

**Synthesis and Structural Characterization of Half-
and Full-Sandwich Group 4 Metallocarboranes**

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(鄺惠鑽)

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Requirements for the Degree of Master of Philosophy
in
Chemistry**

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Abstract

Reaction of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_3$ with $ZrCl_4(THF)_2$ in THF gave $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$. Its reactivity patterns were examined. An equimolar reaction between this chloride complex and $Li[N(SiMe_3)_2]$ gave a cation exchange product $[\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)][Li(THF)_4]$. Compound $ZrCl[N(SiMe_3)_2]_3$ was obtained if 2 equiv of $Li[N(SiMe_3)_2]$ were used. The Zr–Cl bond remained intact even though the Zr–cage bonds were broken, suggesting that the Zr–Cl bond was well protected by the dibenzyl substituents on the carborane cage. Treatment of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_3$ with H_3PO_4 in toluene gave a neutral carborane $(C_6H_5CH_2)_2C_2B_9H_{11}$. An equimolar reaction between $(C_6H_5CH_2)_2C_2B_9H_{11}$ and $M(NEt_2)_4$ ($M = Ti, Zr$) in toluene led to the formation of *exo-nido* compounds $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]M(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ ($M = Ti, Zr$). Interaction between $[\mu-\{o-C_6H_4(CH_2)_2\}C_2B_{10}H_{10}]Na_2$ and $ZrCl_4(THF)_2$ in a 1:1 molar ratio resulted in the formation of two compounds, one was Zr(II) species $\{[\mu-1,2-(o-C_6H_4(CH_2)_2)-1,2-C_2B_{10}H_{10}]_2Zr\}\{Na(THF)_3\}_2$ while the other was Zr(IV) species $\{[\mu-1,2-(o-C_6H_4(CH_2)_2)-1,2-C_2B_{10}H_{10}]_2ZrCl_2\}\{Na(THF)_3\}_2\cdot(THF)$. Both of them have full-sandwich structures. The formation of both Zr(II) and Zr(IV) species was due to the incomplete reduction of the $ZrCl_4(THF)_2$ by carborane dianion.

This work shows that (1) the steric factor plays an important role in the bonding interactions between the carboranyl ligand and group 4 metal ions, and (2) carborane anions are versatile ligands that can bond to group 4 metal ions in η^2- , η^3- , η^4- , η^5- , and η^6 -fashion.

摘要

本文通過 $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_3$ 與 $ZrCl_4(THF)_2$ 在四氫呋喃中反應，獲得了 $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ ，並研究了該化合物的反應特性。該有機鋯氯化物與等摩爾量的 $Li[N(SiMe_3)_2]$ 反應，生成了陽離子交換產物， $[\eta^4:\eta^2-\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)][Li(THF)_4]$ ；然而，該氯化物與二當量的 $Li[N(SiMe_3)_2]$ 反應，卻獲得了 $ZrCl[N(SiMe_3)_2]_3$ 。在該反應過程中，所有 Zr-cage 鍵都斷裂，但 Zr-Cl 鍵保持不變，說明了碳硼烷上二苄基取代基能保護 Zr-Cl 鍵。在甲苯中，通過 $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_3$ 與 H_3PO_4 反應，可以獲得中性碳硼烷 $(C_6H_5CH_2)_2C_2B_9H_{11}$ 。在甲苯中，將 $(C_6H_5CH_2)_2C_2B_9H_{11}$ 與等摩爾量的 $M(NEt_2)_4$ ($M = Ti, Zr$) 反應，獲得了 *exo-nido* 結構的化合物 $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]M(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ ($M = Ti, Zr$)。

$[\{o-C_6H_4(CH_2)_2\}C_2B_{10}H_{10}]Na_2$ 與等量摩爾的 $ZrCl_4(THF)_2$ 反應，生成兩個化合物，一個是二價鋯 (Zr(II)) 化合物， $\{[\mu-1,2-(o-C_6H_4(CH_2)_2)-1,2-C_2B_{10}H_{10}]_2Zr\}\{Na(THF)_3\}_2$ ，而另一個是四價鋯 (Zr(IV)) 化合物， $\{[\mu-1,2-(o-C_6H_4(CH_2)_2)-1,2-C_2B_{10}H_{10}]_2ZrCl_2\}\{Na(THF)_3\}_2(THF)$ ，這是由於碳硼烷二負離子對 $ZrCl_4(THF)_2$ 的不完全還原反應的結果。這兩個化合物都是夾心式結構。

本工作表明：(1)在碳硼烷配體與第IV族金屬離子成鍵方面，立體因素起了重要的作用，(2)碳硼烷負離子是一種多變配體，它能與第IV族金屬離子以 η^2 , η^3 , η^4 , η^5 和 η^6 形式配位。

Abbreviation

Ar	aryl
br	broad
^t Bu	<i>tert</i> -butyl
<i>n</i> -BuLi	<i>n</i> -butyl lithium
Cent	the centroids of the cyclopentadienyl or dicarbollide rings
Cp	cyclopentadienyl
Cp [*]	pentamethylcyclopentadienyl
d	doublet (NMR)
DME	dimethoxyethane
IR	Infrared spectroscopy
NMR	nuclear magnetic resonance spectroscopy
m	multiplet (NMR)
Ph	phenyl
s	singlet (NMR)
t	triplet (NMR)
THF	tetrahydrofuran
TMS	trimethylsilyl
TMEDA	N, N, N', N'-tetramethylethylenediamine

List of Compounds

formula	compound number	page number
$[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_3$	(1)	48
$\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$	(2)	49
$[\eta^4:\eta^2-\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)][Li(THF)_4]$	(3)	54
$ZrCl[N(SiMe_3)_2]_3$	(4)	57
$(C_6H_5CH_2)_2C_2B_9H_{11}$	(5)	62
$[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$	(6)	63
$[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Zr(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$	(7)	63
$[Me_3NH][\mu-\{o-C_6H_4(CH_2)_2\}C_2B_9H_{10}]$	(8)	68
$[\mu-\{o-C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_3$	(9)	69
$[\mu-\{o-C_6H_4(CH_2)_2\}C_2B_9H_9]_2Zr(THF)_2$	(10)	70
$[\mu-\{o-C_6H_4(CH_2)_2\}C_2B_9H_9]_2Hf(THF)_2$	(11)	70
$\{[\mu-1,2-(o-C_6H_4(CH_2)_2)-1,2-C_2B_{10}H_{10}]_2Zr\}\{Na(THF)_3\}_2$	(12)	72
$\{[\mu-1,2-(o-C_6H_4(CH_2)_2)-1,2-C_2B_{10}H_{10}]_2ZrCl_2\}\{Na(THF)_3\}_2\cdot(THF)$	(13)	72

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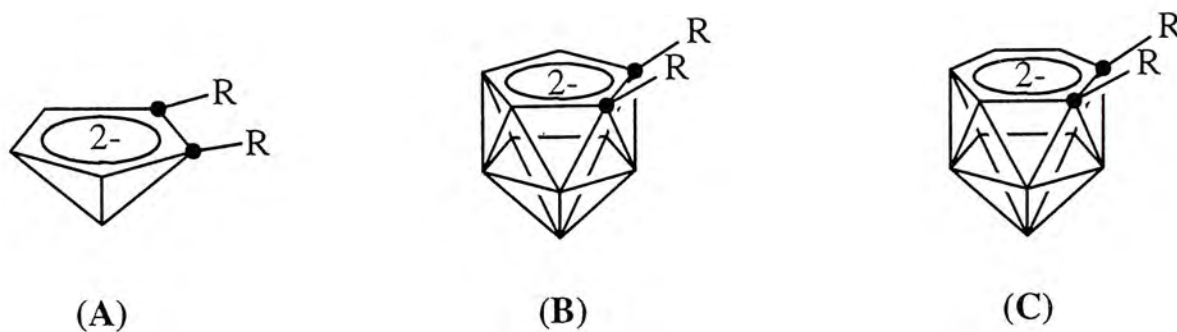
Chapter 1

Introduction

Since the discovery of Ziegler-Natta catalyst, olefin polymerizations have become very important industrial reactions.^{1,2} So, much interest has focused on the development of new olefin polymerization catalysts. Recently, the d^0 metal complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)_2\text{M(L)}]^+$ have received much attention.^{3,4} Traditionally, the cyclopentadienyl (Cp) ligands play an important role in determining catalyst activity, the molecular weight for the resulting polymer, and the ratio of linear polymer to cyclic oligomers.⁵ Sterically hindered ligands such as pentamethylcyclopentadienyl (Cp*) increase the stability of the catalytically active monomeric hydride species, but decrease the accessibility of the metal center. By contrast, the sterically less demanding cyclopentadienyl ligand provides a more accessible metal center but a less stable catalyst.⁵ This leads to the research involved studies of the structural and electronic changes induced by different substituents on the cyclopentadienide ligands and the effect of those changes on the catalytic efficiency of the complex.^{6a} Another way to introduce structural and electronic changes is to replace the cyclopentadienide ligands with other cyclic six electron π -donors.

A class of compounds whose ligation chemistry has been found to parallel with that of Cp are the carborane dianions such as *nido*-[2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_4$]²⁻ (**A**), *nido*-[7,8- $\text{R}_2\text{C}_2\text{B}_9\text{H}_9$]²⁻ (**B**), and *nido*-[7,9- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}$]²⁻ (**C**) (R = alkyl, aryl, H) (Scheme 1.1).⁷ Like Cp, they are donor ligands in which six electrons are delocalized in π -type orbitals around a five-membered ring (or six-membered ring for **C** ligand system). In the case of the carborane, the five metal-binding ring atoms are two

carbons and three borons (or the six metal-binding ring atoms are two carbons and four borons for C ligand system); the presence of the boron atoms allows for stronger, more covalent metal-ligand bonding. Another difference is that of charge; the carboranes are dianions, while the Cp ligands are monovalent. It is confirmed by experiments that the higher negative ligand charges would be expected to favor higher oxidation states in the metallacarboranes compared to the corresponding metallocenes.⁸ Both of these factors should make the early-transition-metal metallacarboranes attractive candidates for catalysts.



Scheme 1.1

1.1 Metallacarboranes of the C₂B₄ Systems

1.1.1 Group 1 Metallacarboranes of the C₂B₄ Systems

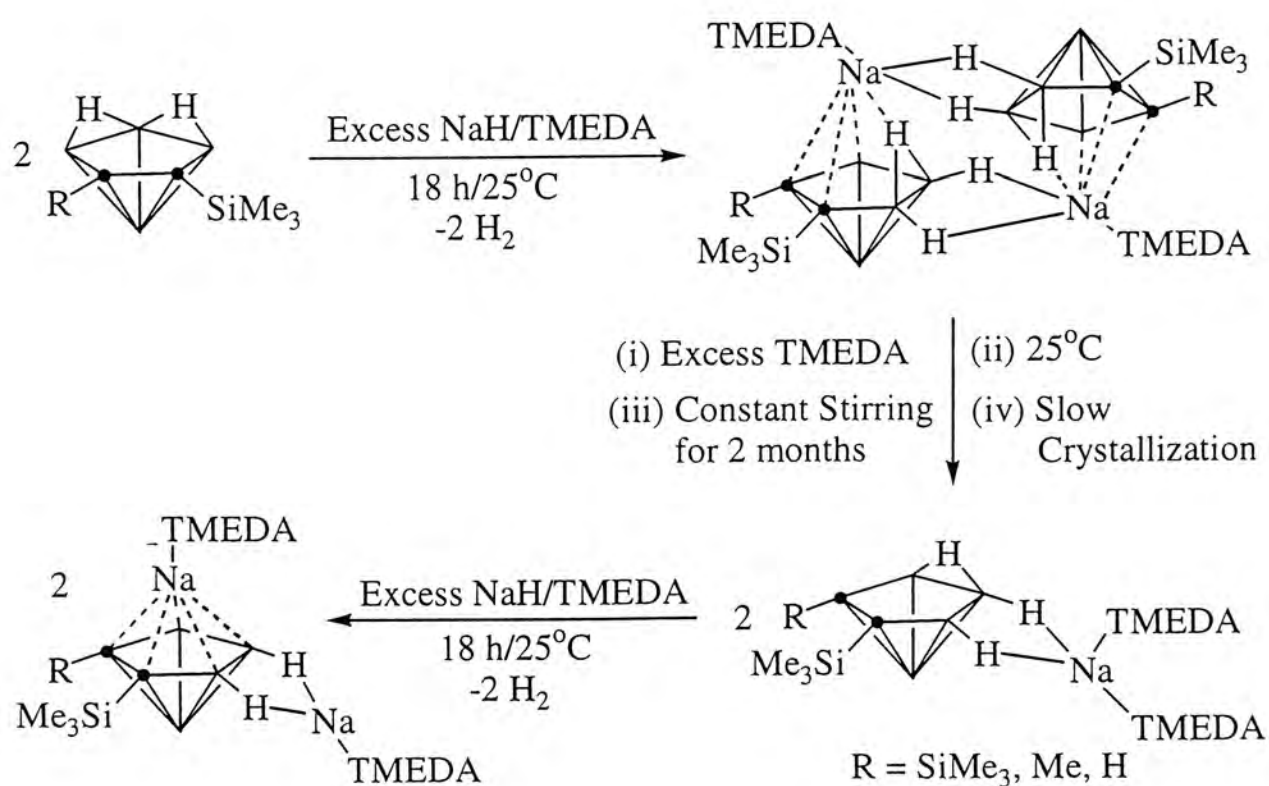
The carborane fragments of the larger cage systems are synthesized via an initial degradation of *closo*-1,2-R₂C₂B₁₀H₁₀ by alcoholic KOH, to produce the monoanions, [R₂C₂B₉H₁₀]⁻, which are assumed to be *nido*-carboranes having a bridging hydrogen. The bridging hydrogen is then removed by the reaction with NaH, to give the dianionic ligands, *nido*-[R₂C₂B₉H₉]²⁻.⁹⁻¹¹ Since similar results are obtained with different alkali metals or when tetraalkylammonium cations are used, the alkali metal ions are assumed to be innocent spectator.^{10,11}

However, the situation in the smaller C₂B₄ cage system is not so straightforward. For example, the carborane monoanion can be obtained by the heterogeneous reaction of *nido*-R₂C₂B₄H₆ with NaH in THF as shown in Scheme 1.2.¹² The main point of interest in this reaction is that, even with the use of excess NaH or a stronger KH base, and at elevated temperatures, the stoichiometry is 1:1.^{13,14} A possible explanation for this behavior is provided by the structures of the monosodium compounds, 1-Na(L)-2,3-(SiMe₃)₂-2,3-C₂B₄H₅ (L = THF or TMEDA).¹⁵ When L = THF, the structure is that of an extended array of Na₂(C₂B₄)₂ dimers that are stacked on top of one another to give a series of – (carborane)⁻ – Na⁺ – (carborane)⁻ – chains,^{12,15,16} while L = TMEDA the chain structure is broken but the ion cluster dimers, *nido*-1-Na(TMEDA)-2,3-(SiMe₃)₂-2,3-C₂B₄H₅, remain.^{12,15,16} These compounds are all fairly soluble in nonpolar and low dielectric constant solvents. This indicates that the isolated ion clusters are quite stable in solution. According to Grimes and coworkers, the deprotonation of *nido*-2,3-RR'C₂B₄H₆ (where R = alkyl, aryl; R' = R, H) with NaH or KH in THF occurred at the surface of MH through the direct reaction of the bridging H with a H⁻ ion in the

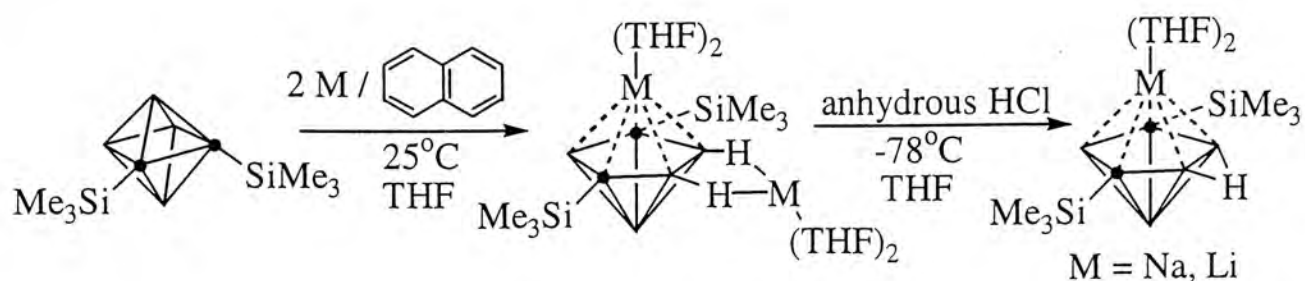
hydride lattice.¹⁷ From *nido*-1-Na(TMEDA)-2,3-(SiMe₃)₂-2,3-C₂B₄H₅, it is apparent that the second bridging hydrogen in an ion pair formed by the carborane monoanion and a solvated sodium ion would be effectively blocked from a direct reaction with a second hydride lattice site, thus preventing a second deprotonation.¹² However, soluble bases, such as BuLi, react readily with either the monosodium compound or the neutral *nido*-carborane to form the mixed sodium/lithium or dilithium complexed dianion.¹⁵ The structures of the extensively solvated species, [Li(TMEDA)₂]⁺[*nido*-2,3-(SiMe₃)₂-2,3-C₂B₄H₅]⁻ and *nido-exo*-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅, show that they are composed of discrete, well separated cation and anion units within the unit cell.¹⁸ It is significant that these monoanions react readily with NaH to give either the mixed-lithium/sodium or disodium compounds of the dianion (Scheme 1.2).¹² For example, constant stirring of the TMEDA solution of the dimeric [*nido*-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅]₂ over a period of two months at room temperature can result in *nido-exo*-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅.¹⁶ This indicates that a more extensively solvated sodium destabilizes the dimer formation and produces the weaker ion pair *nido-exo*-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅. In contrast to the inertness of [*nido*-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅]₂, *nido-exo*-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅ reacts readily with NaH in TMEDA, resulting in the isolation of *closo-exo*-4,5-[(μ-H)₂Na(TMEDA)]-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₄ as shown in Scheme 1.2.¹⁶ These results show that, in the absence of blockage of the second bridge hydrogen by the capping [Na(TMEDA)]⁺ unit, the monosodium compound can react further with a H⁻ site in the NaH lattice to yield the disodium compound. Therefore, it seems that steric effects are as important as inherent acid/base strength

in determining the reactivity of the *nido*-carborane anions. It is of interest to note that while the neutral and monoanionic compounds of the 'carbon-adjacent' *nido*-carboranes were the first ones synthesized, with further deprotonation being reported some 20 years later, the opposite is true for the 'carbons-apart' carboranes; the bimetalated carboranes are the ones produced directly from the cage-opening reactions of *closo*-C₂B₄-carboranes (Scheme 1.3).^{12,19}

Careful reaction of either the disodium or dilithium-complexed carborane dianion with HCl results in the protonation of the two adjacent borons to give the monometallated species. However, attempts at further protonation lead to the decomposition of the carborane.¹²



Scheme 1.2

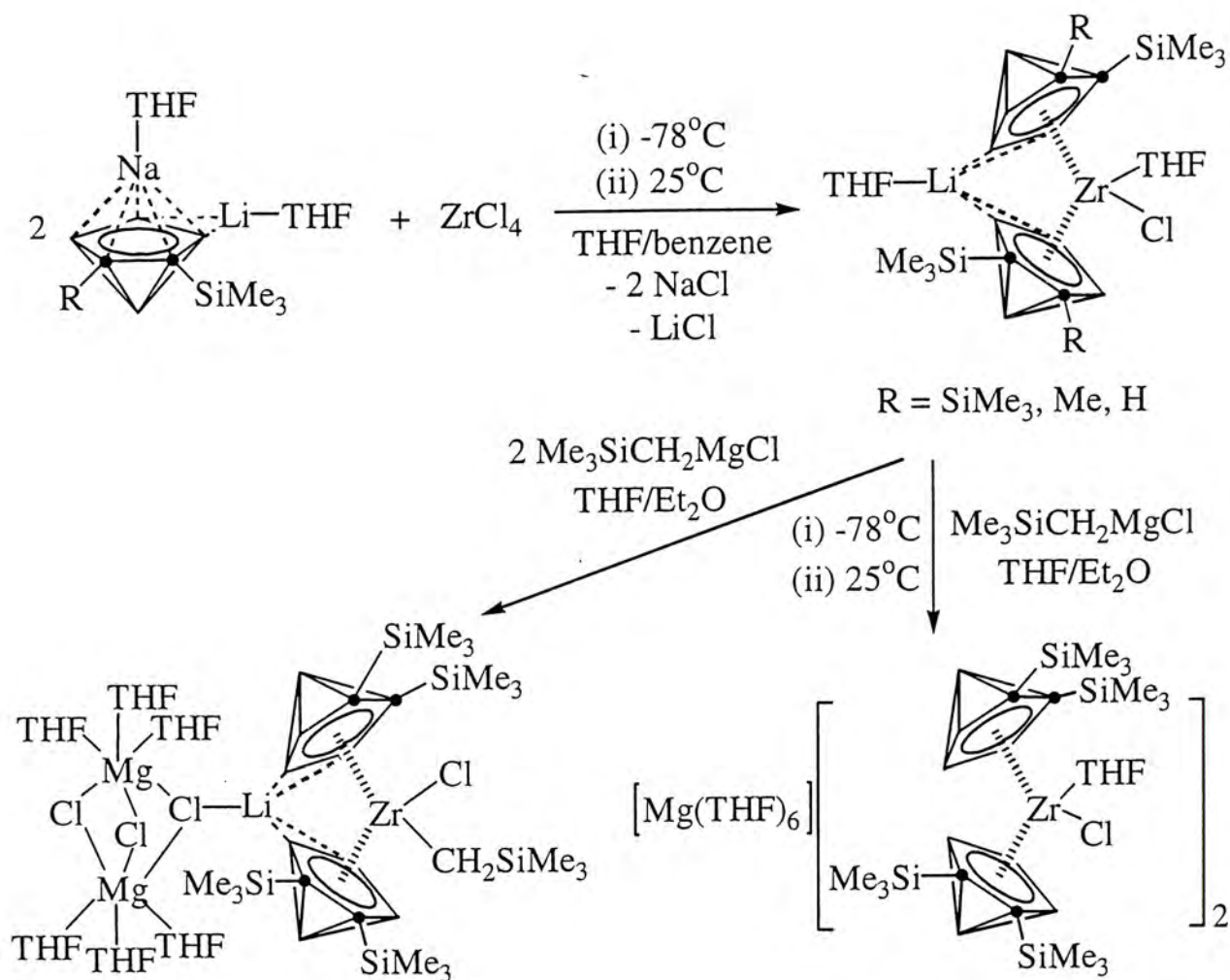


Scheme 1.3

1.1.2 Group 4 Metallacarboranes of the C₂B₄ Systems

In 1995, Hosmane and co-workers reported the syntheses of 1-Cl-1-(C₄H₈O)-2,2'-(SiMe₃)₂-3,3'-(R)₂-4,4',5,5'-Li(C₄H₈O)-1,1'-Zr(2,3-C₂B₄H₄)₂ (R = SiMe₃, Me, H).⁶ The reaction of ZrCl₄ with 2 equiv of the sodium/lithium compounds *closo-exo*-Li(THF)-1-Na-(THF)-2-(SiMe₃)-3-(R)-2,3-C₂B₄H₄ (R = SiMe₃, Me, H) in C₆H₆/THF mixtures produces the zirconacarboranes in 60-70 % yields (Scheme 1.4).^{6a} An equimolar reaction between 1-Cl-1-(C₄H₈O)-2,2',3,3'-(SiMe₃)₄-4,4',5,5'-Li(C₄H₈O)-1,1'-Zr(2,3-C₂B₄H₄)₂ and the Grignard reagent results in the replacement of two Li⁺s by a Mg²⁺, giving the ionic compound [Mg(THF)₆][1-Cl-1-(C₄H₈O)-2,2',3,3'-(SiMe₃)₄-1,1'-Zr(2,3-C₂B₄H₄)₂]₂·4THF.^{6a} The only major alternation is that a cation no longer occupies a bridging position on the zirconacarborane anions. Reaction⁻ of 1-Cl-1-(C₄H₈O)-2,2',3,3'-(SiMe₃)₄-4,4',5,5'-Li(C₄H₈O)-1,1'-Zr(2,3-C₂B₄H₄)₂ with excess Me₃SiCH₂MgCl results in the formation of a complex double salt, 1-Cl-1-CH₂SiMe₃-2,2',3,3'-(SiMe₃)₄-4,4',5,5'-[(μ-H)₄Li](μ₃-Cl)[Mg(μ₂-Cl)(THF)₃]₂-1,1'-Zr(2,3-C₂B₄H₄)₂.^{6a} The 65% yield of this compound indicates that it is the major solid product formed in this reaction. 1-Cl-1-CH₂SiMe₃-2,2',3,3'-(SiMe₃)₄-4,4',5,5'-[(μ-H)₄Li](μ₃-Cl)[Mg(μ₂-Cl)(THF)₃]₂-1,1'-Zr(2,3-C₂B₄H₄)₂ is also the only identified product of the reaction of the chlorozirconacarborane with

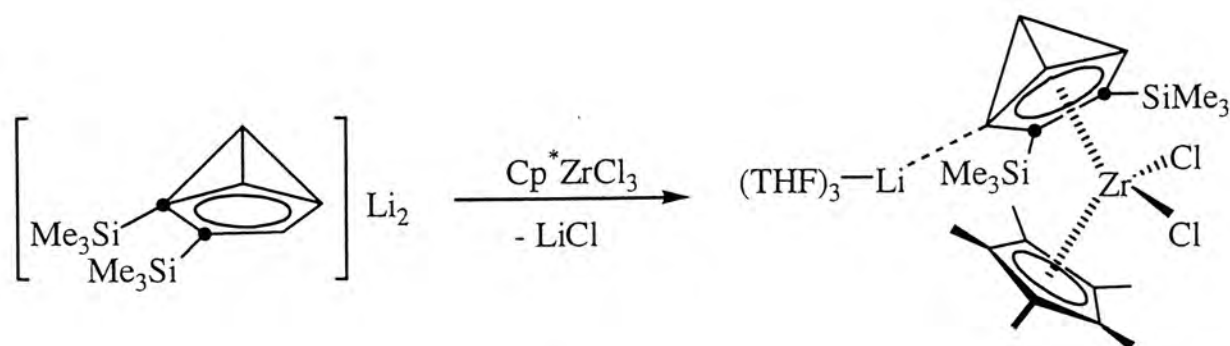
the Grignard reagent, in which $[\text{Me}_3\text{SiCH}_2]^-$ replaces the THF in the primary coordination sphere of the zirconium.



Scheme 1.4

According to Hosmane, an attempted synthesis of $(\eta^5\text{-C}_5\text{Me}_5)[\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{ZrMe}$ was based on the reported method for $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{ZrMe}]_n$, via reaction of the carborane $\text{C}_2\text{B}_9\text{H}_{13}$ with Cp^*ZrMe_3 .²⁰ Unfortunately, reaction of the free ligand $(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_6$ with Cp^*ZrMe_3 in THF or benzene gives a complex mixture of products.⁵ The NMR spectroscopy indicates that the expected product, $(\eta^5\text{-C}_5\text{Me}_5)[\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{ZrMe}$, may be unstable.

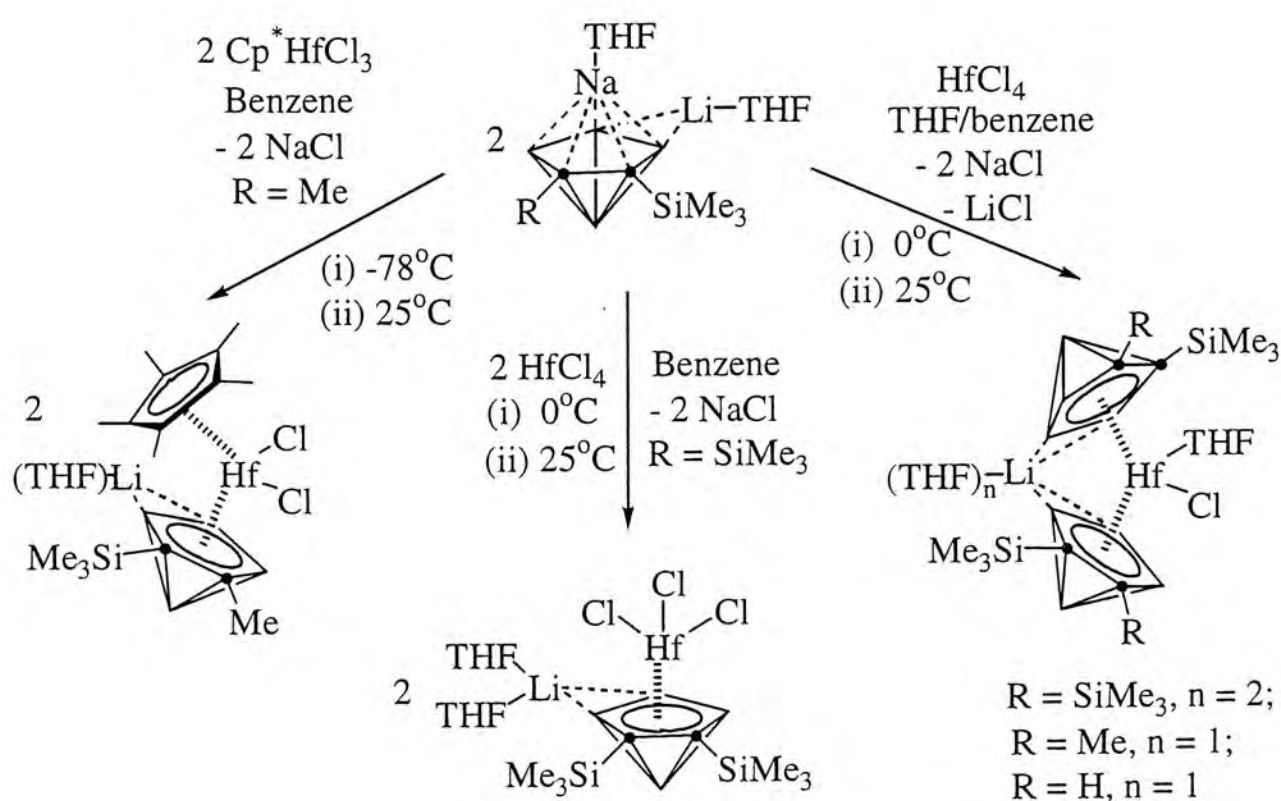
A second synthetic strategy is based on the intermediate metal chloride complex $(\eta^5\text{-C}_5\text{Me}_5)[\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{ZrCl}$, which can potentially serve as a precursor to metal alkyl and hydride derivatives.⁵ Owing to the ability of Cl to act as a four-electron donor, it is expected that this species to be more stable than its alkyl analogue. The in-situ deprotonation of $(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_6$ by 2 equiv. of *n*-BuLi at 0 °C generated the dianion $[(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]^{2-}$ in THF.²¹ Addition of Cp^*ZrCl_3 to this anion solution affords $[\text{Li}(\text{THF})_3]\{(\eta^5\text{-C}_5\text{Me}_5)[\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{ZrCl}_2\}$ (Scheme 1.5).⁵



Scheme 1.5

Besides of the zirconacarboranes, there is also a great interest in the syntheses of hafnacarboranes. In 1999, several full-sandwich, half-sandwich, and mixed-ligand sandwich hafnacarboranes were reported by Hosmane *et al.*²² These hafnacarboranes are synthesized from the reaction of the sodium/lithium compounds *closo-exo*-Li(THF)-1-Na(THF)-2-(SiMe3)-3-(R)-2,3-C2B4H4 (R = SiMe3, Me, H) with the appropriate hafnium reagent (Scheme 1.6). The products of the reactions with HfCl4 are dictated by the beginning stoichiometry used in the synthesis.^{22a} When a 2:1 molar ratio of carborane to hafnium chloride is used, the full-sandwich chlorohafnacarboranes 1-Cl-1-(THF)-2,2'-(SiMe3)2-3,3'-(R)2-4',5,5',6-Li(THF)_n-

$[1,1'-\text{Hf}-(2,3-\text{C}_2\text{B}_4\text{H}_4)_2]$ ($\text{R} = \text{SiMe}_3, \text{Me}, \text{H}$) are produced in yields of 77, 65, and 71% respectively. On the other hand, a 1:1 molar ratio of carborane to HfCl_4 give the trichlorohafnium half-sandwich metallocarborane $[\text{Li}(\text{THF})_2][1,1,1-(\text{Cl})_3\text{-}closo\text{-}1\text{-Hf-}2,3-(\text{SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4]$ in 77% yield. Both 2:1 and 1:1 molar ratios of carborane to Cp^*HfCl_3 produce exclusively the mixed sandwich complex $1,1'-(\text{Cl})_2\text{-}2-(\text{SiMe}_3)\text{-}3-(\text{Me})\text{-}4,5\text{-Li}(\text{THF})\text{-}1,1'\text{-Hf}[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4)]$ in 82% yield.

