethyl ether (20 mL) suspension of **III-19** (63 mg, 0.10 mmol) was treated with aqueous HCl solution (1M, 10 mL) at room temperature. The organic layer was separated and the aqueous solution was extracted with ethyl ether (10 mL × 2). The organic portions were combined and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was subjected to flash column chromatograph on silica gel using hexane as elute to give **III-20** as a colorless solid (29 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 3H), 7.14 (m, 5H), 7.03 (s, 1H), 6.78 (m, 2H) (phenyl and olifinic *H*), 3.28 (brs, 1H, cage C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.6, 134.9 (olefinic *C*), 134.5, 133.7, 129.6, 129.4, 129.3, 129.1, 128.3, 128.2 (phenyl *C*), 78.2,

58.0 (cage *C*). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.6 (1B), -4.2 (1B), -8.7 (2B), -10.2 (2B), -12.4 (2B), -13.8 (2B). HRMS: *m/z* calcd for $C_{16}H_{22}{}^{11}B_8{}^{10}B_2{}^+$ (**III-20**): 322.2719. Found: 322.2707.

Preparation of 1-Ph(CH$_2$)$_2$(1,2-C$_2$B$_{10}$H$_{11}$) (III-21). The reaction mixture of (η^2-$C_2B_{10}H_{10}$)$ZrCl_2(THF)_3$ (**II-6k**, 260 mg, 0.50 mmol) and styrene (78 mg, 0.75 mmol) in toluene was heated to reflux for 48 hours. After treatment with an aqueous HCl solution (1M, 10 mL), the organic phase was separated and the aqueous phase was extracted with diethyl ether three times (3 × 10 mL). The organic portions were combined and dried over Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by flash column chromatography using hexane as eluent to yield the product **III-21** as colorless oil (25 mg, 20%). ^1H NMR ($CDCl_3$): δ 7.30 (m, 3H), 7.13 (d, J = 7.2 Hz, 2H) (phenyl *H*), 3.60 (s, 1H, cage C*H*), 2.80 (m, 2H), 2.51 (m, 2H), (CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.7, 128.8, 128.1, 126.8 (phenyl *C*), 74.6, 61.1 (cage *C*), 39.8, 35.3 (*C*H$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ -2.6 (1B), -6.0 (1B), -9.6 (2B), -11.9 (2B), -12.4 (2B), -13.4 (2B). These data are in agreement with the literature.[141]

Preparation of 1,2-[Cp$_2$ZrCH(Ph)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-2a). To a toluene solution (20 mL) of **I-153** (554 mg, 1.00 mmol) was added styrene (**IV-1a**) (208 mg, 2.00 mmol), and the reaction mixture was heated to reflux for 48 h. After removal of the precipitate (LiCl), the clear solution was concentrated to about 5 mL, from which **IV-2a** was isolated as black crystals after standing at room temperature overnight (405 mg, 87%). ^1H NMR (400 MHz, pyridine-d_5): δ 7.39 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.50 (d, J = 7.6 Hz, 2H) (phenyl), 6.56 (s, 5H, C_5H_5), 5.60 (s, 5H, C_5H_5), 3.67 (m, 1H, CH_2), 3.56 (t, J = 13.6 Hz, 1H, C*H*), 3.06 (dd, J = 13.6 and 5.6 Hz, 1H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 140.3, 131.7, 117.5 (phenyl),

115.1, 114.0 (Cp), 94.8, 90.8 (cage *C*), 65.9 (*C*H), 40.6 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ -1.4 (1B), -2.9 (1B), -6.3 (5B), -9.8 (3B). IR (KBr, cm^{-1}): ν 2567 (BH). Anal. Calcd for $C_{21}H_{30}B_{10}Zr$ (**IV-2a**): C, 51.58; H, 5.63. Found: C, 51.82; H, 6.01.

Preparation of 1,2-[Cp$_2$ZrCH(4-Me-C$_6$H$_4$)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-2b). This complex was prepared as black crystals from **I-153** (554 mg, 1.00 mmol) and 4-methylstyrene (**IV-1b**) (236 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 359 mg (75%). ^{1}H NMR (400 MHz, benzene-d_6): δ 6.83 (d, J = 7.2 Hz, 2H), 5.82 (d, J = 7.2 Hz, 2H), (phenyl), 5.78 (s, 5H, C$_5H_5$), 5.01 (s, 5H, C$_5H_5$), 3.32 (m, 1H, CH_2), 3.15 (t, J = 13.6 Hz, 1H, C*H*), 2.95 (m, 1H, CH_2), 2.10 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 138.2, 132.2, 132.0, 119.1 (phenyl), 115.3, 114.1 (Cp), 94.3, 90.4 (cage *C*), 66.5 (*C*H), 41.9 (*C*H$_2$), 20.6 (*C*H$_3$). ^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ -0.66 (1B), -4.0 (1B), -5.6 (5B), -8.7 (3B). IR (KBr, cm^{-1}): ν 2567 (BH). Anal. Calcd for $C_{21}H_{30}B_{10}Zr$ (**IV-2b**): C, 52.35; H, 6.28. Found: C, 52.53; H, 6.44.

Preparation of 1,2-[Cp$_2$ZrCH(2-Cl-C$_6$H$_4$)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-2c). This complex was prepared as purple crystals from **I-153** (554 mg, 1.00 mmol) and 2-chlorostyrene (**IV-1c**) (277 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 378 mg (75%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.00 (d, J = 8.0 Hz, 1H), 6.98 (m, 2H), 6.56 (m, 2H) (aromatic *H*), 5.99 (s, 5H, C$_5H_5$), 5.53 (s, 5H, C$_5H_5$), 3.85 (t, J = 8.8 Hz, 1H, C*H*), 3.02 (dd, J = 8.4 and 15.0 Hz, 1H, CH_2), 2.84 (dd, J = 8.4 and 15.0 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 149.2, 129.9, 129.1, 127.3, 126.0, 123.2 (aromatic *C*), 117.6, 116.7 (Cp), 88.8, 84.5 (cage *C*), 58.0 (*C*H), 44.4 (*C*H$_2$). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ 0.45 (1B), -5.4 (2B), -6.4 (3B), -7.8 (2B), -9.6 (2B). IR (KBr, cm^{-1}): ν 2566 (BH). Anal. Calcd for

$C_{21.75}H_{29}B_{10}ClZr$ (**IV-2c** + 0.25toluene): C, 49.74; H, 5.57. Found: C, 49.85; H, 5.64.

Preparation of 1,2-[$Cp_2ZrCH(3\text{-}Cl\text{-}C_6H_4)\text{-}CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-2d). This complex was prepared as purple crystals from **I-153** (554 mg, 1.00 mmol) and 3-chlorostyrene (**IV-1d**) (277 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 440 mg (84%). ^{1}H NMR (400 MHz, benzene-d_6): δ 6.75 (m, 2H), 5.95 (s, 1H), 5.87 (d, J = 7.6 Hz, 2H) (aromatic *H*), 5.78 (s, 5H), 5.12 (s, 5H) (C_5H_5), 3.45 (dd, J = 6.0 and 12.0 Hz, 1H, CH_2), 3.05 (t, J = 12.0 Hz, 1H, C*H*), 2.77 (dd, J = 6.0 and 12.0 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 145.8, 136.7, 131.9, 121.9, 120.0, 118.3 (aromatic *C*), 116.1, 115.1 (Cp), 92.2, 87.9 (cage *C*), 63.6 (*C*H), 41.8 (*C*H_2). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ -0.3 (1B), -5.0 (3B), -7.0 (3B), -10.2 (3B). IR (KBr, cm^{-1}): ν 2568 (BH). Anal. Calcd for $C_{21.75}H_{29}B_{10}ClZr$ (**IV-2d**): C, 47.83; H, 5.42. Found: C, 48.07; H, 5.68.

Preparation of 1,2-[$Cp_2ZrCH(4\text{-}Cl\text{-}C_6H_4)CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-2e). This complex was prepared as purple crystals from **I-153** (554 mg, 1.00 mmol) and 4-chlorostyrene (**IV-1e**) (277 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 430 mg (86%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.00 (d, J = 8.4 Hz, 2H), 5.79 (d, J = 8.4 Hz, 2H) (aromatic *H*), 5.74 (s, 5H), 5.16 (s, 5H) (C_5H_5), 3.61 (dd, J = 8.4 and 12.8 Hz, 1H, CH_2), 3.05 (t, J = 12.8 Hz,1H, C*H*), 2.74 (dd, J = 8.4 and 12.8 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 142.9, 129.8, 127.4, 123.4 (aromatic *C*), 116.6, 115.5 (Cp), 91.2, 86.6 (cage *C*), 62.6 (*C*H), 42.4 (*C*H_2). ^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ 0.27 (1B), -5.0 (2B), -6.6 (3B), -10.3 (4B). IR (KBr, cm^{-1}): ν 2574 (BH). Anal. Calcd for $C_{20}H_{27}B_{10}ClZr$ (**IV-2e**): C, 47.83; H, 5.42. Found: C, 48.23; H, 5.11.

Preparation of 1,2-[$Cp_2ZrCH(3\text{-}CF_3\text{-}C_6H_4)CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-2g). This complex was prepared as a pale white solid from **I-153** (554 mg, 1.00 mmol) and

3-CF_3-styrene (**IV-1g**) (344 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 490 mg (91%). ^{1}H NMR (400 MHz, benzene-d_6): δ 6.92 (m, 2H), 6.25 (s, 1H), 6.24(d, J = 8.8 Hz, 2H) (aromatic *H*), 5.79 (s, 5H, C_5H_5), 5.16 (s, 5H, C_5H_5), 3.70 (dd, J = 6.0 and 12.8 Hz, 1H, CH_2), 3.13 (t, J = 12.8 Hz, 1H, C*H*), 2.73 (dd, J = 6.0 and 12.8 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 146.0, 130.4, 129.3, 126.1, 118.2 (aromatic *C*), 116.8, 115.9 (Cp), 90.8, 86.0 (cage *C*), 61.9 (*C*H), 42.2 (CH_2). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ 0.7 (1B), -2.0 (1B), -4.8 (2B), -6.4 (3B), -8.7 (1B), -10.1 (2B). IR (KBr, cm^{-1}): ν 2566 (BH). Anal. Calcd for $C_{24.5}H_{31}B_{10}F_3Zr$ (**IV-2g** + 0.5toluene): C, 50.58; H, 5.37. Found: C, 50.52; H, 5.43.

Preparation of 1,2-[$Cp_2ZrCH(4\text{-}CF_3\text{-}C_6H_4)CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-2h). This complex was prepared as a pale white solid from **I-153** (554 mg, 1.00 mmol) and 4-CF_3-styrene (**IV-1h**) (344 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 391 mg (73%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.27 (d, J = 8.0 Hz, 2H), 5.94 (d, J = 8.0 Hz, 2H) (aromatic *H*), 5.75 (s, 5H), 5.15 (s, 5H) (C_5H_5), 3.76 (dd, J = 5.6 and 12.4 Hz, 1H, CH_2), 3.11 (t, J = 12.4 Hz, 1H, C*H*), 2.71 (dd, J = 5.6 and 12.4 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 149.3, 129.3, 126.4, 122.3 (aromatic *C*), 116.9, 116.0 (Cp), 90.6, 85.8 (cage *C*), 62.2 (*C*H), 42.1 (CH_2). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ 0.6 (1B), -4.7 (3B), -6.4 (3B), -8.8 (1B), -10.1 (2B). IR (KBr, cm^{-1}): ν 2573 (BH). Anal. Calcd for $C_{21}H_{27}B_{10}F_3Zr$ (**IV-2h**): C, 47.08; H, 5.08. Found: C, 46.42; H, 4.94.

Preparation of 1,2-[$Cp_2ZrCH(4\text{-}Br\text{-}C_6H_4)CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-2i). This complex was prepared as purple crystals from **I-153** (554 mg, 1.00 mmol) and 4-Br-styrene (**IV-1i**) (366 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 364 mg (82%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.48 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H) (aromatic *H*), 6.71 (s, 5H, C_5H_5), 6.00 (s, 5H, C_5H_5),

4.12 (dd, J = 6.0 and 12.8 Hz, 1H, CH_2), 3.68 (d, J = 12.8 Hz, 1H, CH), 2.96 (dd, J = 12.8 Hz, and 6.0, 1H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 143.1, 132.4, 123.6, 114.4 (aromatic C), 116.8, 115.9 (Cp), 91.6, 86.9 (cage C), 62.2 (CH), 41.7 (CH$_2$). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ -0.6 (2B), -2.5 (1B), -5.5 (4B), -9.2 (3B). IR (KBr, cm^{-1}): ν 2571 (BH). Anal. Calcd for $C_{20}H_{27}B_{10}BrZr$ (**IV-2i**): C, 43.94; H, 4.98. Found: C, 44.40; H, 5.30.

Preparation of 1,2-[Cp$_2$ZrCH(4-F-C$_6$H$_4$)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-2j). This complex was prepared as purple crystals from **I-153** (554 mg, 1.00 mmol) and 4-fluorostyrene (**IV-1j**) (244 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 393 mg (81%). ^1H NMR (400 MHz, benzene-d_6): δ 6.71 (t, J = 8.5 Hz, 2H), 5.82 (d, J = 8.5 Hz, 2H) (aromatic H), 5.75 (s, 5H), 5.17 (s, 5H) (C$_5H_5$), 3.63 (dd, J = 6.4 and 12.8 Hz, 1H, CH_2), 3.07 (d, J = 12.8 Hz, 1H, CH), 2.79 (dd, J = 12.8 Hz, and 6.4, 1H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 140.3, 129.3, 125.6, 123.5, 123.4, 116.3 (aromatic C), 116.5, 115.5 (Cp), 86.7 (cage C), 62.5 (CH), 42.8 (CH$_2$). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ 0.4 (1B), -5.0 (3B), -6.4 (4B), -9.1 (1B), -10.3 (2B). IR (KBr, cm^{-1}): ν 2569 (BH). Anal. Calcd for $C_{20}H_{27}B_{10}FZr$ (**IV-2j**): C, 49.45; H, 5.60. Found: C, 49.73; H, 5.56.

Preparation of 1,2-[Cp$_2$ZrCH(TMS)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-2k). This complex was prepared as light brown crystals from **I-153** (554 mg, 1.00 mmol) and TMSCH=CH$_2$ (**IV-1k**) (200 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 364 mg (78%). ^1H NMR (400 MHz, benzene-d_6): δ 5.83 (s, 5H, C$_5H_5$), 5.81 (s, 5H, C$_5H_5$), 3.33 (dd, J = 5.1 and 14.1 Hz, 1H, CH_2), 3.05 (t, J = 14.1 Hz, 1H, CH), 2.65 (dd, J = 5.1 and 14.1 Hz, 1H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 116.0, 115.3 (Cp), 89.7, 88.4 (cage C), 64.7 (CH$_2$), 42.9 (CH), 0.28 (TMS). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ -0.0 (1B), -5.6 (4B), -7.8 (2B), -9.6 (1B), -11.4 (2B).

IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{17}H_{32}B_{10}SiZr$ (**IV-2k**): C, 44.02; H, 6.95. Found: C, 43.82; H, 6.85.

Preparation of 1,2-[$Cp_2ZrCH(PPh_2)CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-2l). This complex was prepared as black crystals from **I-153** (554 mg, 1.00 mmol) and diphenylvinylphosphine (**IV-1l**) (424 mg, 2.00 mmol) using the same procedures reported for **IV-2a**: yield 405 mg (59%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.95 (m, 4H), 7.41 (m, 6H) (phenyl), 6.03 (s, 5H, C_5H_5), 5.82 (s, 5H, C_5H_5), 3.95 (m, 1H, CH_2), 2.68 (m, 1H, C*H*), 2.21 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 137.1, 133.4, 131.8, 130.4, 129.3 (phenyl), 107.9, 107.4 (Cp), 101.1, 95.3 (cage *C*), 41.7 (CH_2), 23.3 (*C*H). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ -1.7 (1B), -5.8 (4B), -7.3 (2B), -9.4 (2B), -11.3 (1B). IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{26}H_{33}B_{10}PZr$ (**IV-2l**): C, 54.23; H, 5.78. Found: C, 53.87; H, 5.92.

Preparation of 1,2-[$Cp_2ZrCH_2CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-2m). This complex was prepared as light brown crystals from **I-153** (554 mg, 1.00 mmol) and excess ethylene (gas) (**IV-1m**) using the same procedures reported for **IV-2a**, but the reaction mixture was stirred for 3 d at room temperature: yield 176 mg (45%). ^{1}H NMR (400 MHz, benzene-d_6): δ 5.72 (s, 10H, C_5H_5), 2.76 (t, J = 7.2 Hz, 2H, CH_2), 0.82 (t, J = 7.2 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 115.5 (Cp), 90.2, 88.1 (cage *C*), 44.6, 41.1 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ 0.4 (1B), -5.6 (4B), -7.2 (1B), -8.8 (4B). IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{14}H_{24}B_{10}Zr$ (**IV-2m**): C, 42.93; H, 6.18. Found: C, 42.86; H, 6.17.

Preparation of 1,2-[$Cp_2ZrCH_2CH(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ (IV-3a). To a toluene solution (20 mL) of **I-153** (554 mg, 1.00 mmol) was added 1-hexene (**IV-1o**) (168 mg, 2.00 mmol), and the reaction mixture was heated to reflux for 48 h. After removal of the precipitate (LiCl) by filtration, the clear solution was concentrated to

about 5 mL, from which **IV-3a** was isolated as light yellow crystals after standing at room temperature overnight (367 mg, 82%). ^{1}H NMR (300 MHz, benzene-d_6): δ 5.79 (s, 5H, C_5H_5), 5.76 (s, 5H, C_5H_5), 3.03 (m, 1H, CH_2), 2.12 (t, J = 12.5 Hz, 1H, CH), 1.78 (m, 1H, CH_2), 1.28 (m, 3H, CH_2), 1.12 (m, 2H, CH_2), 0.95 (t, J = 7.0 Hz, H, CH_3), -0.43 (dd, J = 5.0 and 12.5 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 115.8, 115.6 (Cp), 93.9, 91.2 (cage *C*), 54.2, 51.2, 42.5, 30.6, 23.0, 14.4 (Bu^n). ^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ -0.4 (1B), -4.5 (1B), -5.8 (2B), -8.0 (3B), -10.0 (1B), -12.3 (2B). IR (KBr, cm^{-1}): ν 2549 (BH). Calcd for $C_{18}H_{30}B_{10}Zr$ (**IV-3a**): C, 48.28; H, 7.20. Found: C, 48.46; H, 7.21.

Preparation of 1,2-[$Cp_2ZrCH(CH_2PPh_2)CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-3b). This complex was prepared as pale white crystals from **I-153** (554 mg, 1.00 mmol) and allyldiphenylphosphine (**IV-1p**) (271 mg, 1.20 mmol) using the same procedures reported for **IV-2a**: yield 350 mg (59%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.63 (m, 2H), 7.42 (m, 2H), 7.17 (m, 3H), 7.10 (m, 3H) (phenyl), 5.76 (s, 5H), 5.60 (s, 5H) (C_5H_5), 3.12 (m, 1H, CH_2), 2.78 (m, 1H, CH), 2.41(t, J = 12.8 Hz, 1H, CH), 2.07 (m, 1H, CH_2), 0.16 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 140.9, 138.3, 134.5, 132.0, 129.8, 128.8, 128.2 (phenyl), 115.7, 115.4 (Cp), 93.6, 90.8 (cage *C*), 56.2 (*C*H), 48.0, 43.2 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ -0.1 (1B), -5.5 (3B), -7.9 (3B), -11.9 (3B). IR (KBr, cm^{-1}): ν 2560 (BH). Anal. Calcd for $C_{27}H_{35}B_{10}PZr$ (**IV-3b**): C, 54.89; H, 5.98. Found: C, 54.80; H, 6.37.

Preparation of 1,2-[$Cp_2ZrC(Ph)=CCH_2CH=CH_2$]-1,2-$C_2B_{10}H_{10}$ (IV-6) and 1,2-($Cp_2ZrCH_2CHCH_2C\equiv CPh$)-1,2-$C_2B_{10}H_{10}$ (IV-7). Complexes **IV-6** and **IV-7** were prepared as a yellow solid mixture (65/35) from **I-153** (554 mg, 1.00 mmol) and $PhC\equiv CCH_2CH=CH_2$ (170 mg, 1.20 mmol) using the same procedures reported for **IV-2a**: yield 415 mg (82%). They were not separable by crystallization. ^{1}H NMR

(400 MHz, pyridine-d_5): δ 7.38 (m), 7.31 (m), 7.10 (t, J = 7.5 Hz)), 6.97 (d, J = 7.5 Hz) (aromatic *H*), 6.61 (s, C_5H_5), 5.95 (m), 5.80 (m), 5.21 (m), 4.96 (m) (C=C*H*), 3.17 (d, J = 3.4 Hz, CH_2), 2.85 (d, J = 6.0 Hz, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 196.9, 143.7, 139.2, 135.7, 128.7, 128.4, 128.2, 128.0,127.9, 126.1, 124.1 (aromatic *C*), 117.0, 114.6 (Cp), 91.3, 87.9 (cage *C*), 65.1, 61.1(*C*H), 41.7, 38.1, 34.9, 14.8 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ -0.9 (2B), -3.3 (1B), -5.0 (1B), -7.4 (2B), -9.7 (2B), -11.0 (2B), -13.4 (1B). IR (KBr, cm^{-1}): ν 2557 (BH). Anal. Calcd for $C_{23}H_{30}B_{10}Zr$ (**IV-6/7**): C, 54.62; H, 5.98. Found: C, 54.62; H, 5.97.

Preparation of 1-[PhCH=CCH$_2$CH=CH$_2$]-1,2-C$_2$B$_{10}$H$_{11}$ (IV-8) and 1-(CH$_3$CHCH$_2$C≡CPh)-1,2-C$_2$B$_{10}$H$_{11}$ (IV-9). The above mixture of **IV-6** and **IV-7** obtained from the reaction of **I-153** (277 mg, 1.00 mmol) with PhC≡CCH$_2$CH=CH$_2$ (85 mg, 1.20 mmol) was treated with 1M HCl aqueous solution (10 mL). The organic layer was separated, and the aqueous solution was extracted twice with ethyl ether (10 mL × 2). The organic phase was combined, washed with saturated brine aqueous solution (20mL) and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatograph on silica gel using hexane as eluent to give the product **IV-8** as a white solid: 79 mg (55%) and **IV-9** as colorless oil: 35 mg (24 %). The ratio of **IV-8/IV-9** was 65/35 determined by GC-MS. For **IV-8**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 3H), 7.28 (m, 2H) (aromatic *H*), 5.94 (m, 1H, =C*H*), 5.26 (dd, J = 1.3 and 10.3 Hz, 1H, CH_2), 5.19 (dd, J = 1.3 and 17.2 Hz, 1H, CH_2), 3.92 (brs, 1H, cage *H*), 3.13 (m, 2H, CH_2). $^3C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.4, 135.2, 135.0, 131.2, 128.5, 128.3, 117.9 (aromatic and olefinic *C*), 79.1, 59.2 (cage *C*), 35.3 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.0 (1B), -5.4 (1B), -10.4 (2B), -11.6 (2B), -12.9 (2B), -14.4 (2B). HRMS: *m/z* Calcd for $C_{13}H_{22}B_8{}^{10}B_2{}^+$ (**IV-8**): 286.2719. Found: 286.2713. For **IV-9**: ^1H NMR

(400 MHz, $CDCl_3$): δ 7.39 (m, 2H), 7.32 eeew(m, 3H) (aromatic *H*), 3.94 (brs, 1H, cage *H*), 6.72 (s, 1H, C=C*H*), 3.91 (brs, 1H, cage *H*), 2.78 (dd, J = 5.2 and 16.4 Hz, 1H, CH_2), 2.69 (m, 1H, C*H*), 2.52 (dd, J = 7.2 and 16.4 Hz, 1H, CH_2), 1.35 (d, J = 6.8 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 131.5, 128.4, 128.3, 122.8 (aromatic *C*), 85.8, 83.8 (*C*≡*C*), 79.3, 60.0 (cage *C*), 38.8 (*C*H), 27.1 (*C*H_2), 20.3 (*C*H_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.0 (1B), -5.8 (1B), -10.4 (2B), -12.5 (2B), -14.4 (2B). HRMS: *m/z* Calcd for $C_{13}H_{22}B_8{}^{10}B_2{}^+$ (**IV-9**): 286.2719. Found: 286.2712.

Preparation of 1,2-[$Cp_2ZrC(Et)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ (IV-11a). To a toluene solution (20 mL) of **I-153** (554 mg, 1.00 mmol) was added 3-hexyne (**IV-10a**) (164 mg, 2.00 mmol), and the reaction mixture was heated to reflux for 48 h. After removal of the precipitate (LiCl), the clear solution was concentrated to about 5 mL, from which **IV-11a** was isolated as yellow crystals after standing at room temperature overnight (415 mg, 93%). ^1H NMR (300 MHz, pyridine-d_5): δ 6.57 (s, 10H, C_5H_5), 2.17 (q, J = 7.5 Hz, 2H, CH_2), 1.30 (q, J = 7.5 Hz, 2H, CH_2), 1.13 (t, J = 7.5 Hz, 3H, CH_3), 0.81 (t, J = 7.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 195.1, 144.1 (olefinic), 115.8 (Cp), 91.7, 87.1 (cage *C*), 25.7, 22.1, 13.4, 13.0 (Et). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ -0.8 (1B), -5.1 (3B), -7.5 (2B), -9.1 (2B), -10.0 (2B). IR (KBr, cm^{-1}): ν 2572 (BH). Calcd for $C_{18}H_{30}B_{10}Zr$ (**IV-11a**): C, 48.50; H, 6.78. Found: C, 48.25; H, 6.60.

Preparation of 1,2-[$Cp_2ZrC(Pr^n)=C(Pr^n)$]-1,2-$C_2B_{10}H_{10}$ (IV-11b). This complex was prepared as yellow crystals from **I-153** (554 mg, 1.00 mmol) and 4-octyne (**IV-10b**) (220 mg, 2.00 mmol) using the same procedures reported for **IV-11a**: yield 379 mg (80%). ^1H NMR (400 MHz, benzene-d_6): δ 5.88 (s, 10H, C_5H_5), 2.08 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 0.95 (m, 4H, CH_2), 0.92 (t, J = 7.2 Hz, 3H, CH_3), 0.77 (t, J

= 5.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 193.2, 144.7 (olefinic), 115.9 (Cp), 91.7, 87.1 (cage *C*), 36.2, 33.6, 22.9, 22.8 (CH_2), 15.3, 14.8 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ 0.1 (1B), -4.7 (2B), -7.1 (3B), -9.2 (4B). IR (KBr, cm^{-1}): ν 2562 (BH). Anal. Calcd for $C_{20}H_{34}B_{10}Zr$ (**IV-11b**): C, 50.70; H, 7.23. Found: C, 50.58; H, 7.16.

Preparation of 1,2-[$Cp_2ZrC(Bu^n)=C(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ (IV-11c). This complex was prepared as yellow crystals from **I-153** (554 mg, 1.00 mmol) and 5-decyne (**IV-10c**) (207 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 407 mg (81%). ^1H NMR (300 MHz, benzene-d_6): δ 5.88 (s, 10H, C_5H_5), 2.16 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 1.16 (m, 2H, CH_2), 1.02 (m, 4H, CH_2) , 0.96 (t, J = 7.5 Hz, 3H, CH_3), 0.87 (t, J = 7.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 193.3, 145.1 (olefinic), 116.2 (Cp), 92.0, 87.5 (cage *C*), 34.1, 32.0, 31.2, 24.4, 24.0 (CH_2), 14.5, 14.4 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ 0.0 (1B), -4.6 (2B), -7.1 (3B), -9.2 (4B). IR (KBr, cm^{-1}): ν 2635, 2562 (BH). Anal. Calcd for $C_{22}H_{38}B_{10}Zr$ (**IV-11c**): C, 52.65; H, 7.63. Found: C, 52.33; H, 7.52.

Preparation of 1,2-[$Cp_2ZrC(Ph)=C(Ph)$]-1,2-$C_2B_{10}H_{10}$ (IV-11d). This complex was prepared as yellow crystals from **I-153** (554 mg, 1.00 mmol) and PhC≡CPh (**IV-10d**) (267 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 352 mg (65%). ^1H NMR (300 MHz, pyridine-d_5): δ 7.22 (dd, J = 7.2 Hz, 4H, C_6H_5), 7.12 (d, J = 7.2 Hz, 2H, C_6H_5), 7.04 (d, J = 7.2 Hz, 2H, C_6H_5), 6.90 (dd, J = 7.2 Hz, 1H, C_6H_5), 6.80 (dd, J = 7.2 Hz, 1H, C_6H_5), 6.33 (s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 194.8, 153.6 (olefinic), 143.0, 140.0, 131.0, 126.8, 126.2, 126.1, 124.7, 122.1 (C_6H_5), 112.2 (Cp), 94.2, 90.3 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ -2.8 (2B), -5.5 (3B), -8.7 (3B), -11.0 (2B). IR (KBr, cm^{-1}): ν 2564

(BH). Anal. Calcd for $C_{26}H_{30}B_{10}Zr$ (**IV-11d**): C, 57.63; H, 5.58. Found: C, 57.65; H, 5.60.

Preparation of 1,2-[$Cp_2ZrC(Ph)=C(Me)$]-1,2-$C_2B_{10}H_{10}$ (IV-13a). This complex was prepared as orange crystals from **I-153** (554 mg, 1.00 mmol) and PhC≡CMe (**IV-12a**) (174 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 432 mg (90%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.35 (dd, J = 7.5 Hz, 2H, C_6H_5), 7.14 (dd, J = 7.5 Hz, 1H, C_6H_5), 6.93 (d, J = 7.2 Hz, 2H, C_6H_5), 6.54 (s, 10H, C_5H_5), 1.56 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 193.6, 144.8 (olefinic), 137.5, 128.2, 126.0, 124.1 (C_6H_5), 116.9 (Cp), 91.1, 87.9 (cage C), 20.3 (CH_3). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ -0.5 (1B), -5.0 (2B), -7.4 (3B), -8.8 (2B), -10.0 (2B). IR (KBr, cm^{-1}): ν 2638, 2559 (BH). Anal. Calcd for $C_{21}H_{28}B_{10}Zr$ (**IV-13a**): C, 52.57; H, 5.88. Found: C, 52.56; H, 5.87.

Preparation of 1,2-[$Cp_2ZrC(Ph)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ (IV-13b). This complex was prepared as orange crystals from **I-153** (554 mg, 1.00 mmol) and PhC≡CEt (**IV-12b**) (195 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 435 mg (88%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.36 (m, 4H, C_6H_5), 7.14 (dd, J = 7.2 Hz, 1H, C_6H_5), 6.25 (s, 10H, C_5H_5), 2.22 (q, J = 7.2 Hz, 2H, CH_2), 1.05 (t, J = 7.2 Hz, 3H, CH_3. ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 192.1, 153.2 (olefinic), 139.3, 133.3 128.3, 127.0, 126.3 (C_6H_5), 112.4 (Cp), 94.1, 91.6 (cage C), 26.3 (CH_2), 14.9 (CH_3) ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ -2.1 (2B), -4.7 (3B), -8.3 (3B), -10.2 (2B). IR (KBr, cm^{-1}): ν 2637, 2558 (BH). Anal. Calcd for $C_{22}H_{30}B_{10}Zr$ (**IV-13b**): C, 53.51; H, 6.12. Found: C, 53.03; H, 6.21.

Preparation of 1,2-[$Cp_2ZrC(Ph)=C(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ (IV-13c). This complex was prepared as orange crystals from **I-153** (554 mg, 1.00 mmol) and PhC≡CBu^n (**IV-12c**) (237 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield

397 mg (76%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.34 (dd, J = 7.5 Hz, 2H, C_6H_5), 7.11 (dd, J = 7.5 Hz, 1H, C_6H_5), 7.00 (d, J = 7.5 Hz, 2H, C_6H_5), 6.54 (s, 10H, C_5H_5), 2.04 (m, 2H), 1.47 (m, 2H), 1.00 (m, 2H, CH_2), 0.66 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 194.9, 143.9 (olefinic), 143.5, 127.9, 126.2, 124.0 (C_6H_5), 117.0 (Cp), 91.6, 87.6 (cage C), 33.9, 32.0, 22.5 (CH_2), 13.0 (CH_3). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ -0.5 (1B), -5.0 (2B), -7.2 (3B), -8.8 (4B). IR (KBr, cm^{-1}): ν 2557 (BH). Anal. Calcd for $C_{24}H_{34}B_{10}Zr$ (**IV-13c**): C, 55.24; H, 6.57. Found: C, 55.00; H, 6.46.

Preparation of 1,2-[$Cp_2ZrC(Ph)$=$C(C\equiv CPh)$]-1,2-$C_2B_{10}H_{10}$ (IV-13d). This complex was prepared as orange crystals from **I-153** (554 mg, 1.00 mmol) and PhC≡C-C≡CPh (**IV-12d**) (303 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 311 mg (55%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.40 (m, 2H, C_6H_5), 7.22 (m, 8H, C_6H_5), 6.50 (s, 10H, C_5H_5). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 210.8, 148.2 (olefinic), 130.9, 128.7, 128.0, 127.7, 127.5, 125.5, 124.5, 124.2, 123.5 (C_6H_5), 115.9 (Cp), 91.3, 89.5 (cage C), 87.7, 87.5 (-$C\equiv C$-). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ -0.7 (2B), -5.0 (3B), -7.3 (5B). IR (KBr, cm^{-1}): ν 2568 (BH). Anal. Calcd for $C_{28}H_{30}B_{10}Zr$ (**IV-13d**): C, 59.43; H, 5.34. Found: C, 59.57; H, 5.48.

Preparation of 1,2-[$Cp_2ZrC(4\text{-}CH_3C_6H_4)$=$C(Me)$]-1,2-$C_2B_{10}H_{10}$ (IV-13e). This complex was prepared as brown crystals from **I-153** (554 mg, 1.00 mmol) and (4-$CH_3C_6H_4$)C≡CMe (**IV-12e**) (195 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 336 mg (68%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.19 (m, 4H, C_6H_4), 6.23 (s, 10H, C_5H_5), 2.31 (s, 3H, CH_3), 1.76 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 191.3, 152.8 (olefinic), 131.8, 131.2, 128.0, 127.9, 125.9 (C_6H_5), 111.6 (Cp), 95.9, 91.6 (cage C), 20.3 (CH_3). ^{11}B{^{1}H} NMR (96 MHz,

pyridine-d_5): δ -2.5 (2B), -5.1 (3B), -8.7 (3B), -10.0 (2B). IR (KBr, cm^{-1}): ν 2638, 2555 (BH). Anal. Calcd for $C_{22}H_{30}B_{10}Zr$ (**IV-13e**): C, 53.51; H, 6.12. Found: C, 53.75; H, 6.11.

Preparation of 1,2-[$Cp_2ZrC(TMS)=C(Bu^n)$]-1,2-$C_2B_{10}H_{10}$ (IV-13f). This complex was prepared as brown crystals from **I-153** (554 mg, 1.00 mmol) and $TMSC{\equiv}CBu^n$ (**IV-12f**) (231 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 451 mg (87%). ^1H NMR (400 MHz, benzene-d_6): δ 5.94 (s, 10H, C_5H_5), 2.23 (m, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.29 (m, 2H, CH_2), 0.93 (t, J = 7.3 Hz, 3H, CH_3), -0.18 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 205.3, 158.4 (olefinic), 116.9 (Cp), 93.7, 86.7 (cage *C*), 41.0, 34.1, 23.7, 14.5 (Bu^n), 3.3 (TMS). $^{11}B\{^1H\}$ NMR (96MHz, benzene-d_6): δ 0.1 (2B), -3.6 (2B), -6.8 (3B), -8.7 (3B). IR (KBr, cm^{-1}): ν 2620, 2562 (BH). Anal. Calcd for $C_{21}H_{38}B_{10}SiZr$ (**IV-13f**): C, 48.70; H, 7.40. Found: C, 49.02; H, 7.51.

Preparation of 1,2-[$Cp_2ZrC(TMS)=C(Ph)$]-1,2-$C_2B_{10}H_{10}$ (IV-13g). This complex was prepared as yellow crystals from **I-153** (554 mg, 1.00 mmol) and (TMS)C≡CPh (**IV-12g**) (261 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 269 mg (50%). ^1H NMR (300 MHz, pyridine-d_5): δ 7.30 (m, 5H, C_6H_5), 6.69 (s, 10H, C_5H_5), -0.22 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 205.4, 153.9 (olefinic), 143.2, 130.7, 126.5, 126.4 (C_6H_5), 115.8 (Cp), 93.3, 87.6 (cage *C*), 3.3 (TMS). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ -1.0 (2B), -4.4 (3B), -7.5 (5B). IR (KBr, cm^{-1}): ν 2561 (BH). Anal. Calcd for $C_{23}H_{34}B_{10}SiZr$ (**IV-13g**): C, 51.35; H, 6.37. Found: C, 51.36; H, 6.46.

Preparation of 1,2-{$Cp_2ZrC[C(CH_3)=CH_2]=C(Et)$}-1,2-$C_2B_{10}H_{10}$ (IV-13h). This complex was prepared as brown crystals from **I-153** (554 mg, 1.00 mmol) and $CH_2=C(CH_3)-C{\equiv}CEt$ (**IV-12h**) (188 mg, 2.00 mmol) using the same procedures

reported for **IV-11a**: yield 211 mg (46%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 6.26 (s, 10H, C_5H_5), 4.11 (s, 1H, =CH_2), 3.61 (s, 1H, =CH_2), 2.26 (q, J = 7.4 Hz, 2H, CH_2), 1.81 (s, 3H, CH_3), 1.08 (t, J = 7.4 Hz, 3H, CH_3). The ^{13}C NMR spectrum was not obtained due to the poor solubility. ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ -0.5 (2B), -4.9 (3B), -6.4 (3B), -10.3 (2B). IR (KBr, cm^{-1}): ν 2627, 2565 (BH). Anal. Calcd for $C_{19}H_{30}B_{10}Zr$ (**IV-13h**): C, 49.85; H, 6.61 Found: C, 49.69; H, 6.57.

Preparation of 1,2-[Cp$_2$ZrC(PPh$_2$)=C(Bu^n)]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-13i). This complex was prepared as yellow crystals from **I-153** (554 mg, 1.00 mmol) and Ph$_2$PC≡CBu^n (**IV-12i**) (399 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 473 mg (76%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.72 (m, 4H, C_6H_5), 7.52 (m, 6H, C_6H_5), 5.99 (s, 10H, C_5H_5), 2.71 (m, 2H, CH_2), 1.42 (m, 2H), 1.07 (m, 2H, CH_2), 0.64 (t, J = 8.0 Hz, 2H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 170.8, 164.7 (olefinic), 163.7, 132.7, 131.3, 130.0, 129.0 (C_6H_5), 108.4 (Cp), 99.7, 98.4 (cage C), 38.8, 30.7, 22.6 (CH_2), 13.0 (CH_3). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ -0.0 (2B), -4.3 (6B), -9.0 (2B). ^{31}P{^{1}H} NMR (121 MHz, pyridine-d_5): δ -66.7. IR (KBr, cm^{-1}): ν 2558 (BH). Anal. Calcd for $C_{30}H_{39}B_{10}PZr$ (**IV-13i**): C, 57.20; H, 6.24. Found: C, 56.97; H, 6.38.

Preparation of 1,2-{Cp$_2$ZrC(Ph)=C[(CH$_2$)$_3$Cl]}-1,2-C$_2$B$_{10}$H$_{10}$ (IV-13j). This complex was prepared as brown crystals from **I-153** (554 mg, 1.00 mmol) and PhC≡C(CH$_2$)$_3$Cl (**IV-12j**) (268 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 482 mg (89%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.34 (dd, J = 7.2 Hz, 2H, C_6H_5), 7.12 (dd, J = 7.2 Hz, 1H, C_6H_5), 6.99 (d, J = 7.2 Hz, 2H, C_6H_5), 6.52 (s, 10H, C_5H_5), 3.25 (t, J = 6.8 Hz, 2H, CH_2), 2.20 (m, 2H, CH_2), 1.94 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, pyridine-d_5): δ 195.9, 144.2 (olefinic), 141.2, 128.0, 126.0, 124.1 (C_6H_5), 116.8 (Cp), 91.2, 87.8 (cage C), 44.5, 32.7, 31.6 (CH_2). ^{11}B{^{1}H}

NMR (128 MHz, pyridine-d_5): δ -1.0 (1B), -5.5 (2B), -7.8 (3B), -10.0 (4B). IR (KBr, cm^{-1}): ν 2557 (BH). Anal. Calcd for $C_{23}H_{31}B_{10}ClZr$ (**IV-13j**): C, 50.94; H, 5.76. Found: C, 50.80; H, 6.02.

Preparation of 1,2-{$Cp_2ZrC(Ph)=C[CH_2N(CH_3)_2]$}-1,2-$C_2B_{10}H_{10}$ (IV-13k). This complex was prepared as red crystals from **I-153** (554 mg, 1.00 mmol) and $PhC{\equiv}CCH_2N(CH_3)_2$ (**IV-12k**) (239 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 408 mg (78%). ^1H NMR (400 MHz, pyridine-d_5): δ 7.32 (dd, J = 7.2 Hz, 2H, C_6H_5), 7.11 (dd, J = 7.2 Hz, 1H, C_6H_5), 6.92 (d, J = 7.2 Hz, 2H, C_6H_5), 6.53 (s, 10H, C_5H_5), 2.84 (s, 2H, CH_2), 1.99 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 199.1, 143.1 (olefinic), 139.7, 128.5, 127.7, 126.5 (C_6H_5), 116.7 (Cp), 91.6, 89.3 (cage C), 60.1 (CH_2), 44.3 (CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ -1.5 (1B), -5.7 (2B), -7.7 (3B), -10.1 (4B). IR (KBr, cm^{-1}): ν 2628, 2558 (BH). Anal. Calcd for $C_{23}H_{33}B_{10}NZr$ (**IV-13k**): C, 52.84; H, 6.36; N, 2.68. Found: C, 52.35; H, 6.51; N, 2.58.

Preparation of 1,2-[$Cp_2ZrC(Ph)=C(CH_2OCH_3)$]-1,2-$C_2B_{10}H_{10}$ (IV-13l). This complex was prepared as red crystals from **I-153** (554 mg, 1.00 mmol) and $PhC{\equiv}CCH_2OCH_3$ (**IV-12l**) (219 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 188 mg (37%). ^1H NMR (300 MHz, pyridine-d_5): δ 7.43 (d, J = 7.2 Hz, 2H), 7.35 (dd, J = 7.2 Hz, 2H), 7.17 (dd, J = 7.2 Hz, 1H) (C_6H_5), 6.20 (s, 10H, C_5H_5), 3.75 (s, 2H, CH_2), 3.00 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 200.6, 153.7 (olefinic), 126.5, 126.0, (C_6H_5), 111.7 (Cp), 95.4, 90.4 (cage C), 71.4 (OCH_2), 56.6 (CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ -3.1 (2B), -5.3 (2B), -8.5 (5B). IR (KBr, cm^{-1}): ν 2630, 2559 (BH). Anal. Calcd for $C_{22}H_{30}B_{10}OZr$ (**IV-13l**): C, 51.83; H, 5.93. Found: C, 51.66; H, 6.00.

Preparation of 1,2-{$Cp_2ZrC(Ph)=C[(CH_2)_3O$(tetrahydro-

2-pyranyl)]}-1,2-$C_2B_{10}H_{10}$ (IV-13m). This complex was prepared as pale red crystals from **I-153** (554 mg, 1.00 mmol) and PhC≡C[$(CH_2)_3$O(tetrahydro-2-pyranyl)] **(IV-12m)** (366 mg, 1.50 mmol) using the same procedures reported for **IV-11a**: yield 197 mg (35%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.01 (dd, J = 7.2 Hz, 2H), 6.83 (dd, J = 7.2 Hz, 1H), 6.53 (d, J = 7.2 Hz, 2H) (C_6H_5), 5.83 (s, 10H, C_5H_5), 4.41 (t, J = 3.2 Hz, 1H, C*H*), 3.71 (m, 2H, CH_2), 3.56 (m, 2H, CH_2), 3.36 (m, 2H, CH_2), 3.16 (m, 2H, CH_2), 2.14 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 1.25 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 194.5, 145.3 (olefinic), 144.5, 129.3, 126.7, 124.5 (C_6H_5), 116.8 (Cp), 98.0 (CO_2), 91.7, 87.8 (cage *C*), 66.9, 61.4, 31.7, 31.0, 30.9, 26.0, 19.5 (CH_2). ^{11}B{^{1}H} NMR (96 MHz, pyridine-d_5): δ 0.5 (2B), -5.0 (2B), -6.6 (3B), -8.8 (3B). IR (KBr, cm^{-1}): ν 2556 (BH). Anal. Calcd for $C_{31.5}H_{44}B_{10}O_2Zr$ **(IV-13m** + 0.5toluene): C, 57.85; H, 6.78. Found: C, 57.92; H, 6.97.