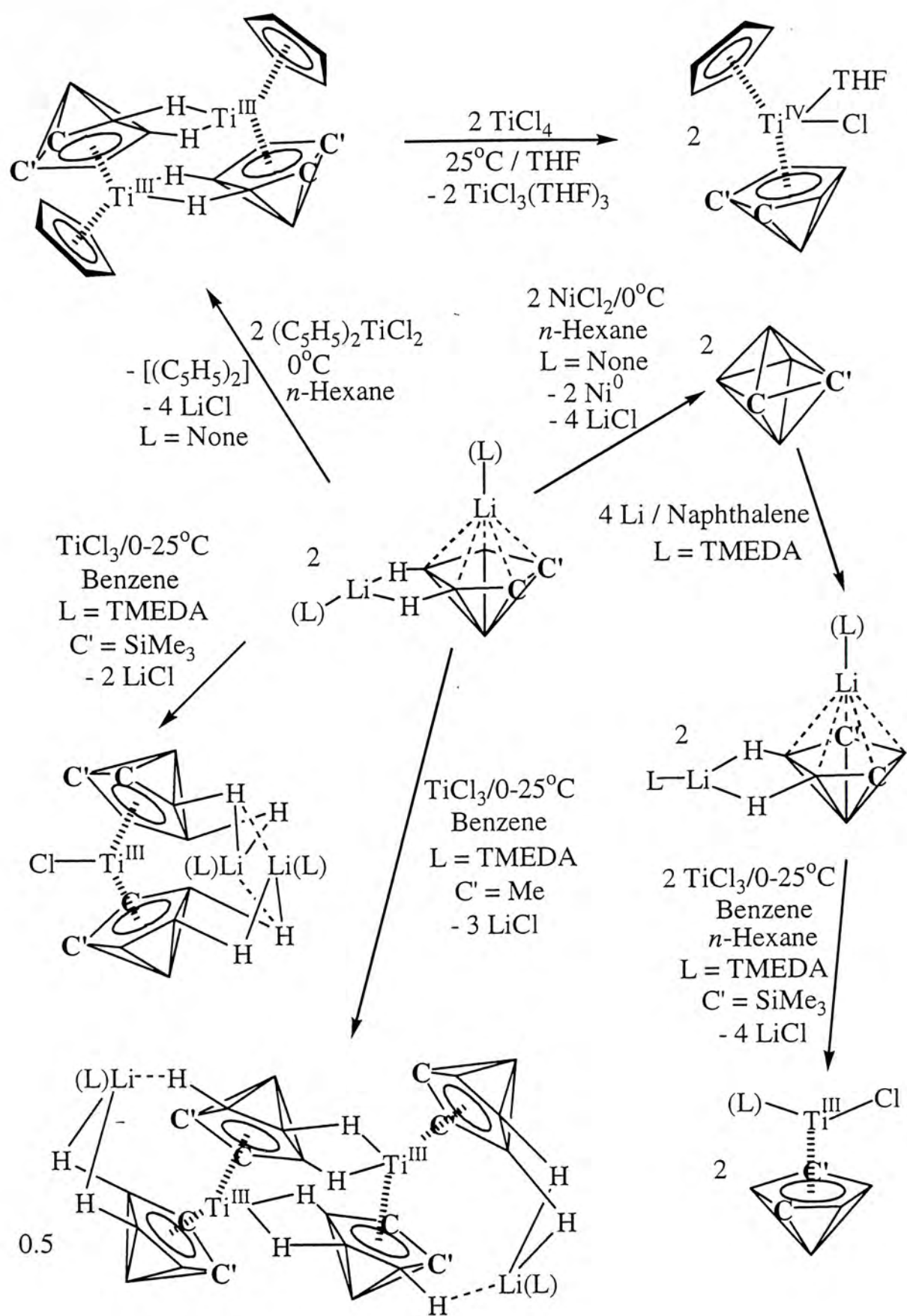


Scheme 1.6

In 1997, the mixed-ligand sandwich titanacarboranes, $[1\text{-Cp-}1\text{-Ti-}2,3\text{-(SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4]_2$ and $1\text{-Cp-}1\text{-Cl-}1\text{-THF-}1\text{-Ti-}2,3\text{-(SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4$ were reported by Hosmane *et al.*^{21,23} The reaction of Cp_2TiCl_2 with the unsolvated 'carbons adjacent' dilithium compounds $closo\text{-}exo\text{-Li-}1\text{-Li-}2\text{-(R)-}3\text{-(SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4$ ($\text{R} = \text{SiMe}_3, \text{Me}, \text{H}$) produces the mixed-ligand sandwich titanacarboranes, $[1\text{-(Cp)-}1\text{-Ti-}2\text{-(R)-}3\text{-(SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4]_2$ ($\text{R} = \text{SiMe}_3, \text{Me}, \text{H}$) in yields of 60%,

54%, and 60%, respectively. Until recently, the crystal structure of [1-(Cp)-1-Ti-2-(Me)-3-(SiMe₃)-2,3-C₂B₄H₄]₂ was also reported.²⁴ The syntheses of these are outlined in Scheme 1.7.²³ In both the syntheses of the mixed-ligand sandwich Ti(III) complexes, [1-Cp-1-Ti-2-(R)-3-(SiMe₃)-2,3-C₂B₄H₄]₂, and their subsequent oxidation to the corresponding Ti(IV) complexes, 1-(Cp)-1-(Cl)-1-(THF)-1-Ti-2-(R)-3-(SiMe₃)-2,3-C₂B₄H₄ (R = SiMe₃, Me, H), the driving forces are most likely the stabilities of the respective Ti(III) products, as well as the dihydrofulvalene formed in the syntheses of, [1-(Cp)-1-Ti-2-(R)-3-(SiMe₃)-2,3-C₂B₄H₄]₂.²³ The products of the reactions of TiCl₃ with the different dilithiacarborane compounds depend on the steric factors arising from the nature of the cage-carbons substituents and the location of the cage-carbons in the C₂B₃ bonding face of the carborane ligand (Scheme 1.7).²³ When the 'carbons adjacent' bis(trimethylsilyl)-carborane (Cb) is a reactant, only the monomeric full-sandwich chlorotitanacarborane, [Li(TMEDA)]₂[1,1'-Ti(Cl)-{2,3-(SiMe₃)₂-2,3-C₂B₄H₄}]₂, is formed, irrespective of the stoichiometry used in the reaction. Replacement of a SiMe₃ group with the smaller Me group affords the [(Cb*)₂Ti]₂²⁻ dimer, [Li(TMEDA)]₂[1,1'-Ti-{2-(Me)-3-(SiMe₃)-2,3-C₂B₄H₄}]₂, exclusively. Similarly, replacement of one of the Cb ligands with the smaller, isolobal and isoelectronic π-donor Cp ligand also results in dimer formation, resulting in the formation of mixed-ligand dimers, [1-(Cp)-1-Ti-2-(R)-3-(SiMe₃)-2,3-C₂B₄H₄]₂. The only half-sandwich titanacarborane that can be formed is that of the carbons apart isomer, 1-(TMEDA)-1-Cl-1-Ti-2,4-(SiMe₃)₂-2,4-C₂B₄H₄. At present, it is not known exactly why the carbons apart and carbons adjacent carboranes should give such different products when reacts with TiCl₃.²³ A possible explanation may be that because of the intervening boron atom, the steric restrictions on additional coordination at the titanium imposed by the cage-carbon

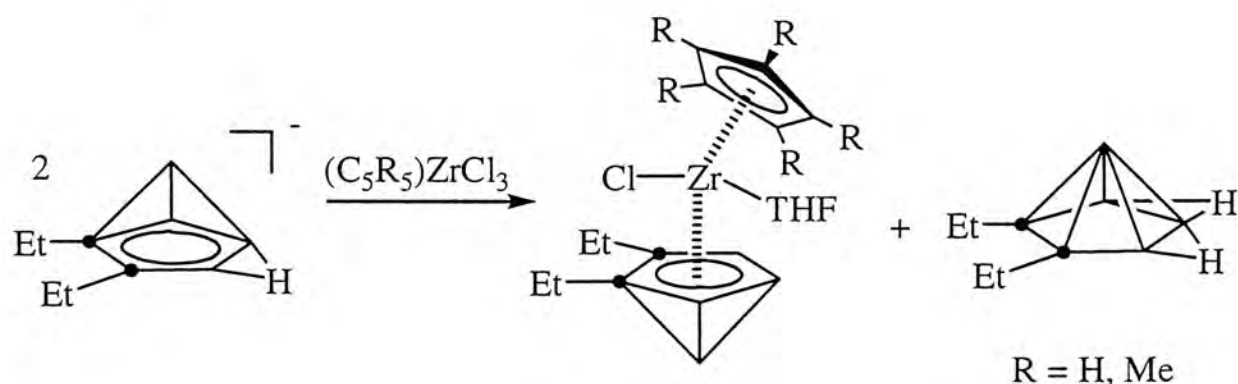
substituents would be somewhat tempered, allowing for the coordination of a chlorine atom and the large TMEDA molecule.²³



$\text{C} = \text{C-SiMe}_3$; $\text{C}' = \text{C-SiMe}_3, \text{Me}, \text{H}$

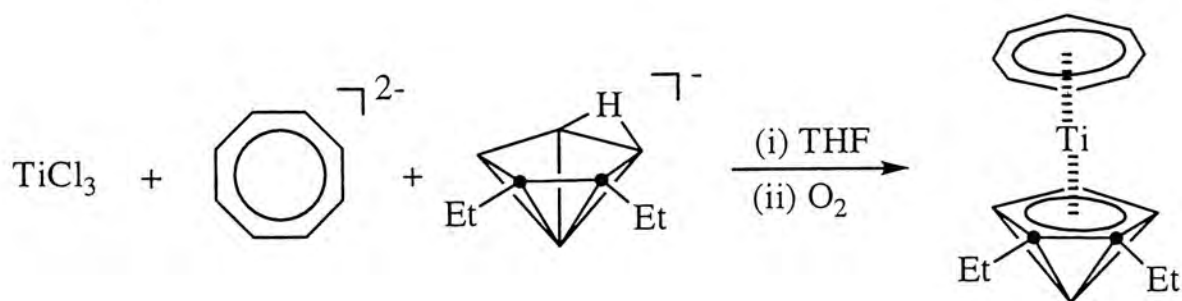
Scheme 1.7

In 1995, the syntheses of $(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}(\text{THF})$ and $(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}(\text{THF})$ were reported by Grimes *et al.*²⁵ Carboranyl-cyclopentadienyl complexes of zirconium are prepared via disproportionation reactions between 2 equiv of *nido*-carborane monoanion $[\text{Et}_2\text{C}_2\text{B}_4\text{H}_5]^-$ and $(\text{C}_5\text{R}_5)\text{ZrCl}_3$ ($\text{R} = \text{H}, \text{Me}$), forming the species $(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}(\text{THF})$ and $(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}(\text{THF})$, together with neutral $\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$, which is recovered (Scheme 1.8).²⁵ The zirconium cyclopentadienyl complex, $(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}(\text{THF})$, is isolated with 1 equiv of THF as solvent of recrystallization. In this compound, the appearance of diastereotopic signals for the carbonyl ethyl groups indicates a comparatively slow process for ligand exchange.²⁵ The permethylcyclopentadienyl complex, $(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}(\text{THF})$, is isolated with 2-3 equiv of THF; in contrast to $(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}(\text{THF})$, its carbonyl ethyl ^1H NMR signals are not split in a diastereotopic pattern, suggesting a more rapid ligand exchange process. This is consistent with the more hindered nature of the metal center, which is expected to enhance the rate of THF dissociation.



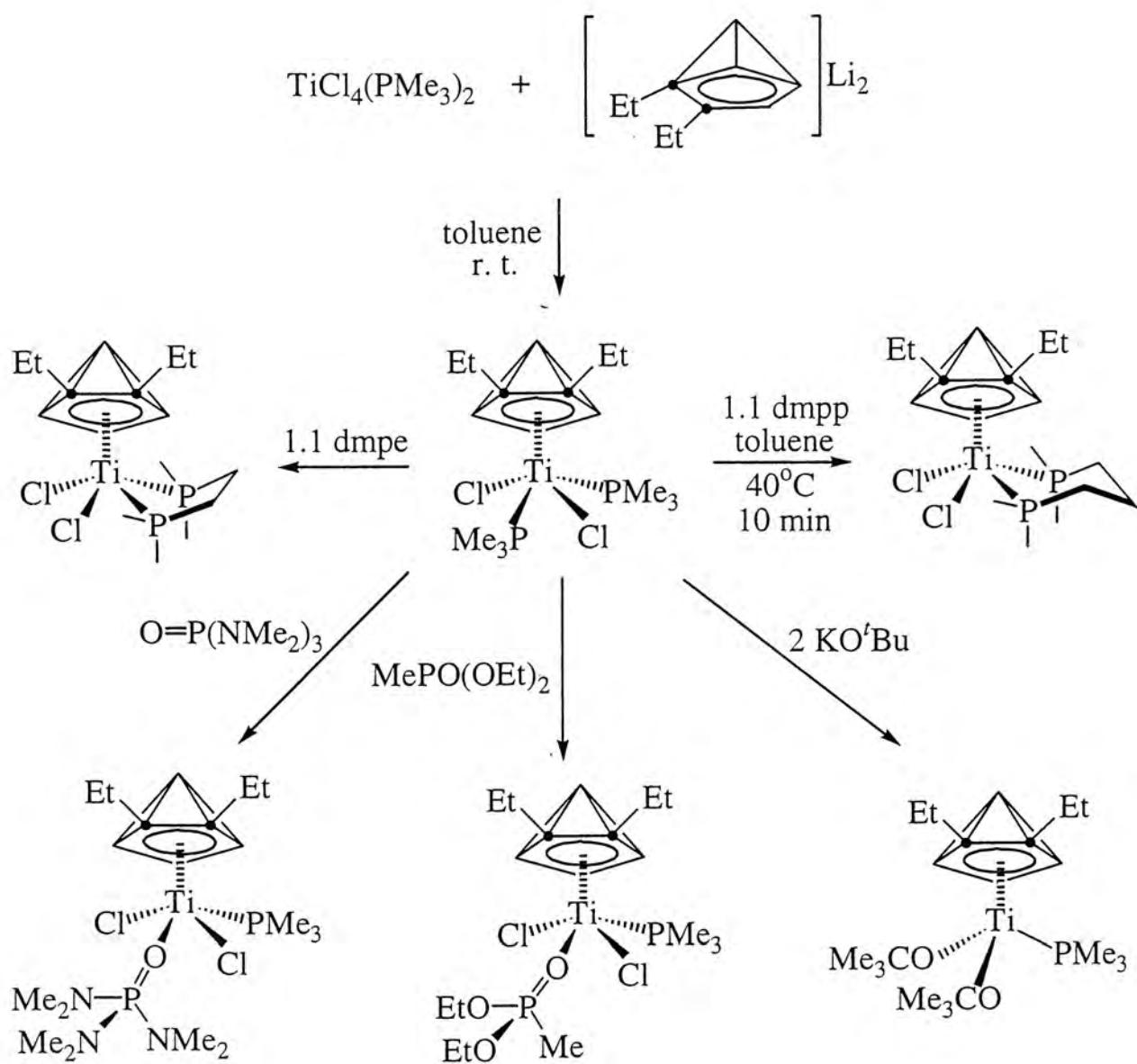
Scheme 1.8

The reaction of $C_8H_8^{2-}$ and $(C_2H_5)_2C_2B_4H_5^-$ ions with $TiCl_3$ in THF gives the major isolobal product $1,2,3-(\eta^8-C_8H_8)Ti[\eta^5-(C_2H_5)_2C_2B_4H_4]$. This reaction was reported by Grimes *et al.* in 1984.²⁶ Approximately equimolar quantities of $TiCl_3$, $K_2C_8H_8$, and $Na^+[(C_2H_5)_2C_2B_4H_5]^-$ are mixed in cold THF and slowly warmed to room temperature. Separation of the products on silica gel in air gives the desired cyclooctatetraene metallocarborane, $1,2,3-(\eta^8-C_8H_8)Ti[\eta^5-(C_2H_5)_2C_2B_4H_4]$ as the major isolated complex (Scheme 1.9). This complex is an air-stable, diamagnetic red solid whose solution decompose slowly (days) on exposure to air. It is also an unreactive complex toward H_2 , CO , CH_3CN , and $(C_6H_5)_3P$ under ambient conditions and is catalytically inactive toward the hydrogenation of 3-hexyne under 1 atm of H_2 .²⁶ In an investigation of the reactivity of the C_8H_8 ring toward methylation, $1,2,3-(\eta^8-C_8H_8)Ti[\eta^5-(C_2H_5)_2C_2B_4H_4]$ is heated with an $AlCl_3/CH_3I$ solution; however, no methylated products are found. Instead, the major product, obtained in 30% yield, is an iodo derivative characterized as $5-I-1,2,3-(\eta^8-C_8H_8)Ti[\eta^5-(C_2H_5)_2C_2B_4H_3]$.²⁶ Direct iodination of $1,2,3-(\eta^8-C_8H_8)Ti[\eta^5-(C_2H_5)_2C_2B_4H_4]$ with I_2 in benzene gives a diiodo derivative, $4,5-I_2-1,2,3-(\eta^8-C_8H_8)Ti[\eta^5-(C_2H_5)_2C_2B_4H_2]$ in 76% yield.²⁶



Scheme 1.9

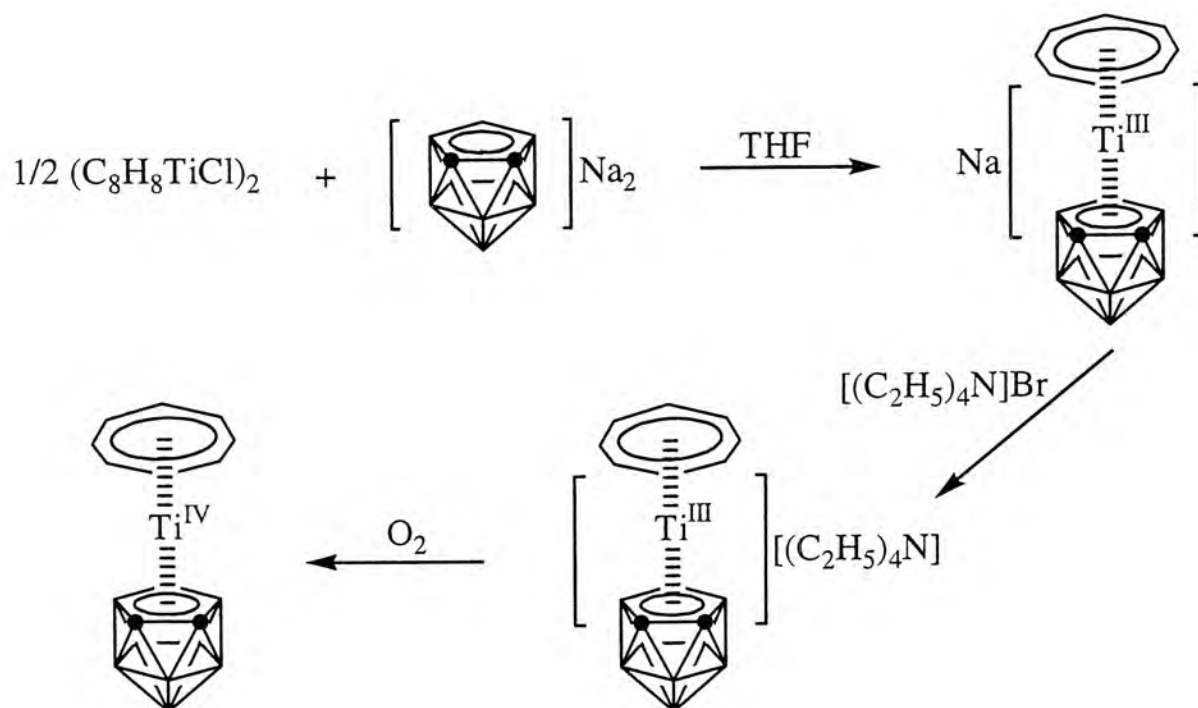
In 2000, Grimes and co-workers have also reported the syntheses of complexes $L(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{MCl}_2$ ($\text{M} = \text{Ti}$, $\text{L} = 2 \text{PMe}_3$, $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$, $\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2$, $[\text{OP}(\text{NMe}_2)_3](\text{PMe}_3)$, $[\text{OP}(\text{OEt})_2\text{Me}](\text{PMe}_3)$; $\text{M} = \text{Zr}$, $\text{L} = 2 \text{PMe}_3$, $\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2$), $(\text{OCMe}_3)_2(\text{PMe}_3)\text{Ti}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ and $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2](\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiMe}_2$ (Scheme 1.10).²⁷ An equimolar reaction between $[\text{Et}_2\text{C}_2\text{B}_4\text{H}_4]^{2-}$ and $\text{TiCl}_4(\text{PMe}_3)_2$ in toluene affords $(\text{PMe}_3)_2(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$. The two phosphine ligands can be replaced by 1,2-bis(dimethylphosphino)ethane (dmpe) or 1,3-bis(dimethylphosphino)propane (dmpp), forming $[\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2](\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$ and $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2](\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$, respectively. Similarly, the zirconium analogues $(\text{PMe}_3)_2(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2$ and $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2](\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2$ can also be prepared. Alkylation of $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2](\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$ with two equiv. of MeLi in toluene can give the complex $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2](\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiMe}_2$. Monodentate phosphine oxide complexes $[\text{OP}(\text{NMe}_2)_3](\text{PMe}_3)(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$ and $[\text{OP}(\text{OEt})_2\text{Me}](\text{PMe}_3)(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$ are accessible via treatment of $(\text{PMe}_3)_2(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$ with excess $\text{OP}(\text{NMe}_2)_3$ or $\text{OP}(\text{OEt})_2\text{Me}$. Besides, the two chloride and one phosphine ligands of $(\text{PMe}_3)_2(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$ can be displaced by *tert*-butoxide to give $(\text{OCMe}_3)_2(\text{PMe}_3)\text{Ti}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$. It is found that the catalytic activity of $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2](\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiMe}_2$ is two orders of magnitude higher than that of $(\text{PMe}_3)_2(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{TiCl}_2$.²⁷ Furthermore, these catalysts produce high-molecular-weight polyethylene of substantially lower melting point than is normally for metallocene systems.²⁷ The stabilities and catalytic activities of all these complexes are dramatically affected by the nature of phosphine, with dmpp proving to be far more effective than either dmpe or trimethylphosphine.²⁷



Scheme 1.10

1.2 Group 4 Metallocarboranes of the C₂B₉ Systems

Hawthorne has developed the coordination chemistry of C₂B₉H₁₁²⁻, which is electronically and sterically comparable to Cp^{*}.²⁰ In 1976, some titanacarboranes based on this ligand were reported by him.²⁸ The reaction of (C₈H₈TiCl)₂ with Na₂C₂B₉H₁₁, prepared by reaction of sodium hydride with 1,2-C₂B₉H₁₂⁻, produces Na[3-(η⁸-C₈H₈)-3-Ti-1,2-C₂B₉H₁₁] (Scheme 1.11). After removal of solvent and addition of [(C₂H₅)₄N]Br, [(C₂H₅)₄N][3-(η⁸-C₈H₈)-3-Ti-1,2-C₂B₉H₁₁] is resulted. This complex can be oxidized to 3-(η⁸-C₈H₈)-3-Ti-1,2-C₂B₉H₁₁. Similarly, [(C₂H₅)₄N][2-(η⁸-C₈H₈)-2-Ti-1,7-C₂B₉H₁₁] and 2-(η⁸-C₈H₈)-2-Ti-1,7-C₂B₉H₁₁ are prepared from 1,7-C₂B₉H₁₂⁻ and (C₈H₈TiCl)₂.²⁸

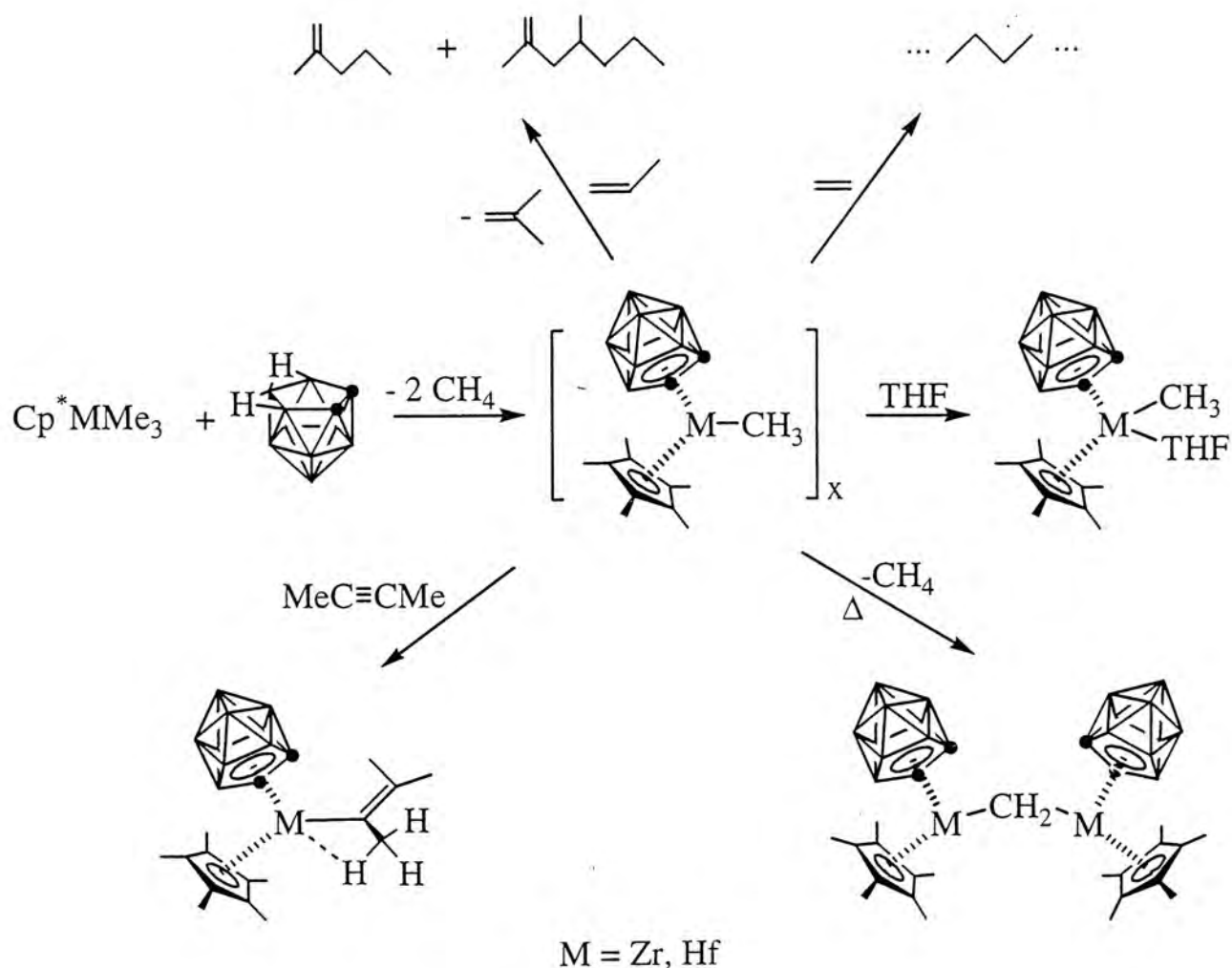


Scheme 1.11

The parent acid C₂B₉H₁₃ contains two acidic hydrogens which can cleave M–C bonds of electrophilic metals.^{20,29} In 1991, Jordan and co-workers have

performed an equimolar reaction between $C_2B_9H_{13}$ and $Cp^*M(Me)_3$ ($M = Zr, Hf$) in aromatic solvent yielding $[(Cp^*)(C_2B_9H_{11})M(Me)]_x$ (Scheme 1.12)²⁰. The methyl complexes $Cp^*_2(C_2B_9H_{11})_2M_2Me_2$, with $M = Zr, Hf$, react with 2-butyne via single insertion to yield the monomeric alkenyl complexes $Cp^*(C_2B_9H_{11})M[C(Me)=CMe_2]$ ($M = Zr, Hf$).²⁰ These monomeric alkenyl complexes do not undergo further insertion chemistry with 2-butyne, and $Cp^*(C_2B_9H_{11})Zr[C(Me)=CMe_2]$ does not coordinate THF. Complexes $Cp^*_2(C_2B_9H_{11})_2Zr_2Me_2$ and $Cp^*_2(C_2B_9H_{11})_2Hf_2Me_2$ form THF adducts $(Cp^*)(C_2B_9H_{11})M(Me)(THF)$ ($M = Zr, Hf$) which do not undergo exchange with free THF on the NMR time scale at 23°C. However, $(Cp^*)(C_2B_9H_{11})Zr(Me)(THF)$ reacts readily with 2-butyne to yield $Cp^*(C_2B_9H_{11})Zr[C(Me)=CMe_2]$. Complexes $Cp^*_2(C_2B_9H_{11})_2Zr_2Me_2$ and $Cp^*_2(C_2B_9H_{11})_2Hf_2Me_2$ are moderately active ethylene polymerization catalysts.²⁰ They can also catalyze the oligomerization of propylene to 2-methylpentene and 2,4-dimethylheptene as major products. Isobutene is detected as a minor product by GC. This product distribution is characteristic of an insertion/ β -H elimination process.

Thermolysis of $Cp^*_2(C_2B_9H_{11})_2Zr_2Me_2$ in toluene-*d*₈ quantitatively yields the methylidene-bridged complex $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu-CH_2)$ and CH_4 .²⁰ $Cp^*_2(C_2B_9H_{11})_2Hf_2Me_2$ undergoes a slower CH_4 elimination reaction to yield $[(Cp^*)(C_2B_9H_{11})Hf]_2(\mu-CH_2)$.



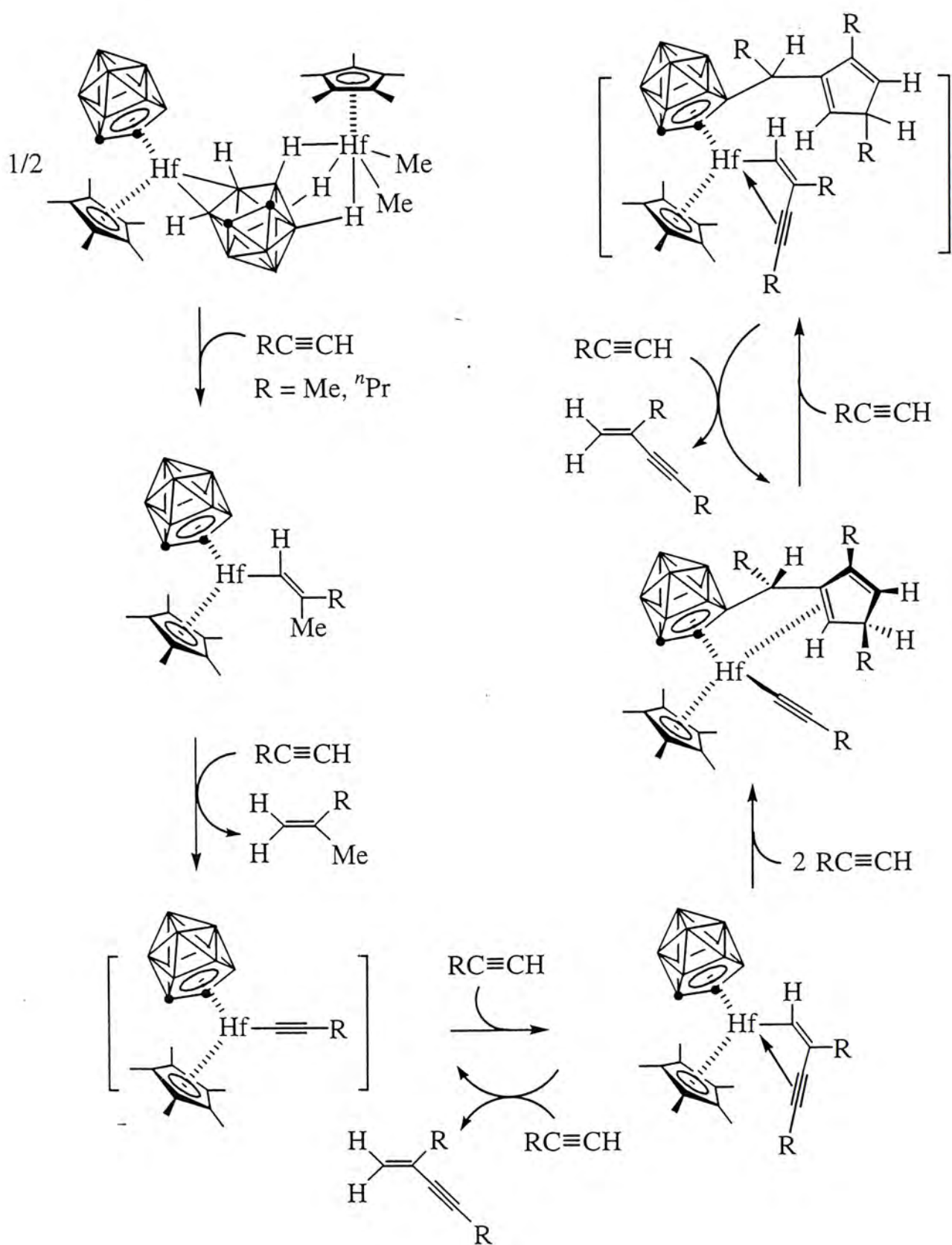
Scheme 1.12

Until 1995, the compound $\text{Cp}^*_2(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Hf}_2\text{Me}_2$ was reported to adopt an unsymmetrical dinuclear structure composed of $[\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{Hf}]^+$ and $[\text{Cp}^*\text{HfMe}_2]^+$ fragments linked by an unusual bridging $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ group (Scheme 1.13).³⁰

Later, Jordan *et. al.* have reported that this dinuclear complex $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^2\text{:}\eta^3\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\text{Cp}^*)\text{Me}_2$ catalyzed the regioselective dimerization of terminal alkynes $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{Me}, \text{}^n\text{Pr}, \text{}^t\text{Bu}$) to 2,4-disubstituted 1-buten-3-yne $\text{CH}_2=\text{C}(\text{R})\text{C}\equiv\text{CR}$.³¹ The selectivity for dimer rather than trimer or higher oligomers results from a 'self-correcting' mechanism in which intermediate **A** (Scheme 1.14), which can potentially produce trimers or higher oligomers, undergoes an

intramolecular cyclization reaction which ultimately yields the boron-alkylated complex $(\text{Cp}^*)\{\eta^5\text{-7-CH(R)(3,5-R}_2\text{-2-C}_5\text{H}_3\text{)-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}\equiv\text{CR}$, which is too crowded to produce trimer in subsequent cycles.³¹

According to Scheme 1.13, $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^2\text{:}\eta^3\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\text{Cp}^*)\text{Me}_2$ reacts with alkyne to yield the alkenyl complex $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC(H)=CRMe}$.³¹ This species is not observed but is directly analogous to $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC(Me)=CMe}_2$. It undergoes rapid σ -bond metathesis with alkyne to yield the unobserved alkynyl species $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC}\equiv\text{CR}$ and $\text{CH}_2\text{=CRMe}$. $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC}\equiv\text{CR}$ then undergoes rapid alkyne insertion to yield $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC(H)=C(R)C}\equiv\text{CR}$. Actually, $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC(H)=C(R)C}\equiv\text{CR}$ can react with alkyne in two ways.³¹ Simple σ -bond metathesis of it and alkyne results in release of dimer 2,4-disubstituted 1-buten-3-yne, regeneration of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC}\equiv\text{CR}$, and formation of one catalytic dimerization cycle. Alternatively, $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC(H)=C(R)C}\equiv\text{CR}$ can react with 2 equiv of alkyne by a more complex mechanism to yield $(\text{Cp}^*)\{\eta^5\text{-7-CH(R)(3,5-R}_2\text{-2-C}_5\text{H}_3\text{)-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}\equiv\text{CR}$. This complex catalyzes the dimerization of alkyne by a second insertion/ σ -bond metathesis cycle involving the unobserved alkenyl intermediate $(\text{Cp}^*)\{\eta^5\text{-7-CH(R)(3,5-R}_2\text{-2-C}_5\text{H}_3\text{)-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC(H)=C(R)C}\equiv\text{CR}$.