Preparation of PhC≡C$(CH_2)_3$O(tetrahydro-2-pyranyl) (IV-12m). To a stirred solution of 5-phenyl-4-pentyn-1-ol (1.60 g, 10.00 mmol), which was prepared from iodobenzene (2.04 g, 10.00 mmol) and 4-pentyn-1-ol (1.18 g, 12.00 mmol) in 98% isolated yield (1.70 g,) as a yellow oil according to the literatute,[139i] and 2,3-dihydropyran (2.10 g, 25.00 mol) in CH_2Cl_2 was added TsOH·H_2O (19 mg, 0.10 mmol) at room temperature. The mixture was stirred for 2 hours. After removal of the solvent, the residue was purified by column chromatography on silica gel using hexane/ether (6/1 in v/v) solution as eluent to afford **IV-12m** (2.20 g, 90%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 2H), 7.28 (m, 3H) (Ph), 4.64 (t, J = 3.4 Hz, 1H), 3.93 (m, 2H), 3.55 (m, 2H), 2.55 (t, J = 7.0 Hz, 2H), 1.92 (m, 3H), 1.72 (m, 1H), 1.61 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 131.5, 128.1, 127.5, 123.9 (Ph), 99.7 (CO_2), 89.6, 80.8 (*C*≡*C*), 65.9, 62.1 (C-O), 30.6, 28.9, 25.4, 19.5, 16.3. HRMS: *m/z* calcd for $C_{16}H_{20}O_2$: 244.1458. Found: 244.1449.

Preparation of 1,3-(PhC=CHCH$_2$)-1,2-$C_2B_{10}H_{10}$ (IV-14). To a solution of **I-153** (277 mg, 0.50 mmol) in toluene (10 mL) was added PhC≡CCH$_2$OCH$_3$ (88 mg, 0.60 mmol) and CuI (190 mg, 1.00 mmol) at room temperature. The mixture was heated to reflux for 24 h, treated with 1 M aqueous HCl and extracted with diethyl ether (3×10 mL). The combined organic phase was dried over Na_2SO_4. After removal of the solvents, the residue was subjected to column chromatography on silica gel using hexane as eluent to afford the title product (35 mg, 27%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.54 (m, 3H) (Ph), 6.19 (t, J = 3.0 Hz, 1H, C*H*), 3.25 (d, J = 3.0 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.5, 134.0, 131.4, 129.2, 128.7, 126.6 (Phenyl and vinyl *C*), 85.7, 78.6 (cage *C*), 41.6 (*C*H$_2$). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -6.9 (4B), -10.4 (2B), -11.9 (2B), -13.8 (2B). HRMS: *m/z* calcd for $C_{11}H_{18}{}^{11}B_8{}^{10}B_2$: 258.2406. Found: 258.2399.

Preparation of $Cp_2Zr(\eta^2$(C,N)-pyridine)(σ-1,2-$C_2B_{10}H_{11}$) (IV-15). To a solution of $Cp_2Zr(\mu$-Cl)(μ-$C_2B_{10}H_{10}$)Li(OEt_2)$_2$ (**I-153**, 554 mg, 1.00 mmol) in toluene (15 mL) was added pyridine (95 mg, 1.20 mmol) at room temperature. After the mixture was stirred at room temperature for 48 h, it was filtrated and concentrated in vacuum to about 5 mL. The product **IV-15** was crystallized from this solution after standing 2 days at room temperature as off-white crystals: yield 400 mg (90%). ^{1}H NMR (400 MHz, benzene-d_6): δ 8.44 (d, J = 5.1 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 6.91 (m, 1H), 6.50 (m, 1H) (pyridinyl *H*), 5.20 (s, 10H, C_5H_5), 3.29 (brs, 1H, cage *H*). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 201.6, 144.5, 136.2, 129.1, 123.8 (pyridine), 109.4 (C_5H_5), 85.6, 66.1 (cage *C*). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ -0.1 (1B), -1.0 (1B), -6.0 (2B), -7.2 (2B), -10.9 (4B). IR (KBr, cm^{-1}): ν 2573, 2545 (BH). Anal. Calcd for $C_{17}H_{25}B_{10}NZr$ (**IV-15**): C, 46.12; H, 5.69; N, 3.16. Found: C, 46.08; H, 5.88; N, 2.88.

Preparation of $Cp_2Zr(\eta^2(C,N)$-pyridine-$d_4)(\sigma$-1,2-$C_2B_{10}H_{10}D)$ (IV-15-d_5). This complex was prepared as off-white crystals from **I-153** (554 mg, 1.00 mmol) and pyridine-d_5 (101 mg, 1.20 mmol) using the same procedures reported for **IV-15**: yield 390 mg (87%). ^{1}H NMR (400 MHz, benzene-d_6): δ 5.20 (s, 10H, C_5H_5). ^{2}H NMR (400 MHz, benzene-d_6): δ 8.45 (1D), 7.18 (1D), 6.93 (1D), 6.52 (1D) (pyridinyl *D*), 3.25 (1D, cage *D*). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ -0.2 (1B), -0.9 (1B), -5.9 (2B), -7.1 (2B), -10.8 (4B). Anal. Calcd for $C_{17}H_{20}D_5B_{10}NZr$ (**IV-15-d_5**): C, 45.60; H+D, 6.75; N, 3.13. Found: C, 45.93; H+D, 6.16; N, 2.70.

Preparation of $Cp_2Zr(\eta^2$-1,6(N,C)-(2-bromopyridine)$(\sigma$-1,2-$C_2B_{10}H_{11})$ (IV-16). This complex was prepared as an off-white solid from **I-153** (554 mg, 1.00 mmol) and 2-bromopyridine (190 mg, 2.00 mmol) using the same procedures reported for **IV-15**: yield 422 mg (81%). ^{1}H NMR (400 MHz, benzene-d_6): δ 7.50 (brs, 1H), 6.70 (m, 2H), (pyridinyl *C*), 5.42 (s, 10H, C_5H_5), 3.57 (brs, 1H, cage *H*). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 198.8, 144.4, 139.7, 131.3, 127.1 (pyridinyl *C*), 111.3 (C_5H_5), 84.2, 67.8 (cage *C*). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ -0.5 (1B), -1.6 (1B), -6.5 (2B), -7.5 (2B), -11.0 (4B). IR (KBr, cm^{-1}): ν 2560 (BH). Anal. Calcd for $C_{17}H_{24}B_{10}BrNZr$ (**IV-16**): C, 39.15; H, 4.64; N, 2.69. Found: C, 39.11; H, 4.49; N, 2.29.

Preparation of $Cp_2Zr(\eta^2$-1,6(N,C)-(2,4-dimethylpyridine)$(\sigma$-1,2-$C_2B_{10}H_{11})$ (IV-17). This complex was prepared as pale white crystals from **I-153** (554 mg, 1.00 mmol) and 2,4-dimethylpyridine (128 mg, 1.20 mmol) using the same procedures reported for **IV-15**: yield 385 mg (82%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 7.70 (s, 1H), 6.81 (s, 1H), (pyridinyl *H*), 5.98 (s, 10H, C_5H_5), 4.39 (brs, 1H, cage *H*), 2.45 (s, 3H), 2.22 (s, 3H), (CH_3). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 187.0, 152.2, 149.2, 129.1, 124.9, (pyridinyl *C*), 110.5 (C_5H_5), 85.7, 68.3 (cage *C*), 20.4, 19.7

(CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ -1.5 (1B), -2.4 (1B), -7.2 (4B), -11.2 (4B). IR (KBr, cm^{-1}): ν 2562 (BH). Anal. Calcd for $C_{19}H_{29}B_{10}NZr$ (**IV-17**): C, 48.48; H, 6.21; N, 2.98. Found: C, 48.41; H, 6.22; N, 2.72.

Preparation of $Cp_2Zr(\eta^2$-1,2(N,C)-quinoline)(σ-1,2-$C_2B_{10}H_{11}$) (IV-18). This complex was prepared as pale white crystals from **I-153** (554 mg, 1.00 mmol) and quinoline (155 mg, 1.20 mmol) using the same procedures reported for **IV-15** but at reflux: yield 418 mg (85%). ^1H NMR (400 MHz, pyridine-d_5): δ 8.26 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.88 (m, 1H), 7.68 (m, 1H), (quinolinyl *H*), 6.04 (s, 10H, C_5H_5), 4.47 (brs, 1H, cage *H*). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 194.7, 142.7, 136.3, 131.0, 129.0, 128.9, 127.1, 126.7, 122.3, (quinolinyl *C*), 85.4, 68.2 (cage *C*). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ 0.9 (1B), -0.2 (1B), -4.9 (4B), -9.0 (4B). IR (KBr, cm^{-1}): ν 2567 (BH). Anal. Calcd for $C_{21}H_{27}B_{10}NZr$ (**IV-18**): C, 51.19; H, 5.52; N, 2.84. Found: C, 51.58; H, 5.46; N, 2.71.

Preparation of $Cp_2Zr\{2$-[9-(η^1-10(N)-dihydroacridine)](σ-1,2-$C_2B_{10}H_{10})\}$ (IV-19). This complex was prepared as yellow crystals from **I-153** (554 mg, 1.00 mmol) and acridine (215 mg, 1.20 mmol) using the same procedures reported for **IV-18**: yield 407 mg (75%). ^1H NMR (400 MHz, pyridine-d_5): δ 7.43 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.26 (m, 2H), 7.08 (m, 2H), (dihydroacridinyl *H*), 6.31 (s, 10H, C_5H_5), 4.85 (s, 1H, cage *H*). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 156.6, 133.7, 128.1, 126.9, 122.0, (dihydroacridinyl *C*), 115.9 (C_5H_5), 86.3, 85.4 (cage *C*), 53.4 (*C*H). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ 1.7 (2B), -6.8 (8B). IR (KBr, cm^{-1}): ν 2554 (BH). Anal. Calcd for $C_{25}H_{29}B_{10}NZr$ (**IV-19**): C, 55.32; H, 5.38; N, 2.58. Found: C, 55.25; H, 5.66; N, 2.58.

Preparation of $Cp_2Zr\{\eta^2$-1,6(N,C)-[2-(1-^{n}BuC≡C)pyridine]}(σ-1,2-$C_2B_{10}H_{11}$)

(IV-20). This complex was prepared as pale white crystals from **I-153** (554 mg, 1.00 mmol) and 2-(1-hexynyl)pyridine (191 mg, 1.20 mmol) using the same procedures reported for **IV-15**: yield 293 mg (56%).^{1}H NMR (300 MHz, benzene-d_6): δ 7.52 (d, J = 6.9 Hz, 1H), 6.99 (m, J = 6.9 Hz, 1H), 6.87 (d, J = 6.9 Hz, 1H), (pyridinyl *H*), 5.55 (s, 10H, C_5H_5), 3.74 (brs, 1H, cage *H*), 2.17 (t, J = 6.6 Hz, 2H, CH_2), 1.40 (m, 4H, CH_2), 0.86 (t, J = 7.2 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 190.8, 139.1, 136.8, 130.8, 126.8 (pyridinyl *C*), 111.0 (C_5H_5), 97.3, 84.7, (C≡C), 77.4, 68.5 (cage *C*), 30.6, 22.2, 19.0, 13.6 (Bu^n). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ -0.3 (1B), -1.4 (1B), -6.1 (2B), -7.5 (2B), -10.6 (4B). IR (KBr, cm^{-1}): ν2601, 2550 (BH). Anal. Calcd for $C_{23}H_{33}B_{10}NZr$ (**IV-20**): C, 52.84; H, 6.36; N, 2.68. Found: C, 52.84; H, 6.35; N, 2.72.

Preparation of $Cp_2Zr\{\eta^2$-1,6(N,C)-[3-(1-^{n}BuC≡C)pyridine]$\}(\sigma$-1,2-$C_2B_{10}H_{11})$ (IV-21a) and $Cp_2Zr\{\eta^2$-1,2(N,C)-[3-(1-^{n}BuC≡C)pyridine]$\}(\sigma$-1,2-$C_2B_{10}H_{11})$ (IV-21b). These two complexes were prepared as pale white crystals from **I-153** (554 mg, 1.00 mmol) and 3-(1-hexynyl)pyridine (191 mg, 1.20 mmol) using the same procedures reported for **IV-15**: yield **IV-21a**: 170 mg (33%), **IV-21b**: 185 mg (35%).^{1}H NMR (300 MHz, benzene-d_6): for **IV-21a**: δ 8.91 (s, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), (pyridinyl *H*), 5.24 (s, 10H, C_5H_5), 3.30 (brs, 1H, cage *H*), 2.22 (t, J = 6.8 Hz, 2H, CH_2), 1.45 (m, 4H, CH_2), 0.86 (t, J = 7.2 Hz, CH_3); for **IV-21b**: δ 8.24 (d, J = 5.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 6.45 (m, 1H), (pyridinyl *H*), 5.40 (s, 10H, C_5H_5), 3.30 (brs, 1H, cage *H*), 2.29 (t, J = 7.2 Hz, 2H, CH_2), 1.48 (m, 4H, CH_2), 0.88 (t, J = 7.2 Hz, CH_3). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): for **IV-21a**: δ 201.7, 146.7, 138.8, 128.8, 121.9, (pyridinyl *C*), 109.5 (C_5H_5), 95.1, 85.5, (C≡C), 77.2, 66.0 (cage *C*), 30.7, 22.3, 19.3, 13.7 (Bu^n); for **IV-21b**: δ 205.3, 142.6, 138.2, 126.8, 123.8, (pyridinyl *C*), 109.5 (C_5H_5), 94.4, 85.4

(C≡C), 79.7, 66.1 (cage *C*), 31.1, 22.2, 19.3, 13.7 (Bu^n);. $^{11}B\{^1H\}$ NMR (96 MHz, benzene-d_6): for **IV-21a**: δ 0.8 (1B), 0.0 (1B), -5.2 (2B), -6.1 (2B), -10.2 (4B); for **IV-21b**: δ 0.5 (1B), -1.0 (1B), -6.0 (2B), -7.1 (2B), -10.9 (4B). IR (KBr, cm^{-1}): ν 2560 (BH). Anal. Calcd for $C_{23}H_{33}B_{10}NZr$ (**IV-21**): C, 52.84; H, 6.36; N, 2.68. Found: C, 52.58; H, 6.73; N, 2.40.

Preparation of 1,2-[$Cp_2ZrC(2\text{-pyridyl})=CBu^n$]-1,2-$C_2B_{10}H_{10}$ (IV-22). To a solution of $Cp_2Zr(\mu\text{-Cl})(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-153**, 554 mg, 1.00 mmol) in toluene (15 mL) was added 2-(1-hexynyl)pyridine (191 mg, 1.20 mmol) and CuI (381 mg, 2.00 mmol). After the mixture was stirred at reflux for 48 h, it was filtrated and concentrated in vacuum to about 5 mL. The product **IV-22** was obtained after standing 2 days at room temperature as light yellow crystals: yield 387 mg (74%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.13 (d, J = 5.4 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 6.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H) (pyridinyl *H*), 6.03 (s, 10H, C_5H_5), 2.43 (t, J = 7.2 Hz, 2H, CH_2), 1.51 (m, 4H, CH_2), 0.96 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2: δ 164.7, 161.8, 155.2, 148.4, 139.0, 122.1, 119.6 (pyridinyl H), 111.9 (C_5H_5), 97.0, 96.2 (cage *C*), 33.9, 31.0, 23.6, 13.9 (Bu^n). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ -1.9 (1B), -5.4 (3B), -7.2 (4B), -11.5 (2B). IR (KBr, cm^{-1}): ν 2550 (BH). HRMS: *m/z* Calcd for $C_{23}H_{33}N^{11}B_8{}^{10}B_2{}^{+}Zr$: 521.2658. Found: 521.2639. Anal. Calcd for $C_{23}H_{33}B_{10}NZr$ (**IV-22**): C, 52.84; H, 6.36; N, 2.68. Found: C, 52.97; H, 6.53; N, 2.59.

Preparation of 1,2-[$Cp_2ZrC(2\text{-pyridyl})=CPh$]-1,2-$C_2B_{10}H_{10}$ (IV-23). This complex was prepared as light brown crystals from **I-153** (554 mg, 1.00 mmol) and 2-(1-phenylacetylenyl)pyridine (215 mg, 1.20 mmol) using the same procedures reported for **IV-22**: yield 418 mg (77%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.08 (d, J = 5.4 Hz, 1H), 7.42 (m, 4H), 7.10 (m, 3H), (aromatic *H*), 6.12 (s, 10H, C_5H_5), 5.81 (d,

J = 8.1 Hz, 1H, pyridinyl H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 166.3, 164.7, 152.8, 148.2, 140.2, 138.5, 129.0, 128.4, 127.9, 122.8 (aromatic *C*), 118.9 (C_5H_5), 96.6, 95.6 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ -1.9 (1B), -5.4 (3B), -7.1 (4B), -11.7 (2B). IR (KBr, cm^{-1}): ν 2556 (BH). Anal. Calcd for $C_{25}H_{29}B_{10}NZr$ (**IV-23**): C, 55.32; H, 5.38; N, 2.58. Found: C, 55.16; H, 5.65; N, 2.30.

Preparation of 2-[trans-(2-pyridyl)C=CBu^n]-1-$C_2B_{10}H_{11}$ (IV-24). The complex **IV-22** (157 mg, 0.30 mmol) in 10 mL of ethyl acetate was treated with an aqueous HCl solution (1M, 10 mL) for 1 h at room temperature. Then the resultant solution was then neutralized using 1 M $NaHCO_3$ aqueous solution (10 mL). The organic layer was separated, and the aqueous solution was extracted twice with ethyl acetate (10 mL × 2). The organic phase was combined, washed with saturated brine aqueous solution (20mL) and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatograph on silica gel using hexane/ethyl acetate (4/1 in v/v) as eluent to give the product as a white solid: 79 mg (87%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J = 4.0 Hz, 1H), 7.72 (m, 1H), 7.21 (m, 2H), (pyridinyl *H*), 6.72 (s, 1H, C=C*H*), 3.91 (brs, 1H, cage *H*), 2.70 (t, J = 8.0 Hz, 2H, CH_2), 1.54 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 0.93 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.5, 149.4, 139.6, 136.3, 131.3, 124.9, 122.3 (vinyl and pyridinyl *C*), 79.1, 59.6 (cage *C*), 31.2, 31.1, 22.7, 13.6 (Bu^n). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -2.9 (1B), -4.3 (1B), -9.3 (2B), -11.2 (4B), -13.4 (2B). HRMS: *m/z* Calcd for $C_{13}H_{23}N^{11}B_8{}^{10}B_2{}^+$ (**IV-24**): 303.2985. Found: 303.2969.

Preparation of 1-[(2-pyridyl)C=CPh]-1-$C_2B_{10}H_{11}$ (IV-25). This compound was prepared as a white solid from **IV-23** (163 mg, 0.30 mmol) using the same procedures reported for **IV-24**: yield 86 mg (89%). ^1H NMR (300 MHz, $CDCl_3$): δ

8.52 (s, 1H), 7.46 (m, 3H), 7.33 (m, 2H), 7.16 (m, 2H), 7.08 (m, 1H), 6.38 (d, J = 7.8 Hz, 1H), (aromatic *H*), 3.42 (brs, 1H, cage *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 153.5, 149.1, 137.7, 135.9, 135.3, 135.2, 129.6, 129.3, 123.4, 122.5, (aromatic *C*), 77.2, 58.4 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.3 (1B), -4.0 (1B), -8.6 (2B), -10.3 (2B), -12.2 (2B), -13.5 (2B). HRMS: *m/z* Calcd for $C_{15}H_{21}N^{11}B_8{}^{10}B_2{}^+$ (**IV-25**): 322.2593. Found: 322.2595.

Preparation of 1,2-[$Cp_2ZrN(Ph)CH(Ph)$]-1,2-$C_2B_{10}H_{10}$ (IV-26). This complex was prepared as brown crystals from **I-153** (277 mg, 0.50 mmol) and PhCH=NPh (109 mg, 0.60 mmol) using the same procedures reported for **IV-15**: yield 170 mg (62%). ^1H NMR (300 MHz, pyridine-d_5): δ 7.51 (d, J = 6.9 Hz, 2H), 7.43 (t, J = 7.5 Hz, 3H), 7.29 (m, 3H), 7.03 (t, J = 7.5 Hz, 2H) (aromatic *H*), 6.62, 5.54 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 144.2, 142.0, 128.0, 127.7, 123.0 (aromatic *C*), 96.2, 90.8 (cage *C*). 70.7 (*C*HN). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ -3.1 (2B), -5.7 (2B), -7.5 (2B), -11.6 (2B). IR (KBr, cm^{-1}): ν 2567 (BH). Anal. Calcd for $C_{25}H_{29}B_{10}NZr$ (**IV-26**): C, 55.11; H, 5.73; N, 2.57. Found: C, 55.26; H, 5.72; N, 2.53.

General Procedures for the Preparation of Benzocarborane (V-2). Method A: To a suspension of zirconacyclopentene **IV-11/13** (0.20 mmol) in toluene (10 mL) was added $NiCl_2(PMe_3)_2$ (62 mg, 0.21 mmol, 97%) and alkyne **V-1** (0.70 mmol) and the reaction vessel was closed and heated at 110 °C for 2 d. The reaction mixture was then cooled to room temperature, and treated with 10 mL of water or 1M aqueous HCl. The organic layer was separated and the aqueous solution was extracted with diethyl ether (20 mL × 2). The organic portions were combined and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was subjected to column chromatographic separation (SiO_2, 300 - 400 mesh) using hexane as eluent to give **V-2** as an oil or white solid.