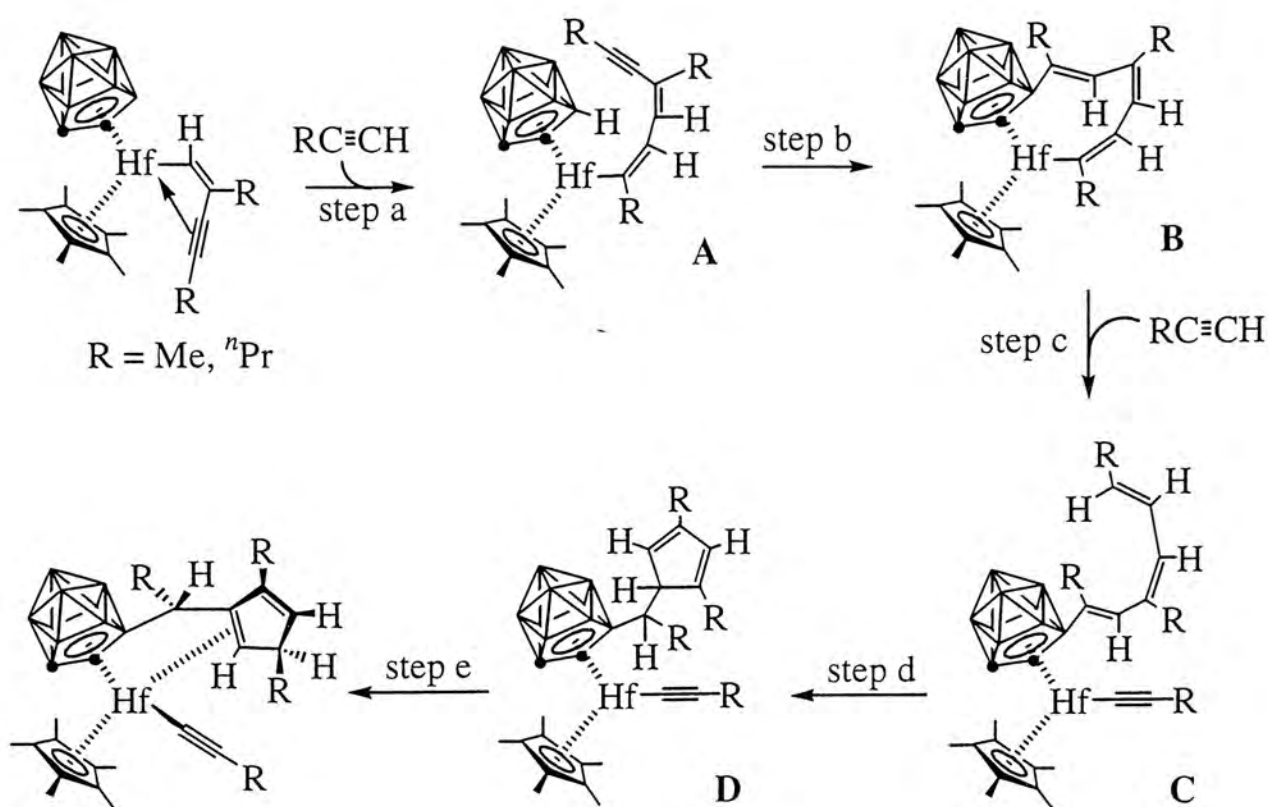


Scheme 1.13

A possible mechanism for the formation of $(\text{Cp}^*)\{\eta^5\text{-7-CH}(\text{R})(3,5\text{-R}_2\text{-2-C}_5\text{H}_3)\text{-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}\equiv\text{CR}$ from $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC}(\text{H})=\text{C}(\text{R})\text{C}\equiv\text{CR}$ is shown

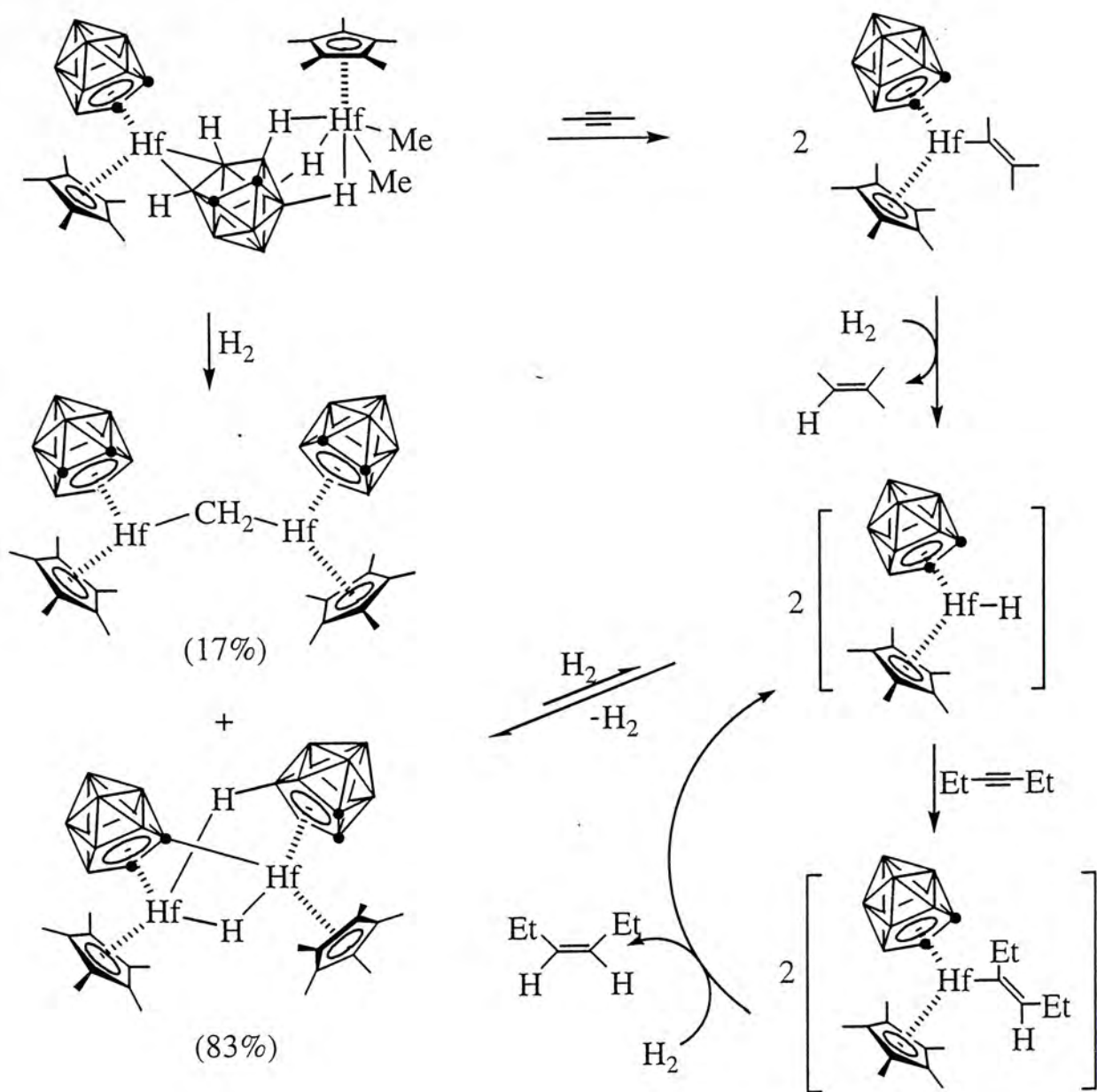
in Scheme 1.14.³¹ Alkyne insertion of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{HfC}(\text{H})=\text{C}(\text{R})\text{C}\equiv\text{CR}$ leads to the formation of alkenyl complex **A** (step a), which undergoes rapid addition of a dicarbollide B–H bond to the pendant alkyne group to yield bridged complex **B** (step b). Complex **B** then undergoes σ -bond metathesis with further alkyne to yield complex **C** (step c), which undergoes subsequent insertion of the C5–C6 double bond into the B–C bond to yield complex **D** (step d). At last, complex **D** undergoes 1,5-H shifts to give $(\text{Cp}^*)\{\eta^5\text{-7-CH}(\text{R})(3,5\text{-R}_2\text{-2-C}_5\text{H}_3)\text{-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}\equiv\text{CR}$ (step e).

Actually, step b is the most important step to the self-correcting property of this catalyst system (Scheme 1.14).³¹ If complex **A** were to undergo σ -bond metathesis with alkyne, the trimer $\text{HRC}=\text{C}-(\text{H})\text{C}(\text{H})=\text{C}(\text{R})\text{C}\equiv\text{CR}$ would be formed and selectively for the dimer would be low. On the other hand, if complex **A** were to undergo alkyne insertion, a precursor to tetramer would be formed. However, neither of these reactions occur because the sequence of reactions initiated by step b ultimately leads to trapping of the alkyne trimer fragment in the form of the B–CHR(3,5-R₂-C₅H₃) substituent in $(\text{Cp}^*)\{\eta^5\text{-7-CH}(\text{R})(3,5\text{-R}_2\text{-2-C}_5\text{H}_3)\text{-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}\equiv\text{CR}$ (and $(\text{Cp}^*)\{\eta^5\text{-7-CH}(\text{R})(3,5\text{-R}_2\text{-2-C}_5\text{H}_3)\text{-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}(\text{H})=\text{C}(\text{R})\text{C}\equiv\text{CR}$). Since the boron-substituent of $(\text{Cp}^*)\{\eta^5\text{-7-CH}(\text{R})(3,5\text{-R}_2\text{-2-C}_5\text{H}_3)\text{-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}(\text{H})=\text{C}(\text{R})\text{C}\equiv\text{CR}$ is bulky, it favors coordination of $\text{RC}\equiv\text{CH}$ through the C–H bond, which leads to σ -bond metathesis and dimer formation, over π -coordination through the $\text{C}\equiv\text{C}$ bond, which would result in insertion and higher oligomers. So, the cycle between $(\text{Cp}^*)\{\eta^5\text{-7-CH}(\text{R})(3,5\text{-R}_2\text{-2-C}_5\text{H}_3)\text{-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}\equiv\text{CR}$ and $(\text{Cp}^*)\{\eta^5\text{-7-CH}(\text{R})(3,5\text{-R}_2\text{-2-C}_5\text{H}_3)\text{-1,2-C}_2\text{B}_9\text{H}_{10}\}\text{HfC}(\text{H})=\text{C}(\text{R})\text{C}\equiv\text{CR}$ also produces only dimer.



Scheme 1.14

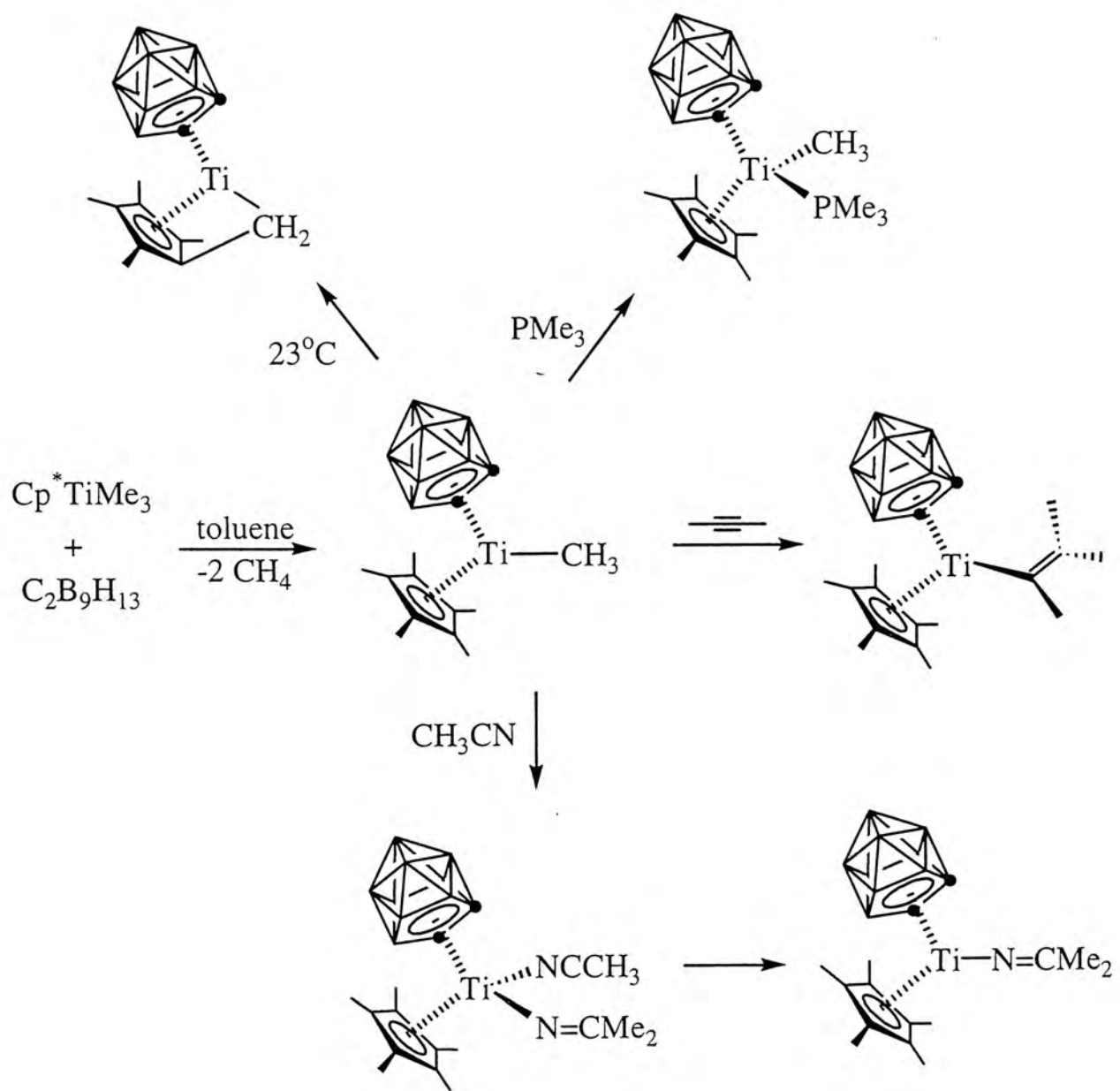
In 1997, Jordan and co-workers have also reported the hafnium carbaboranyl hydride complex $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_2\text{B}_9\text{H}_{10})\text{Hf}(\text{Cp}^*)(\text{H})$, resulting from the reaction of $\text{Cp}^*_2(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Hf}_2\text{Me}_2$ with H_2 , in which the two metal centers are linked by a C-metalated $\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_2\text{B}_9\text{H}_{10}$ ligand and Hf–H–Hf and B–H–Hf bridges (Scheme 1.15).³² This hydride complex catalyzes the hydrogenation of internal alkynes to cis-alkenes. It is proposed that the active species in this reaction is the mononuclear hydride $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{Hf}(\text{H})$, which is formed by hydrogenolysis of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_2\text{B}_9\text{H}_{10})\text{Hf}(\text{Cp}^*)(\text{H})$ and undergoes rapid alkyne or alkene insertion and Hf–C hydrogenolysis steps (Scheme 1.15).³²



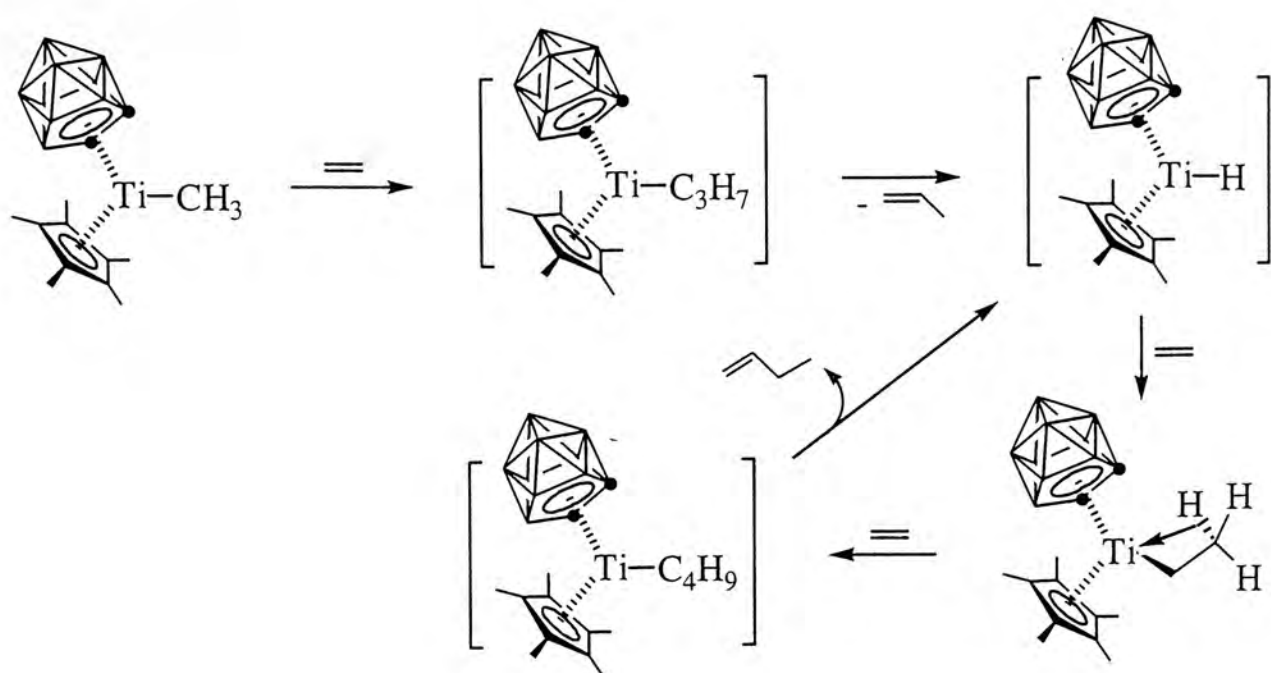
Scheme 1.15

Jordan and co-workers have investigated the chemistry of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$, which is less likely to form dinuclear species due to the smaller Ti radius.^{33,34} The reaction of equimolar amounts of Cp^*TiMe_3 and $\text{C}_2\text{B}_9\text{H}_{13}$ in benzene or toluene results in rapid methane elimination and the formation of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$ (Scheme 1.16).^{33,34} Other reactions related to $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$ are shown in Scheme 1.16.³³ $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$ decomposes at 23°C with further methane elimination to yield the fulvene complex $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ti}$.^{33,34} Addition of PMe_3 to $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$

leads to the formation of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})(\text{PMe}_3)$. Besides, $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$ reacts with excess MeCN to yield the insertion product $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{N}=\text{CMe}_2)(\text{MeCN})$. This product can then be recrystallized from toluene to form the base-free complex $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{N}=\text{CMe}_2)$. $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$ can also undergoes single insertion of 2-butyne to yield the alkenyl complex $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{CMe}=\text{CMe}_2)$. $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{Me})$ reacts rapidly with ethylene to yield propene and $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{CH}_2\text{CH}_3)$, via ethylene insertion, β -H elimination, and rapid ethylene insertion of the resulting hydride $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{H})$ (not observed) (Scheme 1.17).³³ In a secondary process, ethylene is catalytically dimerized to 1-butene via an insertion/ β -H elimination process. The catalyst resting state is ethyl complex $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{CH}_2\text{CH}_3)$. Since it undergoes thermal decomposition to insoluble products, it cannot be isolated.



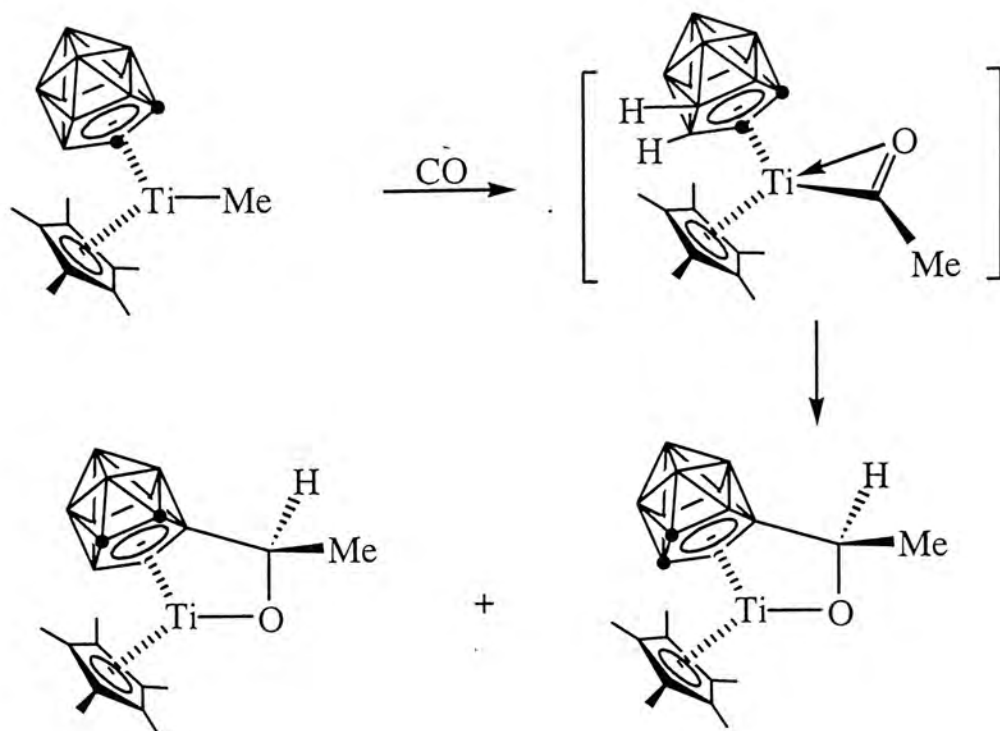
Scheme 1.16



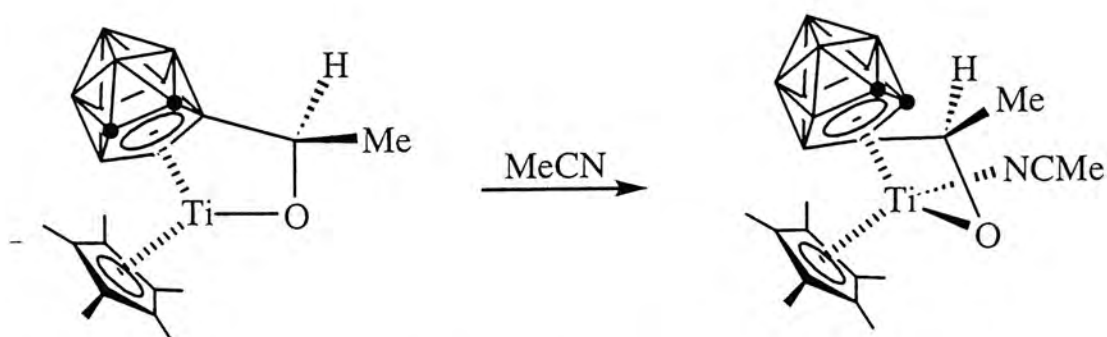
Scheme 1.17

There is another reaction dealing with $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Cp}^*\text{TiMe}$. The reaction of $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Cp}^*\text{TiMe}$ with CO in toluene (-78 to 23°C) yields a mixture of two products, $\text{Cp}^*(\eta^5:\eta^1\text{-8-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ and $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ (Scheme 1.18).³⁵ Both of these complexes contain a linked carborane-alkoxide ligand but differ in the site of attachment of the -CHMeO- linker to the carborane cage. They do not interconvert under the reaction condition. Interestingly, only one of the two possible diastereomers is observed for $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$, and in the absence of coordinating solvents or Lewis bases, $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ is partially dimerized while $\text{Cp}^*(\eta^5:\eta^1\text{-8-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ is monomeric. The anticipated acyl complex, $\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{TiC(=O)Me}$, is not observed. However, experiments with ^{13}CO show that the -BCHMeO- carbon atoms in these two complexes originate from the CO, which implies that $\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{TiC(=O)Me}$ is formed first and rearranges to these two complexes. The

reaction of $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ with CH_3CN yields the acetonitrile adduct $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}(\text{NCMe})$ (Scheme 1.19).³⁵



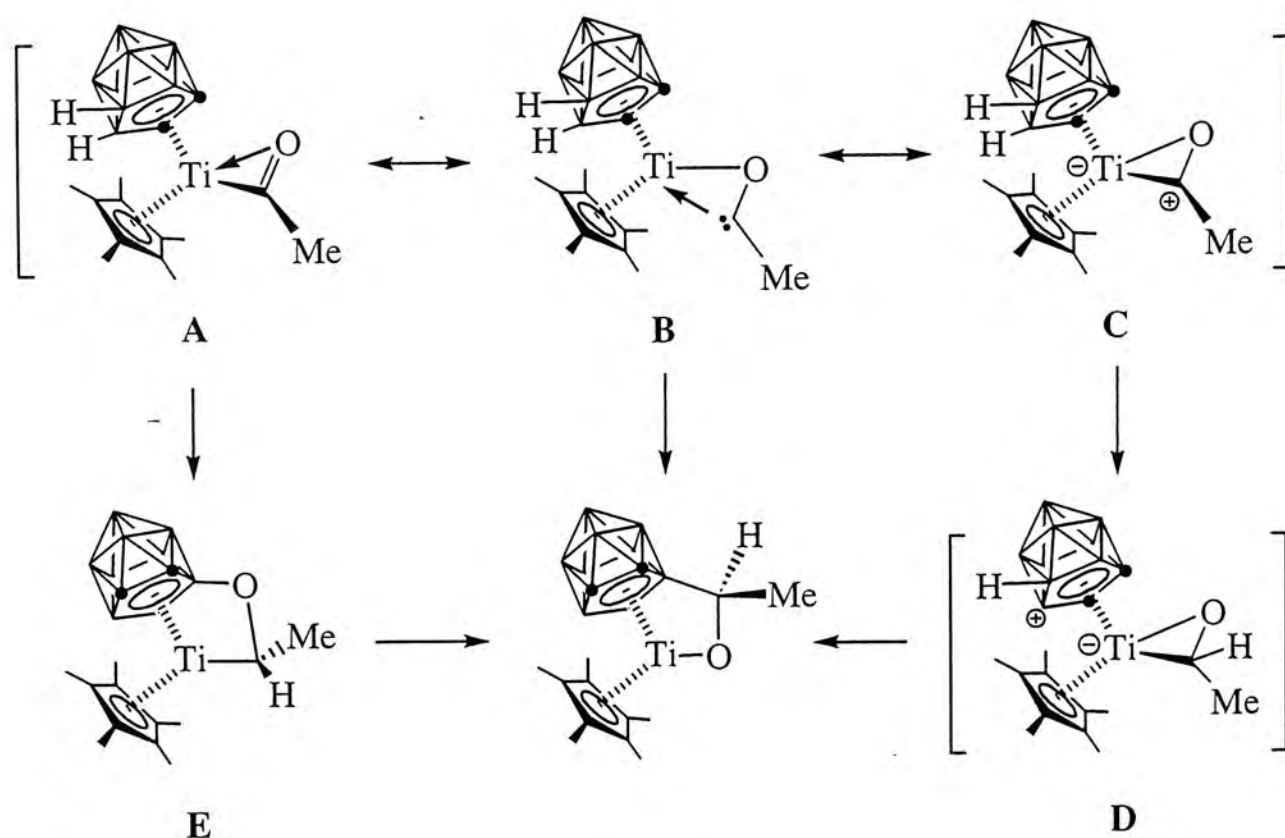
Scheme 1.18



Scheme 1.19

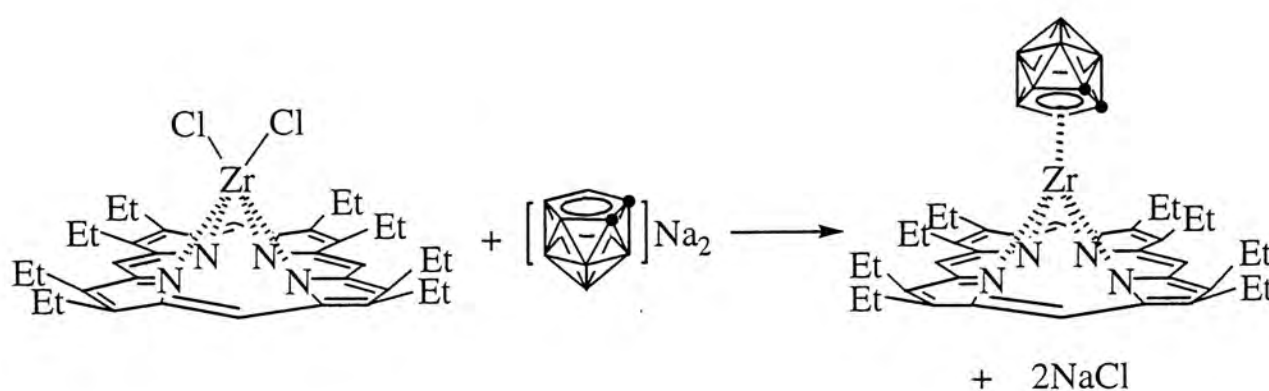
It is reported that the carbonylation of $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Cp}^*\text{TiMe}$ most likely proceeded by initial formation of the acyl species, with the resonance forms **A** to **C** (Scheme 1.20), followed by net insertion of the acyl carbon into a B–H bond to produce $\text{Cp}^*(\eta^5:\eta^1\text{-8-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ or $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$.³⁵

The acyl species is not observed but expected to adopt an η^5 -acyl structure. The acyl bonding of it may be represented by the resonance forms **A** to **C**, the latter two of which emphasize the electrophilic character of the acyl carbon center. The rearrangement to $\text{Cp}^*(\eta^5:\eta^1\text{-8-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ or $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$ involves nucleophilic attack of the central or a lateral B–H bond at the electrophilic acyl carbon. The germinal addition may result from stepwise H transfer followed by B–C bond formation (from **C** to **D** to $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$) or from initial 1,2-B–H addition to the C=O bond followed by rearrangement (from **A** to **E** to $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$). Alternatively, the rearrangement of the acyl species may be viewed as a carbene-like insertion of the acyl carbon into the B–H bond (from **B** to $\text{Cp}^*(\eta^5:\eta^1\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})\text{Ti}$).



Scheme 1.20

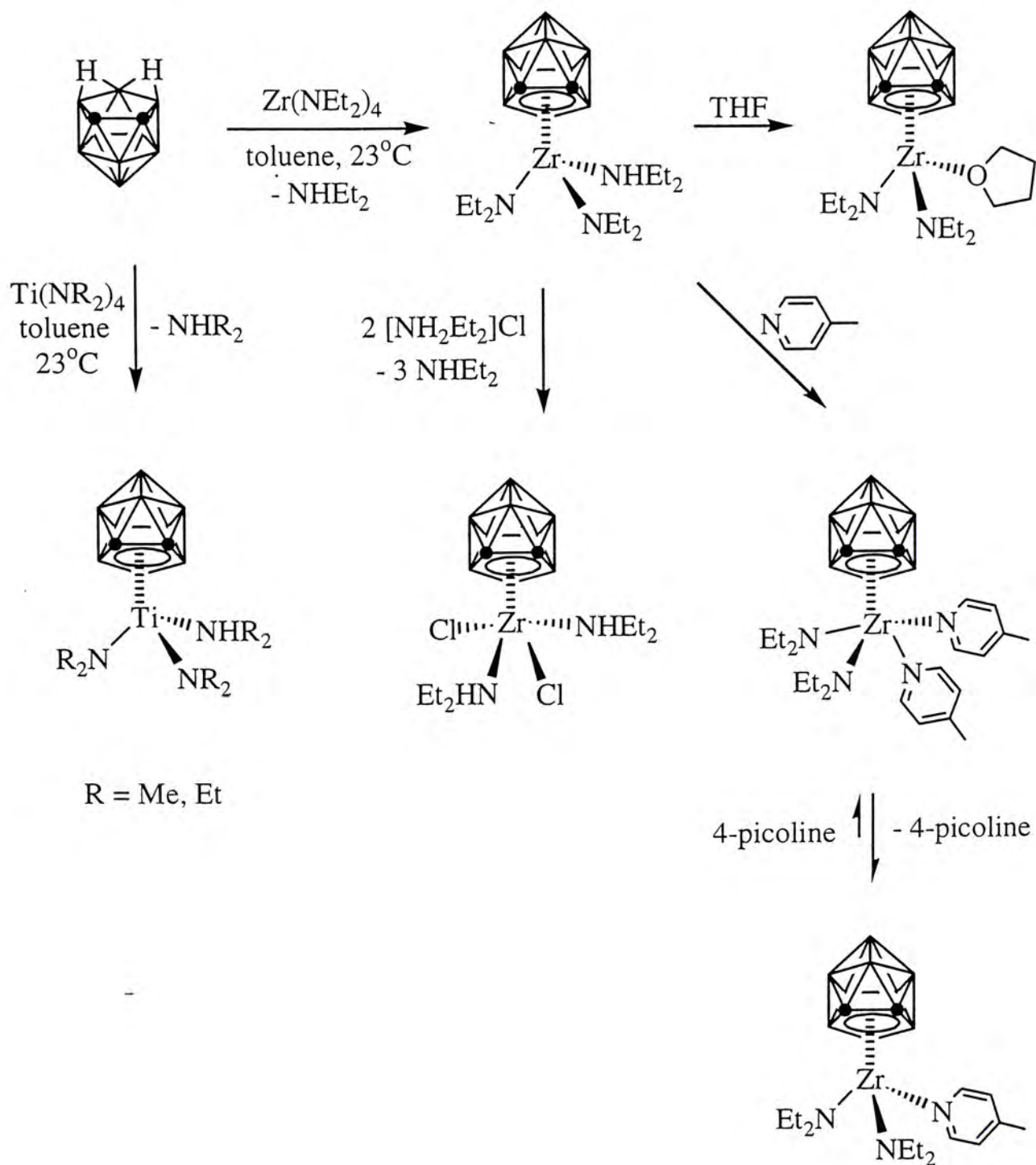
Compounds containing both a porphyrin and a carborane have been studied previously, in particular for their potential use in biochemical applications such as boron neutron capture therapy.³⁶ The simple metathesis reaction between (OEP)ZrCl₂ (OEP = dianion of octaethylporphyrin) and the 7,8-dicarbollide anion [*nido*-7,8-C₂B₉H₁₁]²⁻ in refluxing THF yields (OEP)Zr(η^5 -C₂B₉H₁₁) (Scheme 1.21).³⁷



Scheme 1.21

In 1995, Jordan and co-workers reported the mono-dicarbollide complex (η^5 -C₂B₉H₁₁)Zr(NEt₂)₂(NHEt₂) which is synthesized by the amine elimination reaction of C₂B₉H₁₃ and Zr(NEt₂)₄ (Scheme 1.22).³⁸ This complex can be converted to other mono-dicarbollide Zr(IV) complexes via ligand substitution and protonolysis reactions. (η^5 -C₂B₉H₁₁)Zr(NEt₂)₂(NHEt₂) reacts with neat THF to yield (η^5 -C₂B₉H₁₁)Zr(NEt₂)₂(THF) and with excess 4-picoline to yield (η^5 -C₂B₉H₁₁)Zr(NEt₂)₂(4-picoline)₂. It also reacts with 2 equiv of [NH₂Et₂]Cl to result in selective protonolysis of the Zr–amide bonds and formation of (η^5 -C₂B₉H₁₁)ZrCl₂(NHEt₂)₂. The amine elimination approach also provides access to

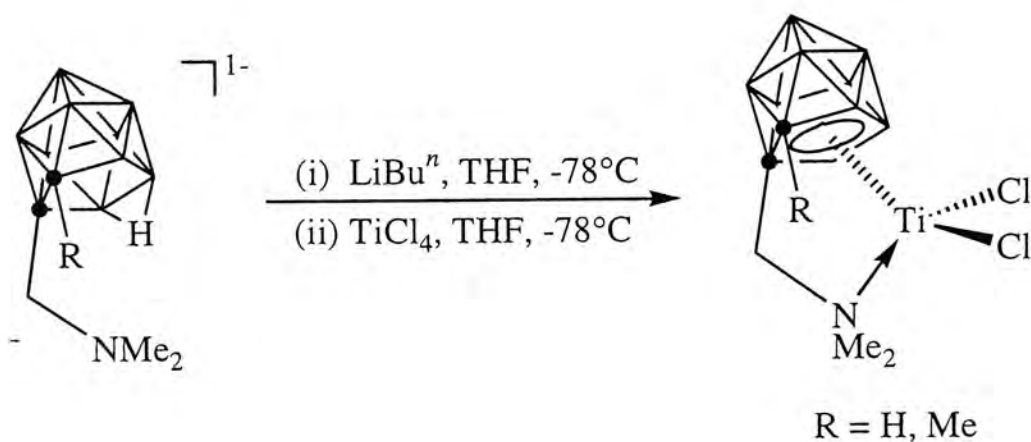
mono-dicarbollide Ti(IV) complexes. Thus, the reaction of $C_2B_9H_{13}$ and $Ti(NR_2)_4$ yields $(\eta^5-C_2B_9H_{11})Ti(NR_2)_2(NHR_2)$.