Method B: To a suspension of zirconacyclopentene **IV-11/13** (0.20 mmol) in a mixed solvent of toluene and THF (10 mL, 2/1 in v/v) was added $FeCl_3$ (65 mg, 0.40 mmol) and alkyne **V-1** (0.40 mmol) and the reaction vessel was closed and heated at 110 °C for 2 d. Using the same workup procedures as above afforded **V-2** as an oil or a white solid.

V-2a: Method A, yield: 84%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (q, J = 7.4 Hz, 2H, CH_2), 2.50 (t, J = 8.0 Hz, 2H, CH_2), 2.32 (q, J = 7.4 Hz, 2H, CH_2), 2.25 (d, J = 8.0 Hz, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.42 (m, 4H, CH_2), 1.31 (m, 2H, CH_2), 1.18 (t, J = 7.4 Hz, 3H, CH_3), 1.02 (t, J = 7.4 Hz, 3H, CH_3), 0.97 (t, J = 7.2 Hz, 3H, CH_3), 0.95 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.9, 134.3, 134.1, 132.6 (aromatic *C*), 77.2, 76.3 (cage *C*), 33.4, 32.7, 32.6, 28.9, 26.3, 23.1, 23.0, 22.1, 15.0, 14.8, 14.0, 13.8, 13.7 (Et and Bu^n). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -7.2 (2B), -10.1 (6B), -12.9 (2B). HRMS: *m/z* Calcd for $C_{18}H_{38}{}^{11}B_8{}^{10}B_2{}^+$: 362.3971. Found: 362.3974.

V-2b: Method A, yield: 81%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (q, J = 7.4 Hz, 2H, CH_2), 2.48 (m, 2H, CH_2), 2.32 (q, J = 7.4 Hz, 2H, CH_2), 2.23 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.36 (m, 2H, CH_2), 1.05 (t, J = 7.4 Hz, 3H, CH_3), 1.01 (t, J = 7.4 Hz, 9H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.9, 134.4, 134.1, 132.6 (aromatic *C*), 77.2, 76.3 (cage *C*), 35.8, 31.2, 26.3, 23.9, 22.1, 15.3, 15.0, 14.8, 14.4, 14.3 (Et and Pr^n). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -7.4 (2B), -10.3 (6B), -13.2 (2B). HRMS: *m/z* Calcd for $C_{16}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 334.3658. Found: 334.3659.

V-2c: Method A, yield: 78%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (q, J = 7.6 Hz, 4H, CH_2), 2.34 (q, J = 7.6 Hz, 4H, CH_2), 1.18 (t, J = 7.6 Hz, 6H, CH_3), 1.03 (t, J = 7.6 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.2, 133.9 (diene *C*), 76.3 (cage *C*), 26.3, 22.0, 15.0, 14.8 (Et). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$):

δ -7.1 (2B), -10.0 (6B), -12.9 (2B). These data are in well agreement with those reported in the literature.[86b]

V-2d: Method A, yield: 30% (70% for the 5 days reacton) for reaction of **IV-11a** with **V-1d**, and 81% for reaction of **IV-11d** with **V-1c**. white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (m, 6H), 6.93 (m, 2H), 6.86 (d, J = 6.5 Hz, 2H), (aromatic *H*), 2.72 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.12 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.29 (t, J = 7.4 Hz, 3H, C*H*$_3$), 0.76 (t, J = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.0, 137.7, 137.3, 136.9, 136.3, 133.7, 130.8, 129.6, 127.3, 127.0, 126.7 (aromatic *C*), 76.2, 74.6 (cage *C*), 26.4, 23.3, 14.9, 13.8 (Et). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -6.9 (2B), -10.2 (5B), -12.8 (3B). HRMS: *m/z* Calcd for $C_{22}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 402.3345. Found: 402.3347.

V-2e: Method B, yield : 20%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H, C*H*$_3$), 3.82 (s, 3H, C*H*$_3$), 2.69 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.37 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.22 (t, J = 7.4 Hz, 3H, C*H*$_3$), 1.01 (t, J = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.7, 163.8 (*C*O$_2$Me), 143.3, 136.2, 129.5, 128.3 (aromatic *C*), 69.1 (cage *C*), 53.0, 52.9 (O*C*H$_3$), 26.7, 22.9, 14.6, 13.9 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -6.0 (1B), -6.7 (1B), -9.8 (2B), -11.2 (2B), -12.9 (4B). HRMS: *m/z* calcd for $C_{14}H_{26}{}^{11}B_8{}^{10}B_2O_4{}^+$: 366.2829. Found: 366.2833.

V-2g: Method A, yield 76%. Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H), 7.12 (m, 2H), (aromatic *H*), 2.68 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.42 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.66 (s, 3H, C*H*$_3$), 1.25 (t, J = 7.4 Hz, 3H, C*H*$_3$), 1.07 (t, J = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 138.4, 136.2, 134.3, 130.3, 130.1, 128.1, 128.0 (aromatic *C*), 75.8, 74.7 (cage *C*), 26.3, 22.6, 18.2, 14.9, 14.0 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -7.1 (2B), -10.3 (5B), -13.0 (3B). HRMS: *m/z* calcd for $C_{17}H_{28}{}^{11}B_8{}^{10}B_2{}^+$: 340.3205. Found: 340.3189.

V-2h: Method A, yield: method A, 81%; method B, 21%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 3H), 7.16 (m, 2H), (aromatic *H*), 2.68 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.40 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.01 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.25 (t, J = 7.4 Hz, 3H, C*H*$_3$), 1.08 (t, J = 7.4 Hz, 3H, C*H*$_3$), 0.84 (t, J = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.6, 137.2, 135.9, 134.3, 133.7, 130.4, 128.0, 127.7 (aromatic *C*), 75.8, 74.7 (cage *C*), 26.4, 23.8, 22.0, 15.0, 14.8 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -8.1 (2B), -11.2 (5B), -14.0 (3B). HRMS: *m/z* calcd for $C_{18}H_{30}{}^{11}B_8{}^{10}B_2{}^{+}$: 354.3345. Found: 354.3340.

V-2h': Method B, yield, 41%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H), 7.09 (m, 2H), 2.62 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.44(q, J = 7.4 Hz, 2H, C*H*$_2$), 1.99 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.20 (t, J = 7.4 Hz, 3H, C*H*$_3$), 0.86 (t, J = 7.4 Hz, 3H, C*H*$_3$), 0.70 (t, J = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2, 137.4, 136.0, 134.8, 133.8, 129.3, 128.1, 127.4 (aromatic and dienyl *C*), 75.8 (cage *C*), 27.3, 26.2, 23.1, 14.8, 14.3, 13.7 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -6.4 (2B), -9.4 (5B), -12.2 (3B). HRMS: *m/z* calcd for $C_{18}H_{30}{}^{11}B_8{}^{10}B_2{}^{+}$: 354.3345. Found: 354.3334.

V-2i: Method A, yield 83%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 3H), 7.14 (m, 2H), (aromatic *H*), 2.67 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.37 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.92 (m, 2H, C*H*$_2$), 1.25 (t, J = 7.4 Hz, 3H, C*H*$_3$), 1.18 (m, 2H, C*H*$_2$), 1.08 (m, 2H, C*H*$_2$), 1.06 (t, J = 7.4 Hz, 3H, C*H*$_3$), 0.70 (t, J = 7.2 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 137.6, 136.9, 134.8, 134.3, 133.9, 130.4, 128.0, 127.7, (aromatic *C*), 75.8, 74.7 (cage *C*), 32.6, 30.5, 26.4, 22.8, 22.1, 15.0, 14.7, 13.4 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -7.2 (2B), -10.4 (5B), -13.1 (3B). HRMS: *m/z* calcd for $C_{20}H_{34}{}^{11}B_8{}^{10}B_2{}^{+}$: 382.3658. Found: 382.3652.

V-2j: Method A. After column chromatography on silica gel, two isomers were

obtained in the yield of 71%. After crystallization the analytically pure product of **V-2i** was obtained in the yield of 31% as colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (m, 4H, CH_2), 1.51 (s, 9H, CH_3), 1.40 (m, 2H, CH_2), 1.15 (t, J = 7.6 Hz, 3H, CH_3), 1.11 (m, 2H, CH_2), 0.96 (t, J = 7.6 Hz, 6H, CH_3), 0.93 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.2, 138.5, 135.6, 133.5 (aromatic *C*), 81.2, 77.6 (cage *C*), 39.7 (*C*(CH_3)$_3$), 34.3 (*C*H_3), 33.9, 32.6, 27.0, 23.1, 22.8, 15.2, 14.6, 13.9 (*C*H_2 and *C*H_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -6.4 (1B), -7.9 (1B), -9.8 (2B), -11.6 (3B), -13.0 (3B). HRMS: *m/z* calcd for $C_{18}H_{38}{}^{11}B_8{}^{10}B_2{}^{+}$: 362.3971. Found: 362.3975.

V-2k: Method A. After column chromatography on silica gel, two isomers were obtained in the yield of 67%. The pure product was not obtained by recrystallization. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (m, 1H, C*H*), 2.57 (q, J = 7.6 Hz, 2H, CH_2), 2.35 (q, J = 7.6 Hz, 2H, CH_2), 2.03 (s, 3H, CH_3), 1.30 (d, J = 7.2 Hz, 3H, CH_3), 1.18 (t, J = 7.6 Hz, 6H, CH_3), 1.03 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.9, 135.1, 134.3, 128.3 (aromatic *C*), 75.9 (cage *C*), 34.5 (*C*H), 26.2, 22.0, 20.9, 20.7, 17.0, 14.7, 14.1 (*C*H_2 and *C*H_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -8.1 (2B), -11.0 (6B), -14.3 (2B). HRMS: *m/z* calcd for $C_{14}H_{30}{}^{11}B_8{}^{10}B_2{}^{+}$: 306.3345. Found: 306.3335.

V-2l: Method A. After column chromatography on silica gel, two isomers were obtained in the yield of 33%. The pure product was not obtained by recrystallization. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (m, 2H, CH_2), 2.37 (m, 4H, CH_2), 1.38 (m, 2H, CH_2), 1.96 (s, 3H, CH_3), 1.18 (t, J = 7.6 Hz, 3H, CH_3), 1.02 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.2, 134.7, 134.5, 134.2, 133.6, 129.3, 128.0 (aromatic *C*), 76.1 (cage *C*), 27.2, 26.3, 26.2, 22.6, 22.5, 22.1, 19.2, 15.9, 14.9, 14.8, 14.5, 14.0, 13.3 (*C*H_2 and *C*H_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -7.9

(2B), -10.8 (4B), -11.5 (2B), -13.7 (2B). HRMS: *m/z* calcd for $C_{13}H_{28}{}^{11}B_8{}^{10}B_2{}^+$: 292.3189. Found: 292.3197.

V-2m: Method A. After column chromatography on silica gel, two isomers were obtained in the yield of 29%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (m, CH_2), 2.36 (m, CH_2), 2.20 (s, CH_2), 2.18 (m, CH_2), 1.96 (s, 3H, CH_3), 1.79 (m, CH_2), 1.55 (m, CH_2), 1.40 (m, CH_2), 1.16 (t, J = 7.2 Hz, CH_3), 1.02 (t, J = 7.2 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.6, 134.5, 134.3, 133.8, 132.2, 129.6, 128.2, (aromatic *C*), 78.7, 78.5, 76.2, 76.0 (cage *C*), 33.8, 29.7, 28.8, 28.1, 27.8, 26.3, 26.2, 22.5, 22.2, 19.5, 18.3, 16.0, 14.9, 14.8, 14.5, 14.0, 3.4, 1.0 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.4 (2B), -11.4 (5B), -14.2 (3B). HRMS: *m/z* calcd for $C_{18}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 358.3658. Found: 358.3655.

V-2n: Method A, yield 21%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H), 7.11 (m, 2H), (aromatic *H*), 2.78 (s, 2H, CH_2), 2.66 (q, J = 7.6 Hz, 2H, CH_2), 2.63 (q, J = 7.6 Hz, 2H, CH_2), 2.01 (s, 6H, CH_3), 1.26 (t, J = 7.6 Hz, 3H, CH_3), 1.08 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.2, 137.0, 136.9, 135.0, 131.1, 128.2, 127.5 (aromatic *C*), 76.1, 74.4 (cage *C*), 58.2, 44.8, 26.1, 21.3, 15.1, 14.9 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.9 (2B), -10.2 (5B), -12.9 (3B). HRMS: *m/z* calcd for $C_{19}H_{33}{}^{11}B_8{}^{10}B_2N^+$: 383.3611. Found: 383.3619.

V-2o: Method A, yield 31%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H), 7.18 (m, 2H), (aromatic *H*), 3.68 (s, 2H, CH_2), 3.05 (s, 3H, CH_3), 2.66 (q, J = 7.4 Hz, 2H, CH_2), 2.47 (q, J = 7.4 Hz, 2H, CH_2), 1.25 (t, J = 7.4 Hz, 3H, CH_3), 1.10 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.0, 137.4, 136.7, 133.6, 130.7, 130.3, 128.4, 127.6 (aromatic *C*), 76.2, 74.2 (cage *C*), 69.6, 58.0, 26.1, 21.8, 14.8, 14.7 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.7 (2B), -10.2 (5B), -12.9 (3B). HRMS: *m/z* calcd for $C_{18}H_{30}{}^{11}B_8{}^{10}B_2O^+$: 370.3294. Found:

370.3292.

V-2p: Method A, yield: 35% (The yield was improved to 74% using 2 equiv of $NiCl_2(PMe_3)_2$ and 1.5 equiv of $PhC{\equiv}CCH_2(CH{=}CH_2)$). Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 3H), 7.14 (m, 2H), (aromatic *H*), 5.70 (m, 1H), 5.00 (dd, J = 1.6 and 10.4 Hz, 1H), 4.73 (dd, J = 1.6 and 17.3 Hz, 1H) (vinyl *H*), 2.74 (m, 2H, C*H*$_2$), 2.68 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.36 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.25 (t, J = 7.4 Hz, 3H, C*H*$_3$), 1.06 (t, J = 7.4 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.5, 137.1, 136.1, 135.9, 134.0, 131.6, 130.0, 128.2, 127.6, 115.6 (aromatic and olifinic *C*), 75.9, 74.6 (cage *C*), 34.4, 26.3, 22.3, 14.9, 14.8 (*C*H$_2$ and *C*H$_3$). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.0 (2B), -10.2 (5B), -12.9 (3B). HRMS: *m/z* calcd for $C_{19}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 366.3345. Found: 366.3345.

V-2q: Method A, yield 83%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (m, 6H), 6.94 (m, 2H), 6.85 (d, J = 8.0 Hz, 2H), (aromatic *H*), 2.63 (m, 2H, C*H*$_2$), 2.03 (m, 2H, C*H*$_2$), 1.67 (m, 2H, C*H*$_2$), 1.48 (m, 2H, C*H*$_2$), 1.14 (m, 2H, C*H*$_2$), 1.01 (t, J = 7.2 Hz, 3H, C*H*$_3$), 0.97 (m, 2H, C*H*$_2$), 0.62 (t, J = 7.2 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.1, 137.9, 137.3, 136.0, 132.5, 130.8, 129.6, 127.3, 127.0, 126.7 (aromatic *C*), 76.4, 74.7 (cage *C*), 33.5, 32.6, 31.3, 30.0, 23.1, 22.5, 13.8, 13.3 (Bu^n). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.6 (2B), -10.9 (5B), -13.4 (3B). HRMS: *m/z* calcd for $C_{20}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 458.3971. Found: 458.3966.

V-2r: Method A, yield 85%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H), 7.01 (m, 2H), (aromatic *H*), 2.53 (m, 2H, C*H*$_2$), 1.93 (m, 2H, C*H*$_2$), 1.84 (s, 3H, C*H*$_3$), 1.53 (m, 2H, C*H*$_2$), 1.44 (m, 2H, C*H*$_2$),1.06 (m, 2H, C*H*$_2$), 0.95 (t, J = 7.2 Hz, 6H, C*H*$_3$), 0.63 (t, J = 7.2 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 139.1, 135.5, 133.5, 132.3, 131.4, 128.8, 128.3, 127.3 (aromatic *C*), 77.2, 75.9 (cage *C*), 33.2, 32.5, 31.2, 30.0, 23.1, 22.6, 21.1, 13.7, 13.3 (*C*H$_2$ and *C*H$_3$). $^{11}B\{^1H\}$ NMR (96

MHz, $CDCl_3$): δ -7.0 (2B), -10.3 (5B), -12.8 (3B). HRMS: *m/z* calcd for $C_{21}H_{36}{}^{11}B_8{}^{10}B_2{}^+$: 396.3815. Found: 396.3805.

4s: Method A, yield 81%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 3H), 7.06 (m, 2H), (aromatic *H*), 2.51 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 1.90 (s, 3H, CH_3), 1.53 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.28 (m, 2H, CH_2), 1.04 (m, 9H, CH_2 and CH_3), 0.64 (t, J = 7.3 Hz, 6H, CH_3), 0.61 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.2, 136.2, 136.1, 133.7, 132.5, 129.4, 128.0, 127.4 (aromatic *C*), 77.0, 76.0 (cage *C*), 34.0, 33.3, 32.5, 31.6, 31.2, 29.8, 23.1, 22.6, 13.7, 13.3 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.2 (2B), -10.2 (5B), -12.9 (3B). HRMS: *m/z* calcd for $C_{24}H_{42}{}^{11}B_8{}^{10}B_2{}^+$: 438.4284. Found: 438.4277.

V-2t: Method A, yield 80%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), (aromatic *H*), 2.62 (q, J = 7.6 Hz, 2H, CH_2), 2.18 (t, J = 8.0 Hz, 2H, CH_2), 2.01 (q, J = 7.4 Hz, 2H, CH_2), 1.29 (m, 2H, CH_2), 1.20 (t, J = 7.4 Hz, 3H, CH_3), 1.03 (m, 2H, CH_2), 0.69 (t, J = 7.4 Hz, 3H, CH_3), 0.65 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.2, 136.5, 135.9, 134.7, 133.8, 129.4, 128.0, 127.4 (aromatic *C*), 76.8, 76.0 (cage *C*), 34.0, 31.7, 26.2, 23.1, 22.7, 14.9, 13.7, 13.3 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.1 (2B), -10.2 (5B), -12.9 (3B). HRMS: *m/z* calcd for $C_{20}H_{34}{}^{11}B_8{}^{10}B_2{}^+$: 382.3658. Found: 382.3645.

V-2u: Method A, yield 36% (Reaction for 5 days improved the yield to73%). Colorless crystals. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 6H), 7.15 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), (aromatic *H*), 2.31 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.19 (s, 3H, CH_3), 1.10 (q, J = 7.2 Hz, 2H, CH_2), 0.69 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.4, 137.9, 137.7, 135.9, 133.5, 130.5, 130.2, 130.0, 129.4, 128.8, 128.4, 128.1, 127.7, 127.5 (aromatic *C*), 75.7, 75.3 (cage *C*), 34.0, 31.9, 22,7, 20.6, 13.3(CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.8

(2B), -10.1 (5B), -12.6 (3B). HRMS: *m/z* calcd for $C_{23}H_{32}{}^{11}B_8{}^{10}B_2{}^+$: 416.3502. Found: 416.3487.

V-2v: Method A, yield 77%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), (aromatic *H*), 3.19 (t, J = 6.6 Hz, 2H, C*H*$_2$), 2.63 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.36 (m, 2H, C*H*$_2$), 2.01 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.76 (m, 2H, C*H*$_2$), 1.19 (t, J = 7.4 Hz, 3H, C*H*$_3$), 0.70 (t, J = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 137.8, 137.0, 135.5, 134.5, 133.7, 129.1, 128.3, 127.7 (aromatic *C*), 76.8, 75.5 (cage *C*), 44.2, 32.2, 31.9, 26.3, 23.1, 14.8, 13.7 (*C*H$_2$ and *C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -6.9 (2B), -10.2 (5B), -12.9 (3B). HRMS: *m/z* calcd for $C_{19}H_{31}{}^{11}B_8{}^{10}B_2Cl^+$: 402.3112. Found: 402.3119.

V-2w: Method **B**, yield 53%. Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (q, J = 7.4 Hz, 2H, C*H*$_2$), 2.40 (m, 2H), 2.34 (m, 2H), 1.40 (m, 2H), (C*H*$_2$), 1.21 (m, 5H, C*H*$_2$ + C*H*$_3$), 0.96 (m, 6H), (C*H*$_3$), 0.41 (s, 9H, TMS). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.3, 138.4, 135.5, 133.5 (dienyl *C*), 78.4, 78.1 (cage *C*), 34.0, 33.6, 26.8, 22.9, 21.8, 15.1, 14.8, 13.9 (*C*H$_2$ and *C*H$_3$), 4.6 (TMS). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -8.2 (2B), -10.2 (2B), -11.7 (3B), -13.7 (3B). HRMS: *m/z* calcd for $C_{17}H_{38}{}^{11}B_8{}^{10}B_2Si^+$: 378.3740. Found: 378.3727.

V-2x: Method B, yield 59%. Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 3H), 7.06 (m, 2H), 2.61 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.84 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.20 (t, J = 7.4 Hz, 3H, C*H*$_3$), 0.69 (t, J = 7.4 Hz, 3H, C*H*$_3$), -0.10 (s, 9H, TMS). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.5, 139.9, 138.8, 137.3, 133.2, 130.1, 127.9, 127.8 (aromatic and dienyl *C*), 78.8, 77.6 (cage *C*), 26.7, 22.7, 14.6, 14.0 (*C*H$_2$ and *C*H$_3$), 3.8 (TMS). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -8.2 (2B), -10.4 (2B), -12.0 (3B), -13.9 (3B). HRMS: *m/z* calcd for $C_{19}H_{34}{}^{11}B_8{}^{10}B_2Si^+$: 398.3427. Found: 398.3419.