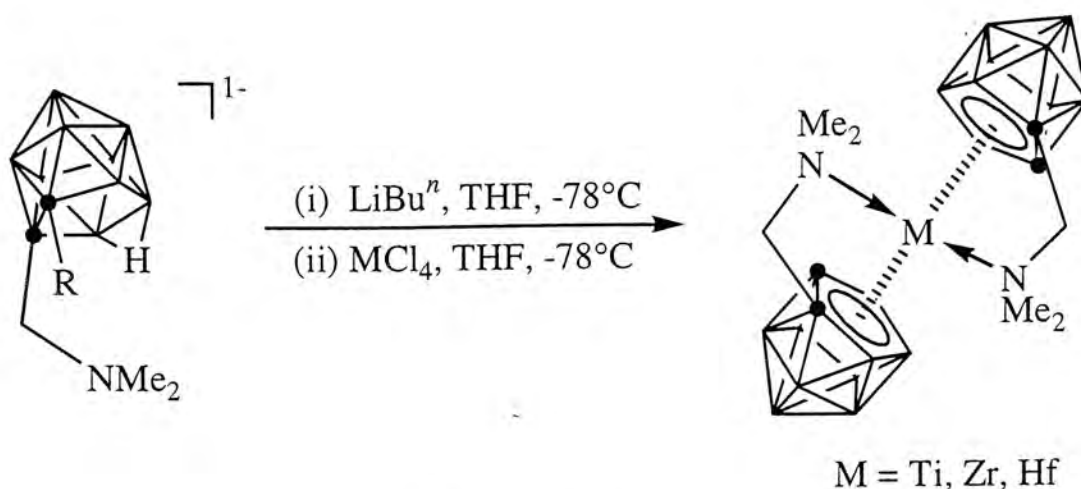
Scheme 1.22

Recently, constrained-geometry complexes, $[\eta^5:\eta^1-RC_2B_9H_9-CH_2NMe_2]TiCl_2$ have been reported by Kang *et. al.*³⁹ The reaction of the ligand

[*nido*-7-NMe₂CH₂-7,8-RC₂B₉H₁₀]⁻ (R = H, Me) with 1 equiv of *n*-BuLi and subsequent reaction with TiCl₄ in toluene yielded the dicarbolly-amino titanium complexes [$\eta^5:\eta^1$ -C₂B₉H₁₀-CH₂NMe₂]⁻TiCl₂ and [$\eta^5:\eta^1$ -MeC₂B₉H₉-CH₂NMe₂]⁻TiCl₂ respectively (Scheme 1.23).³⁹ It is expected to synthesize the dichloro-zirconium and -hafnium complexes in a way analogous to that for the corresponding titanium complexes. However, the reaction of [*nido*-7-NMe₂CH₂-7,8-C₂B₉H₁₁]⁻ with MCl₄ (M = Zr, Hf) in toluene results in [$\eta^5:\eta^1$ -C₂B₉H₁₀-CH₂NMe₂]₂M (M = Zr, Hf) (Scheme 1.24).³⁹ Similarly, the reaction of TiCl₄ with 2 equiv of [*nido*-7-NMe₂CH₂-7,8-C₂B₉H₁₁]⁻ in THF leads to complex [$\eta^5:\eta^1$ -C₂B₉H₁₀-CH₂NMe₂]₂Ti. The preferred formation of a bis(dicarbollyl) over a mono(dicarbollyl) complex can be ascribed to the greater ionic radii of zirconium and hafnium as compared with that of titanium.

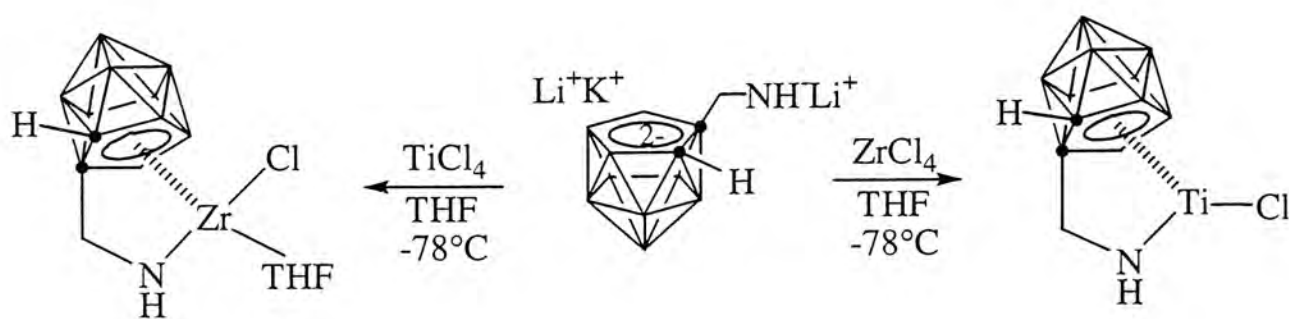


Scheme 1.23



Scheme 1.24

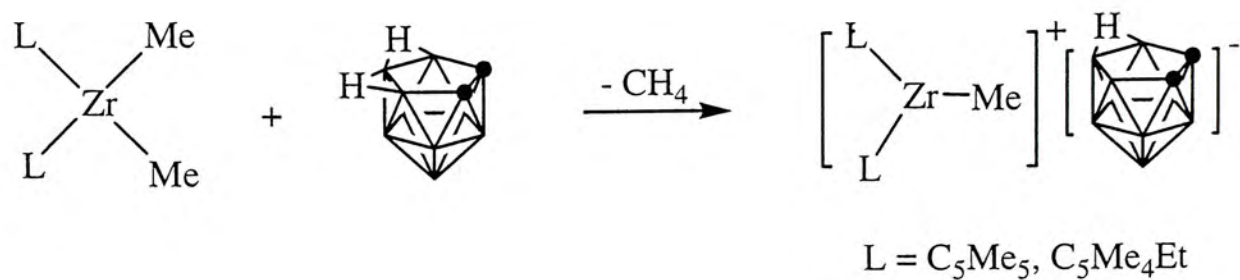
Besides of this method, the complexes can also be prepared by using the carborane trianion.⁴⁰ Lithiation of $[nido-7-(CH_2NH_2)-7,8-C_2B_9H_{11}]^-$ is carried out with 2 equiv of *n*-BuLi in dry THF at -78°C to generate in situ the corresponding trianion that is allowed to react further with $ZrCl_4$ and $TiCl_4$, to produce *closo*-1- $Zr[(Cl)(THF)]-2-(1-\sigma-NHCH_2)-2,3-\eta^5-C_2B_9H_{10}$ and *closo*-1- $Ti(Cl)-2-(1-\sigma-NHCH_2)-2,3-\eta^5-C_2B_9H_{10}$ respectively (Scheme 1.25).



Scheme 1.25

In 1989, the monomethyl complexes $L_2ZrMe(C_2B_9H_{12})$ ($L = C_5Me_5, C_5Me_4Et$) were reported by Hlatky *et. al.*^{29a} Syntheses of these compounds are shown in Scheme 1.26. $(C_5Me_5)_2ZrMe_2$ and $(C_5Me_4Et)ZrMe_2$ react with the diprotic

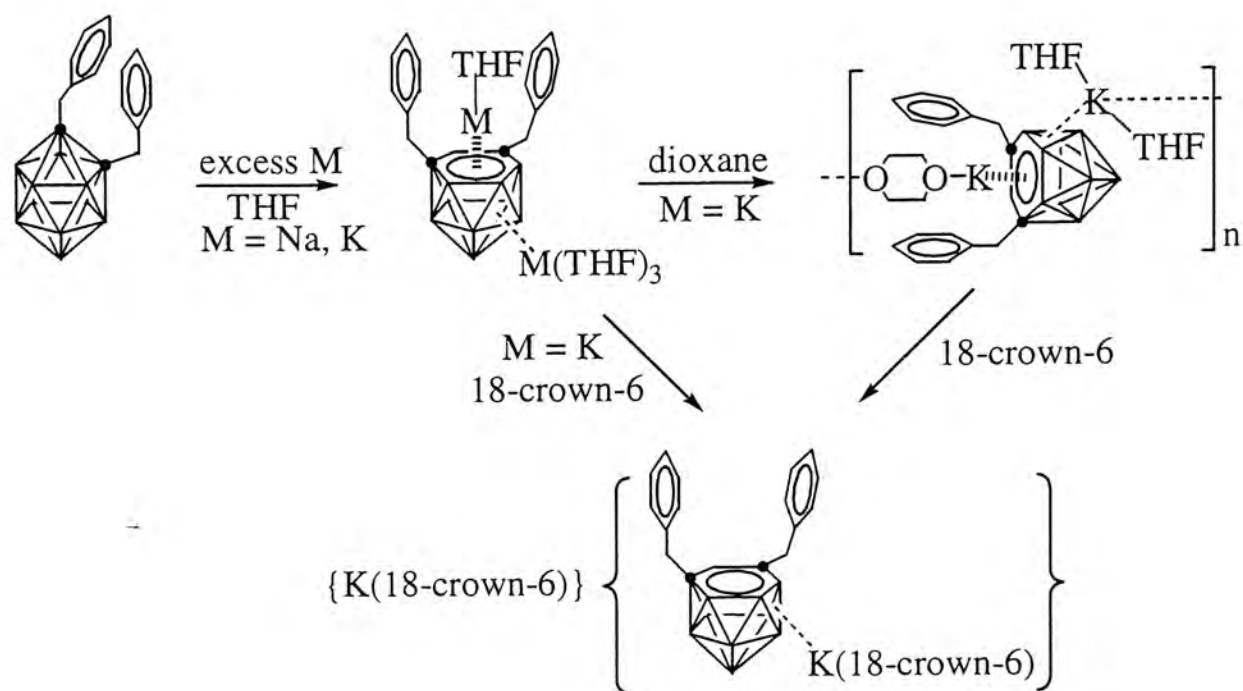
carborane complex *nido*-C₂B₉H₁₃ in pentane to form the monomethyl complexes (η⁵-C₅Me₅)₂(η⁵-C₂B₉H₁₂)ZrMe and (η⁵-C₅Me₄Et)₂(η⁵-C₂B₉H₁₂)ZrMe. These complexes can function as catalysts for the polymerization of ethylene to linear polyethylene under mild condition.



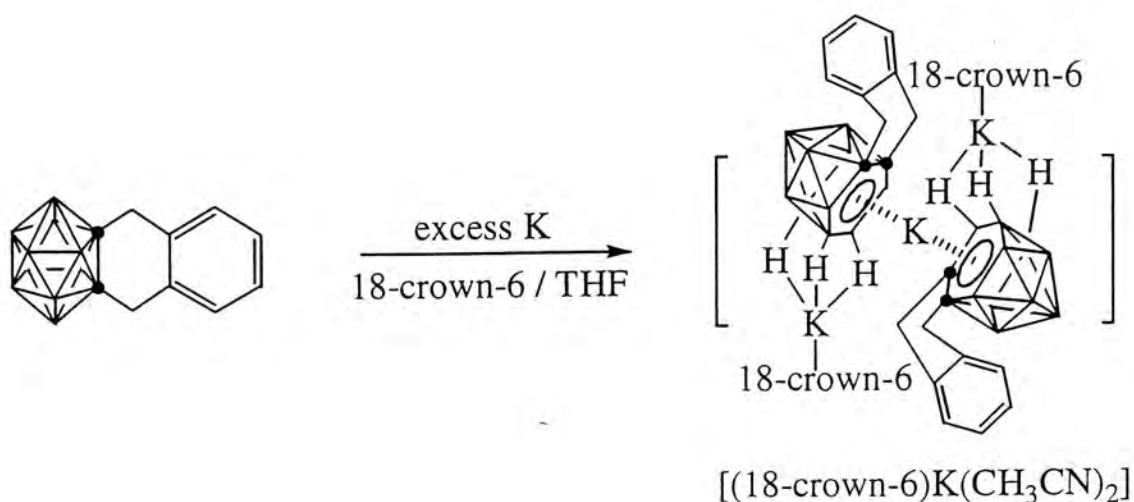
Scheme 1.26

1.3 Group 4 Metallocarboranes of the C_2B_{10} Systems

The dianion of the C_2B_{10} systems can be divided into two species, one is 'carbons-apart', and the other is 'carbons-adjacent'. It has been well documented that o - $R_2C_2B_{10}H_{10}$ ($R = H, \text{alkyl, aryl}$) can be readily reduced by alkali metals to form the $[nido-R_2C_2B_{10}H_{10}]^{2-}$ dianion in which the two cage carbon atoms are in *meta* positions ('carbons-apart' species).⁴¹ The cage C–C bond is completely broken during this two-electron reductive process. When the two cage carbons are linked by a short bridge, they remain adjacent in *ortho* positions during reduction ('carbons-adjacent').⁴² The structures of their alkali metal salts have been reported recently and the synthetic pathway are shown in Schemes 1.27 and 1.28, respectively.^{41,42}



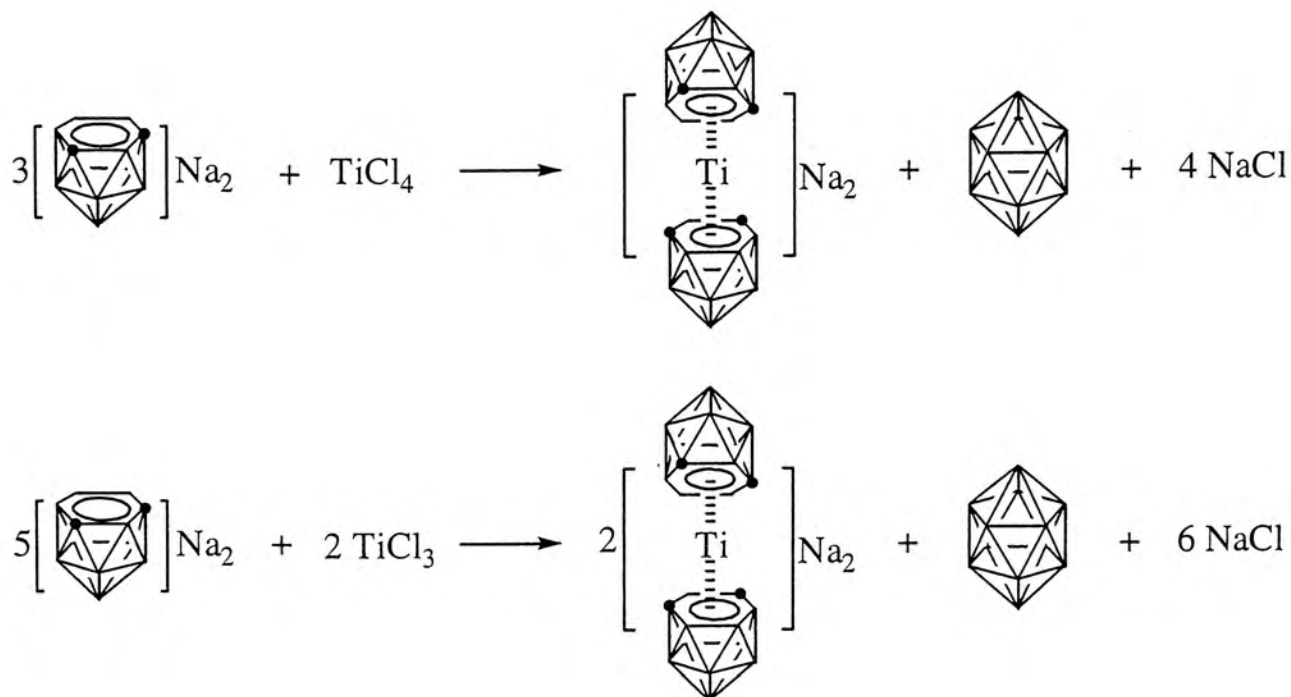
Scheme 1.27



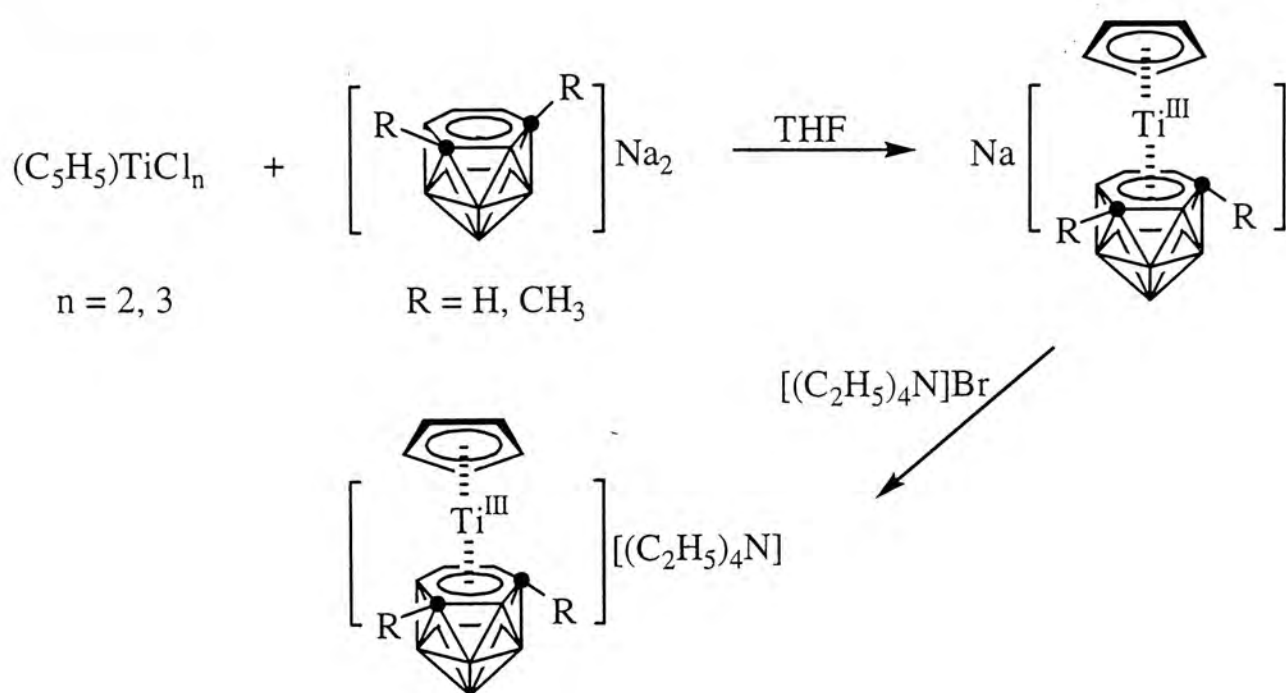
Scheme 1.28

In 1976, complexes of the formula $[\text{M}^{\text{II}}(\text{C}_2\text{B}_{10}\text{H}_{10}\text{R}_2)_2]^{2-}$ ($\text{M} = \text{Ti}$, $\text{R} = \text{H}$; $\text{M} = \text{Ti, Zr, Hf}$, $\text{R} = \text{CH}_3$) were reported as well as the mixed-ligand titanacarboranes $[\text{C}_x\text{H}_x\text{TiC}_2\text{B}_{10}\text{H}_{12}]^{m-}$ ($x = 5$, $m = 1$; $x = 8$, $m = 0$).^{28,43} The reaction of titanium tetrachloride with $\text{Na}_2\text{C}_2\text{B}_{10}\text{H}_{12}$ is instantaneous in THF to yield a red-orange solution. Removal of solvent followed by addition of an ethanol solution of tetraethylammonium bromide results in the formation of $[(\text{C}_2\text{H}_5)_4\text{N}]_2[4,4'\text{-Ti}(1,6\text{-C}_2\text{B}_{10}\text{H}_{12})_2]$.²⁸ Recovery of $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ from the reaction mixture, without exposure to air, identifies the carborane dianion as the reductant responsible for the formal Ti^{II} product (Scheme 1.29).²⁸ $[(\text{C}_2\text{H}_5)_4\text{N}]_2[4,4'\text{-Ti}(1,6\text{-C}_2\text{B}_{10}\text{H}_{12})_2]$ can also be synthesized using titanium trichloride (Scheme 1.29). The dimethylcarboranyl homologue $[(\text{C}_2\text{H}_5)_4\text{N}]_2[4,4'\text{-Ti}(1,6\text{-(CH}_3)_2\text{-}1,6\text{-C}_2\text{B}_{10}\text{H}_{10})_2]$ is similarly isolated. Analogue reaction by using ZrCl_4 and HfCl_4 result in complexes $[(\text{C}_2\text{H}_5)_4\text{N}]_2[4,4'\text{-Zr}(1,6\text{-(CH}_3)_2\text{-}1,6\text{-C}_2\text{B}_{10}\text{H}_{10})_2]$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_2[4,4'\text{-Hf}(1,6\text{-(CH}_3)_2\text{-}1,6\text{-C}_2\text{B}_{10}\text{H}_{10})_2]$, respectively. For the preparation of the mixed-ligand titanacarboranes, addition of $\text{C}_5\text{H}_5\text{TiCl}_n$ ($n = 2$ or 3) to a THF solution of $\text{Na}_2\text{C}_2\text{B}_{10}\text{H}_{12}$ or $\text{Na}_2\text{C}_2(\text{CH}_3)_2\text{B}_{10}\text{H}_{10}$, after the cation exchange process, result in the formation of $[(\text{C}_2\text{H}_5)_4\text{N}][4\text{-(}\eta^5\text{-C}_5\text{H}_5\text{)-}$

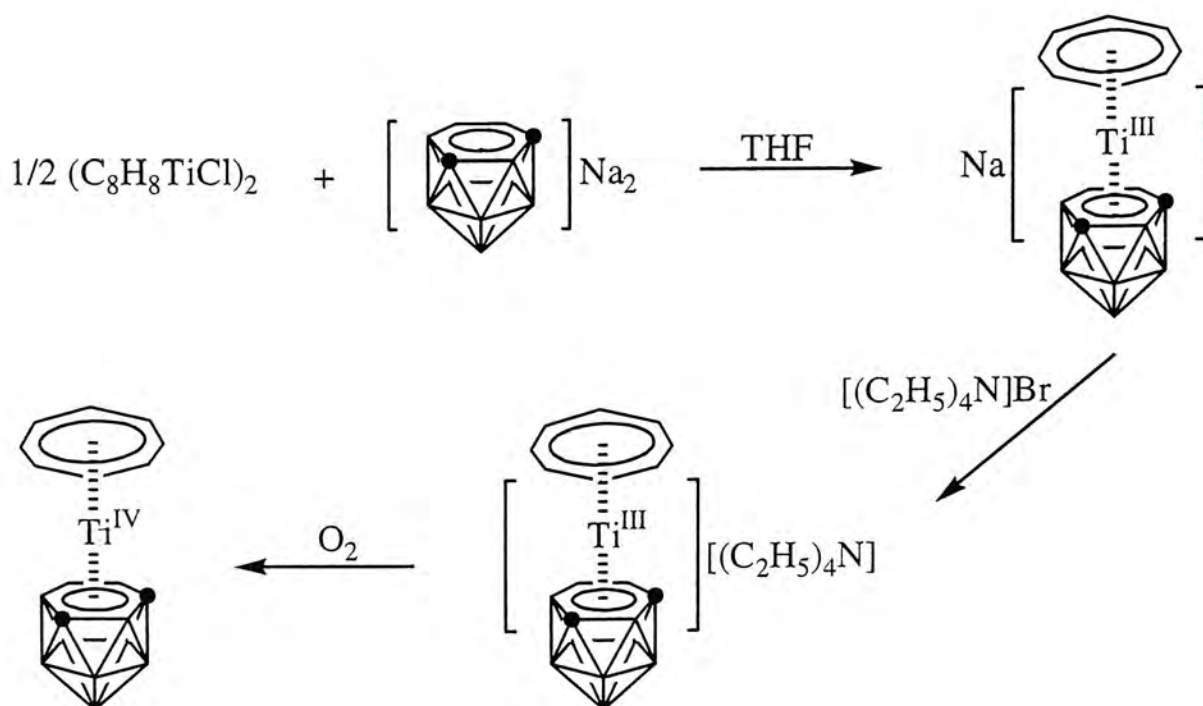
4-Ti-1,6-C₂B₁₀H₁₂] and [(C₂H₅)₄N][(1,6-(CH₃)₂-4-(η^5 -C₅H₅)-4-Ti-1,6-C₂B₁₀H₁₀)] (Scheme 1.30).²⁸ Also, [(C₂H₅)₄N][4-(η^8 -C₈H₈)-4-Ti-1,6-C₂B₁₀H₁₂] is prepared by the reaction of (C₈H₈TiCl)₂ with Na₂C₂B₁₀H₁₂ and this complex is easily oxidized to 4-(η^8 -C₈H₈)-4-Ti-1,6-C₂B₁₀H₁₂ (Scheme 1.31).²⁸



Scheme 1.29



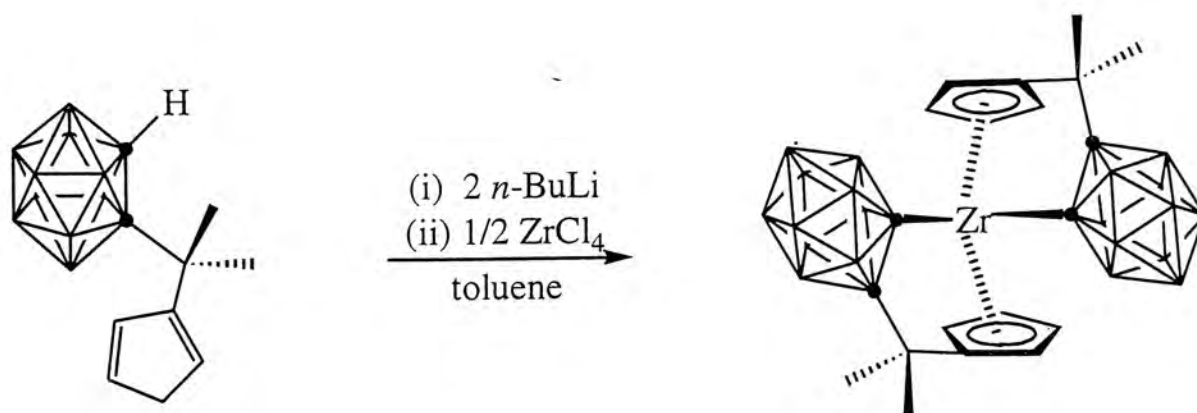
Scheme 1.30



Scheme 1.31

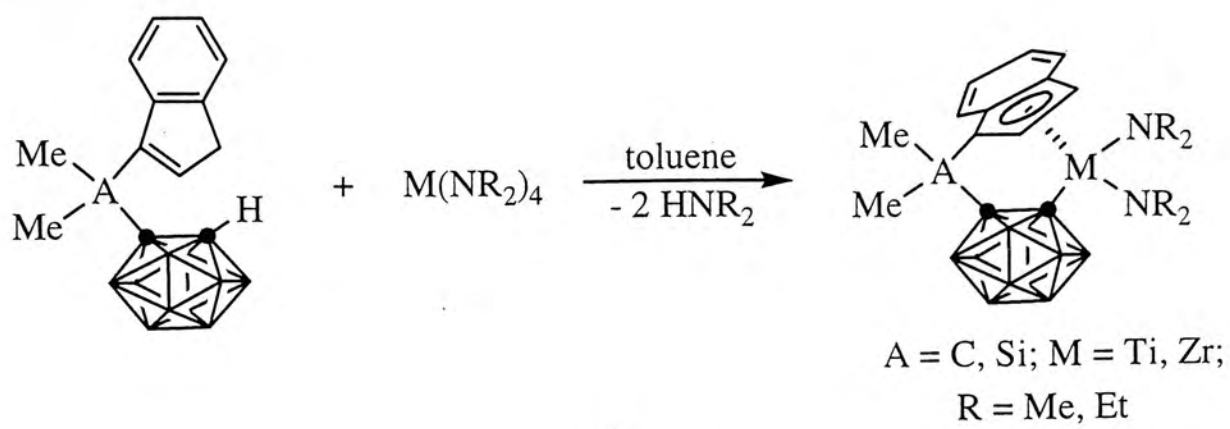
According to Do, *rac*-Zr[η^5 : η^1 -Me₂C(C₅H₄)C₂B₁₀H₁₀]₂ was prepared from the reaction of the dilithium salt of the isopropyl-bridged cyclopentadienyl *o*-

carboranyl ligand $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)\text{C}_2\text{B}_{10}\text{H}_{11}$ with ZrCl_4 (Scheme 1.32).⁴⁴ It is found that it catalyzes the formation of syndiotactic poly(methyl methacrylate) in THF in the absence of any alkylating reagent or cationic center generator.

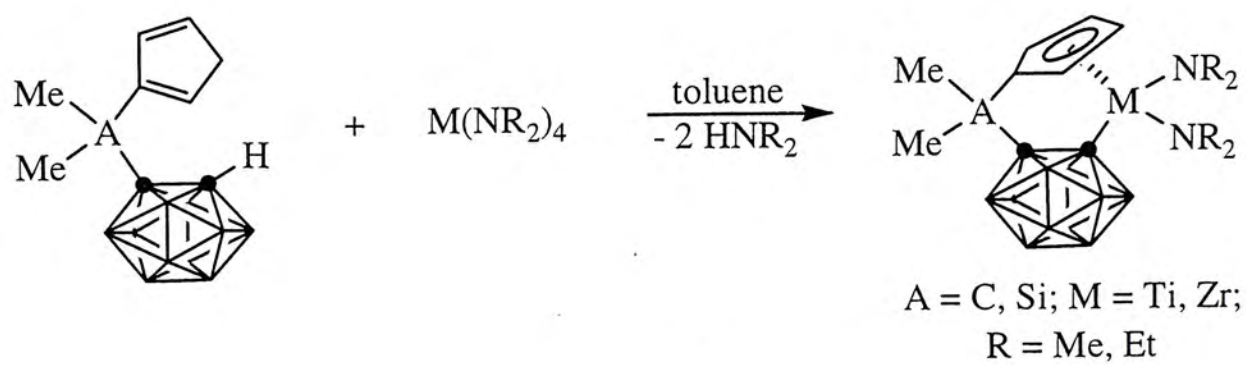


Scheme 1.32

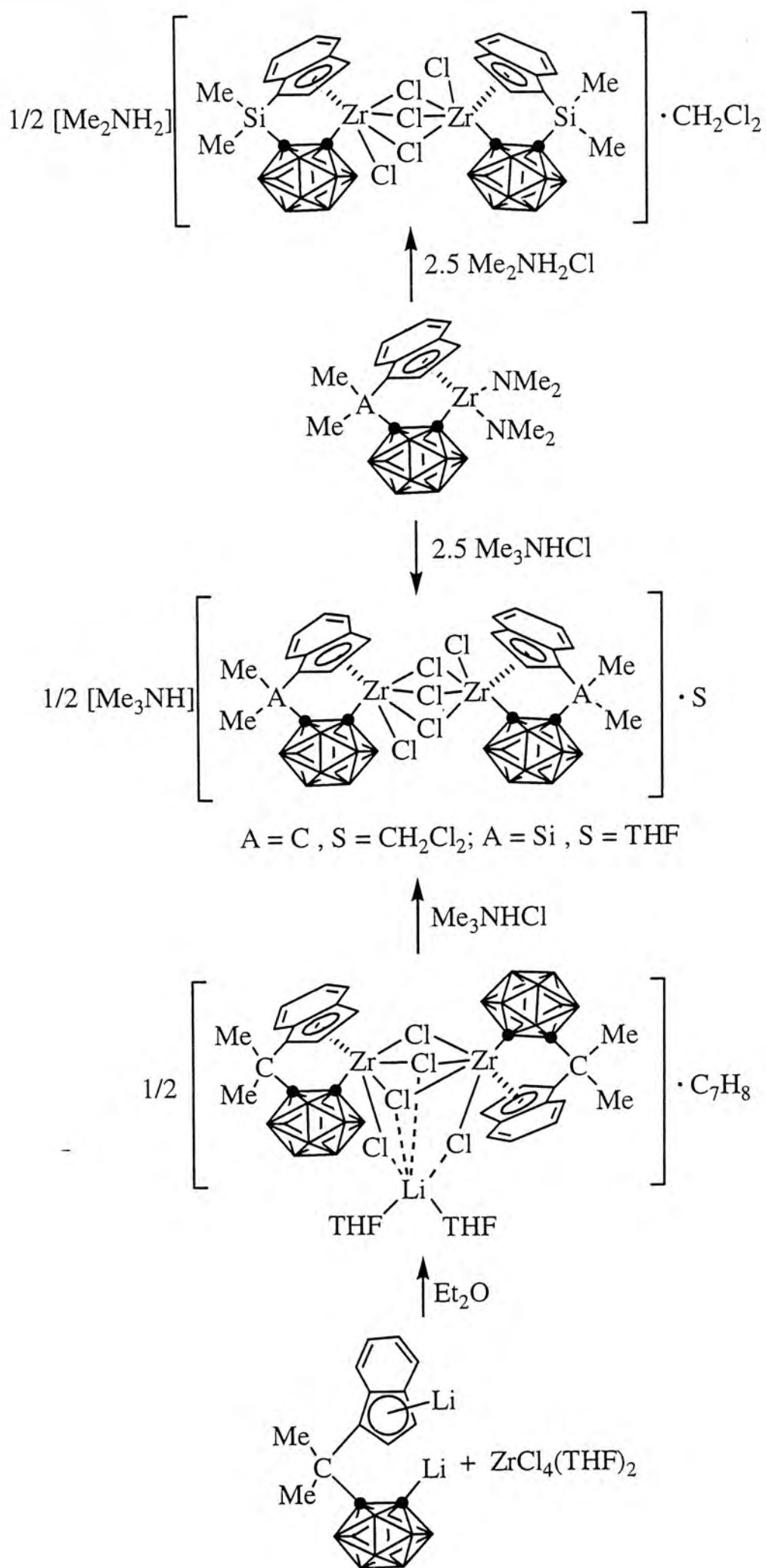
Do and co-workers have also prepared $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{TiCl}_2$ and $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$ via salt metathesis and amine elimination reactions utilizing the ligand $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$ (Scheme 1.33).⁴⁵ The reaction of $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$ with $\text{TiCl}_3(\text{THF})_3$ followed by the oxidation with AgCl in THF yields $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{TiCl}_2$. $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$ also reacts with $\text{Zr}(\text{NMe}_2)_4$ in toluene by undergoing amine elimination reaction to form $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$.



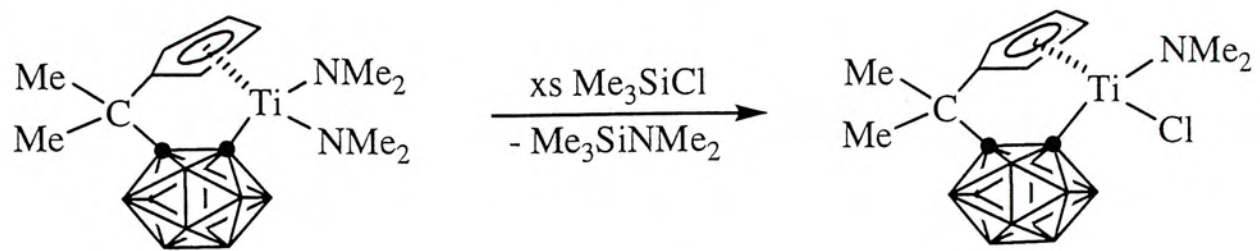
Scheme 1.34



Scheme 1.35



Scheme 1.36



Scheme 1.37

1.4 Applications of Group 4 Metallocarboranes

Metallocarboranes of the early transition metals, especially those of Group 4, are of interest because of the isoelectronic relationship between neutral sandwich complexes of the type $\text{Cp}(\text{R})\text{M}^{\text{IV}}(\eta^5\text{-R}'_2\text{C}_2\text{B}_n\text{H}_n)$ and the $\text{Cp}_2\text{M}^{\text{IV}}\text{R}^+$ cations that are active in the metallocene-catalyzed polymerization of olefins (the electroneutrality of the former arises from the dinegative carborane ligands).⁴⁷ This leads to the development of novel metallocarborane-based catalyst systems.

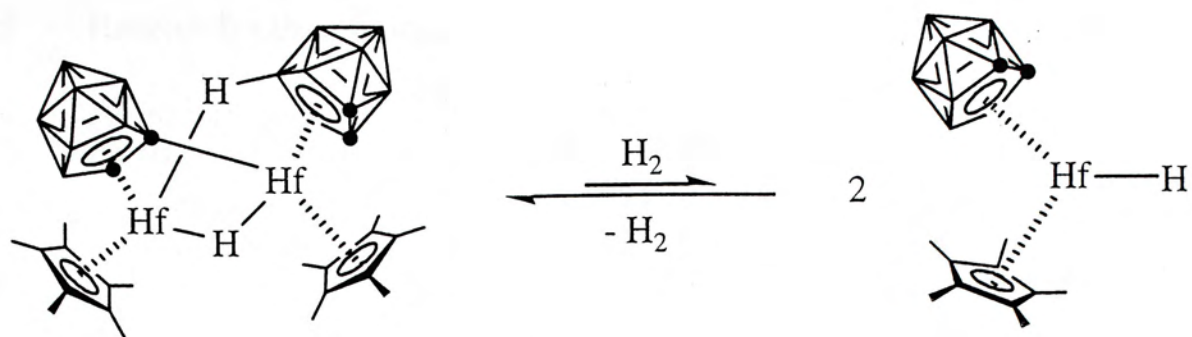
Recently, Jordan and coworkers have explored the catalytic properties of a hydridohafnium-carborane $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_2\text{B}_9\text{H}_{10})\text{Hf}(\text{Cp}^*)(\text{H})$ in the hydrogenation of internal alkynes to *cis*-alkenes, which evidently proceeds via a mononuclear intermediate $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{Hf}(\text{H})$ as shown in Scheme 1.38.^{32,47} The unsymmetrical dimeric structure of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_2\text{B}_9\text{H}_{10})\text{Hf}(\text{Cp}^*)(\text{H})$ in which the two metal centers are linked through Hf–H–Hf, B–H–Hf, and Hf– $\eta^1, \eta^5\text{-C}_2\text{B}_9\text{H}_{10}$ bridges, was determined crystallographically.³² While it reacts with internal alkynes in the presence of H_2 to yield *cis*-alkenes, NMR and other evidence suggest that the catalytically active species is in fact $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{Hf}(\text{H})$ (not isolated).³²

In a different application of hafnium metallocarboranes in catalysis by the same group, the unsymmetrical bridged dinuclear complex $\text{Cp}^*_2(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Hf}_2\text{Me}_2$ catalyzes the regioselective dimerization of terminal alkynes, in which the formation of trimers or higher oligomers is blocked (Scheme 1.13).^{31,47} This comes about because of an internal cyclization of a monohafnium reaction intermediate, formed from $\text{Cp}^*_2(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Hf}_2\text{Me}_2$ in solution, that sterically prevents further interaction of alkyne molecules with the metal center (Scheme 1.14).³¹

In earlier work, chemists at Exxon Corporation have shown that zirconocene-carborane derivatives of the formula $L_2(C_2B_9H_{12})Zr(Me)$ ($L = C_5Me_5$, C_5Me_4Et) polymerize ethylene at 60°C and 300 psi.⁴⁷

Recently, Do and coworkers have demonstrated that CpM (dicarbollyl) complexes of Group 4 metals in which an isopropyl group bridges the Cp and carborane ligands can promote the polymerization of olefins.^{44,47} For example, *rac*- $[\eta^5:\eta^1-Me_2C(C_5H_4)(C_2B_{10}H_{10})]_2M$ catalyzes the formation of syndiotactic poly(methyl methacrylate) in THF in the absence of an alkylating agent,⁴⁴ while $(\eta^5-Cp^*)(\eta^5:\eta^1-Me_2C(C_5H_4)(C_2B_{10}H_{10}))MCl$ and $(\eta^5-Cp^*)(\eta^5:\eta^1-Me_2C(C_5H_4)(C_2B_{10}H_{10}))MCl_2$ in the presence of methylaluminium oxane (MAO) are active in the catalytic polymerization of ethylene and propylene.⁴⁷

Catalytic activity in olefin and alkyne polymerization is also under exploration in small metallacarboranes, e.g. $L_2X_2Ti(Et_2C_2B_4H_4)$ ($X = Cl$, alkyl; $L_2 = 2PR_3$, $R_2P(CH_2)_nPR_2$, etc.; $R = Ph$ or alkyl) in combination with MAO.⁴⁷ Although investigations in this area are continuing, it is still unknown that whether there is commercial potential or not.⁴⁷ However, the MC_2B_4 carborane clusters tend to have higher thermal and oxidative stability than metallocenes. Also, they are soluble in a wide range of media, easily tailored via introduction of functional groups on the carborane cage and/or the metal, and operate under very mild conditions (1 atm and room temperature). These are all good reasons for pursuing these studies.⁴⁷



Scheme 1.38

1.5 Research Objectives

As mentioned above, group 4 metallocarboranes are potential catalysts for olefin polymerization. It is known that there are many factors controlling the activity of the catalysts in the process, for example, the metal size, the charge, the substituent of the ligand, etc. Among these factors, the substituent of ligand is one of the important elements, for it controls the molecular geometry of the catalysts, which in turn affects the catalytic activity in olefin polymerization. Thus, we have interest to study the substituent effect on bonding interactions between group 4 metal ions and carborane anions. In this project, we focus on $1,2-(\text{C}_6\text{H}_5\text{CH}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}$ and $\mu-1,2-[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}$ carborane systems. For the following chapters, we would like to describe the details of our work on this subject.

Chapter 2

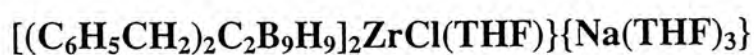
Synthesis and Structural Characterization of Group 4

Metallacarboranes of the C₂B₉ Systems

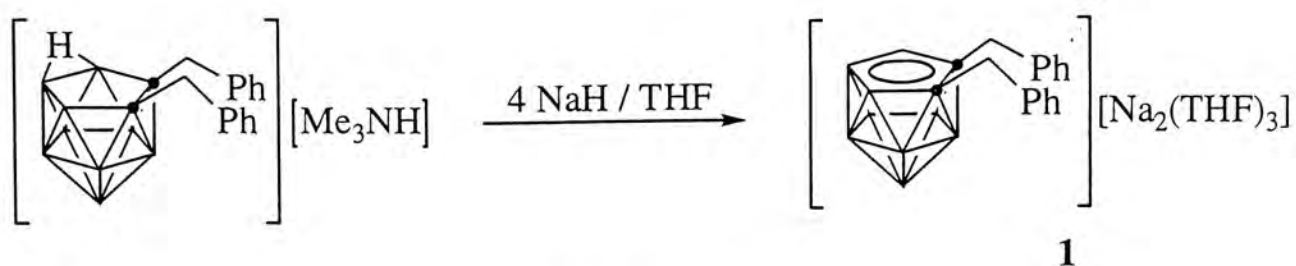
In the past decades, there is much interest in the synthesis of metal-halo species in the field of organometallic chemistry. This is due to the potential of the metal-halo species to act as precursors to a number of organometallic transformations such as the conversions to metal alkyl and hydride derivatives.^{5,6b,21} In recent years, attention is also paid to the preparation of metal amides because of the same reasons.³⁸

Jordan has done a lot of works in this field using unsubstituted dicarbollide ion as the ligand.^{38,48,49} To study the effect of substituents of carborane cage on the molecular structures and reactivity patterns of resultant organometallic complexes, we introduce two benzyl groups onto the carborane cage. In this chapter, we would like to report on the synthesis and structural characterization of some group 4 metallacarboranes derived from dibenzyl substituted carborane anions.

2.1 Synthesis and Structural Characterization of $\{\eta^4:\eta^2-$



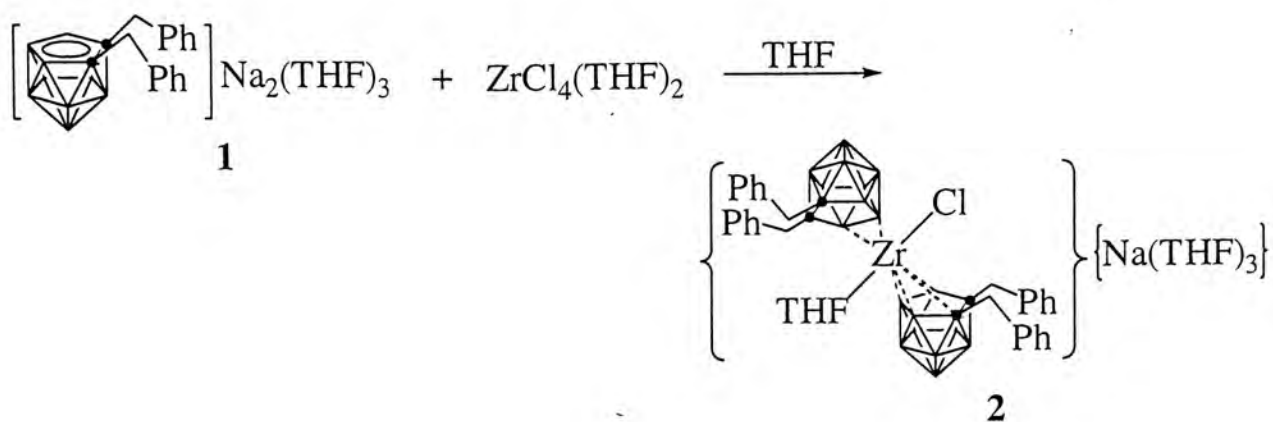
Treatment of [Me₃NH][7,8-(C₆H₅CH₂)₂-*nido*-7,8-C₂B₉H₁₀] with 4 equiv of NaH in THF at reflux temperature afforded a sodium salt [(C₆H₅CH₂)₂C₂B₉H₉]₂Na₂(THF)₃ (**1**) in 79% yield (Scheme 2.1).



Scheme 2.1

Complex **1** was characterized by IR, ^1H , ^{13}C , ^{11}B NMR, and elemental analyses. The solid-state IR spectrum showed a typical strong and broad characteristic B–H absorption at 2510 cm^{-1} . In the ^1H NMR spectrum, there were two doublets with the coupling constant $J = 15.2 \text{ Hz}$, which indicated that the methylene protons on the dibenzyl substituents were non-equivalent. Besides, it also showed the ratio of three THF molecules per carboranyl ligand. It was noted that the coordinated THF molecules in **1** were very labile and could easily be dissociated by other donor solvents. The ^{13}C NMR results were consistent with those of ^1H NMR. The ^{11}B NMR spectrum showed a 3:4:1:1 splitting pattern.

Treatment of $\text{ZrCl}_4(\text{THF})_2$ with 1 equiv of $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (**1**) in THF at room temperature gave, after recrystallization from a toluene/*n*-hexane solution, a complex $\{ \eta^4: \eta^2 - [(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF}) \} \{ \text{Na}(\text{THF})_3 \}$ (**2**) in 73% yield (Scheme 2.2).



Scheme 2.2

Complex **2** was fully characterized by IR, ^1H , ^{13}C , ^{11}B NMR, elemental analyses, and X-ray analyses. The IR spectrum of complex **2** displayed a strong B–H absorption at 2532 cm^{-1} . The ^1H NMR spectrum showed the non-equivalence of the methylene protons on the ligand with a coupling constant $J = 15.3\text{ Hz}$, and the ratio of two THF molecules per cage. The results from ^{13}C NMR spectrum were consistent with those derived from its ^1H NMR spectrum. The ^{11}B NMR spectrum exhibited a 1:2:2:2:2 splitting pattern.

Molecular structure of complex **2** derived from single-crystal X-ray analysis was shown in Figure 2.1. It crystallized in the triclinic $P\bar{1}$ space group with $Z = 2$. It was a ‘slipped’ sandwich structure in which the two carboranyl ligands had different hapticities, while one was η^4 -bonded to the Zr center, the other was bonded to the Zr center in a η^2 -fashion. The coordination sphere of the Zr center was completed by a THF molecule and a chloro ligand. The sodium was bonded to a trigonal B_3 face through three B–H bonds and the coordination sphere around it was then completed by three THF molecules. A possible explanation for the formation of such a ‘slipped’ structure, rather than a full-sandwiched one, was due to the steric bulkiness of the dibenzyl substituents on the carborane ligands.

The Zr–B (η^2 -cage) bond distances ranged from $2.328(6)$ to $2.642(6)\text{ \AA}$ with

an average value of 2.485(6) Å. The Zr–B (η^4 -cage) bond distances ranged from 2.408(5) to 2.634(5) Å with an average value of 2.498(5) Å, which was much shorter than the Zr–C (η^4 -cage) distance of 2.774(4) Å. These values were slightly shorter than the 2.543(6) Å (one η^5 -cage) and 2.554(7) Å (another η^5 -cage) in $\{(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})\}\{\text{Li}(\text{THF})_2\}$,^{6b} and 2.541(10) Å (one η^5 -cage) and 2.530(10) Å (another η^5 -cage) in $[(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})]_2[\text{Mg}(\text{THF})_6]$.^{6a} The Zr–C (η^4 -cage) bond distance of 2.774(4) Å was significantly different from the 2.585(6) Å (one η^5 -cage) and 2.560(6) Å (another η^5 -cage) in $\{(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})\}\{\text{Li}(\text{THF})_2\}$, 2.596(7) Å (one η^5 -cage) and 2.551(8) Å (another η^5 -cage) in $[(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})]_2[\text{Mg}(\text{THF})_6]$, 2.52(8) Å (η^3 -ring) and 2.56(7) Å (η^5 -ring) in $(\eta^3\text{-C}_{13}\text{H}_9)(\eta^5\text{-C}_{13}\text{H}_9)\text{ZrCl}_2$,⁵⁰ 2.49(3) Å (the same for both η^5 -ring) in $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$,⁵¹ and 2.584(5) Å (one η^5 -ring) and 2.563(5) Å (the other η^5 -ring) in $[(\text{C}_2\text{H}_4)(\eta^5\text{-C}_{13}\text{H}_8)_2]\text{ZrCl}_2$ (Table 2.1).⁵²

The Zr–cent distance of 2.944 Å of the η^2 -cage was much longer than that of 2.214 Å of the η^4 -cage. These values were longer than the 2.20 Å (one η^5 -ring) and 2.19 Å (the other η^5 -ring) in $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, 2.175 Å (one η^5 -cage) and 2.173 Å (another η^5 -cage) in $\{(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})\}\{\text{Li}(\text{THF})_2\}$, and 2.173 Å (one η^5 -cage) and 2.152 Å (another η^5 -cage) in $[(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})]_2[\text{Mg}(\text{THF})_6]$, due to the difference in hapticities of the ligand.

The Zr–Cl bond distance of 2.394(2) Å was close to that of 2.407(1) Å in $[(\text{C}_2\text{H}_4)(\eta^5\text{-C}_{13}\text{H}_8)_2]\text{ZrCl}_2$ but was shorter than the 2.420(4) Å in $(\eta^3\text{-C}_{13}\text{H}_9)(\eta^5\text{-C}_{13}\text{H}_9)\text{ZrCl}_2$, 2.441(5) Å in $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, 2.461(1) Å in $\{(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})\}\{\text{Li}(\text{THF})_2\}$, and 2.485(2) Å in $[(\eta^5\text{-}$

(SiMe₃)₂C₂B₄H₄)₂ZrCl(THF)]₂[Mg(THF)₆]. This Zr–Cl distance was at the short end of the reported Zr–Cl bond distances in organozirconium complexes, which suggested that the Zr–Cl bond in **2** was very strong and probably hard to be replaced by other groups.

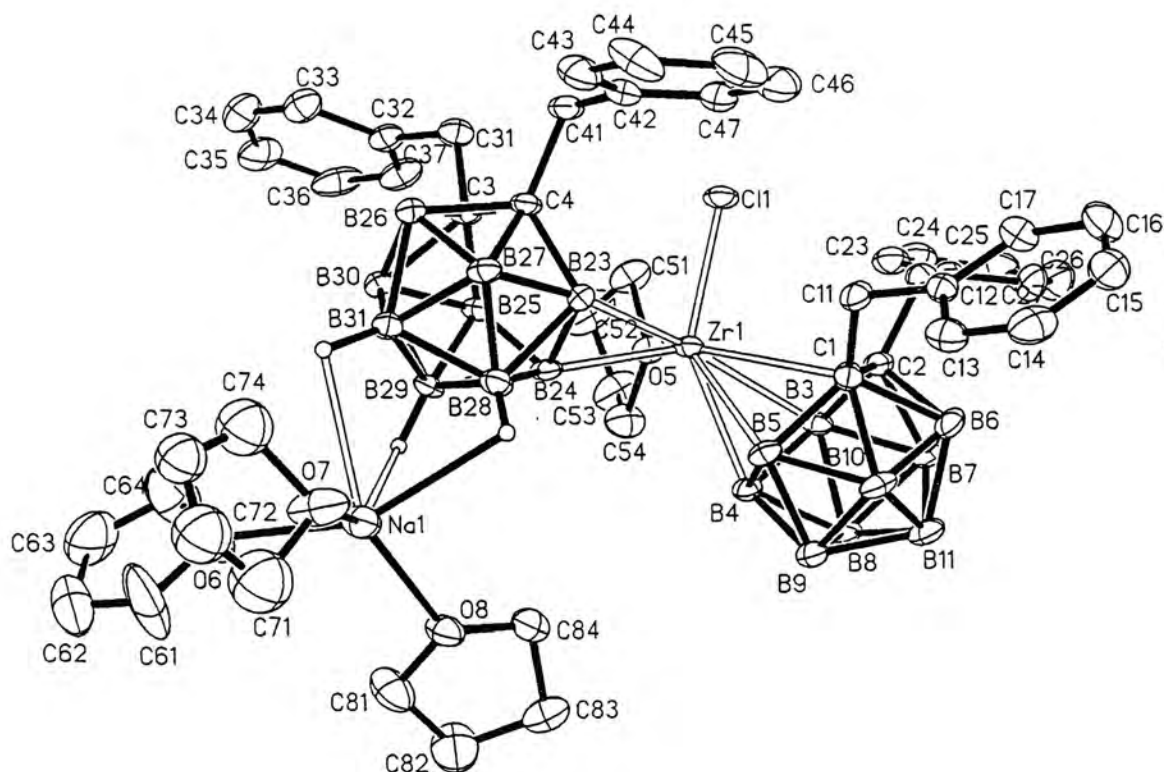


Figure 2.1 Molecular structure of $\{\eta^4:\eta^2-$
 $[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\} \{Na(THF)_3\}$ (**2**)

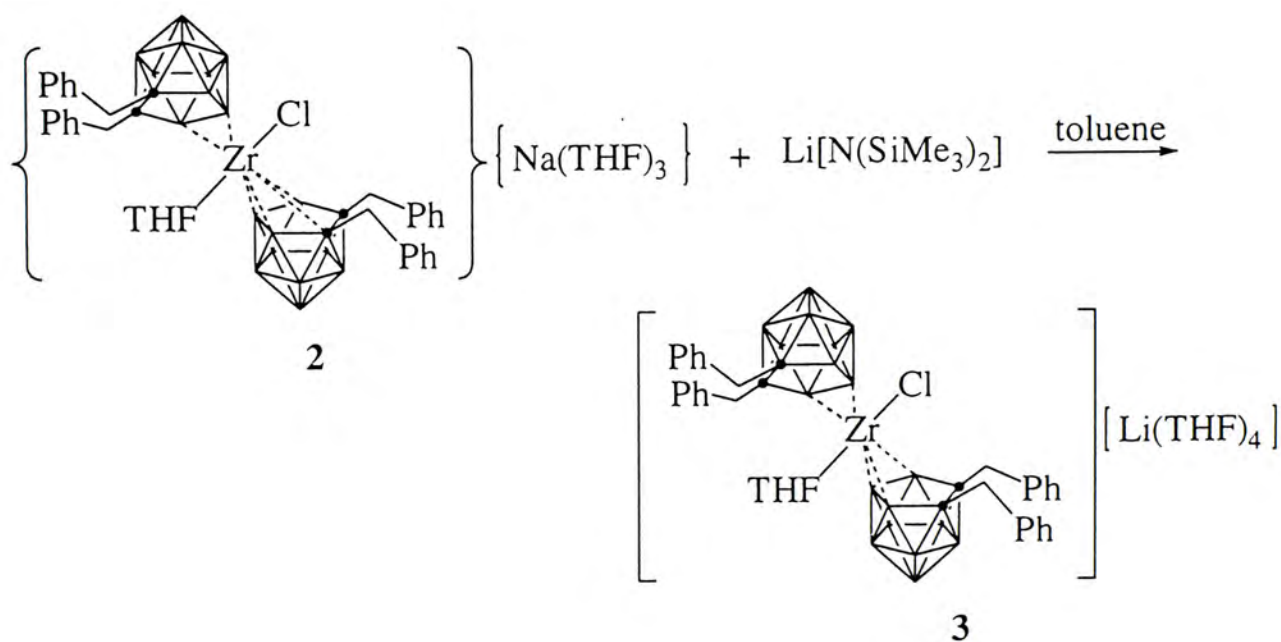
Table 2.1 Selected structural data for some Zr(IV) complexes*

complex	av. Zr-cage atom	av. Zr-Cl	Zr-cent	Ref
$(\eta^3\text{-C}_{13}\text{H}_9)(\eta^5\text{-C}_{13}\text{H}_9)\text{ZrCl}_2$	$\eta^3\text{-C: 2.52(8)}$ $\eta^5\text{-C: 2.56(7)}$	2.420(4)	—	50
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$	$\eta^5\text{-C: 2.49(3), 2.49(3)}$	2.441(5)	2.20, 2.19	51
$[(\text{C}_2\text{H}_4)(\eta^5\text{-C}_{13}\text{H}_8)_2]\text{ZrCl}_2$	$\eta^5\text{-C: 2.563(5), 2.584(5)}$	2.407(1)	—	52
$\{(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})\}\{\text{Li}(\text{THF})_2\}$	$\eta^5\text{-B: 2.543(6), 2.554(7)}$ $\eta^5\text{-C: 2.585(6), 2.560(6)}$	2.461(1)	2.175, 2.173	6b
$[(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})]_2[\text{Mg}(\text{THF})_6]$	$\eta^5\text{-B: 2.541(10), 2.530(10)}$ $\eta^5\text{-C: 2.596(7), 2.551(8)}$	2.485(2)	2.173, 2.152	6a
2	$\eta^2\text{-B: 2.485(6); } \eta^4\text{-B: 2.498(5)}$ $\eta^4\text{-C: 2.774(4)}$	2.394(2)	η^2 :2.944 η^4 :2.214	This work

* All distances are in Å and angles in deg.

2.2 Synthesis and Structural Characterization of $[\eta^4:\eta^2\text{-}((\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9)_2\text{ZrCl}(\text{THF})][\text{Li}(\text{THF})_4]$

To examine the reactivity pattern of the Zr–Cl bond in $\{\eta^4:\eta^2\text{-}((\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9)_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ (**2**), some substitution reactions were attempted. An equimolar reaction between $\{\eta^4:\eta^2\text{-}((\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9)_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ (**2**) and $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ in toluene at room temperature afforded, after recrystallization from a THF solution, $[\eta^4:\eta^2\text{-}((\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9)_2\text{ZrCl}(\text{THF})][\text{Li}(\text{THF})_4]$ (**3**) in 81% yield (Scheme 2.3).



Scheme 2.3

It was assumed that the Cl group in **2** would be displaced by the amido group of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$. However, the result is unexpected and only a cation exchange product was isolated.

Complex **3** was fully characterized by IR, ^1H , ^{13}C , ^{11}B NMR, elemental analyses, and X-ray analyses. The IR spectrum shows the characteristic B–H absorption at 2529 cm^{-1} . The ^1H NMR spectrum shows the non-equivalence of the methylene protons with the coupling constant $J = 15.5\text{ Hz}$. The results from the ^{13}C

NMR spectrum are consistent with those from the ^1H NMR one. The ^{11}B NMR spectrum exhibits four peaks at δ -11.88, -19.49, -35.47 and -38.27 with the ratio of 3:4:1:1, which is different from that observed in **2**.

The X-ray crystal structure of complex **3** is shown in Figure 2.2. The main difference between complexes **3** and **2** is the interactions between the cation complex and the carborane cage, ionic structure versus coordination complex.

Similar to complex **2**, complex **3** also crystallizes in a triclinic $P\bar{1}$ space group with $Z = 2$. The Zr center is tetrahedrally bonded to two carborane cages, a chloride ion and a THF molecule. The hapticity of the two carborane ligands is two and three, respectively. The key structural parameters in both complexes **2** and **3** are very similar (Table 2.2), except for that the average Zr–C bond distance of 3.036 Å of the η^3 -cage is 0.262 Å longer than that of 2.774(4) Å of the η^4 -cage. The longer Zr–C bond may probably be due to the result of crystal packing forces.

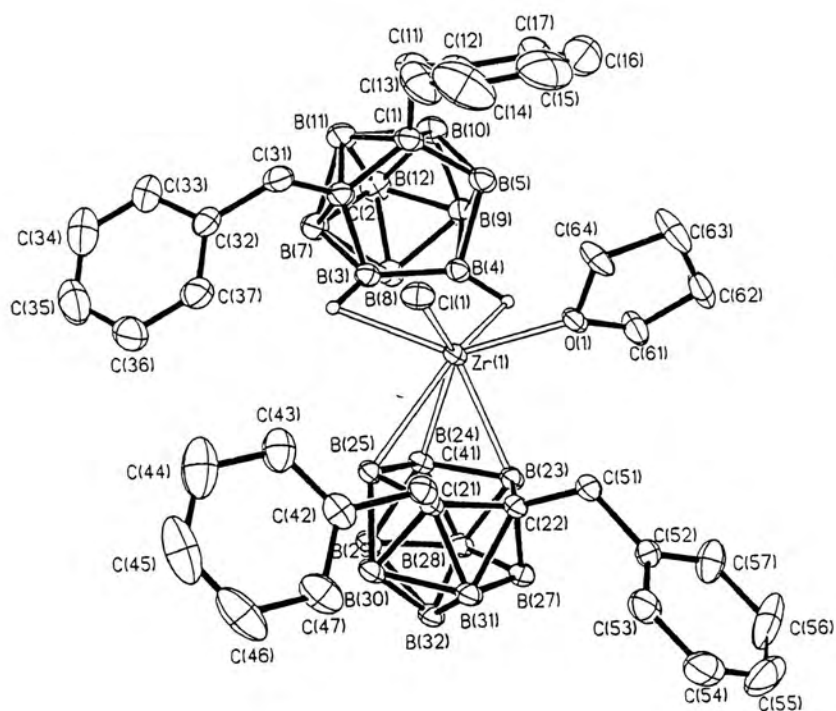


Figure 2.2a Molecular structure of the anion in $[\eta^4:\eta^2-$
 $\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)][Li(THF)_4]$ (3)

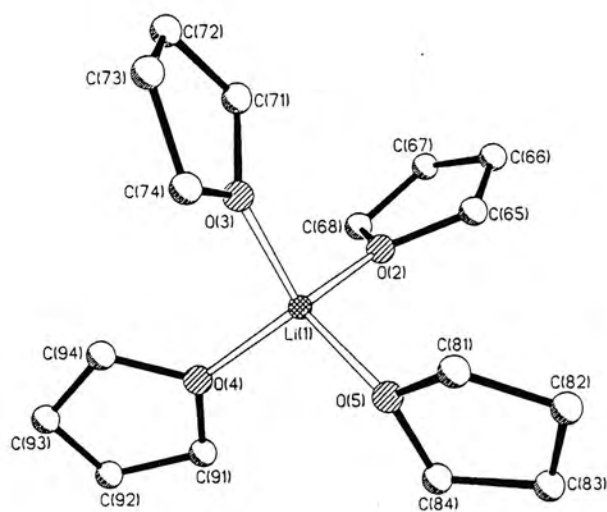


Figure 2.2b Molecular structure of the cation in $[\eta^4:\eta^2-$
 $\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)][Li(THF)_4]$ (3)

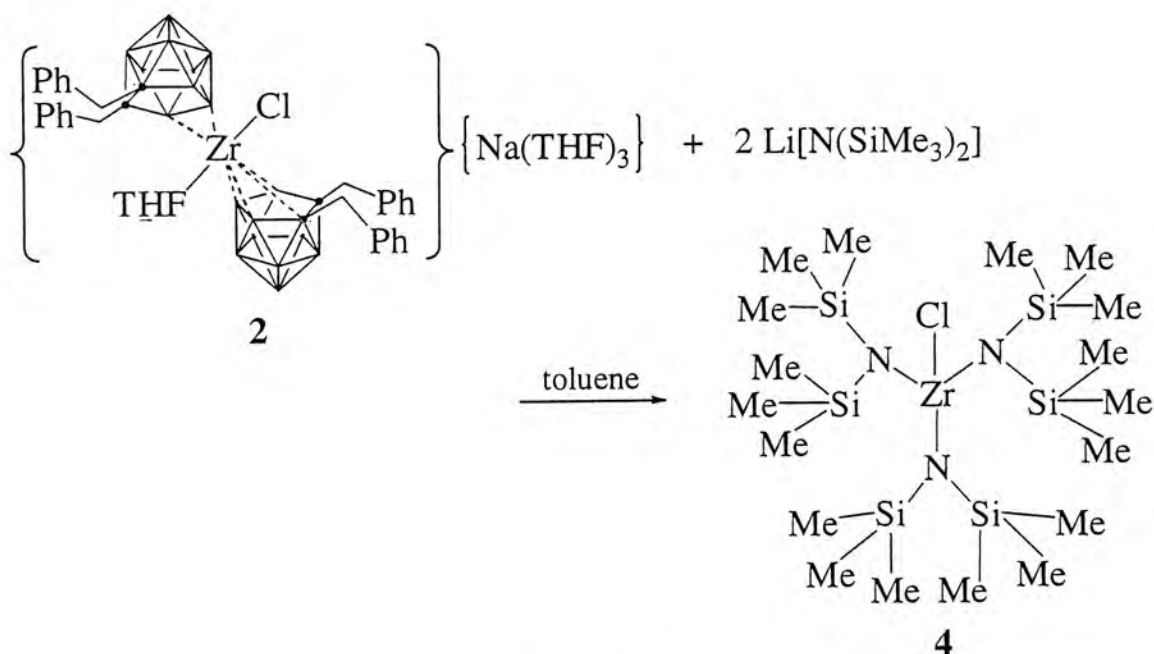
Table 2.2 Selected structural data for **2** and **3***

complex	av. Zr-C	av. Zr-B	Zr-Cl	Zr-cent	cent-Zr -cent	cent-Zr- Cl
2	η^4 -C:	η^2 -B: 2.493(6)	2.394(2)	η^2 :2.944	151.2	η^2 :82.7
	2.774(4)	η^4 -B: 2.498(5)		η^4 :2.214		η^4 :110.2
3	η^3 -C: 3.036	η^2 -B: 2.418(4)	2.388(1)	η^2 :2.973	155.9	η^2 :85.4
		η^3 -B: 2.471(3)		η^3 :2.308		η^3 :106.2

* All distances are in Å and angles in deg.