V-2y: Method B, yield 44%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (m, 4H), 2.20 (m, 2H), 1.59 (m, 4H), 1.35 (m, 4H), (CH_2), 1.00 (t, J = 7.4 Hz, 6H, CH_3), 0.98 (t, J = 7.4 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.1, 132.8 (dienyl *C*), 76.4 (cage *C*), 35.8, 31.4, 23.9, 23.8, 14.4, 14.3 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -8.5 (2B), -11.3 (6B), -14.2 (3B). These data are in agreement with the literature.[86b]

Preparation of 1-[CH(CH=CH$_2$)=C(Et)]-1,2-C$_2$B$_{10}$H$_{11}$ (V-3). To a suspension of 1,2-[Cp$_2$ZrC(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (**IV-11a**) (89 mg, 0.20 mmol) in toluene (10 mL) was added $NiCl_2(PMe_3)_2$ (62 mg, 0.21 mmol, 97%). The mixture was heated to reflux for 2 days. Then the reaction mixture was concentrated and subjected to column chromatography on silica gel to give **V-3** as a white solid (21 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51 (m, 1H), 6.25 (d, J = 8.0 Hz, 1H), 5.41 (m, 2H), (vinyl *H*), 3.78 (brs, 1H, cage C*H*), 2.36 (q, J = 7.6 Hz, 2H, CH_2), 1.08 (t, J = 7.6 Hz, 2H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.9, 132.1, 131.3, 122.2, (vinyl *C*), 78.4, 59.8, (cage *C*), 24.5, 14.2 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -2.7 (1B), -4.4 (1B), -9.2 (2B), -11.2 (4B), -13.2 (2B). HRMS: *m/z* calcd for $[C_8H_{10}{}^{11}B_8{}^{10}B_2{}^+$-2H] (**V-3**-2H): 222.2406, Found: 222.2396.

Preparation of 1,2-[(dppe)NiC(Ph)=C(Ph)]-1,2-C$_2$B$_{10}$H$_{10}$ (V-4). A suspension of 1,2-[$Cp_2ZrC(Ph)=C(Ph)$]-1,2-$C_2B_{10}H_{10}$ (**IV-11d**) (108 mg, 0.20 mmol) and $NiCl_2$(dppe) (110 mg, 0.21 mmol) in toluene (10 mL) was heated to reflux for 24 h with stirring. The mixture was filtrated to yield a brown solution. The product **V-4** was isolated as light brown crystals after standing the solution for 2 days at room temperature (120 mg, 69%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 8.09 (m, 1H), 7.66 (m, 1H), 7.54 (m, 1H), 7.46 (m, 6H), 7.30 (m, 12H), 7.22 (m, 1H), 7.12 (t, J = 7.5 Hz, 2H), 7.02 (m, 1H), 6.93 (m, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.61 (t, J = 7.5 Hz, 2H),

6.52 (m, 1H) (aromatic *H*), 2.31 (t, J = 4.2 Hz, 4H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 164.5, 147.3, 139.7, 138.3, 138.2, 138.1, 134.2, 134.1, 133.9, 132.8, 132.6, 132.5, 132.4, 131.0, 130.2, 129.8, 128.4, 128.3, 126.9, 126.7, 126.5,126.2, 125,7, 125.6 (aromatic and olefinic *C*), 90.4, 74.7 (cage *C*), 23.7 (*C*H$_2$). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ -1.7 (3B), -4.7 (2B), -7.5 (4B), -10.3 (1B). $^{31}P\{^1H\}$ NMR (121 MHz, pyridine-d_5): δ -53.9 (d, J = 2.4 Hz), 44.6 (d, J = 2.4 Hz), -11.1 (s). IR (KBr, cm^{-1}): ν 2563 (BH), 1595 (C=C). Anal. Calcd for $C_{49}H_{52}B_{10}NiP_2$ (**V-4**+toluene): C, 67.67; H, 6.03. Found: C, 67.41; H, 5.95.

Preparation of Naphthalocarboranes V-6a, V-6b and V-6c. To a solution of **IV-11/13** (0.40 mmol) in THF (15 mL) was added 1,2-diiodidebenzene or ortho-iodo-bromobenzene (0.41 mmol), HMPA (215 mg, 1.20 mmol) and CuCl (80 mg, 0.80 mmol). The mixture was heated to reflux for 24 h. The resulting suspension was treated with HCl (3.0 M, 20 mL), and extracted with ether twice (30 mL × 2). The combined organic solutions were washed with a saturated NaCl aqueous solution and then dried over anhydrous Na_2SO_4. After filtration and concentration, the crude product was purified by chromatography on silica gel using hexane as elute to afford **V-6** as colorless crystals. X-ray-quality crystals of **V-6a** were grown from a hexane solution.

V-6a: yield 83%. colorless crystals. ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (dd, J = 1.2 and 7.8 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.46 (m, 1H), 7.40 (m, 1H) (phenyl), 2.71 (m, 4H, C*H*$_2$), 1.28 (t, J = 7.2 Hz, 3H, C*H*$_3$), 1.18 (t, J = 7.2 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 134.0, 132.3, 131.5, 129.5, 128.2, 127.7, 125.7(aromatic *C*), 75.0, 72.7 (cage *C*), 26.7, 21.6, 14.6, 13.8 (Et). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.5 (2B), -8.7 (2B), -11.4 (6B). HRMS: *m/z* calcd for $C_{14}H_{24}{}^{11}B_8{}^{10}B_2{}^+$: 300.2876. Found: 300.2875.

V-6b: yield 85%. colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (dd, J = 1.2 Hz and 7.5 Hz, 1H), 7.50 (m, 2H), 7.37 (m, 1H) (Ph), 2.61 (m, 4H), 1.63 (m, 4H), 1.06 (t, J = 7.2 Hz, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 133.3, 131.4, 130.9, 129.4, 128.2, 128.0, 125.8 (aromatic *C*), 75.1, 72.7 (cage *C*), 36.1, 30.6, 23.5, 22.6, 14.3, 14.2. $^{11}B\{^{1}H\}$ NMR (96 MHz, $CDCl_3$): δ -6.6 (2B), -9.0 (2B), -11.6 (6B). HRMS: *m/z* calcd for $C_{16}H_{28}{}^{11}B_8{}^{10}B_2{}^{+}$: 328.3189. Found: 328.3186.

V-6c: yield 85%. colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (dd, J = 1.2 and 7.5 Hz, 1H), 7.48 (m, 3H), 7.34 (m, 1H), 7.26 (m, 1H), 7.14 (m, 2H), 6.71 (m, 1H) (Ph), 2.44 (m, 2H), 1.41 (m, 2H), 1.11 (m, 2H), 0.69 (t, J = 7.2 Hz, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 137.1, 135.2, 134.4, 130.8, 129.6, 129.1, 128.7, 128.4, 127.8, 127.7 (aromatic *C*), 75.0, 73.3 (cage *C*), 34.0, 31.8, 22.7, 13.3. $^{11}B\{^{1}H\}$ NMR (96 MHz, $CDCl_3$): δ -6.2 (2B), -8.9 (2B), -11.2 (6B). HRMS: *m/z* calcd for $C_{20}H_{28}{}^{11}B_8{}^{10}B_2{}^{+}$: 376.3189. Found: 376.3192.

Preparation of [(Et)C=C(Et)C$_6$H$_2$(Et)C=C(Et)]-(1,2-C$_2$B$_{10}$H$_{10}$)$_2$ (V-8). To a solution of **IV-11a** (89 mg, 0.20 mmol) in THF (15 mL) was added 1,2,4,5-tetraiodidebenzene (59 mg, 0.10 mmol), HMPA (121 mg, 0.68 mmol) and CuCl (45 mg, 0.45 mmol). The mixture was heated to reflux for 24h. Using the same workup procedures as **V-6**, **V-8** (30 mg) were obtained as colorless crystals in 57% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.67 (s, 1H), 2.69 (m, 8H), 1.25 (t, J = 7.6 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 136.1, 131.4, 131.1, 128.6, 127.9, 123.0, 74.4, 71.4 (cage *C*), 26.9, 21.7, 14.6, 13.7. $^{11}B\{^{1}H\}$ NMR (96 MHz, $CDCl_3$): δ -6.0 (6B), -8.7 (4B), -11.2 (10B). HRMS: *m/z* calcd for $C_{22}H_{42}{}^{11}B_{16}{}^{10}B_4{}^{+}$: 522.5287. Found: 522.5284.

Preparation of 1,2-[(R^1)C=C(R^2)]-1,2-C$_2$B$_{10}$H$_{10}$ (V-9). To a suspension of **IV-11/11** (0.20 mmol) in toluene was added $Cu(OTf)_2$ (73 mg, 0.20 mmol). The

mixture was stirred at room temperature for 48 hours. After removal of the precipitate (Cu) by filtration and the solvent in vacuum, the crude product was purified by flash chromatography on silica gel using hexane as elute to give **V-9**.

V-9a: Colorless oil. (24 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (q, J = 7.5 Hz, 4H, CH_2), 1.03 (t, J = 7.5 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.9 (*C*=*C*), 74.6 (cage *C*), 20.7, 10.3 (Et). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ 7.6 (2B), -0.4 (2B), -11.5 (2B), -16.3 (4B). HRMS: *m/z* calcd for $C_8H_{20}{}^{11}B_8{}^{10}B_2{}^{+}$: 224.2563. Found: 224.2561.

V-9b: Colorless oil. (34 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (t, J = 7.5 Hz, 4H, CH_2), 1.48 (m, 4H), 0.94 (t, J = 7.5 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.7 (*C*=*C*), 75.0 (cage *C*), 29.3, 19.2, 13.9 (Pr). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ 8.0 (2B), 0.1 (2B), -11.0 (2B), -15.9 (4B). HRMS: *m/z* calcd for $C_{10}H_{24}{}^{11}B_8{}^{10}B_2{}^{+}$: 252.2876. Found: 252.2864.

V-9c: Colorless oil. (34 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (t, J = 7.2 Hz, 4H, CH_2), 1.39 (m, 8H, CH_2), 0.92 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.6 (*C*=*C*), 75.0 (cage *C*), 29.7, 27.8, 27.0, 22.4, 13.6 (Bu). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ 7.7 (2B), -0.1 (2B), -11.2 (2B), -16.1 (4B). HRMS: *m/z* calcd for $C_{12}H_{28}{}^{11}B_8{}^{10}B_2{}^{+}$: 280.3189. Found: 280.3200.

V-9d: Colorless crystals. (52 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (m, 4H), 7.41 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 138.9, 130.1, 129.7, 129.1, 126.0 (*C*=*C* and phenyl *C*), 73.9 (cage *C*). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ 7.6 (2B), 1.1 (2B), -10.7 (2B), -14.6 (4B). HRMS: *m/z* calcd for $C_{16}H_{20}{}^{11}B_8{}^{10}B_2{}^{+}$: 320.22563. Found: 320.2565.

V-9e: Colorless crystals. (34 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40(m, 3H), 7.19(m, 2H), 2.00 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.1, 138.7

(*C*=*C*), 129.4, 129.1, 129.0, 125.5 (phenyl *C*), 75.2, 73.9 (cage *C*), 14.3. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ 8.1 (2B), 0.9 (2B), -10.6 (2B), -15.3 (4B).These data are in agreement with the reported.

V-9f: Colorless crystals. (47 mg, 78%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.43(m, 3H), 7.21(m, 2H) (phenyl *H*), 2.41 (t, J = 7.2 Hz, 2H), 1.61(m, 2H), 1.49(m, 2H) (CH_2), 1.00 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.5, 140.3 (*C*=*C*), 129.5, 129.1, 129.0, 125.6 (phenyl *C*), 74.6, 73.7 (cage *C*), 28.8, 27.9, 22.7, 13.7. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ 7.9 (2B), 0.8 (2B), -10.8 (2B), -15.1 (4B). HRMS: *m/z* calcd for $C_{14}H_{24}{}^{11}B_8{}^{10}B_2$: 300.2876. Found: 300.2877.

V-9g: Colorless crystals. (53 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.06 (t, J = 7.2 Hz, 2H), 1.43 (m, 4H) (CH_2), 0.94 (t, J = 7.2 Hz, 3H, CH_3), 0.11 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.9, 150.1 (*C*=*C*), 78.5, 75.1 (cage *C*), 30.0, 28.0, 22.4, 13.7 (Bu), -2.2 (TMS). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ 7.9 (2B), 1.4 (1B), -0.4 (1B), -10.4 (2B), -14.9 (4B). HRMS: *m/z* calcd for $C_{11}H_{28}{}^{11}B_8{}^{10}B_2Si^+$: 296.2958. Found: 296.2943.

V-9h: Colorless crystals. Reaction for 10 days afforded **V-11h** (45 mg) in 71% isolated yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 3H), 7.22 (m, 2H) (phenyl *H*), 0.25 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.3, 130.2, 129.0, 127.9, 126.0 (*C*=*C* and phenyl *C*), 75.2 (cage *C*), -1.9 (TMS). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 6.5 (2B), 0.6 (1B), -1.0 (1B), -11.7 (2B), -15.5 (4B). HRMS: *m/z* calcd for $C_{13}H_{24}{}^{11}B_8{}^{10}B_2Si^+$: 316.2645. Found: 316.2645.

V-9i: White solid. (57 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 3H), 7.22 (m, 2H) (phenyl *H*), 3.63 (t, J = 6.0 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2H), 2.06 (m, 2H) (CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.0, 141.0, 129.5, 129.1, 125.8 (*C*=*C* and phenyl *C*), 74.2, 73.5 (cage *C*), 43.8, 28.5, 26.1. $^{11}B\{^1H\}$ NMR (128 MHz,

$CDCl_3$): δ 7.2 (2B), 0.3 (2B), -11.3 (2B), -15.7 (4B). HRMS: *m/z* calcd for $C_{13}H_{21}{}^{11}B_8{}^{10}B_2Cl^+$: 320.2329. Found: 320.2326.

V-9j: White solid. (14 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 3H), 7.24 (m, 2H) (phenyl *H*), 4.10 (s, 2H, C*H*$_2$), 3.40 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.2, 138.4, 130.0, 129.1, 128.6, 126.5 (*C*=*C* and phenyl *C*), 73.8, 73.3 (cage *C*), 66.2 (C*H*$_2$), 59.2 (C*H*$_3$). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ 7.7 (2B), 0.8 (2B), -10.8 (2B), -15.2 (4B). HRMS: *m/z* calcd for $C_{12}H_{20}{}^{11}B_8{}^{10}B_2O^+$: 288.2512. Found: 288.2510.

Preparation of 1-[HC(R^1)=C(R^2)]-1,2-$C_2B_{10}H_{11}$ (V-10/V-10'). A typical procedure is described as follows. A toluene suspension (20 mL) of **IV-11/13**, prepared from the reaction of **I-153** (1.00 mmol) and **IV-10/12** (2.00 mmol), was treated with aqueous HCl (10 mL, 1M) at room temperature. The organic layer was separated and the aqueous solution was extracted with ethyl ether (20 mL × 2). The organic portions were combined and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was subjected to flash column chromatograph on silica gel to give **V-10/V-10'**.

V-10a: Colorless oil (170 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 (t, J = 7.2 Hz, 1H, olifinic *H*), 3.74 (brs, 1H, cage C*H*), 2.22 (q, J = 7.6 Hz, 2H, C*H*$_2$), 2.08 (m, 2H, C*H*$_2$), 1.03 (m, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.6, 134.0 (olefinic *C*), 78.7, 60.1 (cage *C*), 24.0, 21.8, 13.8, 13.5 (Et). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -3.5 (1B), -5.6 (1B), -10.1 (2B), -12.0 (4B), -14.0 (2B). HRMS: *m/z* calcd for $C_8H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 226.2719. Found: 226.2714.

V-10b: Colorless oil (196 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (t, J = 7.2 Hz, 1H, olifinic *H*), 3.72 (brs, 1H, cage C*H*), 2.13 (m, 2H), 2.05 (q, J = 7.2 Hz, 2H), 1.43 (m, 2H) (C*H*$_2$), 0.94 (m, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ

134.8, 133.0 (olefinic *C*), 79.0, 60.2 (cage *C*), 33.0, 30.6, 22.3, 22.2, 14.0, 13.7. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.1 (1B), -5.1 (1B), -9.6 (2B), -11.4 (4B), -13.5 (2B). HRMS: *m/z* calcd for $C_{10}H_{26}{}^{11}B_8{}^{10}B_2{}^+$: 254.3032. Found: 254.3029.

V-10c: Colorless oil (214mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.73 (t, J = 7.2 Hz, 1H, olifinic *H*), 3.72 (brs, 1H, cage C*H*), 2.14 (m, 2H), 2.05 (q, J = 7.2 Hz, 2H), 1.37 (m, 8H) (CH_2), 0.95 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.8, 133.0 (olefinic *C*), 79.1, 60.2 (cage *C*), 31.1, 30.7, 28.3, 22.7, 22.3, 13.9, 13.7. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.1 (1B), -5.1 (1B), -9.7 (2B), -11.4 (4B), -13.5 (2B). HRMS: *m/z* calcd for $C_{12}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 282.3345. Found: 282.3342.

V-10d: White solid (109 mg, 34%). NMR data are identical with those of **III-20**.

V-10e: Colorless oil (151 mg, 58%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H) (phenyl *H*), 6.85(s, 1H, olefinic *H*), 3.91 (brs, 1H, cage C*H*), 1.97 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.7, 132.7, 130.6, 128.9, 128.4, 127.8(olefinic and phenyl *C*), 79.0, 59.2 (cage *C*), 18.1. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.5 (1B), -6.3 (1B), -10.7 (2B), -12.5 (2B), -13.3 (2B), -14.9 (2B). HRMS: *m/z* calcd for $C_{11}H_{20}{}^{11}B_8{}^{10}B_2{}^+$: 260.2563. Found: 260.2558.

V-10e': Colorless oil (15 mg, 6%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42(m, 3H), 7.04 (dd, J = 8.0 Hz and 2.0 Hz, 2H) (phenyl *H*), 6.27 (q, J = 6.8 Hz, 1H, olefinic *H*), 3.23 (brs, 1H, cage C*H*), 1.43 (d, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.6, 135.2, 131.9, 129.2, 129.0, 128.6, 127.9 (olefinic and phenyl *C*), 77.5, 58.5 (cage *C*), 15.6. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.2 (1B), -5.4 (1B), -9.5 (2B), -11.0 (2B), -13.0 (2B), -14.3 (2B). HRMS: *m/z* calcd for $C_{11}H_{20}{}^{11}B_8{}^{10}B_2{}^+$: 260.2563. Found: 260.2553.

V-10f: Colorless oil (162 mg, 59%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 2H),

7.32 (m, 1H), 7.22 (d, J = 7.2 Hz, 2H) (phenyl *H*), 6.78 (s, 1H, olefinic), 3.88 (brs, 1H, cage C*H*), 2.37 (q, J = 7.6 Hz, 2H, CH_2), 1.20 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.7, 135.5, 133.4, 128.5, 128.4, 127.9(olefinic and phenyl *C*), 78.8, 60.0 (cage *C*), 24.4, 14.5 (Et). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -5.9 (1B), -7.5 (1B), -12.3 (2B), -14.4 (4B), -16.4 (2B). HRMS: *m/z* calcd for $C_{12}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 274.2719. Found: 274.2716.

V-10f': Colorless oil (19 mg, 7%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 3H), 7.04 (dd, J = 4.4 and 2.4 Hz, 2H) (phenyl *H*), 6.17 (t, J = 7.6 Hz, 1H, olefinic *H*), 3.21 (brs, 1H, cage C*H*), 1.75 (m, 2H, CH_2), 0.90 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.7, 135.6, 133.8, 129.1, 129.0, 128.5 (olefinic and phenyl *C*), 58.5 (cage *C*), 23.3, 13.4 (Et). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.5 (1B), -7.8 (1B), -11.9 (2B), -13.4 (2B), -15.4 (2B), -16.7(2B). HRMS: *m/z* calcd for $C_{12}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 274.2719. Found: 274.2705.

V-10g: Colorless oil (196 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, J = 7.2 Hz, 2H), 7.35 (dd, J = 7.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 2H) (Ph), 6.81 (s, 1H, olefinic *H*), 3.89 (brs, 1H, cage C*H*), 2.33 (t, J = 8.0 Hz, 2H), 1.58 (m, 2H, CH_2), 1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.6, 133.6, 128.4, 127.9 (olefinic and phenyl *C*), 79.0, 60.3 (cage *C*), 31.6, 31.2, 22.6, 13.6. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -5.6 (1B), -7.3 (1B), -12.1 (2B), -13.9 (4B), -16.0 (2B). HRMS: *m/z* calcd for $C_{14}H_{26}{}^{11}B_8{}^{10}B_2{}^+$: 302.3032. Found: 302.3025.

V-10g': Colorless oil (15 mg, 5%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 3H), 7.03 (dd, J = 7.2 and 2.4 Hz, 2H), (phenyl *H*), 6.17 (t, J = 7.2 Hz, 1H, olefinic *H*), 3.20 (brs, 1H, cage C*H*), 1.73 (m, 2H), 1.29 (m, 2H), 1.21 (m, 2H) (CH_2), 0.82 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.6, 135.7, 134.1, 129.2, 128.9, 128.5 (olefinic and phenyl *C*), 58.4 (cage *C*), 30.1, 29.5, 22.1, 13.8 (^{n}Bu).

$^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.3 (1B), -7.6 (1B), -11.6 (2B), -13.1 (2B), -15.1 (2B), -16.5 (2B). HRMS: *m/z* calcd for $C_{14}H_{26}{}^{11}B_8{}^{10}B_2{}^+$: 302.3032. Found: 302.3033.

V-10h: White solid (152 mg, 44%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.2 and 1.0 Hz, 2H), 7.49 (m, 2H), 7.42 (m, 6H) (phenyl *H*), 7.20 (s, 1H, olefinic *H*), 4.30 (brs, 1H, cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.3, 134.4, 131.5, 129.9, 129.6, 129.4, 128.7, 128.5, 121.5, 114.9 (olefinic and phenyl *C*), 99.8, 84.4, 75.2, 58.7(*C*≡*C* and cage *C*). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.3 (1B), -4.8 (1B), -9.0 (2B), -11.0 (4B), -13.6 (2B). HRMS: *m/z* calcd for $C_{18}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 346.2719. Found: 346.2707.

V-10h': White solid (104 mg, 30%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 3H), 7.23 (m, 5H), 7.03 (dd, J = 7.8 and 1.2 Hz, 2H) (phenyl *H*), 6.38 (s, 1H, olefinic *H*), 3.36 (brs, 1H, cage C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.0, 135.6, 131.5, 129.1, 128.9, 128.8, 128.2, 122.2, 116.4 (olefinic and phenyl *C*), 97.6, 85.6, 76.1, 58.4 (*C*≡*C* and cage *C*). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.5 (2B), -8.6 (2B), -10.4 (2B), -12.7 (2B), -13.6 (2B). HRMS: *m/z* calcd for $C_{18}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 346.2719. Found: 346.2712.