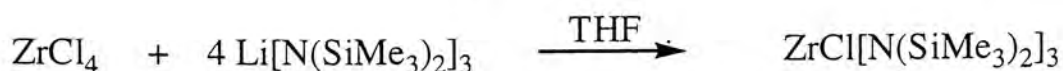
2.3 Synthesis and Structural Characterization of $\text{ZrCl}[\text{N}(\text{SiMe}_3)_2]_3$

Treatment of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\} \{\text{Na}(\text{THF})_3\}$ (**2**) with two equiv of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ in toluene at room temperature afforded $\text{ZrCl}[\text{N}(\text{SiMe}_3)_2]_3$ (**4**) in 79% yield after recrystallization from a THF solution (Scheme 2.4).



Scheme 2.4

Complex **4** is a known compound, and its structure was reported by Airoidi *et. al.* in 1980.⁵³ According to Airoidi, **4** was prepared from the reaction of ZrCl_4 with four equiv of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ in THF at 0°C , followed by sublimation and recrystallization from pentane (Scheme 2.5).⁵³



Scheme 2.5

Molecular structure of complex **4** is shown in Figure 2.3. It crystallizes in monoclinic space group Cc with $Z = 4$. It is a distorted tetrahedron in which the three $\text{N}(\text{SiMe}_3)_2$ ligands are σ -bonded to the Zr center. The coordination sphere of the Zr center is completed by a chloro ligand. The crystal data of our work was similar to those reported.

The Zr–Cl bond distance of $2.397(2) \text{ \AA}$ in **4** is very close to the $2.394(2) \text{ \AA}$ in **2** and $2.388(1) \text{ \AA}$ in **3** (Table 2.3).

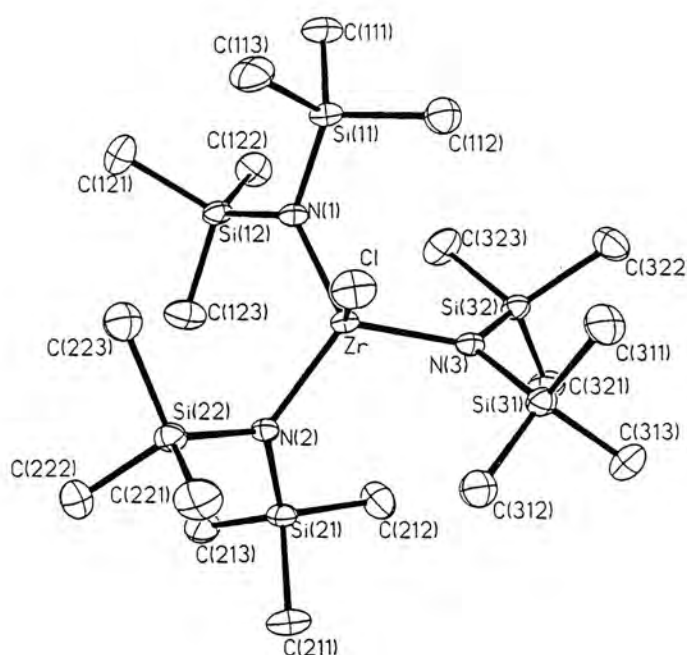


Figure 2.3 Molecular structure of $\text{ZrCl}[\text{N}(\text{SiMe}_3)_2]_3$ (**4**)

Table 2.3 The Zr–Cl bond distances in complexes **2**, **3** and **4**

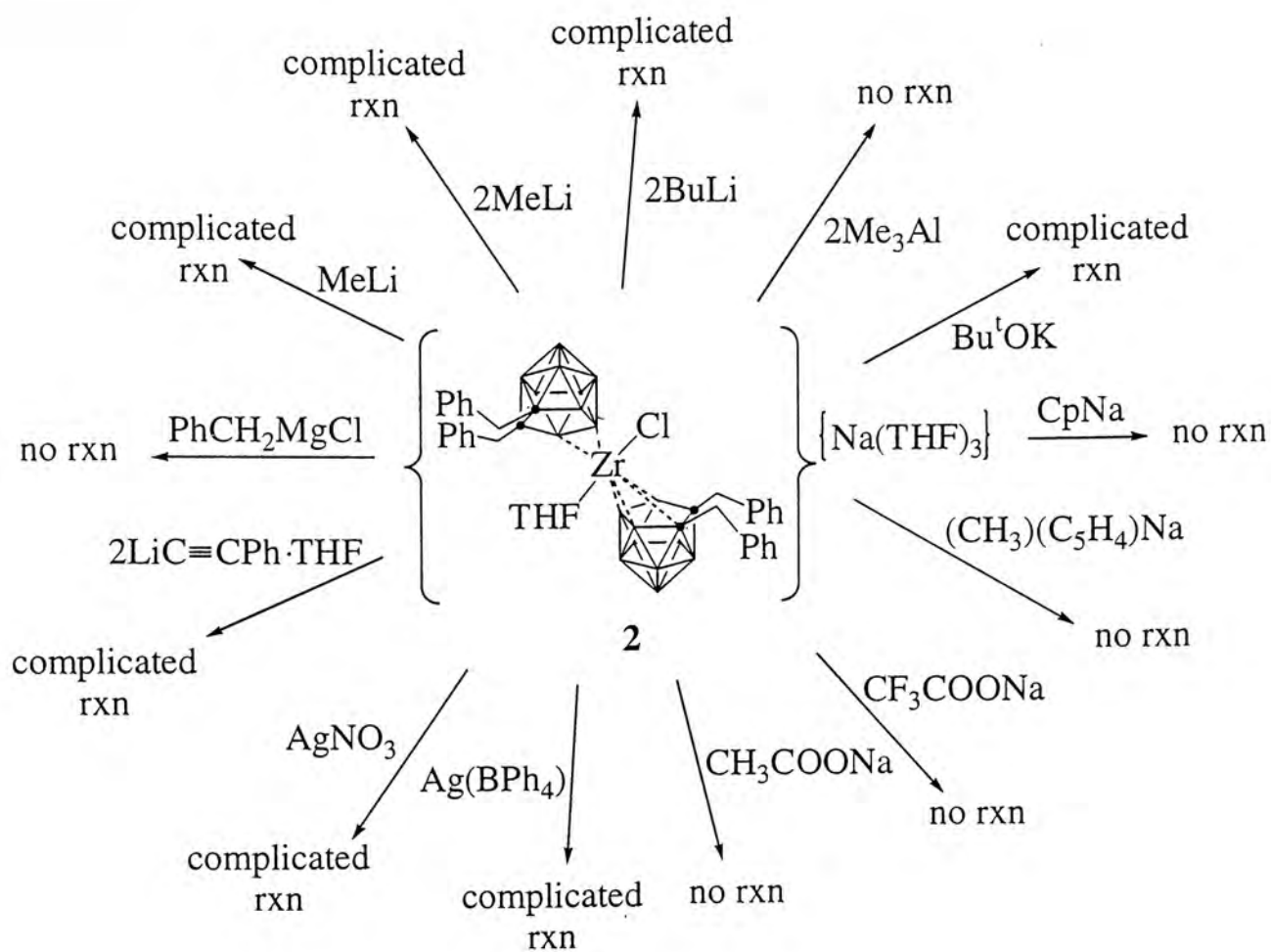
complex	Zr–Cl
2	2.394(2)
3	2.388(1)
4	2.397(2)

* Distances are in Å

Again, this result shows that the Zr–Cl bond remains intact even though the carborane ligands are replaced by the N(SiMe₃)₂ groups, implying that the Zr–Cl bond is well protected by the bulky dibenzyl carborane ligands.

Other Attempts to Substitute the Chloro Group in Complex **2**

Many attempts have been made to substitute the chloro group in **2**, shown in Scheme 2.6. However, these reactions either were very complicated or did not proceed at all on the basis of ¹¹B NMR analyses. For simple comparison, if the splitting pattern of the ¹¹B NMR spectrum of the product is quite different from that of the starting material, the reaction is assigned to be ‘complicated’. ‘No reaction’ means that no changes in the ¹¹B NMR spectrum are observed. Unfortunately, no pure products were isolated from the above mentioned ‘complicated’ reactions. It was not possible to propose the products from these reactions.



Scheme 2.6

Reaction of Complex 2 with PhCH_2MgCl

To an orange solution of $\{\eta^4:\eta^2\text{-}[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ in toluene was added a colourless ether solution of PhCH_2MgCl at -78°C . The reaction mixture was allowed to warm to room temperature and stirred overnight. After removal of solvent, the yellow solid was extracted with THF. The THF solutions were combined and concentrated, to which was added *n*-hexane. There was no change in the ^{11}B NMR spectrum of this solution. $\{\eta^4:\eta^2\text{-}[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ was obtained as orange crystals in 59% yield after this solution stood at room temperature for a week.

Reaction of Complex 2 with CpNa

To an orange solution of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ in THF was slowly added 1 equiv of THF solution of CpNa at room temperature. The mixture was stirred overnight. The ^{11}B NMR of this solution was the same as that of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ in THF solution.

Reaction of Complex 2 with MeLi

To an orange solution of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ in THF was slowly added 1 equiv of THF solution of MeLi at $-78^\circ C$. The reaction mixture was allowed to warm to room temperature and stirred overnight. A yellow solution with white precipitate was observed. After removal of the precipitate and solvent, the residue was extracted with toluene. The toluene solutions were combined and concentrated, to which was added *n*-hexane. No pure products were isolated. The ^{11}B NMR exhibited a 1:1:2:2:2:1 splitting pattern.

Reaction of Complex 2 with AgNO₃

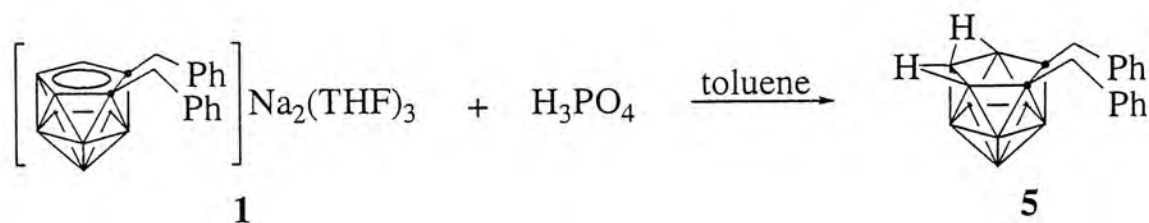
To an orange solution of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ in THF was added AgNO₃ as a solid at room temperature. The reaction mixture was stirred for 15 min to give a greynish-green suspension. The reaction mixture was stirred overnight at room temperature. After removal of the black precipitate (AgCl) and solvent, the residue was extracted with toluene. The toluene solutions were combined and concentrated, to which was added *n*-hexane. No pure products were isolated from this solution. The ^{11}B NMR displayed a 1:1:2:2:2:1 splitting pattern.

It is noteworthy that similar results were also observed in the

metallacarboranes of the C_2B_4 systems. For example, the coordinated chloro ligands in $\{[\eta^5\text{-R}(\text{SiMe}_3)\text{C}_2\text{B}_4\text{H}_4]_2\text{ZrCl}(\text{THF})\}\{\text{Li}(\text{THF})\}$ ($\text{R} = \text{SiMe}_3, \text{Me}, \text{H}$) were found to be substitutionally inert in the presence of the Grignard reagent $\text{Me}_3\text{SiCH}_2\text{MgCl}$ or other alkylating agents, such as AlMe_3 and LiR' ($\text{R}' = \text{Me}, t\text{-Bu}, \text{Me}_3\text{SiCH}_2$) (Section 1.1.2).^{6a} Also, according to Hosmane, $\{(\eta^5\text{-C}_5\text{Me}_5)[\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{ZrCl}_2\}\{\text{Li}(\text{THF})_3\}$ did not react with sterically hindered reagents such as $\text{LiSi}(\text{SiMe}_3)_3$, even at elevated temperatures. Reactions with MeLi or MeMgBr afforded many products (Section 1.1.2).⁵

2.4 Synthesis and Structural Characterization of $[\eta^2\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{M}(\text{NEt}_2)_2(\text{NHEt}_2)\cdot(\text{CH}_2\text{Cl}_2)$ ($\text{M} = \text{Ti}, \text{Zr}$)

Treatment of $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (**1**) with H_3PO_4 in toluene at room temperature afforded $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ (**5**) in 75% yield (Scheme 2.7).

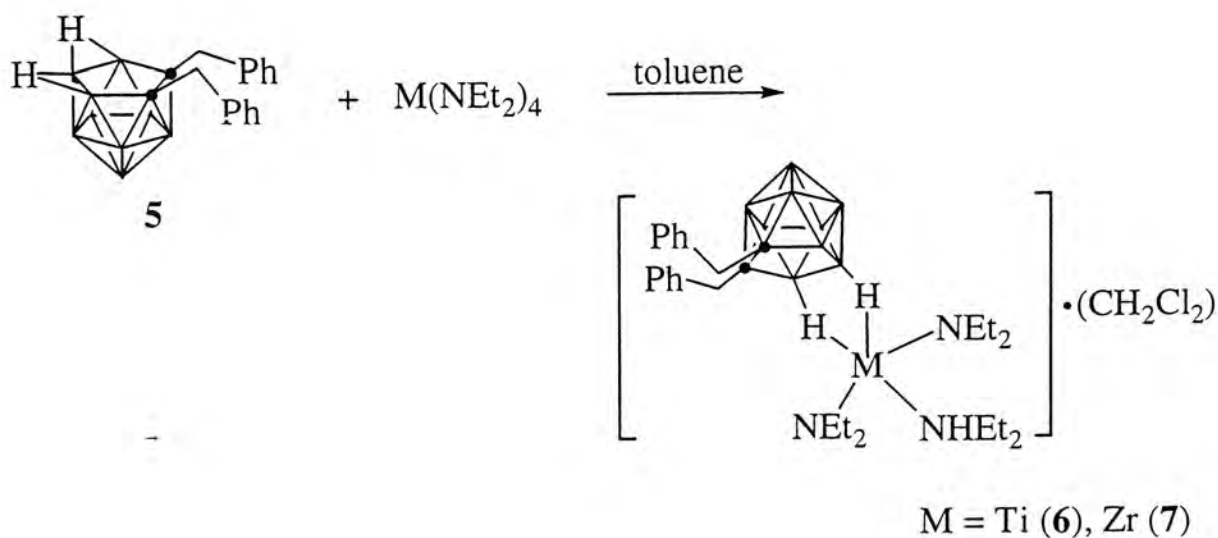


Scheme 2.7

Complex **5** was characterized by IR, ^1H , ^{13}C , ^{11}B NMR, and elemental analyses. The IR spectrum shows a typical strong and broad characteristic B–H absorption at 2552 cm^{-1} . The results from both ^1H NMR and ^{13}C NMR spectra are consistent with each other. The ^{11}B NMR spectrum shows five distinct peaks with the ratio of 2:2:1:1:3.

$(C_6H_5CH_2)_2C_2B_9H_{11}$ is a thermally unstable species and it decomposes upon heating. A toluene solution of $(C_6H_5CH_2)_2C_2B_9H_{11}$ was heated at $50^\circ C$ for 3 hr. ^{11}B NMR of the solution was run and the pattern was different from that at room temperature. This showed the decomposition of $(C_6H_5CH_2)_2C_2B_9H_{11}$ upon heating. ^{11}B NMR (the solution): δ 6.70 (1), -3.63 (1), -6.33 (1), -10.57 (1), -12.91 (1), -16.55 (2), -25.33 (1), -38.47 (1).

An equimolar reaction between $M(NEt_2)_4$ ($M = Ti, Zr$) and $(C_6H_5CH_2)_2C_2B_9H_{11}$ in toluene at room temperature gave, after recrystallization from CH_2Cl_2 , gave $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ (**6**) as orange crystals and $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Zr(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ (**7**) as orange solid in 83% and 85% yield, respectively (Scheme 2.8).



Scheme 2.8

Complex **6** was fully characterized by IR, 1H , ^{13}C , ^{11}B NMR, elemental analyses, and X-ray analyses. In the IR spectrum, the strong absorption at 2524 cm^{-1} indicates the B–H stretching. In the 1H NMR spectrum, the non-equivalence of the methylene protons is indicated by the two doublets at δ 3.18 and 3.08, respectively

(with $J = 15.3$ Hz). The quartet at $\delta 2.72$ and the triplet at $\delta 1.13$ are assigned to the methylene and methyl protons of the NCH_2CH_3 group, respectively ($J = 7.2$ Hz). The multiplicity of these peaks shows the presence of coupling between these two types of protons. In the ^{13}C NMR, the methylene carbons of the NCH_2CH_3 and HNCH_2CH_3 groups are assigned to the peaks at $\delta 42.85$ and $\delta 40.87$, respectively, but the methyl carbons of these two groups overlap at $\delta 13.08$. The ^{11}B NMR spectrum shows four distinct peaks at $\delta 1.15$, -7.03 , -23.08 and -25.67 , with a splitting pattern of 3:4:1:1. The spectroscopic data of complex **7** are very similar to those of complex **6**.

The molecular structure of complex **6** is shown in Figure 2.4. Complex **6** crystallizes in the triclinic space group $\text{P}\bar{1}$. It is an *exo-nido* complex with a carborane being η^2 -bonded to the d^0 Ti center. A possible explanation for the formation of η^2 -bonding is due to the steric effect of the bulky benzyl ligands.

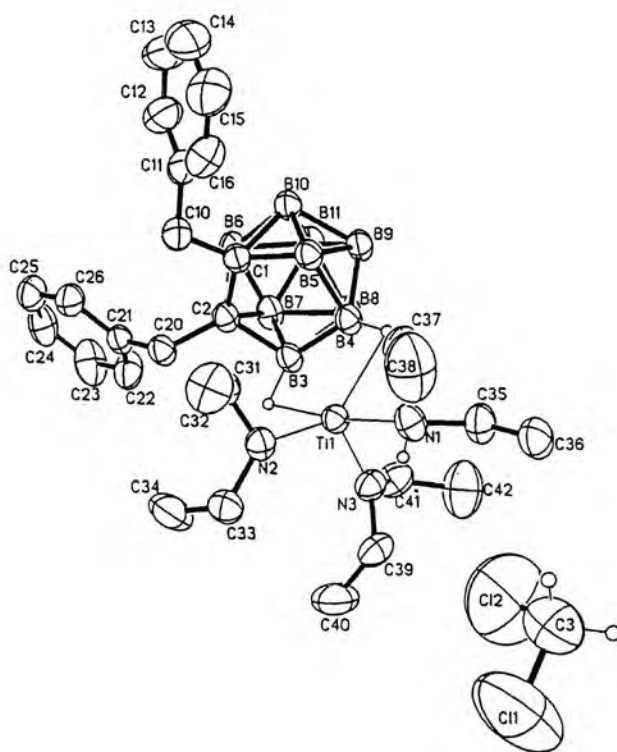


Figure 2.4 Molecular structure of [η^2 -
 $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9$]Ti(NEt₂)₂(NHet₂)·(CH₂Cl₂) (**6**)

Selected structural data for complex **6** and some other Ti(IV) complexes are listed in Table 2.4. The average Ti–B bond distance of 2.328(3) Å in **6** is shorter than the 2.423(2) Å in $[\text{Cp}^*(\eta^1:\eta^5\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})]\text{Ti}(\text{NCMe})$, 2.48(2) Å in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)(\text{NCMe})$, and 2.41(3) Å in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)$. However, the Ti–cent distance of 2.920 Å is much longer than the 1.961 Å in $[\text{Cp}^*(\eta^1:\eta^5\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})]\text{Ti}(\text{NCMe})$, 2.02 Å in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)(\text{NCMe})$, 1.91 Å in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)$, and 2.051 Å and 2.036 Å in $[\{\text{Ti}_2\text{Cp}^*_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$, due to the low hapticity of the ligand in **6**. The Ti–N(1) bond distance of 2.235(2) Å is comparable to the 2.174(2) Å in $[\text{Cp}^*(\eta^1:\eta^5\text{-4-CHMeO-C}_2\text{B}_9\text{H}_{10})]\text{Ti}(\text{NCMe})$, 2.19 (1) Å in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)(\text{NCMe})$, and 2.158 Å in $[\{\text{Ti}_2\text{Cp}^*_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$. The Ti–N(2) distance of 1.879(2) Å and the Ti–N(3) distance of 1.871(2) Å are comparable to the 1.85(1) Å in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)(\text{NCMe})$ and 1.89(2) Å in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)$.

The N(2)–Ti–N(3) bond angle of 112.69(10)° is the largest among three N–Ti–N angles. Both the N(1)–Ti–N(3) and N(1)–Ti–N(2) bond angles of 95.22(9)° and 98.86(9)° are larger than the 85.6(5)° in $[\text{Cp}^*(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Ti}](\text{N}=\text{CMe}_2)(\text{NCMe})$, but are comparable to the 101.6(2)° in $[\{\text{Ti}_2\text{Cp}^*_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$.

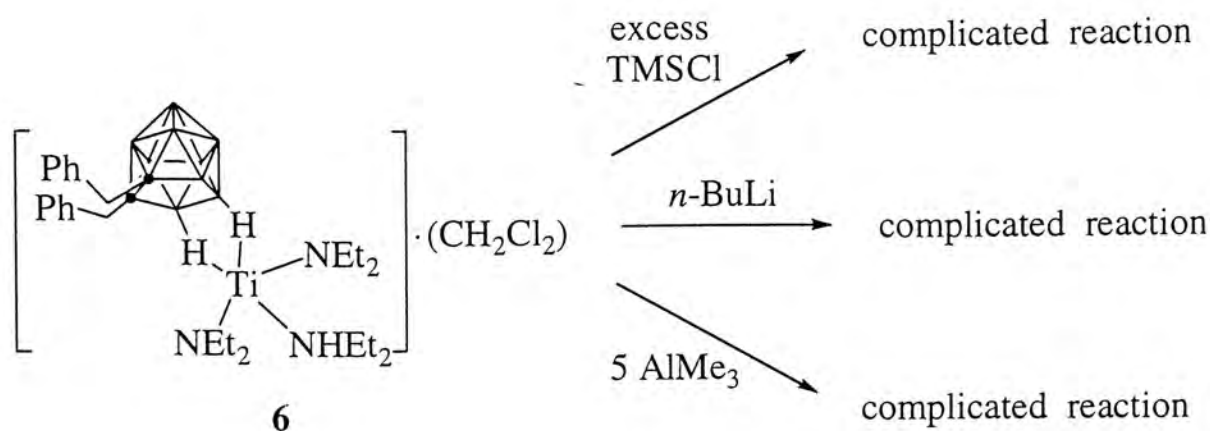
Table 2.4 Selected structural data for **6** and other Ti(IV) complexes*

complex	av. Ti-cage atom	Ti-cent	Ti-N	cent-Ti-N	N-Ti-N	Ref
[Cp [*] (η^5 -4-CHMeO-C ₂ B ₉ H ₁₀)]Ti(NCMe)	2.423(2)	1.961	2.174(2)	105.0	—	35
[Cp [*] (η^5 -C ₂ B ₉ H ₁₁)Ti](N=CMMe ₂)(NCMe)	2.48(2)	2.02	NCMe ₂ : 1.85(1) NCMe: 2.19(1)	NCMe ₂ : 107.8 NCMe: 105.0	85.6(5)	33
[Cp [*] (η^5 -C ₂ B ₉ H ₁₁)Ti](N=CMMe ₂)	2.41(3)	1.91	1.89(2)	111.0	—	33
[Ti ₂ Cp [*] ₂ Cl ₃ (NH ₃)](μ -N)]	—	2.051	2.158(4)	115.5	101.6(2)	54
		2.036		117.1 115.9		
6	2.328(3)	2.920	N(1):2.235(2)	N(1): 122.3	N(2,3): 112.69(10)	This work
			N(2): 1.879(2)	N(2): 95.2	N(1,3): 95.22(9)	
			N(3): 1.871(2)	N(3):129.2	N(1,2): 98.86(9)	

* All distances are in Å and angles in deg.

Attempted Derivatization of Complex 6

To examine the reactivity patterns of complex **6**, some reactions were attempted (Scheme 2.9).



Scheme 2.9

Reaction of Complex 6 with TMSCl

To a reddish-brown solution of $[\eta^2\text{-}(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHEt}_2)\cdot(\text{CH}_2\text{Cl}_2)$ in toluene was slowly added excess TMSCl at -78°C . The reaction mixture was allowed to warm to room temperature and stirred overnight. The ^{11}B NMR spectrum of this solution: δ 19.76 (1), -3.98 (2), -12.56 (2), -19.28 (2), -27.70 (2), which is different from **6**. After removal of precipitate and the solvent, the residue was extracted with CH_2Cl_2 . The CH_2Cl_2 solutions were combined and concentrated, to which was added *n*-hexane. The resulting brown solution was stood at room temperature for days. No pure products were obtained.

Reaction of complex 6 with *n*-BuLi

To a reddish-brown solution of $[\eta^2\text{-}(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHEt}_2)\cdot(\text{CH}_2\text{Cl}_2)$ in toluene was added 1 equiv of *n*-

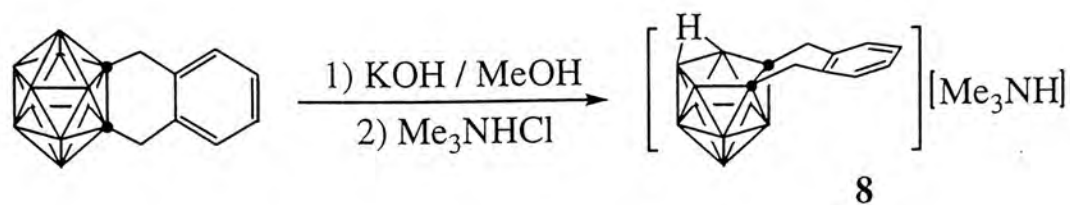
BuLi at -78°C . The reaction mixture was allowed to warm to room temperature and stirred overnight to give a brown solution with white precipitate. ^{11}B NMR spectrum of this solution: δ -22.86 (3), -26.09 (2), -27.36 (3), -46.45 (1), which is different from **6**. After removal of precipitate and the solvent, the residue was extracted with CH_2Cl_2 . The CH_2Cl_2 solutions were combined and concentrated, to which was added *n*-hexane. The resulting brown solution was stood for days. No pure products were isolated for further characterization.

Reaction of Complex **6** with AlMe_3

To a reddish-brown solution of $[\eta^2\text{-}(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHEt}_2)\cdot(\text{CH}_2\text{Cl}_2)$ in toluene was added 5 equiv of AlMe_3 at -78°C . The reaction mixture was allowed to warm to room temperature and stirred overnight to give a brown solution. The ^{11}B NMR spectrum of this solution: δ -7.82 (3), -11.71 (4), -21.20 (1), -22.11 (1), which is different from **6**. After removal of precipitate and the solvent, the residue was extracted with CH_2Cl_2 . The CH_2Cl_2 solutions were combined and concentrated, to which was added *n*-hexane. The resulting brown solution was stood at room temperature for days. No pure products were isolated.

2.5 Synthesis and Characterization of $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]_2\text{M}(\text{THF})_2$ (M = Zr, Hf)

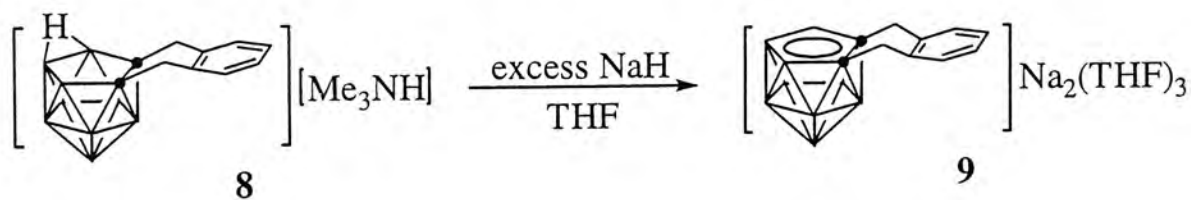
Treatment of $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ with KOH in distilled CH_3OH at reflux temperature for two days gave, after addition of Me_3NHCl solution, $[\text{Me}_3\text{NH}][\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_{10}]$ (**8**) in 72% yield (Scheme 2.10).



Scheme 2.10

Complex **8** was characterized by IR, ^1H , ^{13}C , ^{11}B NMR, and elemental analyses. The IR spectrum exhibits a strong B–H absorption at 2501 cm^{-1} . The ^1H NMR spectrum shows the presence of methyl and aromatic protons with the ratio of 9 to 4. The non-equivalence of the methylene protons is shown by two singlets at δ 3.20, and δ 3.07, respectively. The ^{13}C NMR results are consistent with those of the ^1H NMR. The splitting pattern of the ^{11}B NMR spectrum is 2:1:2:2:1:1, which is similar to that of $[\text{Me}_3\text{NH}][7,8-(\text{C}_6\text{H}_5\text{CH}_2)_2\text{-nido-7,8-C}_2\text{B}_9\text{H}_{10}]$.

Reaction of $[\text{Me}_3\text{NH}][\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_{10}]$ (**8**) with excess NaH in THF at reflux temperature gave $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (**9**) in 81% yield (Scheme 2.11).

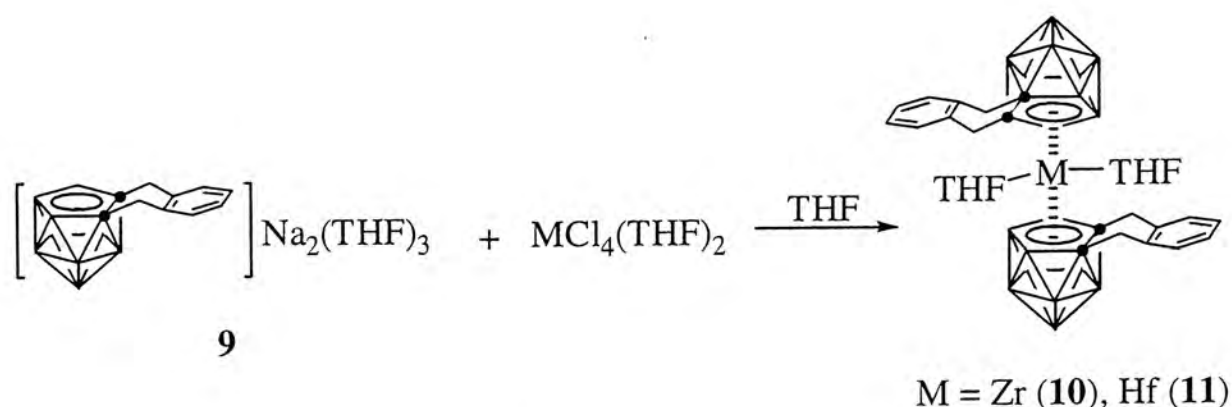


Scheme 2.11

Complex **8** was characterized by IR, ^1H , ^{13}C , ^{11}B NMR, and elemental analyses. In the IR spectrum, the characteristic strong absorption at 2509 cm^{-1} indicates the presence of B–H bond. The ratio of three THF molecules per carborane

ligand is supported by the ^1H NMR spectrum. In contrast to complex **7**, two doublets at δ 3.55 and 3.47 with $J = 15.3$ Hz were observed and assigned to the methylene protons. The results of the ^{13}C NMR spectrum are in line with those of the ^1H NMR. The ^{11}B NMR spectrum exhibits five peaks at δ -1.13, -5.86, -9.50, -12.06 and -32.51 with a splitting pattern of 2:2:3:1:1.

Treatment of $\text{MCl}_4(\text{THF})_2$ ($\text{M} = \text{Zr}, \text{Hf}$) with 1 equiv of $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (**9**) in THF at room temperature afforded, after recrystallization from a toluene/*n*-hexane solution, $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9\}_2\text{M}(\text{THF})_2$ ($\text{M} = \text{Zr}$ (**10**), Hf (**11**)) in good yield (Scheme 2.12).



Scheme 2.12

Complexes **10** and **11** were characterized by IR, ^1H , ^{13}C , ^{11}B NMR, and elemental analyses. The spectroscopic results of these complexes are similar. Like other complexes, their IR spectra show a strong B–H absorption around 2500 cm^{-1} . The ^1H NMR spectra support the ratio of one THF molecule per ligand and show the non-equivalence of the methylene protons. The results from ^{13}C NMR are consistent with those of ^1H NMR spectra. The ^{11}B NMR spectra are more complicated than those of the above-mentioned complexes.

Complexes **10** and **11** are proposed to have full-sandwich structures, in which the central metal center is η^5 -bound to each of the two carborane cages and two THF molecules in a tetrahedral arrangement.

2.6 Conclusion

Unlike the unsubstituted $C_2B_9H_{11}^{2-}$ dicarbollide ion which usually forms η^5 - π bonding with d^0 group 4 metal centers, the dibenzyl-substituted one prefers to form σ -bond with the group 4 metal center via M–H–B bonding, leading to the formation of the ‘slipped’ or *exo-nido* structures. The steric bulkiness of the dibenzyl groups is believed to be responsible for the formation of these structures. Due to the steric effects of the dibenzyl substituents, the Zr–Cl bond of zirconacarboranes is well-protected, which limits the further exploration.

On the other hand, less steric demanding carboranyl ligand [μ - $\{o$ - $C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_3$ resembles the dicarbollide ion, probably forming η^5 - π bonding with group 4 metal centers.

Chapter 3

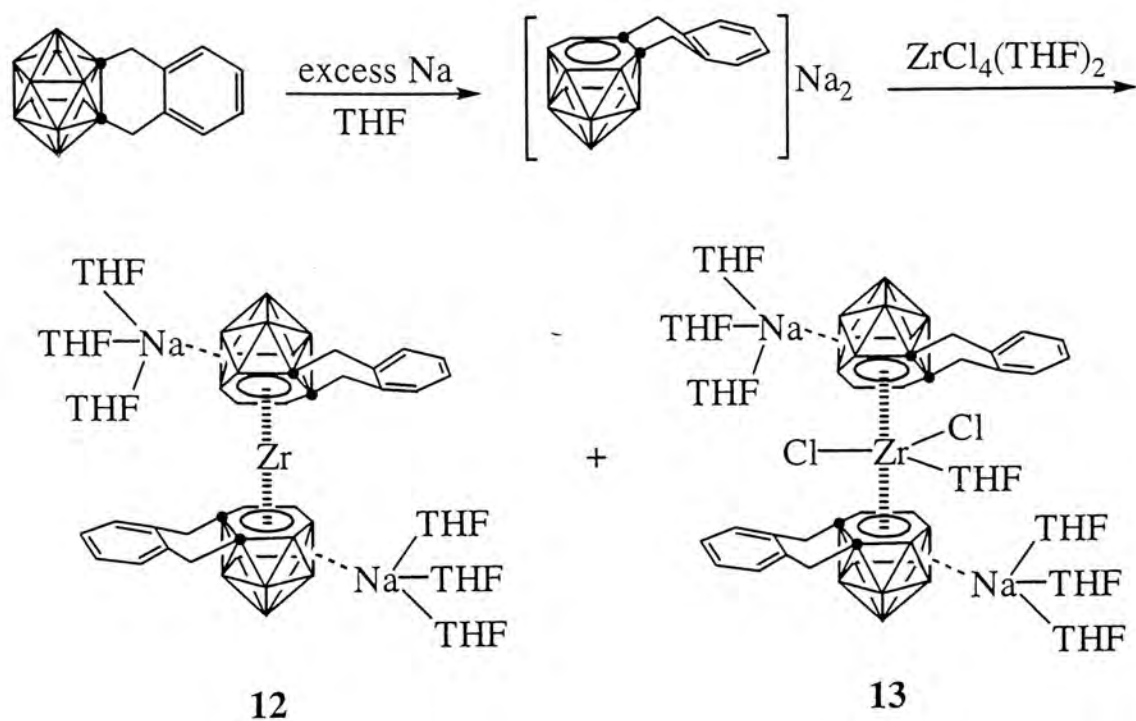
Synthesis and Structural Characterization of Group 4

Metallacarboranes of the C₂B₁₀ Systems

In the previous chapter, the substituent effect of the C₂B₉ ligand on the structures of group 4 metallacarboranes has been discussed. In this chapter, the focus is on the cage carbons-linked ligand, μ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₂, which is recently synthesized by our group. Normally, *closo*-carboranes undergo reduction to give the 'carbons-apart' dianions. However, the cage carbon adjacency of this ligand remains during the two-electron reductive process. We report in this chapter the synthesis and structural characterization of group 4 metal complexes with this new ligand.

3.1 Synthesis and Structural Characterization of $\{[\mu$ -1,2-(*o*-C₆H₄(CH₂)₂)-1,2-C₂B₁₀H₁₀]₂Zr}\{Na(THF)₃\}₂ and $\{[\mu$ -1,2-(*o*-C₆H₄(CH₂)₂)-1,2-C₂B₁₀H₁₀]₂ZrCl₂\}\{Na(THF)₃\}₂·(THF)

Reaction of μ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀ with excess Na in THF at room temperature gave, after work-up, the disodium salt $[\mu$ -{*o*-C₆H₄(CH₂)₂}-C₂B₁₀H₁₀]₂Na₂. Treatment of ZrCl₄(THF)₂ with this dianionic salt in THF at room temperature gave $\{[\mu$ -1,2-(*o*-C₆H₄(CH₂)₂)-1,2-C₂B₁₀H₁₀]₂Zr}\{Na(THF)₃\}₂ (**12**) as dark red crystals and $\{[\mu$ -1,2-(*o*-C₆H₄(CH₂)₂)-1,2-C₂B₁₀H₁₀]₂ZrCl₂\}\{Na(THF)₃\}₂·(THF) (**13**) as orange crystals in 76% and 10% isolated yield, respectively (Scheme 3.1). These two complexes were separated according to their color.



Scheme 3.1

According to Hawthorne, the reaction of TiCl_4 with $[\text{C}_2\text{B}_{10}\text{H}_{12}]\text{Na}_2$ in THF resulted in, after removal of solvent and addition of an ethanol solution of tetraethylammonium bromide, the formation of $[(\text{C}_2\text{H}_5)_4\text{N}]_2[4,4'\text{-Ti}(1,6\text{-C}_2\text{B}_{10}\text{H}_{12})_2]$.²⁸ In the reaction, the carborane dianion was found to be the reductant responsible for the formation of Ti(II) product (Scheme 1.29) by the recovery of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ from the reaction mixture without exposure to air.²⁸ Similarly, neutral 1,2- $(\text{CH}_3)_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}$ was also recovered from the reaction of ZrCl_4 with $[(\text{CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}_2$ (Section 1.3).²⁸ Therefore, the redox reaction is also present in the reaction of $\text{ZrCl}_4(\text{THF})_2$ with $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}_2$. Unlike Hawthorne's reaction in which only Zr(II) species was isolated, the present reaction resulted in the formation of both Zr(II) and Zr(IV) complexes with Zr(II) as the major product. This is due to the differences in the molar ratio of the reactants. For the reported one, 3 equiv. of dianionic salt was used resulting in the complete

reduction of Zr(IV) to Zr(II). In the present case, only 1 equiv of dianionic salt was used, leading to the incomplete reduction.

Complexes **12** and **13** were fully characterized by IR, ^1H , ^{13}C , ^{11}B NMR, elemental analyses and X-ray analyses. In the IR spectra of these two complexes, the B–H stretching was shown by a strong absorption peak around 2530 cm^{-1} . They have similar ^1H and ^{13}C NMR spectra. However, the splitting patterns of the ^{11}B NMR spectra are different, 1:2:2:1:1:1:1:1 for **12**, and 1:1:3:2:1:1:1 for **13**.

The molecular structures of complexes **12** and **13** are shown in Figures 3.1 and 3.2, respectively. They are full-sandwich complexes in which the two carborane ligands are η^6 -bonded to the metal center. Complex **12** crystallizes in a triclinic space group $P\bar{1}$. Complex **13** crystallizes in a monoclinic space group $C2/c$. In complex **12**, each sodium ion is bonded to the trigonal B_3 face through three B–H bonds, while in complex **13** the Na^+ ion is bonded to two B–H bonds and one chloro group. The coordination sphere around the sodium ion is then completed by three THF molecules in both complexes.

The average Zr–C bond distance of $2.437(3)\text{ \AA}$ in complex **12** is much shorter than that of $2.751(4)\text{ \AA}$ in complex **13** (Table 3.1). The measured value can be compared with the $2.49(3)\text{ \AA}$ in $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, $2.574(5)\text{ \AA}$ in $[(\text{C}_2\text{H}_4)(\eta^5\text{-C}_{13}\text{H}_8)_2]\text{ZrCl}_2$ and $2.573(6)\text{ \AA}$ in $\{(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl(THF)}\}\{\text{Li(THF)}_2\}$. The average Zr–B bond distance of $2.539(4)\text{ \AA}$ in complex **12** is comparable to the $2.537(10)\text{ \AA}$ in $\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2\}\{\text{Li(THF)}_3\}$ and $2.548(7)\text{ \AA}$ in $\{(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl(THF)}\}\{\text{Li(THF)}_2\}$, but is shorter than that of 2.649 \AA in complex **13**. The Zr–cent distance of 2.140 \AA in complex **13** is 0.276 \AA longer than that of 1.864 \AA in complex **12**. It is close to that of 2.151 \AA (Zr–Cb) in $\{(\eta^5\text{-$

$\text{C}_5\text{Me}_5)(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2\{\text{Li(THF)}_3\}$ and 2.174 Å in $\{(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl(THF)}\}\{\text{Li(THF)}_2\}$, but is shorter than that of 2.244 Å (Zr–Cp) in $\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2\}\{\text{Li(THF)}_3\}$ and 2.20 Å in $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$. The average Zr–Cl bond distance of 2.534(1) in complex **12** is longer than those of 2.441(5) Å in $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, 2.407(1) Å in $[(\text{C}_2\text{H}_4)(\eta^5\text{-C}_{13}\text{H}_8)_2]\text{ZrCl}_2$, 2.455(3) Å in $\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2\}\{\text{Li(THF)}_3\}$ and 2.461(1) Å in $\{(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl(THF)}\}\{\text{Li(THF)}_2\}$.

The Cl–Zr–Cl angle of 84.97(6)° in complex **13** is smaller than that of 97.1(2)° in $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, 96.9(1)° in $[(\text{C}_2\text{H}_4)(\eta^5\text{-C}_{13}\text{H}_8)_2]\text{ZrCl}_2$ and 94.6(1)° in $\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2\}\{\text{Li(THF)}_3\}$. The cent–Zr–Cl angles of 106.1° and 110.0° in complex **13** are smaller than those of 110.1° and 130.4° in $\{(\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl(THF)}\}\{\text{Li(THF)}_2\}$.

Table 3.1 Selected structural data for some organozirconium complexes*

complex	av. Zr-C	av. Zr-B	av Zr-cent	av Zr-Cl	Cl-Zr-Cl	cent-Zr-Cl	ref
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$	2.49(3)	—	2.20	2.441(5)	97.1(2)	—	51
$[(\text{C}_2\text{H}_4)(\eta^5\text{-C}_{13}\text{H}_8)_2]\text{ZrCl}_2$	2.574(5)	—	—	2.407(1)	96.9(1)	—	52
$\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)\text{ZrCl}_2\} \{\text{Li}(\text{THF})_3\}$	—	2.537(10)	Zr-Cp: 2.244 Zr-Cb: 2.151	2.455(3)	94.6(1)	—	5
$\{(\eta^5\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4)_2\text{ZrCl}(\text{THF})\} \{\text{Li}(\text{THF})_2\}$	2.573(6)	2.548(7)	2.174	2.461(1)	—	110.1, 130.4	6b
12	2.437(3)	2.539(4)	1.864	—	—	—	This work
13	2.751(4)	2.649(6)	2.140	2.534(1)	84.97(6)	106.1, 110.0	This work

* All distances are in Å and angles in deg.

Reaction of $\text{ZrCl}_4(\text{THF})_2$ with 2 Equiv of $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}_2$

To a THF solution of $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ was added finely cut Na metal, and the mixture was stirred at room temperature for four days. After removal of excess Na, the resulting clear orange solution was slowly added to a THF solution of $\text{ZrCl}_4(\text{THF})_2$ at room temperature to give a deep blue solution. This solution was stirred at room temperature for two days. Removal of precipitate and the solvent gave a deep blue solid that was extracted with toluene. The clear deep blue toluene solutions were combined and concentrated. The ^{11}B NMR showed the presence of **12**, **13** and $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ in a molar ratio of 8:1:1.

Reaction of $\text{ZrCl}_4(\text{THF})_2$ with $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}_2$ at Low Temperature

On the basis of ^{11}B NMR analyses, low temperature reaction did not change the molar ratio of the products.

3.2 Conclusion

An equimolar reaction between $\text{ZrCl}_4(\text{THF})_2$ and $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}_2$ resulted in an incomplete reduction of Zr(IV) to Zr(II), leading to a mixture of Zr(II) and Zr(IV) complexes with Zr(II) one as the major product. The formation of the full-sandwich metallocarboranes indicates that $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_{10}\text{H}_{10}]^{2-}$ is a less sterically demanding ligand than $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]^{2-}$.

Chapter 4

Summary

Some group 4 metallocarboranes with 'slipped', *exo-nido* and full-sandwich structures were prepared and structurally characterized. Both the salt metathesis and amine elimination are effective methods for the preparation of these complexes.

Reaction of $\text{ZrCl}_4(\text{THF})_2$ with $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (**1**) resulted in the formation of a 'slipped' complex, $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ (**2**), in which one carborane cage is σ -bonded (η^2 -bonding) to the Zr center while the other one is π -bonded (η^4 -bonding) to the Zr. Because of steric and electronic effects, the Zr-Cl bond in complex **2** is very strong and remains intact during the reactions with various nucleophiles. For example, **2** reacted with 1 or 2 equiv of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ affording a cation exchange product $[\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})][\text{Li}(\text{THF})_4]$ (**3**) or $\text{ZrCl}[\text{N}(\text{SiMe}_3)_2]_3$ (**4**), respectively. There were no reactions between **2** and PhCH_2MgCl or CpNa or $(\text{CH}_3)(\text{C}_5\text{H}_4)\text{Na}$ or CF_3COONa or CH_3COONa or Me_3Al . The reactions of **2** with MeLi , *n*-BuLi, AgNO_3 , $\text{Ag}(\text{BPh})_4$, $\text{LiC}\equiv\text{CPh}\cdot\text{THF}$, or Bu^tOK were complicated, and no pure products were isolated.

Treatment of $\text{M}(\text{NEt}_2)_4$ with $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ (**5**) gave $[\eta^2-(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{M}(\text{NEt}_2)_2(\text{NHEt}_2)\cdot(\text{CH}_2\text{Cl}_2)$ ($\text{M} = \text{Ti}$ (**6**), Zr (**7**)). These are *exo-nido* complexes in which the carboranes are η^2 -bonded to the metal center. The formation of these species, rather than half-sandwich complexes, is due to the steric effect of the bulky ligand. The reactions between **6** and TMSCl , *n*-BuLi, or AlMe_3 were complicated, and no pure products were isolated.

An equimolar reaction between $\text{ZrCl}_4(\text{THF})_2$ and $[\mu\{-o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}_2$ afforded a mixture of Zr(II) and Zr(IV) complexes, $[\{\mu\text{-}1,2\text{-}(o\text{-C}_6\text{H}_4(\text{CH}_2)_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}_2\text{Zr}][\text{Na}(\text{THF})_3]_2$ (**12**) and $[\{\mu\text{-}1,2\text{-}(o\text{-C}_6\text{H}_4(\text{CH}_2)_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}_2\text{ZrCl}_2][\text{Na}(\text{THF})_3]_2 \cdot (\text{THF})$ (**13**), respectively. This is due to the incomplete reduction of Zr(IV) to Zr(II) by the carborane dianion. They are all full-sandwich complexes. The ratio of **12** to **13** is almost independent upon the reaction temperature and the molar ratio of the reactants.

This work shows that (1) the steric factor plays an important role in the bonding interactions between the carboranyl ligand and group 4 metal ions, and (2) carborane anions are versatile ligands that can bond to group 4 metal ions in η^2 -, η^3 -, η^4 -, η^5 -, and η^6 -fashion, respectively.

Chapter 5

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except CH_2Cl_2) were freshly distilled from sodium benzophenone ketyl immediately prior to use. $\text{MCl}_4(\text{THF})_2$ ($\text{M} = \text{Hf}, \text{Zr}$) and $\text{Ti}(\text{NEt}_2)_4$ were prepared according to the literature methods.⁵⁵ All other chemicals were purchased from Aldrich Chemical Company and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Nicolet Magna 550 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Valian Inova 400 spectrometer at 128.32 MHz. All chemical shifts are reported in δ units with reference to internal and external TMS (0.00 ppm) or with respect to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external $\text{BF}_3 \cdot \text{OEt}_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd, Brunel University, Middlesex, U. K.

Preparation of 1,2-($\text{C}_6\text{H}_5\text{CH}_2$)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$.¹¹ To a solution of *o*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ (5.20 g, 36.1 mmol) in dry toluene/ Et_2O (2:1) mixture (150 mL) at 0°C was added a 1.60 M solution of *n*-BuLi in *n*-hexane (46.5 mL, 74.4 mmol) dropwise with stirring. The mixture was allowed to warm up to room temperature and stirred for 30 min. The solution was then cooled to 0°C, and freshly distilled $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (8.60 mL, 72.3 mmol) in toluene (30 mL) was added rapidly. The reaction mixture was

refluxed overnight and then quenched with 100 mL of water. The organic layer was separated, and the aqueous layer was extracted with Et₂O (3 x 15 mL). The combined organic portions were dried over anhydrous MgSO₄. Removal of the solvent and addition of *n*-hexane gave 1,2-(C₆H₅CH₂)₂-1,2-C₂B₁₀H₁₀ as a white solid (9.02 g, 77%). ¹H NMR (acetone-*d*₆): δ 7.38 (m, 10H, C₆H₅), 3.89 (s, 4H, C₆H₅CH₂). ¹³C NMR (acetone-*d*₆): δ 136.96, 131.87, 129.61, 129.04 (C₆H₅), 81.84 (cage C), 41.69 (C₆H₅CH₂). ¹¹B NMR (acetone-*d*₆): δ -5.99 (2), -10.56 (2), -11.82 (6).

Preparation of [Me₃NH][7,8-(C₆H₅CH₂)₂-*nido*-7,8-C₂B₉H₁₀].¹¹ To a mixture of 1,2-(C₆H₅CH₂)₂-1,2-C₂B₁₀H₁₀ (5.00 g, 15.4 mmol) and KOH (3.00 g, 53.6 mmol) was added distilled CH₃OH (150 mL) with stirring at 0°C. The reaction mixture was allowed to warm up to room temperature within 30 min and then refluxed overnight. After removal of the solvent, water (100 mL) was added. The aqueous solution was neutralized with diluted HCl. Addition of aqueous Me₃NHCl solution gave a white precipitate. The product was filtered off, washed with water (3 x 30 mL), and dried in vacuum to give [Me₃NH][7,8-(C₆H₅CH₂)₂-*nido*-7,8-C₂B₉H₁₀] as a white solid (5.29 g, 92%). ¹H NMR (acetone-*d*₆): δ 7.19 (m, 10H, C₆H₅), 3.19 (s, 9H, HN(CH₃)₃), 3.12 (s, 2H, C₆H₅CH₂), 3.04 (s, 2H, C₆H₅CH₂), 2.99 (s, 1H, HN(CH₃)₃). ¹³C NMR (acetone-*d*₆): δ 143.98, 130.74, 128.48, 126.17 (C₆H₅), 46.48 (HN(CH₃)₃), 42.86 (C₆H₅CH₂), the cage carbons were not observed. ¹¹B NMR (acetone-*d*₆): δ -10.55 (2), -11.94 (1), -18.63 (2), -19.81 (2), -35.10 (1), -37.74 (1).

Preparation of [(C₆H₅CH₂)₂C₂B₉H₉]Na₂(THF)₃ (1). To a suspension of NaH (0.36 g, 15.0 mmol) in 20 mL of THF was added a THF solution (10 mL) of [Me₃NH][7,8-(C₆H₅CH₂)₂-*nido*-7,8-C₂B₉H₁₀] (1.40 g, 3.75 mmol), and the mixture was refluxed for two days. Removal of excess NaH gave a pale yellow solution. Concentration of the solution and addition of *n*-hexane afforded a white solid (1.70

g, 79%). ^1H NMR (CD_2Cl_2): δ 7.35-7.21 (m, 10H, C_6H_5), 3.68 (m, 8H, THF), 3.22 (d, $J = 15.2$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 3.05 (d, $J = 15.2$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 1.85 (m, 8H, THF). ^{13}C NMR (CD_2Cl_2): δ 141.30, 129.34, 127.40, 125.37 (C_6H_5), 68.00 (THF), 40.62 ($\text{C}_6\text{H}_5\text{CH}_2$), 25.10 (THF), the cage carbons were not observed. ^{11}B NMR (CD_2Cl_2): δ 0.95 (3), -7.46 (4), -23.31 (1), -25.83 (1). IR (KBr, cm^{-1}): ν 2510 (m), 2350 (w), 2316 (w), 1602 (w), 1492 (w), 1447 (w), 1260 (m), 1092 (s), 1030 (s), 897 (w), 801 (s), 701 (m), 538 (w). Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{B}_{18}\text{Na}_4\text{O}$ (**1** - 2.5THF): C, 54.77; H, 6.90. Found: C, 55.07; H, 7.38.

Preparation of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ (2**).**

To a solution of $\text{ZrCl}_4(\text{THF})_2$ (0.37 g, 0.98 mmol) in THF (20 mL) was slowly added a THF (15 mL) solution of $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (0.35 g, 0.98 mmol) at room temperature. The mixture was stirred overnight. After removal of the solvent, the residue was extracted with toluene (2 x 10 mL). The toluene solutions were combined and concentrated to about 15 mL to which was added *n*-hexane (2 mL). $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ was isolated as orange crystals after this solution stood at room temperature for a week (0.38 g, 73%, based on $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$). ^1H NMR (CD_2Cl_2): δ 7.35-7.16 (m, 10H, C_6H_5), 3.63 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 3.54 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 3.66 (br s, 8H, THF), 1.85 (br s, 8H, THF). ^{13}C NMR (CD_2Cl_2): δ 138.09, 129.31, 127.93, 126.52 (C_6H_5), 52.57 (THF), 41.34 ($\text{C}_6\text{H}_5\text{CH}_2$), 25.25 (THF), the cage carbons were not observed. ^{11}B NMR (CD_2Cl_2): δ 17.52 (1), 4.03 (2), 0.27 (2), -5.57 (2), -14.26 (2). IR (KBr, cm^{-1}): ν 2532 (s), 2321 (w), 1616 (w), 1451 (m), 1258 (m), 1042 (s), 807 (m), 716 (m), 527 (m). Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{B}_{18}\text{ClNaOZr}$ (**2** - 3THF): C, 51.04; H, 6.43. Found: C, 50.60; H, 7.35.

Preparation of $[\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})][\text{Li}(\text{THF})_4]$ (3**).**

To a solution of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ (0.38 g, 0.36 mmol) in toluene (20 mL) was slowly added a toluene (15 mL) solution of $LiN(TMS)_2$ (0.061 g, 0.36 mmol) at room temperature. The reaction mixture was stirred at room temperature for two days. After removal of the solvent, the residue was extracted with THF (20 mL). The THF solutions were combined and concentrated to about 15 mL. $[\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)][Li(THF)_4]$ was isolated as orange crystals after this solution stood at room temperature for a week (0.32 g, 81%). 1H NMR (CD_2Cl_2): δ 7.23 (m, 10H, C_6H_5), 3.77 (br s, 8H, THF), 3.19 (d, $J = 15.5$ Hz, 2H, $C_6H_5CH_2$), 3.03 (d, $J = 15.5$ Hz, 2H, $C_6H_5CH_2$), 1.91 (br s, 8H, THF). ^{13}C NMR (CD_2Cl_2): δ 141.80, 129.39, 127.24, 125.09 (C_6H_5), 68.24 (THF), 40.81 ($C_6H_5CH_2$), 25.11 (THF), the cage carbons were not observed. ^{11}B NMR (CD_2Cl_2): δ -11.88 (3), -19.49 (4), -35.47 (1), -38.27 (1). IR (KBr, cm^{-1}): ν 2529 (s), 2298 (w), 1607 (w), 1457 (m), 1037 (s), 890 (w), 815 (m), 700 (m). Anal. Calcd for $C_{44}H_{70}B_{18}ClLiO_3Zr$ (**3** - 2THF): C, 54.19; H, 7.24. Found: C, 54.28; H, 7.41.

Preparation of $ZrCl[N(SiMe_3)_2]_3$ (4). To a solution of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ (0.53 g, 0.50 mmol) in toluene (20 mL) was slowly added a toluene (15 mL) solution of $LiN(TMS)_2$ (0.18 g, 1.10 mmol) at room temperature. The reaction mixture was stirred at room temperature for two days. After removal of the solvent, the residue was extracted with THF (2 x 10 mL). The THF solutions were combined and concentrated to about 15 mL. $ZrCl[N(SiMe_3)_2]_3$ was isolated as yellow crystals after this solution stood at room temperature for a week (0.24 g, 79%, based on $LiN(TMS)_2$). 1H NMR (pyridine- d_5): δ 0.26 (s, TMS). ^{13}C NMR (pyridine- d_5): δ 31.02, 22.15, 13.55. IR (KBr, cm^{-1}): ν 2401 (w), 2307 (w), 1622 (w), 1441 (w), 1259 (m), 1090 (s), 1030 (s), 804 (s), 679

(w), 506 (w). Anal. Calcd for $C_{18}H_{54}ClN_3Si_6Zr$: C, 35.56; H, 8.95; N, 6.91. Found: C, 35.67; H, 8.71; N, 6.89.

Reaction of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ with $PhCH_2MgCl$. To an orange solution of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ (0.34 g, 0.32 mmol) in toluene (20 mL) was added a colourless toluene (15 mL) solution of 0.091 M $PhCH_2MgCl$ (3.52 mL, 0.32 mmol) at $-78^\circ C$. The reaction mixture was allowed to warm up to room temperature within 30 min and the mixture became a sticky fresh orange mixture. The mixture was stirred overnight at room temperature and the mixture became turbid fresh orange solution. After filtration, a yellow solid and a colourless solution were collected. The ^{11}B NMR spectrum showed that there was no carborane in the colourless solution. The yellow solid was extracted with THF (2 x 10 mL). The THF solutions were combined and concentrated to about 15 mL to which was added *n*-hexane (2 mL). $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ was recovered as orange crystals after the solution stood at room temperature for a week (0.20 g, 59% recovery yield). 1H NMR (CD_2Cl_2): δ 7.19 (m, 10H, C_6H_5), 3.66 (d, $J = 13.2$ Hz, 2H, $C_6H_5CH_2$), 3.64 (m, 8H, THF), 3.60 (d, $J = 13.2$ Hz, 2H, $C_6H_5CH_2$), 1.60 (m, 8H, THF). ^{13}C NMR (CD_2Cl_2): δ 142.68, 129.85, 127.23, 124.99 (C_6H_5), 67.13 (THF), 41.77 ($C_6H_5CH_2$), 28.50 (THF), the cage carbons were not observed. ^{11}B NMR (pyridine- d_5): δ 2.78 (2), 1.43 (1), -5.08 (2), -6.27 (2), -21.56 (1), -24.20 (1). IR (KBr, cm^{-1}): ν 2529 (m), 2415 (w), 2321 (m), 1622 (m), 1448 (m), 1387 (m), 1266 (m), 1034 (s), 808 (m), 689 (w), 628 (w), 506 (s).

Reaction of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ with $CpNa$. To an orange solution of $\{\eta^4:\eta^2-[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$ (0.53 g, 0.50 mmol) in THF (20 mL)

was slowly added a pale orange THF (15 mL) solution of CpNa (0.060 g, 0.68 mmol) at room temperature. The reaction solution was allowed to warm up to room temperature and an orange solution was observed. The solution was stirred overnight and the colour of it remained unchanged. ^{11}B NMR of the solution was run and the pattern was similar to that of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ in THF solution. ^{11}B NMR (the solution): δ 5.52 (1), 2.90 (1), -13.35 (2), -15.76 (1), -18.68 (2), -23.93 (1), -24.87 (1). The solution was stirred at 50°C for 3 hr and the colour remained the same. ^{11}B NMR of the solution was run and the pattern was similar to that was done before. ^{11}B NMR (the solution): δ 5.61 (1), 2.99 (1), -13.15 (2), -15.70 (1), -18.50 (2), -23.88 (1), -24.87 (1). The solution was stirred at 50°C overnight and there was no further observable change. ^{11}B NMR of the solution was run and the result was similar to the previous one. ^{11}B NMR (the mixture): δ 10.95 (1), 8.57 (1), -8.00 (2), -10.31 (1), -13.28 (2), -18.48 (1), -19.48 (1). During the reaction, there was no colour change and no precipitate came out. Also, the patterns of the ^{11}B NMR spectra of the reaction solution were similar to that of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ in THF solution. These showed that there was no reaction between $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ and CpNa.

Reaction of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ with MeLi. To an orange solution of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ (0.53 g, 0.50 mmol) in THF (20 mL) was added a colourless THF (15 mL) solution of 0.4246 mmol/g MeLi/THF/ether solution (1.17 g, 0.50 mmol) at -78°C. The reaction mixture was allowed to warm up to room temperature within 30 min and yellow mixture was observed. The mixture was stirred overnight at room temperature and a yellow solution with a layer of white

precipitate was observed. ^{11}B NMR of the solution was run and the pattern was different from that of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ in THF solution. ^{11}B NMR (the solution): δ 4.02 (1), -9.60 (1), -12.38 (2), -14.79 (2), -17.84 (2), -22.89 (1). After removal of precipitate and solvent, the residue was extracted with toluene (2 x 10 mL). The toluene solutions were combined and concentrated to about 15mL to which was added *n*-hexane (2 mL). The yellow solution resulted was stood at room temperature for crystallization.

Reaction of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ with AgNO_3 . To an orange solution of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ (0.53 g, 0.50 mmol) in THF (20 mL) was added white AgNO_3 (0.065 g, 0.38 mmol) at room temperature. The reaction mixture was stirred for 15 min and turned greynish-green. The mixture was stirred for 1.5 hr and ^{11}B NMR was run. The pattern of the spectrum was complicated and different from that of $\{\eta^4:\eta^2-[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]_2\text{ZrCl}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ in THF solution. The reaction mixture was stirred overnight at room temperature and there was no further observable change. ^{11}B NMR was run and the pattern was similar to the one was done before. After filtration, a yellow solution and a black residue were obtained. The IR spectrum showed the absence of carborane in the black residue. After removal of solvent, the yellow solid was extracted with toluene (2 x 10 mL). The toluene solutions were combined and concentrated to about 15mL to which was added *n*-hexane (2 mL). The yellow solution resulted was stood at room temperature for crystallization.

Preparation of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ (5). To a solution of $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (1.20 g, 3.35 mmol) in toluene (25 mL) was added H_3PO_4 (6 mL, 85%). The resulting two-phase mixture was vigorously stirred

overnight at room temperature. The toluene layer was decanted and the H_3PO_4 layer was extracted with toluene (2 x 15 mL). The toluene extracts were combined and dried over MgSO_4 . After removal of toluene under vacuum, the residue was recrystallized from toluene/*n*-hexane at -30°C to give $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ as a white solid (0.76 g, 72%). ^1H NMR (CD_2Cl_2): δ 7.35-7.16 (m, 10H, C_6H_5), 3.64 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 3.54 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), -1.0 (v br s, 2H, $\mu\text{-H}$). ^{13}C NMR (CD_2Cl_2): δ 137.94, 129.29, 128.04, 126.60 (C_6H_5), 86.91 (cage C), 41.34 ($\text{C}_6\text{H}_5\text{CH}_2$). ^{11}B NMR (CD_2Cl_2): δ 3.50 (2), -9.79 (2), -13.72 (1), -19.37 (1), -28.33 (3). IR (KBr, cm^{-1}): ν 2621 (w), 2552 (m), 1261 (m), 1090 (s), 1023 (s), 802 (s), 751 (m), 696 (m), 540 (w). Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{B}_{19}$: C, 61.07; H, 8.01. Found: C, 61.85; H, 7.96.

Decomposition of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ upon heating. A toluene solution of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ was heated at 50°C for 3 hr. ^{11}B NMR of the solution was run and the pattern was different from that at room temperature. This showed the decomposition of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ upon heating. ^{11}B NMR (the solution): δ 6.70 (1), -3.63 (1), -6.33 (1), -10.57 (1), -12.91 (1), -16.55 (2), -25.33 (1), -38.47 (1).

Preparation of $[\eta^2\text{-}(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHEt}_2)\cdot(\text{CH}_2\text{Cl}_2)$ (6). A solution of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ (0.79 g, 2.51 mmol) in toluene (15 mL) was added to a toluene (10 mL) solution of $\text{Ti}(\text{NEt}_2)_4$ (0.84 g, 2.51 mmol) dropwise over a period of 10 min with vigorous stirring at room temperature. The reaction mixture was stirred overnight. Removal of the precipitate and solvent gave an orange solid. Recrystallization from a CH_2Cl_2 solution gave orange crystals (1.37 g, 83%). ^1H NMR (CD_2Cl_2): δ 7.20 (s, 10H, C_6H_5), 4.21 (s, 1H, HNCH_2CH_3), 3.18 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 3.03 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 2.72 (q, $J = 7.2$ Hz, 12H, NCH_2CH_3), 1.13 (t, $J = 7.2$ Hz, 18H, NCH_2CH_3). ^{13}C NMR (CD_2Cl_2): δ 141.85,

129.47, 127.27, 125.14 (C_6H_5), 42.85 (NCH_2CH_3), 40.87 ($HNCH_2CH_3$), 13.08 ($HNCH_2CH_3$ and NCH_2CH_3), the cage carbons were not observed. ^{11}B NMR (CD_2Cl_2): δ 1.15 (3), -7.03 (4), -23.08 (1), -25.67 (1). IR (KBr, cm^{-1}): ν 2524 (m), 2393 (w), 2354 (w), 2314 (w), 1602 (w), 1450 (w), 1387 (w), 1260 (m), 1093 (s), 1025 (s), 802 (s), 701 (w), 518 (m). Anal. Calcd for $C_{57}H_{110}B_{18}Cl_2N_6Ti_2$ ($6 - 0.5CH_2Cl_2$): C, 55.17; H, 8.94; N, 6.77. Found: C, 55.66; H, 8.92; N, 6.97.

Reaction of $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ with TMSCl. To a reddish-brown solution of $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ (0.66 g, 1.00 mmol) in toluene (20 mL) was added TMSCl (0.55 g, 5.06 mmol) at $-78^\circ C$. The reaction mixture was allowed to warm up to room temperature and a brown mixture was observed. The reaction mixture was stirred overnight and there was no further observable change. ^{11}B NMR of the mixture was run and the pattern was different from that of $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ in CH_2Cl_2 solution. ^{11}B NMR (the mixture): δ 19.76 (1), -3.98 (2), -12.56 (2), -19.28 (2), -27.70 (2). After removal of precipitate and the solvent, the residue was extracted with CH_2Cl_2 (2 x 10 mL). The CH_2Cl_2 solutions were combined and concentrated to about 15 mL to which was added *n*-hexane (2 mL). The brown solution resulted was stood at room temperature for crystallization.