V-10i: White solid (140 mg, 51%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.21 (d, J = 7.8 Hz, 2H), 7.11 (d, 2H, J = 7.8 Hz, 2H) (phenyl *H*), 6.81 (s, 1H, olefinic *H*), 3.91 (brs, 1H, cage C*H*), 2.32 (s, 3H), 1.98 (s, 3H) (C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.7, 132.7, 132.6, 129.8, 129.60, 128.8 (olefinic and phenyl *C*), 79.2, 59.2 (cage *C*), 21.2, 18.1 (*C*H$_3$). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.2 (1B), -5.0 (1B), -9.5 (2B), -11.3 (4B), -13.6 (2B). HRMS: *m/z* calcd for $C_{12}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 274.2719. Found: 274.2712.

V-10i': White solid (22 mg, 8%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.21 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 7.8 Hz, 2H) (phenyl *H*), 6.24 (q, J = 6.9 Hz, 1H, olefinic *H*),

3.21(brs, 1H, cage C*H*), 2.37 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.4, 135.0, 132.4, 131.7, 129.7, 129.0 (olefinic and phenyl *C*), 77.4, 58.4 (cage *C*), 21.1, 15.7 (*C*H$_3$). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.8 (1B), -5.1 (1B), -9.0 (2B), -10.5 (2B), -12.6 (2B), -13.9 (2B). HRMS: *m/z* calcd for $C_{12}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 274.2719. Found: 274.2718.

V-10j: White solid (211 mg, 71%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.71 (s, 1H, olefinic *H*), 3.75 (brs, 1H, cage C*H*), 2.24 (m, 2H, CH_2), 1.46 (m, 4H, CH_2), 0.95 (t, 3H, J = 7.2 Hz, CH_3), 0.13 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.4, 133.3 (olefinic *C*), 79.5, 60.4 (cage *C*), 35.5, 32.7, 23.0, 13.7 (^{n}Bu), -0.3 (TMS). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.4 (1B), -5.0 (1B), -9.8 (2B), -11.7 (4B), -13.8 (2B). HRMS: *m/z* calcd for $[C_{11}H_{30}{}^{11}B_8{}^{10}B_2Si - CH_3]^+$: 283.2880. Found: 283.2882.

V-10k: White solid (105 mg, 33%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (m, 3H), 7.08 (m, 2H) (phenyl *H*), 6.34 (s, 1H, olefinic *H*), 3.19 (brs, 1H, cage C*H*), -0.25 (s, 9H, TMS). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.2, 137.4, 130.7, 129.3, 128.8, 128.5 (olefinic and phenyl *C*), 78.7, 58.1 (cage *C*), -0.9 (TMS). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.1 (1B), -5.1 (1B), -9.3 (2B), -10.8 (2B), -12.9 (2B), -14.2 (2B). HRMS: *m/z* calcd for $C_{13}H_{26}{}^{11}B_8{}^{10}B_2Si^+$: 318.2801. Found: 318.2804.

V-10l: Colorless oil (50 mg, 21%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.85 (s, 1H), 5.06 (s, 1H), 4.87 (s, 1H) (olifinic *H*), 4.90 (brs, 1H, cage C*H*), 2.29 (q, J = 7.2 Hz, 2H, CH_2), 2.07 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H) (CH_3). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.6, 133.6, 131.0, 115.7 (olefinic *C*), 59.3 (cage *C*), the other cage carbon was not observed, 31.6, 23.2, 14.3 (*C*H$_3$). $^{11}B\{1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.2 (2B), -11.1 (4B), -12.3 (2B), -14.4 (2B). HRMS: m/z calcd for $[C_9H_{22}{}^{11}B_8{}^{10}B_2 - 2H]^+$: 236.2563. Found: 236.2566.

V-10m: White solid (235 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H),

7.19 (d, 2H, J = 7.2 Hz) (phenyl *H*), 6.86 (s, 1H, olefinic *H*), 3.92 (brs, 1H, cage C*H*), 3.50 (t, J = 6.0 Hz, 2H), 2.50 (m, 2H), 2.01 (m, 2H) (CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 135.1, 134.5, 134.1, 128.6, 128.3, 128.2 (olefinic and phenyl *C*), 78.4, 60.5 (cage *C*), 44.4, 31.8, 29.0 (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -2.8 (1B), -4.4 (1B), -9.3 (2B), -11.4 (4B), -13.3 (2B). HRMS: m/z calcd for $C_{13}H_{23}{}^{11}B_8{}^{10}B_2Cl^+$: 322.2486. Found: 322.2499.

V-10n: White solid (197 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 3H), 7.29 (d, J = 7.6 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H) (phenyl and olifnic *H*), 5.02 (brs, 1H, cage C*H*), 3.11 (s, 2H, CH_2), 2.04 (s, 6H, CH_3). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.5, 135.4, 130.8, 128.6, 128.3, 127.8 (phenyl and olefinic *C*), 77.9, 59.0 (cage *C*), 57.2 (CH_2), 44.7 (CH_3). $^{11}B\{1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.5 (2B), -12.5 (4B), -14.7 (2B), -16.4 (2B). HRMS: m/z calcd for $C_{13}H_{24}N^{11}B_8{}^{10}B_2{}^+$: 303.2985. Found: 303.2982.

V-10o: Colorless oil. (73 mg, 25%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.38 (m, 3H), 7.25 (m, 3H) (phenyl and alkenyl *H*), 4.11 (brs, 1H, cage C*H*), 3.96 (s, 2H, CH_2), 3.28 (s, 3H, CH_3). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.0, 134.9, 130.4, 128.7, 128.6, 128.5 (phenyl and olefinic *C*), 77.6, 69.4 (cage *C*), 59.4 (CH_2), 57.9 (CH_3). $^{11}B\{1H\}$ NMR (96 MHz, $CDCl_3$): δ -2.9 (1B), -4.4 (1B), -9.6 (2B), -10.6 (2B), -12.0 (2B), -13.2 (2B). HRMS: m/z calcd for $C_{12}H_{22}{}^{11}B_8{}^{10}B_2O^+$: 290.2668. Found: 290.2660.

V-10o': Colorless oil. (9 mg, 3%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 3H), 7.06 (m, 2H) (phenyl *H*), 6.30 (t, J = 6.2 Hz, 1H, olefinic *H*), 3.58 (d, J = 6.2 Hz, 2H, CH_2), 3.24 (brs, 1H, cage C*H*), 3.20 (s, 3H, CH_3). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.6, 134.6, 133.5, 129.1, 129.0, 128.7 (phenyl and olefinic *C*), 76.4, 70.0 (cage *C*), 58.3 (CH_2), 58.2 (CH_3). $^{11}B\{1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.5 (1B), -4.4 (1B),

-8.8 (2B), -10.4 (2B), -12.6 (2B), -13.7 (2B). HRMS: m/z calcd for $C_{12}H_{22}{}^{11}B_8{}^{10}B_2O^+$: 290.2668. Found: 290.2657.

V-10-A: Colorless crystals (14%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 3H), 7.25 (m, 2H) (phenyl *H*), 5.18 (s, 2H, allenyl *H*), 3.67 (brs, 1H, cage C*H*). ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 208.1 (C=*C*=CH_2), 133.2, 129.2, 128.8, 128.7 (phenyl *C*), 104.1 (*C*=C=CH_2), 80.3 (C=C=*C*H_2), 72.9, 59.7 (cage *C*). ^{11}B{1H} NMR (96 MHz, $CDCl_3$): δ -3.4 (1B), -5.4 (1B), -9.8 (2B), -12.1 (4B), -13.9 (2B). HRMS: m/z calcd for $C_{11}H_{18}{}^{11}B_8{}^{10}B_2{}^+$: 258.2406. Found: 258.2405.

V-10p: Colorless oil. (77 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H), 7.24 (m, 2H), (phenyl *H*), 6.85 (s, 1H, olefinic *H*), 4.54 (t, *J* = 4.0 Hz, 1H, OC*H*), 4.25 (brs, 1H, cage C*H*), 3.80 (m, 2H), 3.51 (m, 1H), 3.38 (m, 1H), 2.45 (m, 2H), 1.86 (m, 4H), 1.57 (m, 4H) (*C*H_2). ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 135.6, 134.6, 134.2, 128.5, 127.9, (phenyl and olefinic *C*), 99.1 (O*C*H), 79.0, 66.7 (cage *C*), 62.4, 59.2,30.6, 29.6, 27.9, 25.3, 19.6 (*C*H_2). ^{11}B{1H} NMR (96 MHz, $CDCl_3$): δ -3.0 (1B), -4.1 (1B), -8.9 (2B), -10.4 (4B), -13.1 (2B). HRMS: m/z calcd for $C_{18}H_{32}{}^{11}B_8{}^{10}B_2O^+$: 388.3400. Found: 388.3405.

Preparation of 1-[Cl(Et)=C(Et)]-1,2-$C_2B_{10}H_{11}$ (V-11a). To a THF solution (20 mL) of I_2 (254 mg, 1.00 mmol, freshly sublimed) was added **IV-11a** (89 mg, 0.20 mmol) and CuCl (20 mg, 0.20 mmol) at 0 ℃. The mixture was stirred at room temperature for 24 h. The solution was then treated with a saturated aqueous $Na_2S_2O_3$ solution (10 mL), and extracted with diethyl ether (20 mL × 2). The organic portions were combined and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified by flash chromatograph on silica gel using hexane as elute to give **V-11a** as colorless oil (50 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.41 (brs, 1H, cage C*H*), 2.82 (q, *J* = 7.2 Hz, 2H, CH_2), 2.48 (q, *J* = 7.2 Hz, 2H, CH_2),

1.16 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.3, 104.3 (olefinic *C*), 76.4, 57.9 (cage *C*), 41.3, 29.6, 14.1 13.6 (Et). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -2.6 (2B), -10.0 (6B), -13.4 (2B). HRMS: *m/z* calcd for $C_8H_{21}{}^{11}B_8{}^{10}B_2I^+$: 352.1686. Found: 352.1684.

Preparation of 1,2-[$Cp_2Zr(NCPh)C(Et)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ (V-12). To a suspension of **IV-11a** (446 mg, 1.00 mmol) in toluene (20 mL) was added phenylnitrile (206 mg, 2.0 mmol), and the mixture was heated to reflux for 24 h. The resulting clear solution was concentrated to about 5 mL, from which **V-12** was isolated as pale white crystals (505 mg, 92%) after standing overnight. ^1H NMR (300 MHz, pyridine-d_5): δ 7.85 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 1H), 7.44 (dd, J = 7.8 Hz, 2H) (phenyl *H*), 6.19 (s, 10H, Cp), 2.34 (q, J = 7.5 Hz, 2H, CH_2), 1.95 (q, J = 7.2 Hz, 2H, CH_2), 1.21 (t, J = 7.5 Hz, 3H, CH_3), 1.11 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-d_5): δ 190.8, 142.4 (olefinic), 133.9, 132.0, 129.1, 109.9, 107.9 (aromatic *C*), 125.1 (CN), 111.0 (Cp), 93.7, 89.9 (cage *C*), 28.1, 25.0, 14.8, 13.1(Et). $^{11}B\{^1H\}$ NMR (128 MHz, pyridine-d_5): δ -2.2 (2B), -5.4 (3B), -8.6 (3B), -10.3 (2B). IR (KBr, cm^{-1}): ν 2568, 2545 (BH), 2261(C≡N). Anal. Calcd for $C_{25}H_{35}B_{10}NZr$ (**V-12**): C, 54.71; H, 6.43; N, 2.55. Found: C, 54.78; H, 6.27; N, 2.22.

Preparation of 1,2-{$Cp_2Zr[NC(2',6'-\{Me\}_2C_6H_3)]C(Et)=C(Et)\}$-1,2-$C_2B_{10}H_{10}$ (V-13). The complex **V-13** was prepared as pale white crystals from the reaction of **IV-11a** (446 mg, 1.00 mmol) and 2,6-dimethylphenylisonitrile (262 mg, 2.00 mmol) in toluene (30 mL) using the similar procedure for **V-12** but at room temperature. Yield: 519 mg (90%). ^1H NMR (400 MHz, benzene-d_6): δ 6.75 (dd, J = 7.6 Hz, 1H), 6.56 (t, J = 7.6 Hz, 2H) (aromatic *H*), 5.64 (s, 10H, C_5H_5), 2.40 (q, J = 7.4 Hz, 2H, CH_2), 2.10 (s, 6H, CH_3), 1.96 (q, J = 7.4 Hz, 2H, CH_2), 1.24 (t, J = 7.4 Hz, 3H, CH_3), 1.12 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 187.2, 145.2

(olefinic *C*), 135.4, 130.0 (aromatic *C*), 108.4 (C_5H_5), 96.5, 87.6 (cage *C*), 30.4, 25.7, 18.6, 15.7, 13.9 (Et). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ -1.1 (2B), -4.5 (3B), -7.7 (5B). IR (KBr, cm^{-1}): ν 2564 (BH), 2169 (C≡N). Anal. Calcd for $C_{27}H_{39}B_{10}NZr$ **(V-13)**: C, 56.21; H, 6.81; N, 2.43. Found: C, 56.13; H, 6.93; N, 2.09.

Preparation of 1,2-[(2',6'-$Me_2C_6H_3N$=)CC(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ (V-14). To a suspension of **IV-11a** (45 mg, 0.1 mmol) in toluene (10 mL) was added 2,6-dimethylphenylisonitrile (26 mg, 0.2 mmol), and the mixture was heated to reflux for 24 h. The resulting dark solution was treated with water (10 mL) and extracted with diethyl ether (10 mL × 2). The combined organic solutions were washed with a saturated aqueous NaCl solution and then dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the crude product was purified by chromatography on silica gel using hexane/diethyl ether (10/1 in v/v) as elute to afford **V-14** as a yellow solid (28 mg, 77%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.97 (m, 3H, C_6H_3), 2.35 (m, 4H, CH_2), 2.06 (s, 6H, CH_3), 1.22 (t, J = 7.8 Hz, 3H, CH_3), 1.12 (t, J = 7.8 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 157.6, 150.4, 144.8, 144.7, 127.2, 126.0, 124.3, (olefinic and aromatic *C*), 79.4, 70.1 (cage *C*), 21.3, 18.9, 18.3, 13.2, 12.9 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.7 (1B), -2.0 (1B), -6.4 (1B), -10.2 (3B), -12.5 (2B), -16.0 (2B). HRMS: *m/z* calcd for $C_{17}H_{29}{}^{11}B_8{}^{10}B_2{}^+$: 355.3298. Found: 355.3300.

Preparation of 1,2-[(R^1)C=C(R^2)-(Ph)CH-CH_2)]-1,2-$C_2B_{10}H_{10}$ (VI-2) and 1,2-[(R^1)C=C(R^2)-CH_2-CH(^{n}Bu)]-1,2-$C_2B_{10}H_{10}$ (VI-3). Compounds **VI-2** and **VI-3** were prepared from the reaction of **IV-2a/3a** (0.20 mmol) with alkyne (0.60 mmol) in the presence of $NiCl_2(PMe_3)_2$ (62 mg, 0.20 mmol) in toluene (10 mL) at 110 ℃ for 2 d in a closed vessel. After standard workup, the pure product was obtained by column chromatography on silica gel using hexane as eluent.

VI-2a: White solid (19 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 2H), 7.28 (m, 1H), 7.09 (d, J = 8.4 Hz, 2H) (C_6H_5), 3.70 (m, 1H, C*H*), 2.78 (m, 1H), 2.54 (m, 2H), 2.33 (m, 1H), 2.22 (m, 1H), 1.65 (m, 1H) (CH_2), 1.16 (t, J = 7.4 Hz, 3H CH_3), 0.77 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 142.0, 137.7, 130.8, 128.8, 128.7, 127.1 (olefinic and aromatic *C*), 73.4, 69.2 (cage *C*), 42.2, 39.2, 25.5, 23.7, 14.8, 12.5 (*C*H, CH_2 and CH_3). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ -5.3 (1B), -6.5 (2B), -11.8 (4B), -12.8 (3B). HRMS: *m/z* calcd for $C_{16}H_{28}{}^{11}B_8{}^{10}B_2{}^{+}$: 328.3189. Found: 328.3180.

VI-2b: White solid (25 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 2H), 7.27 (m, 1H), 7.07 (d, J = 8.4 Hz, 2H) (C_6H_5), 3.64 (m, 1H, C*H*), 2.77 (m, 1H, CH*H*), 2.51 (m, 1H, C*H*H), 2.45 (m, 2H), 2.19 (m, 1H), 2.10 (m, 1H), 1.63 (m, 2H), 1.39 (m, 3H), 1.16 (m, 1H), 1.11 (m, 2H) (6CH_2), 1.02 (t, J = 7.0 Hz, 3H, CH_3), 0.72 (t, J = 7.0 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 142.1, 136.6, 130.0, 128.8, 128.7, 127.1 (olefinic and aromatic *C*), 73.6, 69.3 (cage *C*), 42.8, 39.3, 32.5, 32.4, 30.4, 30.0, 22.9, 22.3, 13.8, 13.7 (*C*H, CH_2 and CH_3). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ -4.4 (2B), -5.5 (2B), -10.8 (4B), -11.2 (2B). HRMS: *m/z* calcd for $C_{20}H_{36}{}^{11}B_8{}^{10}B_2{}^{+}$: 384.3815. Found: 384.3815.

VI-3a: Colorless oil (41 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (m, 1H, C*H*), 2.30 (m, 1H), 2.26 (m, 1H), 2.15 (m, 2H), 2.03 (m, 2H, C*H*), 1.75 (m, 2H), 1.41 (m, 4H), 1.23 (m, 1H) (CH_2), 1.07 (t, J = 7.5 Hz, 3H, CH_3), 1.00 (t, J = 7.5 Hz, 3H, CH_3), 0.94 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 135.2, 128.4 (*C*=*C*), 76.9, 76.2 (cage *C*), 38.7, 35.9, 32.2, 29.5, 24.8, 22.5, 14.6, 13.9, 12.4 (*C*H, CH_2 and CH_3). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ -4.1 (3B), -10.8 (3B), -11.2 (4B). HRMS: *m/z* calcd for $C_{14}H_{32}{}^{11}B_8{}^{10}B_2{}^{+}$: 308.3502. Found: 308.3494.

VI-3b: Colorless oil (42 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (m, 2H),

2.25 (m, 1H), 2.14 (m, 2H), 1.98 (m, 2H), 1.75 (m, 1H), 1.54 (m, 1H), 1.43 (m, 7H), 1.22 (m, 1H) (CH_2), 0.94 (m, 9H, $3CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.0, 127.8 (*C*=*C*), 76.3 (cage *C*), 38.6, 36.3, 35.9, 34.0, 32.7, 29.5, 23.2, 22.5, 20.9, 14.1, 13.9, 13.8 (*C*H, CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -5.3 (1B), -6.0 (2B), -12.2 (3B), -12.9 (4B). HRMS: *m/z* calcd for $C_{16}H_{36}{}^{11}B_8{}^{10}B_2{}^+$: 336.3815. Found: 336.3818.

VI-3c: Colorless oil (51 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.37 (m, 2H, C*H*), 2.21 (m, 2H), 1.98 (m, 2H), 1.76 (m, 1H), 1.50 (m, 1H), 1.36 (m, 12H), 1.22 (m, 1H), 1.23 (m, 1H) (CH_2) 0.94 (m, 9H, $3CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.1, 127.5 (*C*=*C*), 77.2, 76.3, (cage *C*), 38.7, 35.9, 34.1, 32.8, 32.0, 31.6, 29.9, 29.7, 29.4, 22.8, 22.6, 22.5, 14.0, 13.9, 13.8 (*C*H, CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.8 (3B), -11.9 (7B). HRMS: *m/z* calcd for $C_{18}H_{40}{}^{11}B_8{}^{10}B_2{}^+$: 364.4128. Found: 364.4121.

VI-3d: white solid (62 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (m, 3H), 7.13 (m, 4H), 7.05 (m, 1H), 6.93 (m, 1H), 6.92 (m, 1H) (Ph), 2.80 (m, 2H), 2.57 (dd, J = 11.0 16.0 Hz, 1H, CH*H*), 1.96 (m, 1H), 1.58 (m, 5H), 0.98 (t, J = 7.0 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.0, 137.9, 137.1, 132.0, 130.9, 130.8, 127.9, 127.8,127.7, 127.6,127.5, 127.0 (olifinic and phenyl *C*), 77.4, 75.2 (cage *C*), 39.3, 36.0, 35.6, 29.5, 22.5, 13.9 (*C*H, CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.7 (1B), -5.5 (2B), -12.2 (7B). HRMS: *m/z* calcd for $C_{22}H_{32}{}^{11}B_8{}^{10}B_2{}^+$: 404.3502. Found: 404.3497.

VI-3e: Colorless oil (33 mg, 48%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 3H), 7.11 (m, 1H), 7.06 (m, 1H) (Ph), 2.54 (m, 1H), 2.37 (dd, J = 5.6 and 17Hz, 1H, C*H*H), 2.17 (dd, J = 12 and 17 Hz, 1H,CH*H*), 1.85 (m, 1H), 1.46 (s, 3H, CH_3), 1.45 (m, 3H), 1.27 (m, 1H), 0.96 (t, J = 7.1 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$): δ 137.6, 133.2, 129.9, 129.8, 128.3, 128.1, 127.8 (*C*=*C* and phenyl *C*), 77.0, 75.2 (cage *C*), 38.7, 36.0, 34.5, 29.4, 22.5, 22.2, 13.9 (*C*H, CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -6.6 (3B), -13.3 (7B). HRMS: *m/z* calcd for $C_{17}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 342.3345. Found: 342.3351.

VI-3e': Colorless oil (15 mg, 22%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.30 (m, 1H), 7.07 (m, 2H) (Ph), 2.56 (m, 1H), 2.35 (m, 1H), 1.84 (m, 5H), 1.41 (m, 4H), 1.20 (m, 1H) (C*H* and CH_2), 0.91 (t, *J* = 7.0 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.7, 134.5, 128.5, 127.5, 127.4, 125.5 (*C*=*C* and phenyl *C*), 77.6, 75.9 (cage *C*), 39.1, 36.0, 35.5, 29.4, 22.5, 19.6, 13.9 (*C*H, CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -6.0 (3B), -13.1 (7B). HRMS: *m/z* calcd for $C_{17}H_{30}{}^{11}B_8{}^{10}B_2{}^+$: 342.3345. Found: 342.3347.

VI-3f: Colorless oil (34 mg, 44%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 3H), 7.09 (m, 2H) (Ph), 2.50 (m, 1H, C*H*), 2.40 (dd, *J* = 5.4 and 17.2 Hz, 1H, CH*H*), 2.14 (dd, *J* = 11.6 and 17.2 Hz, 1H, C*H*H), 1.86 (m, 1H), 1.74 (m, 2H, CH_2), 1.46 (m, 4H), 1.27 (m, 3H), 1.12 (m, 2H) (C*H* and CH_2), 0.96 (t, *J* = 7.0 Hz, 3H, CH_3), 0.77 (t, *J* = 7.3 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.3, 137.2, 130.1, 130.0, 129.6, 128.2, 128.0, 127.8 (*C*=*C* and phenyl *C*), 75.2 (cage *C*), 38.9, 35.9, 35.2, 32.2, 29.8, 29.5, 22.5, 22.3, 13.9, 13.8 (*C*H, CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -5.9 (3B), -12.6 (7B). HRMS: *m/z* calcd for $C_{20}H_{36}{}^{11}B_8{}^{10}B_2{}^+$: 384.3815. Found: 384.3819.

VI-3f': Colorless oil (18 mg, 24%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 2H), 7.30 (m, 1H), 7.06 (m, 1H) (Ph), 2.51 (m, 1H, C*H*), 2.27 (m, 1H), 2.01 (m, 1H), 1.79 (m, 1H), 1.42 (m, 6H), 1.20 (m, 2H), 1.13 (m, 2H) (C*H* and CH_2), 0.90 (t, *J* = 6.8 Hz, 3H, CH_3), 0.69 (t, *J* = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.7, 135.9, 130.6, 128.6, 127.3 (*C*=*C* and phenyl *C*), 75.7 (cage *C*), 39.1, 36.4, 35.9, 32.2,

31.8, 29.4, 22.5, 22.4, 13.9, 13.4 (*C*H, *C*H$_2$ and *C*H$_3$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -5.0 (1B), -5.8 (2B), -12.6 (7B). HRMS: *m/z* calcd for $C_{20}H_{36}{}^{11}B_8{}^{10}B_2{}^+$: 384.3815. Found: 384.3813.

VI-3g: Colorless oil (24 mg, 33%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H), 7.12 (m, 1H),7.06 (m, 1H) (Ph), 3.59 (ab, J = 11.8 Hz, 2H, C*H*$_2$), 2.71 (s, 3H, C*H*$_3$), 2.69 (dd, J = 5.6 and 17.4 Hz, 1H, C*H*H), 2.50 (m, 1H), 2.10 (dd, J = 11.7 and 17.4 Hz, 1H, CH*H*), 1.85 (m, 1H), 1.86 (m, 1H), 1.49 (m, 6H, C*H*$_2$), 0.96 (t, J = 7.0 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.1, 134.0, 132.8, 129.9, 129.6, 128.3, 128.1 (*C*=*C* and phenyl *C*), 74.5 (cage *C*), 72.4, 57.9 (*C*H$_3$OCH$_2$), 38.8, 36.1, 29.5, 29.4, 22.5, 13.9 (*C*H, *C*H$_2$ and *C*H$_3$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -5.4 (1B), -6.4 (2B), -13.1 (7B). HRMS: *m/z* calcd for $C_{20}H_{36}{}^{11}B_8{}^{10}B_2{}^+$: 372.3451. Found: 372.3445.

VI-3g': Colorless oil (13 mg, 24%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 3H), 7.22 (m, 2H) (Ph), 3.78 (ab, J = 10.3 Hz, 2H, C*H*$_2$), 3.19 (s, 3H, C*H*$_3$), 2.60 (m, 3H), 1.81 (m, 1H), 1.40 (m, 4H), 1.21 (m, 1H), 0.90 (t, J = 7.1 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.2, 140.4, 128.3, 128.0, 127.3, 126.8 (*C*=*C* and phenyl *C*), 74.4 (cage *C*), 70.5, 57.6 (*C*H$_3$OCH$_2$), 38.8, 35.8, 35.6, 29.7, 29.4, 22.5, 13.8 (*C*H, *C*H$_2$ and *C*H$_3$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -5.4 (1B), -6.4 (2B), -13.1 (7B). HRMS: *m/z* calcd for $C_{19}H_{32}{}^{11}B_8{}^{10}B_2O^+$: 372.3451. Found: 372.3454.

Preparation of [(R^2)CH-CH(R^1)C$_6$H$_4$]-1,2-C$_2$B$_{10}$H$_{10}$ (VI-4a, R^1 = Ph, R^2 = H; VI-4b, R^1 = 3-CF$_3$C$_6$H$_4$, R^2 = H; VI-4c, R^1 = H, R^2 = Bu^n). Compounds **VI-4a - c** were prepared from the reaction of **IV-2a, IV-2g** or **IV-3a** (0.20 mmol) with 1,2-diiodobenzene (66 mg, 0.20 mmol) in the presence of CuCl (40 mg, 0.40 mmol) and HMPA (108 mmg, 0.60 mmol) in THF (10 mL) at reflux for 24 h. Using the same workup procedures as reported for **V-6** gave **VI-4a,b,c**.

VI-4a: Colorless crystals (97 mg, 30%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, J = 6.9 Hz, 1H), 7.41 (m, 3H), 7.24 (m, 1H), 7.22 (m, 3H), 6.66 (d, J = 7.8 Hz, 1H) (aromatic *H*), 4.27 (dd, J = 6.9 and 12.9 Hz, 1H, C*H*), 3.11 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.1, 134.9, 131.2, 129.2, 129.1, 129.0, 128.9, 127.7, 127.6, 127.4 (aromatic *C*), 72.3, 70.5 (cage *C*), 43.4 (*C*H), 39.1 (*C*H_2). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -3.4 (1B), -5.4 (1B), -8.8 (4B), -9.9 (2B), -11.2 (2B). HRMS: *m/z* calcd for $C_{16}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 322.2719. Found: 322.2710.

VI-4b: Colorless crystals (86 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (m, 2H), 7.55 (t, J = 8.0 Hz, 2H), 7.47 (s, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.30 (dd, J = 7.7 Hz, 1H), 7.21 (m, 1H), 6.59 (d, J = 8.0 Hz, 1H) (aromatic *H*), 4.36 (dd, J = 6.4 and 13.0 Hz, 1H, C*H*), 2.96 (dd, J = 6.4 and 14.6 Hz, 1H, C*H*H), 2.82 (dd, J = 13.0 and 14.6 Hz, 1H, C*H*H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.2, 133.9, 132.6, 131.4, 129.7, 129.2, 128.6 127.9, 127.8, 125.9, 124.8 (aromatic *C*), 72.1, 70.0 (cage *C*), 43.4 (*C*H), 39.1 (*C*H_2). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -3.8 (1B), -5.8 (1B), -9.2 (4B), -10.4 (2B), -11.7 (2B). HRMS: *m/z* calcd for $C_{17}H_{21}{}^{11}B_8{}^{10}B_2F_3{}^+$: 390.2593. Found: 390.2587.

VI-4c: Colorless crystals (39 mg, 13%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (m, 1H), 7.29 (m, 2H), 7.24 (m, 1H) (aromatic *H*), 3.01 (m, 1H, C*H*), 2.69 (m, 2H), 1.86 (m, 1H), 1.48 (m, 5H) (CH_2), 0.97 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 131.7, 131.0, 129.2, 129.0, 127.5 (aromatic *C*), 77.6, 74.5 (cage *C*), 39.5 (*C*H), 36.0, 33.3, 29.4, 22.5, 13.9 (*C*H_2 and *C*H_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -3.7 (1B), -4.9 (1B), -8.6 (1B), -9.6 (1B), -10.2(1B), -11.7 (4B). HRMS: *m/z* calcd for $C_{14}H_{26}{}^{11}B_8{}^{10}B_2{}^+$: 302.3032. Found: 302.3035.

Preparation of (RCH-CH$_2$)-1,2-C$_2$B$_{10}$H$_{10}$ (VI-5a, R = Ph; VI-5b, R = Bu^n). Compounds **VI-5a** and **VI-5b** were prepared from the reaction of **IV-2a** and **IV-3a**

(0.20 mmol) with $Cu(OTf)_2$ (73 mg, 0.20 mmol) in toluene (10 mL) at room temperature for 48 h, respectively. Using the same workup procedures as reported for **V-11** gave **VI-5a** and **VI-5b**.

VI-5a: Colorless crystals (41%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (m, 3H), 7.12 (m, 2H) (phenyl *H*), 4.62 (t, J = 6.0 Hz, 1H, C*H*), 3.21(d, J = 6.0 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136.7, 128.7, 127.6, 126.0 (phenyl *C*), 81.4, 74.4 (cage *C*), 50.4 (*C*H), 40.1 (*C*H and CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.5 (1B), -5.2 (2B), -10.8 (7B). HRMS: *m/z* calcd for $C_{10}H_{18}{}^{11}B_8{}^{10}B_2{}^+$: 246.2406. Found: 246.2405.

VI-5b: Colorless crystals (44%). ^1H NMR (400 MHz, $CDCl_3$): δ 3.27 (dd, J = 4.4 and 8.4 Hz, 1H, C*H*), 2.89 (dd, J = 8.4 and 11.6 Hz, 1H, C*H*H, 2.49 (dd, J = 4.4 and 11.6 Hz, 1H, CH*H*), 1.81 (m, 2H), 1.63 (m, 2H), 1.33 (m, 3H), 1.17 (m, 1H), 0.91(t, J = 6.9 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 82.3, 74.6 (cage *C*), 48.7 (*C*H), 41.6, 31.4, 28.5, 22.2, 13.8 (CH_2 and CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -5.0 (3B), -10.5 (7B). HRMS: *m/z* calcd for $[C_8H_{22}{}^{11}B_8{}^{10}B_2 - 2H]^+$: 224.2563. Found: 224.2560.

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.[142] 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.[143] For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[144] 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 I. Publications Based on the Research Findings

1. 'Synthesis and Structural Characterization of Zirconium-Carboryne Complexes'
   Shikuo Ren, Liang Deng, Hoi-Shan Chan, and Zuowei Xie*
   Organometallics **2009**, *28*, 5749–5756.
2. 'Reaction of Zirconocene-Carboryne Precursor with Alkynes: An Efficient Route to Zirconacyclopentenes Incorporating a Carboranyl Unit'
   Shikuo Ren, Hoi-Shan Chan, and Zuowei Xie*
   Organometallics **2009**, *28*, *4106–4114*.
3. 'Synthesis, Structure, and Reactivity of Zirconacyclopentene Incorporating a Carboranyl Unit'
   Shikuo Ren, Hoi-Shan Chan, and Zuowei Xie
   J. Am. Chem. Soc. **2009**, *131*, 3862–3863.
4. 'A Facile and Practical Synthetic Route to 1,1'-Bis(*o*-carborane)'
   Shikuo Ren and Zuowei Xie*
   Organometallics **2008**, *27*, 5167–5168.
5. 'Synthesis, Structure, and Reactivity of Zirconacyclopentene Incorporating a Carboranyl Unit'
   Shikuo Ren and Zuowei Xie*
   The 1st Singapore Hong Kong Bilateral Graduate Student Congress in Chemical Scieces, Singapore, 2009, P23.
6. 'Synthesis, Structure, and Reactivity of Zirconium-Carboryne Complexes'
   Shikuo Ren and Zuowei Xie*
   The 2nd International Symposium for Young Elements Chemists: 2007 Workshops on Organometallic Chemistry, Japan, P55.

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

	II-5b	**II-5d**	**II-5e**	**II-5f**
formula	$C_{38}H_{54}Cl_2N_4Zr$	$C_{38}H_{54}Cl_2N_4Ti$	$C_{16}H_{34}Cl_2N_4Zr$	$C_{26}H_{38}Cl_2N_4Zr$
crystal size (mm)	0.50x0.40x 0.30	0.50x0.30x0.20	0.40x0.30x0.20	0.50x0.40x0.40
fw	729.0	685.7	444.6	568.7
crystal system	orthorhombic	triclinic	monoclinic	orthorhombic
space group	*P*2(1)2(1)2(1)	*P*(-1)	*P*2(1)/*n*	*Pbcn*
a, Å	11.835(2)	11.513(2)	9.974(2)	20.524(4)
b, Å	15.803(3)	13.605(2)	31.110(5)	8.553(2)
c, Å	23.401(5)	14.146(3)	14.936(3)	16.881(3)
α, deg	90	95.11(1)	90	90
β, deg	90	108.58(1)	101.02(1)	90
γ, deg	90	111.22(1)	90	90
V, Å^3	4376.6(15)	1904.7(6)	4549.4(14)	2963.5(10)
Z	4	2	8	4
D_{calcd}, Mg/m^3	1.106	1.196	1.298	1.275
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.3 to 50.0	3.1 to 50.0	3.8 to 50.0	4.8 to 50.0
μ, mm^{-1}	0.400	0.395	0.723	0.571
F(000)	1536	732	1856	1184
no. of obsd reflns	4294	6669	7988	2611
no. of params refnd	406	406	415	150
goodness of fit	1.006	1.048	0.988	0.985
R1	0.103	0.050	0.049	0.049
*w*R2	0.274	0.117	0.132	0.116

	II-5i	**II-6a**	**II-6b**	**II-6e**
formula	$C_{22}H_{46}Cl_2N_4Ti$	$C_{30}H_{60}B_{10}N_4Zr$	$C_{44}H_{72}B_{10}N_4OZr$	$C_{22}H_{52}B_{10}N_4OZr$
cryst size (mm)	0.50x0.50x0.40	0.50x0.40x0.30	0.40x0.30x0.20	0.50x0.40x0.30
fw	485.4	676.14	872.38	588.00
cryst syst	orthorhombic	monoclinic	monoclinic	Monoclinic
space group	*Pccn*	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	15.927(4)	10.794(2)	20.600(2)	16.333(2)
b, Å	11.063(2)	29.126(5)	10.889(1)	9.890(1)
c, Å	15.906(3)	12.214(2)	21.547(2)	20.157(3)
α, deg	90	90	90	90
β, deg	90	101.03(1)	92.19(1)	91.06(1)
γ, deg	90	90	90	90
V, Å^3	2802.8(11)	3769(1)	4829.9(8)	3255.6(7)
Z	4	4	4	4
Dcalcd,Mg/m^3	1.150	1.192	1.200	1.200
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.5 to 56.1	2.8 to 50.0	2.0 to 56.0	4.0 to 56.0
μ, mm-1	0.510	0.318	0.265	0.360
F(000)	1048	1432	1848	1240
no. of obsd reflns	3398	6644	11672	7871
no. of params refnd	132	407	541	343
goodness of fit	1.073	1.059	0.987	1.022
R1	0.047	0.031	0.058	0.041
wR2	0.124	0.080	0.129	0.105

	II-6g	**II-6h**	**II-6i**	**II-6j**
formula	$C_{24}H_{56}B_{10}N_4Zr$	$C_{28}H_{66}B_{10}N_6Zr$	$C_{24}H_{56}B_{10}N_4Ti$	$C_{24}H_{56}B_{10}N_4Hf$
crystal size (mm)	0.50x0.40x0.30	0.40x0.30x0.20	0.50x0.30x0.20	0.40x0.30x0.30
fw	600.05	686.19	556.73	687.32
crystal system	monoclinic	orthorhombic	monoclinic	Monoclinic
space group	$C2/c$	$P2_12_12_1$	$C2/c$	$C2/c$
a, Å	17.853(2)	12.383(2)	18.043(3)	17.815(4)
b, Å	11.837(2)	16.059(3)	11.732(2)	11.853(2)
c, Å	17.036(2)	20.427(3)	16.682(3)	16.961(3)
α, deg	90	90	90	90
β, deg	103.46(1)	90	102.95(1)	103.71(1)
γ, deg	90	90	90	90
V, Å^3	3501.3(8)	4062(1)	3441.5(11)	3479.6(12)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.138	1.122	1.074	1.312
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.2 to 50.0	3.2 to 56.1	4.2 to 56.1	4.2 to 56.1
μ, mm^{-1}	0.334	0.297	0.269	3.018
F(000)	1272	1464	1200	1400
no. of obsd reflns	3089	9807	4148	4202
no. of params refnd	178	406	177	177
goodness of fit	1.096	0.998	1.053	1.020
R1	0.026	0.057	0.076	0.023
wR2	0.068	0.130	0.206	0.057

	II-6k	**II-6l**	**II-6m**	**III-1**•2THF
formula	$C_{14}H_{34}B_{10}Cl_2O_3Zr$	$C_{36}H_{88}B_{20}O_8Zr_2$	$C_{32}H_{64}B_{10}O_6Zr$	$C_{61}H_{90}B_{10}N_4O_3Zr$
crystal size (mm)	0.40x0.30x0.20	0.50x0.40x0.30	0.40x0.30x0.20	0.50x0.30x0.20
fw	520.63	1047.70	744.15	1126.69
crystal system	orthorhombic	monoclinic	monoclinic	Monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	11.001(2)	10.989(3)	10.545(2)	21.486(2)
b, Å	13.832(2)	30.219(7)	23.298(4)	12.487(1)
c, Å	16.716(3)	17.541(4)	18.315(3)	24.828(2)
α, deg	90	90	90	90
β, deg	90	92.04 (1)	93.49(1)	109.40(1)
γ, deg	90	90	90	90
V, Å^3	2543.5(7)	5822(2)	4491(1)	6283.1(11)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.360	1.195	1.101	1.191
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 56.1	2.7 to 50.0	2.8 to 50.0	2.2 to 50.0
μ, mm^{-1}	0.656	0.399	0.280	0.221
F(000)	1064	2192	1576	2392
no. of obsd reflns	6101	10234	7914	11057
no. of params refnd	271	595	442	712
goodness of fit	1.037	1.023	1.064	1.036
R1	0.038	0.060	0.041	0.062
wR2	0.088	0.142	0.110	0.147

	III-2	**III-3**	**III-5**	**III-7**•0.5THF •0.5toluene
formula	$C_{46}H_{74}B_{10}N_4Zr$	$C_{37}H_{63}B_{10}N_5Zr$	$C_{36}H_{73}B_{10}N_5OZr$	$C_{52.5}H_{86}B_{10}N_6O_{0.5}Zr$
crystal size (mm)	0.50x0.40x0.30	0.40x0.30x0.20	0.40x0.30x0.30	0.50x0.40x0.30
fw	898.41	779.26	791.31	1008.59
crystal system	monoclinic	monoclinic	monoclinic	Triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P(-1)$
a, Å	11.984(1)	17.135(2)	12.186(2)	10.686(2)
b, Å	21.114(2)	13.970(2)	21.069(3)	13.291(2)
c, Å	20.507(3)	18.013(2)	17.956(3)	21.843(3)
α, deg	90	90	90	86.81(1)
β, deg	99.44(1)	97.64(1)	97.37(1)	88.16(1)
γ, deg	90	90	90	69.05(3)
V, Å^3	5118.7(10)	4273.5(10)	4571.9(12)	2892.6(7)
Z	4	4	4	2
D_{calcd}, Mg/m^3	1.166	1.211	1.150	1.158
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.8 to 50.0	2.4 to 56.0	3.0 to 56.1	1.9 to 50.0
μ, mm^{-1}	0.252	0.290	0.274	0.230
F(000)	1904	1648	1688	1074
no. of obsd reflns	9017	10328	11073	10157
no. of params refnd	559	478	478	658
goodness of fit	1.059	1.019	0.995	1.021
R1	0.043	0.050	0.063	0.066
wR2	0.108	0.116	0.141	0.172

	III-8	**III-9**•0.5THF	**III-10**	**III-12**
formula	$C_{31}H_{70}B_{10}HfN_6$	$C_{39}H_{69}B_{10}N_5O_{1.5}Zr$	$C_{45}H_{73}B_{10}N_5SZr$	$C_{25}H_{56}B_{10}HfN_4S_2$
crystal size (mm)	0.50x0.40x0.30	0.50x0.20x0.20	0.40x0.30x0.20	0.50x0.40x0.30
fw	813.52	831.31	915.46	763.45
crystal system	monoclinic	orthorhombic	orthorhombic	Monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a, Å	21.370(4)	10.493(1)	13.597(3)	12.655(4)
b, Å	17.528(3)	21.436(2)	18.556(4)	11.085(4)
c, Å	23.837(4)	23.573(2)	23.349(5)	27.091(9)
α, deg	90	90	90	90
β, deg	105.76(1)	90	90	92.15(1)
γ, deg	90	90	90	90
V, Å^3	8593(2)	5302.2(9)	5891(2)	3798(2)
Z	8	4	4	4
D_{calcd}, Mg/m^3	1.258	1.041	1.032	1.335
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.0 to 50.0	2.6 to 50.0	2.8 to 56.1	3.0 to 50.0
μ, mm^{-1}	2.456	0.239	0.253	2.879
F(000)	3360	1760	1936	1074
no. of obsd reflns	15134	9346	14130	6658
no. of params refnd	865	532	559	379
goodness of fit	0.99	1.049	0.989	1.006
R1	0.036	0.088	0.077	0.035
wR2	0.093	0.232	0.196	0.088

	III-13b	**III-13d**	**III-13e**	**III-14**
formula	$C_{24}H_{56}B_{10}N_4S_2Zr$	$C_{24}H_{56}B_{10}HfN_4S_2$	$C_{24}H_{56}B_{10}N_4Se_2Zr$	$C_{36}H_{66}B_{10}N_{10}Zr$
crystal size (mm)	0.50x0.40x0.30	0.50x0.40x0.30	0.50x0.40x0.30	0.50x0.40x0.30
fw	664.17	751.44	757.97	838.31
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	10.470(2)	10.469(2)	10.461(2)	19.456(3)
b, Å	17.560(3)	17.488(4)	17.824(3)	18.780(3)
c, Å	21.038(4)	20.976(4)	21.047(4)	27.717(4)
α, deg	90	90	90	90
β, deg	99.28(1)	99.03(1)	100.35(1)	110.39(1)
γ, deg	90	90	90	90
V, Å^3	3817.5(12)	3792.9(14)	3860.4(11)	9493(2)
Z	4	4	4	8
D_{calcd}, Mg/m^3	1.156	1.316	1.304	1.173
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 56.1	3.0 to 50.0	3.0 to 56.1	3.1 to 56.1
μ, mm^{-1}	0.418	2.881	2.191	0.269
F(000)	1400	1528	1544	3536
no. of obsd reflns	9227	6683	9285	11475
no. of params refnd	370	370	370	514
goodness of fit	1.019	1.040	1.005	1.024
R1	0.049	0.029	0.048	0.050
wR2	0.114	0.074	0.112	0.127

	III-15a	III-16a	III-16b	III-16d
formula	$C_{41}H_{61}B_{10}N_7Zr$	$C_{51}H_{83}B_{10}N_7Zr$	$C_{48}H_{74}B_{10}Cl_3N_7Zr$	$C_{51}H_{83}B_{10}HfN_7$
crystal size (mm)	0.50x0.40x0.30	0.40x0.30x0.20	0.50x0.40x0.30	0.40x0.30x0.20
fw	851.29	993.56	1054.81	1080.83
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P(-1)$	$P2_1/c$	$P(-1)$
a, Å	14.092(2)	14.357(2)	21.664(4)	10.339(2)
b, Å	13.669(2)	14.423(2)	14.105(3)	14.429(2)
c, Å	24.899(4)	16.948(3)	20.704(4)	17.020(4)
α, deg	90	88.70(1)	90	88.54(1)
β, deg	96.28(1)	77.29(1)	110.25(1)	77.23(1)
γ, deg	90	65.85(1)	90	65.94(1)
V, Å^3	4767.4(12)	3115.0(8)	5935(2)	3127.7(9)
Z	4	2	4	2
D_{calcd}, Mg/m^3	1.186	1.059	1.180	1.148
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 56.1	2.5 to 50.0	2.0 to 50.0	2.5 to 50.0
μ, mm^{-1}	0.267	0.213	0.358	1.704
F(000)	1784	1056	2208	1120
no. of obsd reflns	11493	10910	10454	10979
no. of params refnd	595	622	631	622
goodness of fit	1.015	1.053	1.004	0.964
R1	0.052	0.053	0.072	0.049
wR2	0.125	0.149	0.188	0.112

	III-16e	III-17	III-18	IV-2a
formula	$C_{52}H_{82}B_{10}Cl_3HfN_7O$	$C_{58}H_{128}B_{20}Cu_2N_{10}O_2Zr_2$	$C_{24}H_{36}B_{10}Cl_2O_2Zr$	$C_{20}H_{28}B_{10}Zr$
crystal size (mm)	0.40x0.30x0.20	0.50x0.40x0.40	0.50x0.40x0.30	0.40x0.30x0.20
fw	1214.19	1523.42	626.75	467.74
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P(-1)$	$P(-1)$	$P2_1/n$	$P2_1/n$
a, Å	12.391(4)	10.824(2)	11.897(2)	14.939(2)
b, Å	17.294(6)	14.136(2)	14.014(3)	8.212(1)
c, Å	17.849(10)	17.222(4)	19.674(4)	19.487(3)
α, deg	118.31(1)	107.55(1)	90	90
β, deg	100.01(1)	92.93(1)	102.19(1)	110.40(1)
γ, deg	100.88(1)	102.88(1)	90	90
V, Å^3	3150(2)	2429.3(7)	3206.2(11)	2241.0(6)
Z	2	1	4	4
D_{calcd}, Mg/m^3	1.280	1.041	1.298	1.386
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	3.12 to 50.0	3.6 to 56.0	3.0 to 56.1
μ, mm^{-1}	1.824	0.677	0.531	0.497
F(000)	1248	800	1280	952
no. of obsd reflns	10986	8514	7744	5420
no. of params refnd	667	442	352	280
goodness of fit	1.039	0.973	1.018	1.035
R1	0.044	0.049	0.050	0.035
wR2	0.121	0.128	0.138	0.086

	IV-2c•0.25 toluene	**IV-2j**	**IV-2k**	**IV-2l**
formula	$C_{21.75}H_{29}B_{10}ClZr$	$C_{20}H_{27}B_{10}FZr$	$C_{17}H_{32}B_{10}SiZr$	$C_{33}H_{40}B_{10}PZr$
crystal size (mm)	0.40x0.30x0.20	0.40x0.30x0.20	0.40x0.30x0.20	0.50x0.40x0.30
fw	525.22	485.74	463.84	666.94
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	*P(-1)*	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	7.973(1)	13.651(6)	11.085(2)	10.662(2)
b, Å	10.444(2)	8.427(4)	9.066(1)	11.731(2)
c, Å	31.469(5)	20.131(8)	23.525(4)	28.371(5)
α, deg	84.83(1)	90	90	90
β, deg	84.65(1)	102.88(1)	99.12(1)	94.83(1)
γ, deg	75.81(1)	90	90	90
V, Å^3	2523.2(8)	2257.5(17)	2334.4(6)	3535.8(10)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.383	1.429	1.320	1.253
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	1.3 to 56.1	3.1 to 56.1	3.5 to 56.1	2.9 to 56.1
μ, mm^{-1}	0.552	0.502	0.525	0.379
F(000)	1066	984	952	1372
no. of obsd reflns	11911	5435	5596	8541
no. of params refnd	613	289	262	406
goodness of fit	1.030	0.997	1.046	1.033
R1	0.048	0.052	0.035	0.056
*w*R2	0.113	0.121	0.088	0.146

	IV-2m	IV-3a	IV-3b	IV-11a
formula	$C_{14}H_{24}B_{10}Zr$	$C_{18}H_{32}B_{10}Zr$	$C_{27}H_{35}B_{10}PZr$	$C_{18}H_{30}B_{10}Zr$
cryst size (mm)	0.40x0.30x0.30	0.40x0.30x0.20	0.40x0.30x0.20	0.40x0.30x0.20
fw	391.65	447.76	589.84	445.74
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P(-1)$	$C2/c$
a, Å	11.620(2)	10.488(2)	11.725(2)	26.251(2)
b, Å	8.158(1)	26.632(4)	12.272(2)	9.445(1)
c, Å	20.357(3)	19.416(3)	12.396(2)	18.280(2)
α, deg	90	90	105.27(1)	90
β, deg	101.04(1)	104.78(1)	90.06(1)	105.53(1)
γ, deg	90	90	118.13(1)	90
V, Å^3	1894.0(5)	5243.6(14)	1500.8(4)	4366.9(6)
Z	4	8	2	8
Dcalcd, Mg/m^3	1.373	1.134	1.305	1.356
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.1 to 50.0	3.1 to 56.1	3.4 to 50.0	3.2 to 56.0
μ, mm^{-1}	0.573	0.422	0.437	0.506
F(000)	792	1840	604	1824
no. of obsd reflns	3332	12679	5269	5280
no. of params refnd	226	523	352	262
goodness of fit	1.057	0.950	1.023	1.048
R1	0.031	0.079	0.038	0.031
wR2	0.078	0.215	0.096	0.078

	IV-11c	**IV-11d**	**IV-13a**	**IV-13c**
formula	$C_{22}H_{38}B_{10}Zr$	$C_{26}H_{30}B_{10}Zr$	$C_{21}H_{28}B_{10}Zr$	$C_{24}H_{34}B_{10}Zr$
cryst size (mm)	0.40x0.40x0.30	0.40x0.40x0.30	0.40x0.30x0.20	0.50x0.40x0.30
fw	501.84	541.82	479.75	521.83
cryst syst	monoclinic	monoclinic	triclinic	tetragonal
space group	$P2_1/c$	$P2_1/n$	$P(-1)$	$P4/n$
a, Å	15.956(3)	8.264(1)	8.938(2)	23.044(1)
b, Å	8.313(1)	19.753(3)	10.478(2)	23.044(1)
c, Å	20.484(3)	16.705(3)	13.004(2)	10.426(1)
α, deg	90	90	91.02(1)	90
β, deg	100.94(1)	96.54(1)	102.78(1)	90
γ, deg	90	90	93.48(1)	90
V, Å^3	2667.8(8)	2709.4(8)	1185.0(4)	5536.8(3)
Z	4	4	2	8
Dcalcd, Mg/m^3	1.249	1.328	1.345	1.252
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.0 to 56.0	3.2 to 56.0	3.2 to 56.2	3.9 to 50
μ, mm^{-1}	0.422	0.421	0.472	0.409
F(000)	1040	1104	488	2144
no. of obsd reflns	6413	6527	5643	4869
no. of params refnd	298	334	289	316
goodness of fit	1.056	1.023	1.038	1.184
R1	0.039	0.039	0.045	0.053
wR2	0.100	0.100	0.110	0.155

	IV-13d•1.5 toluene	**IV-13f**	**IV-13g**	**IV-13h**
formula	$C_{38.50}H_{42}B_{10}Zr$	$C_{21}H_{38}B_{10}SiZr$	$C_{23}H_{34}B_{10}SiZr$	$C_{19}H_{30}B_{10}Zr$
cryst size (mm)	0.40x0.40x0.30	0.40x0.40x0.30	0.50x0.4x0.30	0.50x0.4x0.30
fw	704.04	517.92	537.91	457.75
cryst syst	Triclinic	monoclinic	triclinic	monoclinic
space group	*P*(-1)	$P2_1/n$	*P*(-1)	*C*2/c
a, Å	11.137(3)	15.400(1)	10.244(1)	26.326(4)
b, Å	12.012(3)	9.770(2)	10.566(2)	9.445(1)
c, Å	14.742(3)	19.293(4)	14.281(2)	18.317(3)
α, deg	83.26(1)	90	105.07(1)	90
β, deg	88.17(1)	110.00(1)	100.16(1)	102.69(1)
γ, deg	71.80(1)	90	109.89(2)	90
V, Å^3	1860.5(7)	2727.6(9)	1342.6(3)	4443.3(1)
Z	2	4	2	8
Dcalcd, Mg/m^3	1.257	1.261	1.331	1.369
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.8 to 56.2	2.8 to 56.0	3.1 to 56.1	3.2 to 50.0
μ, mm^{-1}	0.323	0.456	0.467	0.499
F(000)	726	1072	552	1872
no. of obsd reflns	8859	6565	6359	3913
no. of params refnd	460	298	316	271
goodness of fit	1.017	1.038	1.043	1.030
R1	0.064	0.036	0.045	0.032
wR2	0.156	0.089	0.113	0.085

	IV-13i	IV-13j	IV-13k	IV-13l
formula	$C_{30}H_{39}B_{10}PZr$	$C_{23}H_{31}B_{10}ClZr$	$C_{23}H_{33}B_{10}NZr$	$C_{22}H_{30}B_{10}OZr$
cryst size (mm)	0.50x0.4x0.30	0.40x0.30x0.20	0.40x0.30x0.20	0.50x0.40x0.30
fw	629.90	542.25	522.82	509.78
cryst syst	triclinic	Triclinic	triclinic	triclinic
space group	*P*(-1)	*P*(-1)	*P*(-1)	*P*(-1)
a, Å	11.227(3)	10.480(2)	10.432(2)	9.105(1)
b, Å	11.761(3)	10.630(2)	14.015(2)	10.434(1)
c, Å	13.983(4)	12.757(2)	18.515(3)	13.234(2)
α, deg	67.01(1)	74.93(1)	90.89(1)	91.46(1)
β, deg	78.57(1)	81.51(1)	99.70(1)	104.86(1)
γ, deg	74.34(1)	76.40(1)	96.73(1)	92.93(1)
V, Å^3	1627.6(8)	1328.1(3)	2648.2(7)	1212.6(3)
Z	2	2	4	2
Dcalcd, Mg/m^3	1.285	1.356	1.311	1.057
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.2 to 50.0	3.3 to 56.1	2.2 to 56.0	3.2 to 50.0
μ, mm^{-1}	0.407	0.527	0.429	0.468
F(000)	648	552	1072	520
no. of obsd reflns	5706	6295	12565	4247
no. of params refnd	379	326	631	326
goodness of fit	1.032	1.012	1.014	1.057
R1	0.048	0.054	0.051	0.039
wR2	0.132	0.118	0.117	0.100

	IV-13m·0.5 toluene	**IV-14**	**IV-15**	**IV-17**
formula	$C_{31.5}H_{44}B_{10}O_2Zr$	$C_{11}H_{18}B_{10}$	$C_{17}H_{25}B_{10}NZr$	$C_{19}H_{29}B_{10}NZr$
cryst size (mm)	0.40x0.30x0.20	0.50x0.40x0.30	0.40x0.30x0.20	0.50x0.4x0.30
fw	653.99	258.35	442.70	470.75
cryst syst	triclinic	monoclinic	Orthorhombic	monoclinic
space group	*P*(-1)	$P2_1/n$	*P*bca	$P2_1/m$
a, Å	10.468(3)	7.904(1)	14.383(3)	10.490(1)
b, Å	13.040(4)	22.997(4)	14.605(3)	10.605(2)
c, Å	14.143(5)	8.3407(1)	20.451(4)	11.092(2)
α, deg	91.38(1)	90	90	90
β, deg	107.33(1)	91.34(1)	90	109.05(1)
γ, deg	91.20(1)	90	90	90
V, Å^3	1841.7(10)	1515.6(4)	4295.9(13)	1166.5(3)
Z	2	4	8	2
Dcalcd, Mg/m^3	1.179	1.132	1.369	1.340
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	3.5 to 56.1	4.0 to 56.1	3.9 to 50.0
μ, mm^{-1}	0.325	0.054	0.515	0.479
F(000)	678	536	1792	480
no. of obsd reflns	6447	3650	5205	2175
no. of params refnd	415	190	262	160
goodness of fit	1.052	1.015	1.036	1.194
R1	0.058	0.058	0.041	0.044
wR2	0.150	0.155	0.097	0.116

	IV-18	IV-19	IV-20	IV-21a
formula	$C_{21}H_{27}B_{10}NZr$	$C_{25}H_{29}B_{10}NZr$	$C_{23}H_{33}B_{10}NZr$	$C_{23}H_{33}B_{10}NZr$
cryst size (mm)	0.40x0.3x0.10	0.40x0.30x0.20	0.40x0.30x0.20	0.40x0.30x0.20
fw	492.76	542.81	522.82	522.82
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/m$	*P*nma	*C*c	$P2_1/n$
a, Å	10.811(3)	15.571(3)	12.806(1)	11.020(2)
b, Å	10.573(3)	15.993(3)	28.139(1)	19.964(3)
c, Å	14.089(4)	10.228(2)	8.488(1)	13.013(2)
α, deg	90	90	90	90
β, deg	112.16(1)	90	120.85(1)	111.46(1)
γ, deg	90	90	90	90
V, Å^3	1491.6(7)	2546.9(8)	2625.8(1)	2664.2(8)
Z	2	4	4	4
Dcalcd, Mg/m^3	1.097	1.416	1.322	1.303
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.1 to 50.0	4.7 to 50.0	4.0 to 56.0	3.9 to 56.1
μ, mm^{-1}	0.377	0.449	0.433	0.427
F(000)	500	1104	1072	1072
no. of obsd reflns	2771	2328	5335	6435
no. of params refnd	172	178	316	316
goodness of fit	1.088	1.044	1.014	1.018
R1	0.052	0.031	0.026	0.052
wR2	0.134	0.078	0.067	0.135

	IV-23	**IV-26**	**V-2j**	**V-2o**
formula	$C_{25}H_{29}B_{10}NZr$	$C_{25}H_{31}B_{10}NZr$	$C_{18}H_{38}B_{10}$	$C_{18}H_{30}B_{10}O$
cryst size (mm)	0.50x0.20x0.20	0.40x0.30x0.20	0.30x0.30x0.20	0.50x0.40x0.30
fw	542.81	544.83	362.58	370.52
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	*Pc*	*P*(-1)	*P*(-1)	$P2_1/c$
a, Å	10.375(1)	10.584(2)	9.777(2)	11.337(2)
b, Å	23.269(3)	10.645(2)	10.179(2)	10.624(2)
c, Å	11.481(1)	14.127(2)	13.111(2)	19.108(3)
α, deg	90	85.39(1)	82.25(1)	90
β, deg	108.18(1)	70.62(1)	81.31(1)	106.54(1)
γ, deg	90	61.18(1)	62.98(1)	90
V, Å^3	2633.3(5)	1309.4(4)	1145.8(3)	2206.0(6)
Z	4	2	2	4
Dcalcd, Mg/m^3	1.369	1.382	1.051	1.116
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	1.7 to 50.6	3.1 to 50.0	3.2 to 49.9	3.7 to 50.0
μ, mm^{-1}	0.435	0.437	0.052	0.059
F(000)	1104	556	392	784
no. of obsd reflns	11224	4590	4007	3885
no. of params refnd	667	334	253	262
goodness of fit	0.997	1.032	1.004	1.026
R1	0.060	0.038	0.065	0.052
wR2	0.100	0.097	0.156	0.133

	V-2p	V-2u	V-2w	V-2x
formula	$C_{19}H_{30}B_{10}$	$C_{23}H_{32}B_{10}$	$C_{17}H_{38}B_{10}Si$	$C_{19}H_{34}B_{10}Si$
cryst size (mm)	0.40x0.30x0.20	0.40x0.30x0.20	0.50x0.40x0.30	0.50x0.40x0.30
fw	366.53	416.59	378.66	398.65
cryst syst	monoclinic	monoclinic	hexagonal	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P6_5$	$P2_1/c$
a, Å	9.533(2)	11.829(2)	10.693(3)	13.579(2)
b, Å	18.412(4)	16.137(2)	10.693(3)	13.033(2)
c, Å	13.318(3)	14.117(2)	37.114(11)	14.930(2)
α, deg	90	90	90	90
β, deg	102.60(1)	108.30(1)	90	113.18(1)
γ, deg	90	90	120	90
V, Å^3	2281.5(8)	2558.4(7)	3675.1(18)	2428.8(7)
Z	4	4	6	4
Dcalcd, Mg/m^3	1.067	1.082	1.027	1.090
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.8 to 55.9	3.6 to 50.0	4.4 to 50.0	3.6 to 50.0
μ, mm^{-1}	0.053	0.055	0.097	0.101
F(000)	776	880	1224	848
no. of obsd reflns	5475	4506	4322	4285
no. of params refnd	262	298	254	271
goodness of fit	1.001	1.016	1.066	1.062
R1	0.055	0.062	0.055	0.054
wR2	0.138	0.159	0.136	0.140

	V-4·toluene	V-6a	V-8	V-9d
formula	$C_{49}H_{52}B_{10}NiP_2$	$C_{14}H_{24}B_{10}$	$C_{22}H_{42}B_{20}$	$C_{16}H_{20}B_{10}$
cryst size (mm)	0.50x0.40x0.30	0.40x0.30x0.20	0.40x0.30x0.20	0.40x0.30x0.20
fw	869.66	300.43	522.76	320.42
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P(-1)$	$P(-1)$
a, Å	11.068(16)	10.182(2)	10.735(4)	9.869(2)
b, Å	21.30(3)	17.545(4)	11.351(4)	10.739(2)
c, Å	20.99(3)	10.182(2)	14.898(5)	10.739(2)
α, deg	90	90	110.22(1)	75.10
β, deg	90.45(3)	107.19	106.49(1)	63.66(1)
γ, deg	90	90	98.50(1)	63.66(1)
V, Å^3	4948(13)	1737.9(6)	1517.2(10)	911.5(3)
Z	4	4	2	2
Dcalcd, Mg/m^3	1.167	1.148	1.105	1.168
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	4.2 to 56.2	3.1 to 50.0	4.1 to 50.0
μ, mm^{-1}	0.489	0.056	0.052	0.058
F(000)	1816	632	548	332
no. of obsd reflns	8543	4149	5341	3043
no. of params refnd	559	217	379	235
goodness of fit	1.008	1.019	1.085	1.031
R1	0.058	0.067	0.118	0.046
wR2	0.148	0.159	0.347	0.117

	V-10-A	**V-12·0.5toluene**	**V-13**	**VI-4a**
formula	$C_{11}H_{18}B_{10}$	$C_{28.50}H_{39}B_{10}NZr$	$C_{27}H_{39}B_{10}NZr$	$C_{16}H_{22}B_{10}$
cryst size (mm)	0.40x0.30x0.20	0.50x0.40x0.20	0.40x0.30x0.10	0.40x0.30x0.20
fw	258.35	594.93	576.91	322.44
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
space group	$Pna2_1$	$P2_1/c$	$P(-1)$	$P(-1)$
a, Å	13.128(3)	10.230(2	8.217(1)	7.413(1)
b, Å	15.315(4)	18.885(3)	9.397(1)	10.265(2)
c, Å	7.812(2)	16.192(3)	21.221(1)	24.831(4)
α, deg	90	90	96.42(1)	83.23(1)
β, deg	90	100.10(1)	95.86(1)	87.53(1)
γ, deg	90	90	110.43(1)	83.26(1)
V, Å^3	1570.6(6)	3079.7(9)	1508.3(1)	1862.7(5)
Z	4	4	2	4
Dcalcd, Mg/m^3	1.093	1.283	1.270	1.150
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.1 to 56.1	3.34 to 56.04	3.90 to 56.02	4.9 to 50.0
μ, mm^{-1}	0.052	0.378	0.383	0.057
F(000)	536	1228	596	672
no. of obsd reflns	3696	7418	7241	6299
no. of params refnd	198	379	352	469
goodness of fit	1.019	1.035	1.017	1.067
R1	0.054	0.042	0.028	0.101
wR2	0.135	0.106	0.070	0.237

	VI-4c	VI-5a
formula	$C_{14}H_{26}B_{10}$	$C_{10}H_{18}B_{10}$
cryst size (mm)	0.50x0.40x0.30	0.40x0.30x0.20
fw	302.45	246.34
cryst syst	triclinic	monoclinic
space group	$P(-1)$	$P2_1/n$
a, Å	9.176(1)	9.042(2)
b, Å	10.177(1)	14.042(3)
c, Å	11.731(1)	11.669(2)
α, deg	64.61(1)	90
β, deg	72.18(1)	98.04(1)
γ, deg	71.82(1)	90
V, Å^3	921.20(9)	1466.9(5)
Z	2	4
Dcalcd, Mg/m^3	1.090	1.115
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.9 to 50.0	4.6 to 50.0
μ, mm^{-1}	0.053	0.052
F(000)	320	512
no. of obsd reflns	3144	2589
no. of params refnd	217	181
goodness of fit	1.079	1.088
R1	0.090	0.056
wR2	0.275	0.163