Reaction of $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ with *n*-BuLi. To a reddish-brown solution of $[\eta^2-(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot(CH_2Cl_2)$ (0.31 g, 0.47 mmol) in toluene (20 mL) was added 1.57 M *n*-BuLi (0.30 mL, 0.47 mmol) at $-78^\circ C$. The reaction mixture was allowed to warm up to room temperature and a brown mixture was observed. The reaction mixture was stirred overnight and brown solution with white precipitate

was observed. ^{11}B NMR of the solution was run and the pattern was different from that of $[\eta^2\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHET}_2)\cdot(\text{CH}_2\text{Cl}_2)$ in CH_2Cl_2 solution. ^{11}B NMR (the solution): δ -22.86 (3), -26.09 (2), -27.36 (3), -46.45 (1). After removal of precipitate and the solvent, the residue was extracted with CH_2Cl_2 (2 x 10 mL). The CH_2Cl_2 solutions were combined and concentrated to about 15mL to which was added *n*-hexane (2 mL). The brown solution resulted was stood at room temperature for crystallization.

Reaction of $[\eta^2\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHET}_2)\cdot(\text{CH}_2\text{Cl}_2)$ with AlMe_3 . To a reddish-brown solution of $[\eta^2\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHET}_2)\cdot(\text{CH}_2\text{Cl}_2)$ (0.30 g, 0.45 mmol) in toluene (20 mL) was added 2.0 M AlMe_3 (1.13 mL, 2.25 mmol) at -78°C . The reaction mixture was allowed to warm up to room temperature and a brown mixture was observed. The reaction mixture was stirred overnight and there was no further observable change. ^{11}B NMR of the solution was run and the pattern was different from that of $[\eta^2\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHET}_2)\cdot(\text{CH}_2\text{Cl}_2)$ in CH_2Cl_2 solution. ^{11}B NMR (the solution): δ -7.82 (3), -11.71 (4), -21.20 (1), -22.11 (1). After removal of precipitate and the solvent, the residue was extracted with CH_2Cl_2 (2 x 10 mL). The CH_2Cl_2 solutions were combined and concentrated to about 15mL to which was added *n*-hexane (2 mL). The brown solution resulted was stood at room temperature for crystallization.

Preparation of $[\eta^2\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Zr}(\text{NEt}_2)_2(\text{NHET}_2)\cdot(\text{CH}_2\text{Cl}_2)$ (7). A solution of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{11}$ (0.31 g, 1.0 mmol) in toluene (15 mL) was added to a toluene (10 mL) solution of $\text{Zr}(\text{NEt}_2)_4$ (0.38 g, 1.0 mmol) dropwise over a period of 10 min with vigorous stirring at room temperature. The reaction mixture was stirred overnight. After removal of precipitate and solvent, the residue was extracted

with CH_2Cl_2 (2 x 10 mL). The CH_2Cl_2 solutions were combined and concentrated to about 15 mL to which was added *n*-hexane (2 mL). $[\eta^2\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9\text{]Zr(NEt}_2)_2\text{(NHEt}_2\text{)·(CH}_2\text{Cl}_2\text{)}$ was isolated as orange solid (0.60 g, 85%). $^1\text{H NMR (CD}_2\text{Cl}_2\text{): } \delta$ 7.21 (s, 10H, C_6H_5), 4.69 (s, 1H, HNCH_2CH_3), 3.32 (m, 4H, HNCH_2CH_3), 3.19 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 3.03 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$), 2.90 (m, 8H, NCH_2CH_3), 1.30 (t, $J = 7.2$ Hz, 6H, HNCH_2CH_3), 1.20 (t, $J = 7.2$ Hz, 12H, NCH_2CH_3). $^{13}\text{C NMR (CD}_2\text{Cl}_2\text{): } \delta$ 141.91, 130.75, 129.38, 127.18, 125.01 (C_6H_5), 44.62 (HNCH_2CH_3), 40.79 (NCH_2CH_3), 31.23 ($\text{CH}_2\text{C}_6\text{H}_5$), 13.54 (HNCH_2CH_3), 12.70 (NCH_2CH_3), the cage carbons were not observed. $^{11}\text{B NMR (CD}_2\text{Cl}_2\text{): } \delta$ -10.24 (3), -18.41 (4), -34.56 (1), -37.14 (1). IR (KBr, cm^{-1}): ν 2518 (s), 2354 (w), 2314 (w), 1576 (w), 1452 (m), 1387 (w), 1260 (m), 1101 (w), 1023 (m), 803 (m), 760 (w), 702 (m). Anal. Calcd for $\text{C}_{29}\text{H}_{56}\text{B}_9\text{Cl}_2\text{N}_3\text{Zr}$: C, 49.32; H, 7.99; N, 5.95. Found: C, 48.74; H, 7.75; N, 4.55.

Preparation of $[\text{Me}_3\text{NH}][\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_{10}]$ (8). To a mixture of $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (0.62 g, 2.52 mmol) and KOH (0.56 g, 10.7 mmol) was added distilled CH_3OH (40 mL) with stirring at 0°C . The reaction mixture was allowed to warm to room temperature within 30 min and then refluxed for two days. After removal of the solvent, water (15 mL) was added. The aqueous solution was neutralized with diluted HCl. Addition of aqueous Me_3NHCl solution gave a greynish-brown precipitate. The product was filtered off, washed with water (3 x 30 mL), and dried in vacuum to give $[\text{Me}_3\text{NH}][\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_{10}]$ as a pale brown solid (0.53 g, 72%). $^1\text{H NMR (acetone-}d_6\text{): } \delta$ 7.01 (m, 4H, C_6H_4), 3.20 (s, 9H, $\text{HN(CH}_3)_3$), 3.12 (s, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$), 3.07 (s, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$). $^{13}\text{C NMR (acetone-}d_6\text{): } \delta$ 144.28, 132.17, 130.83 (C_6H_4), 50.68 ($\text{C}_6\text{H}_4(\text{CH}_2)$), 44.90 ($\text{HN(CH}_3)_3$), the cage carbons were not observed. $^{11}\text{B NMR (acetone-}d_6\text{): } \delta$ -11.19

(2), -12.43 (1), -20.87 (2), -21.79 (2), -35.88 (1), -38.16 (1). IR (KBr, cm^{-1}): ν 3130 (s), 3019 (w), 2946 (w), 2838 (w), 2737 (w), 2576 (s), 2501 (s), 1466 (m), 1385 (w), 1260 (w), 1172 (w), 1041 (w), 976 (w), 752 (m), 548 (w), 413 (w). Anal. Calcd for $\text{C}_{13}\text{H}_{28}\text{B}_9\text{N}$: C, 52.81; H, 9.55; N, 4.74. Found: C, 52.39; H, 9.69; N, 4.20.

Preparation of $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (9). To a suspension of NaH (0.23 g, 9.58 mmol) in 20 mL of THF was slowly added a THF solution (10 mL) of $[\text{Me}_3\text{NH}][\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_{10}]$ (0.50 g, 1.70 mmol) at room temperature, and the mixture was refluxed for two days. Removal of excess NaH and the solvent gave a yellow solid that was washed with *n*-hexane and dried in vacuum, resulting $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ as golden yellow solid (1.37 g, 81%). ^1H NMR (pyridine- d_5): δ 6.96 (s, 4H, C_6H_4), 3.65 (m, 8H, THF), 3.55 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$), 3.47 (d, $J = 15.3$ Hz, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$), 1.60 (m, 8H, THF). ^{13}C NMR (pyridine- d_2): δ 140.13, 127.12, 124.73 (C_6H_4), 67.15 (THF), 40.46 ($\text{C}_6\text{H}_4(\text{CH}_2)$), 25.11 (THF), the cage carbons were not observed. ^{11}B NMR (pyridine- d_2): δ -1.13 (2), -5.86 (2), -9.50 (3), -12.06 (1), -32.51 (1). IR (KBr, cm^{-1}): ν 2509 (s), 2354 (m), 2321 (m), 1690 (w), 1640 (m), 1542 (w), 1452 (m), 1260 (s), 1092 (s), 1025 (s), 917 (w), 801 (s), 749 (w), 669 (w), 539 (m). Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{B}_9\text{Na}_2\text{O}$ (9 - 2THF): C, 47.68; H, 7.15. Found: C, 48.33; H, 7.36.

Preparation of $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]_2\text{Zr}(\text{THF})_2$ (10). To a solution of $\text{ZrCl}_4(\text{THF})_2$ (0.20 g, 0.72 mmol) in THF (10 mL) was slowly added a THF (10 mL) solution of $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (0.27 g, 0.72 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. After removal of precipitate and the solvent, the residue was extracted with toluene (2 x 10 mL). The toluene solutions were combined and concentrated to about 15 mL to which was added *n*-hexane (2 mL). $[\mu\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]_2\text{Zr}(\text{THF})_2$ was

isolated as needle-shape white microcrystals after the solution stood at room temperature for two days (0.11 g, 67%, based on $[\mu\{-o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$). ^1H NMR (pyridine- d_5): δ 6.95 (m, 4H, C_6H_4), 3.63 (m, 8H, THF), 3.29 (s, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$), 3.24 (s, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$), 1.59 (m, 8H, THF). ^{13}C NMR (pyridine- d_2): δ 139.30, 128.0, 126.95, 125.31 (C_6H_4), 70.11 (cage C), 67.14 (THF), 39.71 ($\text{C}_6\text{H}_4(\text{CH}_2)$), 25.13 (THF). ^{11}B NMR (pyridine- d_2): δ -7.03 (2), -8.48 (1), -10.16 (1), -14.10 (1), -16.15 (1), -18.92 (2), -35.29 (1). IR (KBr, cm^{-1}): ν 2526 (s), 2388 (w), 2348 (w), 2314(w), 1676 (w), 1616 (m), 1488 (w), 1454 (m), 1259(m), 1094 (s), 1036 (s), 917 (w), 816 (s), 750 (m), 682 (w), 528 (m). Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{B}_{18}\text{Zr}$ (**10** - 2THF): C, 42.87; H, 6.11. Found: C, 43.36; H, 6.65.

Preparation of $[\mu\{-o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]_2\text{Hf}(\text{THF})_2$ (11**).** To a solution of $\text{HfCl}_4(\text{THF})_2$ (0.15 g, 0.54 mmol) in THF (10 mL) was slowly added a THF (10 mL) solution of $[\mu\{-o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$ (0.25 g, 0.54 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. After removal of precipitate and the solvent, the residue was extracted with toluene (2 x 10 mL). The toluene solutions were combined and concentrated to about 15 mL to which was added *n*-hexane (2 mL). $[\mu\{-o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]_2\text{Hf}(\text{THF})_2$ was isolated as needle-shape white microcrystals after the solution stood at room temperature for two days (0.14 g, 62%, based on $[\mu\{-o\text{-C}_6\text{H}_4(\text{CH}_2)_2\}\text{C}_2\text{B}_9\text{H}_9]\text{Na}_2(\text{THF})_3$). ^1H NMR (pyridine- d_5): δ 6.97 (m, 4H, C_6H_4), 3.63 (m, 8H, THF), 3.29 (s, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$), 3.24 (s, 2H, $\text{C}_6\text{H}_4(\text{CH}_2)$), 1.59 (m, 8H, THF). ^{13}C NMR (pyridine- d_2): δ 139.79, 127.61, 126.20 (C_6H_4), 70.75 (cage C), 67.84 (THF), 40.38 ($\text{C}_6\text{H}_4(\text{CH}_2)$), 25.81 (THF). ^{11}B NMR (pyridine- d_2): δ -8.54 (1), -9.94 (2), -18.13 (1), -18.99 (3), -32.93 (1), -35.34 (1). IR (KBr, cm^{-1}): ν 2551 (s),

2349 (w), 2313 (w), 1612 (w), 1489 (w), 1446 (m), 1260 (w), 1091 (m), 1043 (m), 845 (w), 802 (s), 750 (m), 523 (w), 462 (w). Anal. Calcd for C₂₀H₃₄B₁₈Hf (11 - 2THF): C, 37.09; H, 5.29. Found: C, 37.36; H, 5.90.

Preparation of $\{[\mu\text{-}1,2\text{-}(o\text{-C}_6\text{H}_4(\text{CH}_2)_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}]_2\text{Zr}\}\{\text{Na}(\text{THF})_3\}_2$ (12) and $\{[\mu\text{-}1,2\text{-}(o\text{-C}_6\text{H}_4(\text{CH}_2)_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}]_2\text{ZrCl}_2\}\{\text{Na}(\text{THF})_3\}_2\cdot(\text{THF})$ (13).

To a THF solution (25 mL) of $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (0.25 g, 1.00 mmol) was added finely cut Na metal (0.35 g, 15.2 mmol), and the mixture was stirred at room temperature for four days. After removal of excess Na, the resulting clear orange solution was slowly added to a THF solution (20 mL) of ZrCl₄(THF)₂ (0.38 g, 1.00 mmol) at room temperature. The reaction mixture was stirred for two days. Removal of precipitate and the solvent gave a deep blue solid that was extracted with toluene (3 x 15 mL). The clear deep blue toluene solutions were combined and concentrated to about 15 mL. $\{[\mu\text{-}1,2\text{-}(o\text{-C}_6\text{H}_4(\text{CH}_2)_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}]_2\text{Zr}\}\{\text{Na}(\text{THF})_3\}_2$ and $\{[\mu\text{-}1,2\text{-}(o\text{-C}_6\text{H}_4(\text{CH}_2)_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}]_2\text{ZrCl}_2\}\{\text{Na}(\text{THF})_3\}_2\cdot\text{THF}$ were isolated as dark red crystals (0.80 g, 76%, based on $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$) and orange crystals (0.12 g, 10%, based on $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$), respectively, after this solution stood at room temperature for 2 days. For $\{[\mu\text{-}1,2\text{-}(o\text{-C}_6\text{H}_4(\text{CH}_2)_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}]_2\text{Zr}\}\{\text{Na}(\text{THF})_3\}_2$: ¹H NMR (pyridine-*d*₅): δ 7.20-7.12 (m, 4H, C₆H₄), 4.24 (d, *J* = 15.3 Hz, 2H, C₆H₄(CH₂)), 4.16 (d, *J* = 15.3 Hz, 2H, C₆H₄(CH₂)), 3.63 (m, 24H, THF), 1.60 (m, 24H, THF). ¹³C NMR (pyridine-*d*₅): δ 142.11, 137.92, 128.75, 128.00, 126.45, 126.94, 125.71, 125.34, 125.09, 124.47 (C₆H₄), 67.17 (THF), 48.60 (C₆H₄(CH₂)), 25.14 (THF), the cage carbons were not observed. ¹¹B NMR (pyridine-*d*₅): δ 3.54 (1), -2.59 (2), -11.27 (2), -18.30 (1), -20.08 (1), -21.69 (1), -23.70 (1), -25.16 (1). IR (KBr, cm⁻¹): ν 2535 (m), 2355 (w), 2314 (w), 1640

(w), 1453 (w), 1260 (m), 1093 (s), 1042 (s), 904 (w), 802 (s), 695 (w), 669 (w), 540 (m). Anal. Calcd for $C_{40}H_{76}B_{20}Na_2O_5Zr$ (**12** - THF): C, 48.51; H, 7.73. Found: C, 48.95; H, 7.46. For $\{[\mu-1,2-(o-C_6H_4(CH_2)_2)-1,2-C_2B_{10}H_{10}]_2ZrCl_2\}\{Na(THF)_3\}_2 \cdot (THF)$: 1H NMR (pyridine- d_5): δ 7.19 (m, 4H, C_6H_4), 4.24 (d, $J = 15.3$ Hz, 2H, $C_6H_4(CH_2)$), 4.16 (d, $J = 15.3$ Hz, 2H, $C_6H_4(CH_2)$), 3.63 (m, 16H, THF), 1.59 (m, 16H, THF). ^{13}C NMR (pyridine- d_5): δ 137.88, 125.70, 125.33 (C_6H_4), 67.13 (THF), 48.58 ($C_6H_4(CH_2)$), 25.11 (THF), the cage carbons were not observed. ^{11}B NMR (pyridine- d_5): δ 17.60 (1), 11.55 (1), 2.79 (3), -4.34 (2), -7.61 (1), -9.56 (1), -10.82 (1). IR (KBr, cm^{-1}): ν 2522 (m), 2392 (w), 2314 (w), 1636 (w), 1535 (w), 1260 (m), 1093 (s), 1028 (s), 877 (w), 802 (s), 749 (w), 675 (w), 544 (w), 514 (w), 405 (w). Anal. Calcd for $C_{48}H_{92}B_{20}Cl_2Na_2O_7Zr$: C, 47.82; H, 7.69. Found: C, 47.90; H, 7.45.

Reaction of $ZrCl_4(THF)_2$ with 2 equiv of $[\mu\{-o-C_6H_4(CH_2)_2\}C_2B_{10}H_{10}]Na_2$. To a THF solution (25 mL) of $\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}$ (0.25 g, 1.00 mmol) was added finely cut Na metal (0.35 g, 15.2 mmol), and the mixture was stirred at room temperature for four days. After removal of excess Na, the resulting clear orange solution was slowly added to a THF solution (20 mL) of $ZrCl_4(THF)_2$ (0.19 g, 0.50 mmol) at room temperature and the reaction solution became deep blue in colour. The solution was stirred for two days and there was no further observable change. ^{11}B NMR of the solution was run and the pattern of the spectrum was different from that of $[\mu\{-o-C_6H_4(CH_2)_2\}C_2B_{10}H_{10}]Na_2$ in THF solution. ^{11}B NMR (the solution): δ 16.33 (2), 9.94 (2), 1.96 (1), -9.98 (2), -12.05 (1), -19.10 (2). Removal of precipitate and the solvent gave a deep blue solid that was extracted with toluene (3 x 15 mL). The clear deep blue toluene solutions were combined and concentrated to about 15 mL to which was added *n*-hexane (2 mL).

The solution was allowed to stand at room temperature overnight. After filtration, black solid was isolated. ^{11}B NMR was run and the pattern was similar to the previous one. ^{11}B NMR: δ 17.60 (1), 11.55 (2), 2.79 (2), -4.34 (2), -7.61 (1), -9.56 (2). The remaining pale black solution was concentrated to about 15 mL to which was added *n*-hexane (2 mL). The solution was allowed to stand at room temperature overnight. After filtration, μ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀ was recovered as white solid. ^1H NMR (pyridine-*d*₅): δ 7.22 (m, 4H, C₆H₄), 3.68 (s, 4H, C₆H₄(CH₂)), 3.63 (m, 8H, THF), 1.60 (m, 8H, THF). ^{13}C NMR (pyridine-*d*₅): δ 128.72, 128.39, 127.97, 127.13 (C₆H₄), 67.13 (THF), 36.61 (C₆H₄(CH₂)), 25.11 (THF), the cage carbons were not observed. ^{11}B NMR (pyridine-*d*₅): δ 6.21 (3), 1.80 (7). IR (KBr, cm⁻¹): ν 2585 (m), 2401 (w), 2348 (w), 2314 (w), 1616 (w), 1535 (w), 1495 (w), 1448 (w), 1260 (m), 1092 (s), 1023 (s), 802 (s), 545 (m), 427 (m).

Reaction of ZrCl₄(THF)₂ with [μ -{*o*-C₆H₄(CH₂)₂}C₂B₁₀H₁₀]Na₂ at low temperature. To a THF solution (25 mL) of μ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀ (0.25 g, 1.00 mmol) was added finely cut Na metal (0.35 g, 15.2 mmol), and the mixture was stirred at room temperature for four days. After removal of excess Na, the resulting clear orange solution was slowly added to a THF solution (20 mL) of ZrCl₄(THF)₂ (0.38 g, 1.00 mmol) at -78°C. The solution was allowed to warm up to room temperature and became deep blue in colour. The solution was stirred overnight and there was no further observable change. ^{11}B NMR was run and the pattern of the spectrum was different from that of μ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀ in THF solution. ^{11}B NMR (the solution): δ 18.43 (2), 11.65 (1), 9.18 (1), 3.83 (1), -6.09 (1), -8.18 (1), -10.31 (2), -17.36 (1). Removal of precipitate and the solvent gave a deep blue solid that was extracted with toluene (3 x 15 mL). The clear deep blue toluene solutions were combined and concentrated to about 15 mL to

which was added *n*-hexane (2 mL). The solution was allowed to stand at room temperature for crystallization.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N₂ in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-K α radiation. An empirical absorption correction was applied using the SADABS program. 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.⁵⁶ Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For the noncentrosymmetric structure, the appropriate enantiomorph was chosen by refining Flack's parameter x towards zero.⁵⁷ Crystal data and details of data collection and structure refinements are given in Appendix I. Atomic coordinates and thermal parameters are given in Appendix II. Bond distances and angles are listed in Appendix III.

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

2	
Empirical formula	C ₄₈ H ₇₈ B ₁₈ ClNaO ₄ Zr
Formula weight	1063.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 14.287(7)$ Å, $b = 15.103(7)$ Å, $c = 15.133(8)$ Å, $\alpha = 63.35(1)^\circ$, $\beta = 86.49(1)^\circ$, $\gamma = 83.52(1)^\circ$
Volume, Z	2900(2) Å ³ , 2
Density (calculated)	1.218 Mg/m ³
Absorption coefficient	0.284 mm ⁻¹
F(000)	1112
Crystal size	0.34 x 0.32 x 0.21 mm
θ range for data collection	1.51 to 24.00°
Limiting indices	$-13 \leq h \leq 16$, $-14 \leq k \leq 17$, $-15 \leq l \leq 17$
Reflections collected	14457
Independent reflections	9081 ($R_{\text{int}} = 0.0803$)
Completeness to $\theta = 24.00^\circ$	99.7 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.6248
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9081 / 9 / 719
Goodness-of-fit on F ²	0.949
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0803, wR2 = 0.1802
R indices (all data)	R1 = 0.1911, wR2 = 0.2420
Extinction coefficient	0.0016(4)
Largest diff. peak and hole	0.828 and -1.121 eÅ ⁻³

3	
Empirical formula	C ₅₂ H ₈₆ B ₁₈ ClLiO ₅ Zr
Formula weight	1119.40
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 11.5719(8)$ Å, $b = 13.5746(9)$ Å, $c = 19.778(1)$ Å, $\alpha = 87.143(1)^\circ$, $\beta = 85.830(1)^\circ$, $\gamma = 86.252(1)^\circ$
Volume, Z	3088.9(4) Å ³ , 2
Density (calculated)	1.204 Mg/m ³
Absorption coefficient	0.264 mm ⁻¹
F(000)	1176
Crystal size	0.64 x 0.45 x 0.25 mm
θ range for data collection	1.77 to 28.04°
Limiting indices	$-15 \leq h \leq 14$, $-17 \leq k \leq 16$, $-23 \leq l \leq 26$
Reflections collected	20908
Independent reflections	14613 ($R_{\text{int}} = 0.0350$)
Completeness to $\theta = 24.00^\circ$	97.5 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.4415
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14613 / 0 / 703
Goodness-of-fit on F ²	0.942
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0605, wR2 = 0.1487
R indices (all data)	R1 = 0.1025, wR2 = 0.1702
Largest diff. peak and hole	0.910 and -1.207 eÅ ⁻³

4	
Empirical formula	$C_{18}H_{54}ClN_3Si_6Zr$
Formula weight	607.85
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	$a = 15.5562(7)$ Å, $b = 18.3342(13)$ Å, $c = 12.0222(5)$ Å, $\alpha = 90^\circ$, $\beta = 104.5790(10)^\circ$, $\gamma = 90^\circ$
Volume, Z	3318.5(3) Å ³ , 4
Density (calculated)	1.217 Mg/m ³
Absorption coefficient	0.640 mm ⁻¹
F(000)	1296
Crystal size	1.06 x 1.31 x 1.03 mm
θ range for data collection	1.75 to 27.98°
Limiting indices	$-20 \leq h \leq 20$, $-24 \leq k \leq 17$, $-13 \leq l \leq 15$
Reflections collected	11265
Independent reflections	6943 ($R_{int} = 0.0825$)
Completeness to $\theta = 24.00^\circ$	99.5 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.6248
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6943 / 2 / 248
Goodness-of-fit on F^2	1.079
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0684$, $wR2 = 0.1977$
R indices (all data)	$R1 = 0.0704$, $wR2 = 0.2009$
Absolute structure parameter	0.94(6)
Extinction coefficient	0.0013(5)
Largest diff. peak and hole	1.526 and -0.993 eÅ ⁻³

6	
Empirical formula	C ₂₉ H ₅₆ B ₉ Cl ₂ N ₃ Ti
Formula weight	662.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 10.2490(11)$ Å, $b = 11.3742(13)$ Å, $c = 17.818(2)$ Å, $\alpha = 85.430(2)^\circ$, $\beta = 88.300(2)^\circ$, $\gamma = 65.134(2)^\circ$
Volume, Z	1878.6(4) Å ³ , 2
Density (calculated)	1.172 Mg/m ³
Absorption coefficient	0.394 mm ⁻¹
F(000)	704
Crystal size	0.62 x 0.47 x 0.31 mm
θ range for data collection	1.98 to 25.00°
Limiting indices	$-12 \leq h \leq 11$, $-13 \leq k \leq 13$, $-21 \leq l \leq 19$
Reflections collected	10050
Independent reflections	6564 ($R_{\text{int}} = 0.0666$)
Completeness to $\theta = 24.00^\circ$	99.1 %
Absorption correction	SADABS
Max. and min. transmission	1.000 and 0.075523
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6564 / 0 / 434
Goodness-of-fit on F ²	1.065
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0660, wR2 = 0.1829
R indices (all data)	R1 = 0.0744, wR2 = 0.1917
Largest diff. peak and hole	0.745 and -0.452 eÅ ⁻³

11	
Empirical formula	C ₄₄ H ₈₄ B ₂₀ Na ₂ O ₆ Zr
Formula weight	1062.51
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 10.9907(8)$ Å, $b = 12.6526(9)$ Å, $c = 12.7972(9)$ Å, $\alpha = 61.5540(10)^\circ$, $\beta = 79.743(2)^\circ$, $\gamma = 72.676(2)^\circ$
Volume, Z	1492.36(18) Å ³ , 1
Density (calculated)	1.182 Mg/m ³
Absorption coefficient	0.240 mm ⁻¹
F(000)	558
Crystal size	0.82 x 0.47 x 0.26 mm
θ range for data collection	1.81 to 25.00°
Limiting indices	$-13 \leq h \leq 11$, $-15 \leq k \leq 15$, $-14 \leq l \leq 15$
Reflections collected	8089
Independent reflections	5222 ($R_{\text{int}} = 0.0699$)
Completeness to $\theta = 25.00^\circ$	99.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5222 / 30 / 371
Goodness-of-fit on F ²	1.027
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0678, wR2 = 0.1791
R indices (all data)	R1 = 0.0784, wR2 = 0.1889
Largest diff. peak and hole	0.937 and -0.431 eÅ ⁻³

12

Empirical formula	$C_{48}H_{92}B_{20}Cl_2Na_2O_7Zr$
Formula weight	1205.52
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 15.9343(12)$ Å, $b = 24.1026(19)$ Å, $c = 17.6490(13)$ Å, $\alpha = 90^\circ$, $\beta = 101.953(2)^\circ$, $\gamma = 90^\circ$
Volume, Z	6631.3(9) Å ³ , 4
Density (calculated)	1.207 Mg/m ³
Absorption coefficient	0.303 mm ⁻¹
F(000)	2528
Crystal size	0.59 x 0.52 x 0.30 mm
θ range for data collection	1.56 to 25.00°
Limiting indices	$-17 \leq h \leq 18$, $-26 \leq k \leq 28$, $-20 \leq l \leq 20$
Reflections collected	17912
Independent reflections	5842 ($R_{int} = 0.0779$)
Completeness to $\theta = 25.00^\circ$	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5842 / 33 / 362
Goodness-of-fit on F^2	1.105
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0699$, $wR2 = 0.1835$
R indices (all data)	$R1 = 0.1095$, $wR2 = 0.2042$
Largest diff. peak and hole	0.721 and -0.656 eÅ ⁻³

Appendix II. Atomic Coordinates and Thermal Parameters

2				
atom	x	y	z	U(eq)
Zr(1)	7301(1)	7821(1)	5938(1)	43(1)
Cl(1)	5896(1)	8912(1)	5752(1)	59(1)
Na(1)	9725(2)	7331(1)	2598(1)	70(1)
O(5)	8046(2)	8778(2)	6334(2)	55(1)
O(6)	10811(4)	8258(3)	1538(3)	127(2)
O(7)	9143(3)	6865(2)	1485(2)	117(2)
O(8)	10501(3)	6407(2)	4095(2)	72(1)
C(1)	6331(3)	6149(3)	6942(3)	47(2)
C(2)	6371(3)	6535(3)	7769(3)	46(2)
C(3)	7322(3)	10069(3)	3202(3)	44(1)
C(4)	6629(3)	9296(3)	3313(3)	44(1)
C(11)	5429(3)	6388(3)	6308(3)	55(2)
C(12)	4721(3)	5635(3)	6606(3)	46(2)
C(13)	4833(4)	4889(3)	6312(3)	67(2)
C(14)	4155(4)	4209(4)	6567(4)	85(2)
C(15)	3407(4)	4265(4)	7110(5)	98(3)
C(16)	3264(4)	5001(4)	7411(4)	90(2)
C(17)	3935(4)	5669(4)	7153(4)	66(2)
C(21)	5464(4)	7088(3)	7985(3)	65(2)
C(22)	5533(4)	7389(3)	8790(3)	57(2)
C(23)	5952(4)	8229(3)	8628(4)	75(2)
C(24)	6003(5)	8499(4)	9372(5)	95(2)
C(25)	5648(5)	7939(4)	10315(4)	107(3)
C(26)	5207(5)	7110(4)	10478(4)	105(3)
C(27)	5159(4)	6861(4)	9725(3)	76(2)
C(31)	6873(4)	11105(3)	3046(4)	64(2)
C(32)	7528(4)	11898(3)	2701(3)	59(2)
C(33)	7653(4)	12515(3)	1694(4)	76(2)
C(34)	8275(5)	13223(4)	1385(5)	102(3)
C(35)	8833(5)	13325(4)	2034(5)	108(3)
C(36)	8707(5)	12755(3)	3005(5)	100(2)
C(37)	8058(5)	12050(3)	3358(4)	84(2)
C(41)	5563(3)	9659(3)	3212(3)	56(2)
C(42)	4902(4)	8941(3)	3248(3)	57(2)
C(43)	4741(4)	8828(4)	2406(4)	79(2)
C(44)	4148(4)	8141(4)	2450(5)	106(2)
C(45)	3704(4)	7567(4)	3343(5)	104(3)
C(46)	3839(4)	7713(4)	4159(5)	95(3)
C(47)	4441(4)	8389(4)	4112(4)	74(2)
C(51)	7679(4)	9814(3)	6145(4)	81(2)
C(52)	8549(6)	10232(4)	6294(5)	135(3)
C(53)	9142(5)	9396(4)	6967(5)	118(3)
C(54)	9018(4)	8596(4)	6666(4)	87(2)
C(61)	11466(7)	7937(5)	1011(6)	271(4)
C(62)	12109(7)	8549(6)	565(6)	177(5)
C(63)	11855(7)	9405(5)	793(6)	171(5)
C(64)	11002(6)	9200(5)	1316(6)	168(4)
C(71)	9814(9)	6292(9)	1165(6)	219(10)
C(72)	9451(10)	6407(6)	205(6)	168(7)
C(73)	8934(8)	7383(6)	-219(5)	106(5)
C(74)	8763(11)	7683(6)	589(6)	155(7)

C(71')	9264(8)	5999(6)	1380(6)	54(3)
C(72')	8932(11)	6150(9)	476(9)	112(5)
C(73')	8339(12)	6968(10)	193(10)	126(5)
C(74')	8283(9)	7321(7)	900(8)	78(4)
C(81)	11475(5)	6469(5)	4054(5)	109(3)
C(82)	11844(6)	5850(7)	5072(5)	155(4)
C(83)	11014(5)	5519(4)	5743(4)	100(3)
C(84)	10211(4)	6173(4)	5089(4)	87(2)
B(3)	7467(4)	6752(4)	7864(3)	43(2)
B(4)	8210(4)	6352(4)	7087(4)	44(2)
B(5)	7418(4)	6022(3)	6477(4)	48(2)
B(6)	6245(5)	5294(4)	8184(4)	63(2)
B(7)	6999(5)	5668(4)	8791(4)	58(2)
B(8)	8158(5)	5542(4)	8372(4)	54(2)
B(9)	8110(4)	5105(4)	7476(4)	54(2)
B(10)	6924(5)	4942(4)	7354(4)	58(2)
B(11)	7356(5)	4668(4)	8528(4)	63(2)
B(23)	7048(4)	8178(3)	4089(4)	47(2)
B(24)	8132(4)	8263(4)	4452(4)	52(2)
B(25)	8246(4)	9528(4)	3910(4)	49(2)
B(26)	7239(4)	9805(4)	2226(4)	49(2)
B(27)	7089(4)	8526(3)	2778(4)	47(2)
B(28)	8091(4)	7876(4)	3512(4)	52(2)
B(29)	8869(4)	8777(3)	3383(4)	46(2)
B(30)	8339(4)	9931(3)	2597(4)	51(2)
B(31)	8211(4)	8930(3)	2339(4)	51(2)

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atom	x	y	z	U(eq)
Cl(1)	-4722(1)	5793(1)	1737(1)	64(1)
Zr(1)	-5306(1)	7514(1)	1697(1)	42(1)
O(1)	-3614(2)	7813(2)	1141(1)	53(1)
C(1)	-3599(3)	7020(3)	3427(2)	64(1)
C(2)	-4911(3)	6764(3)	3462(2)	56(1)
C(11)	-2659(4)	6187(4)	3574(2)	87(1)
C(12)	-2094(3)	5666(4)	2970(2)	78(1)
C(13)	-2486(5)	4805(4)	2749(4)	122(2)
C(14)	-1978(8)	4328(6)	2201(5)	167(4)
C(15)	-1055(8)	4670(8)	1873(4)	158(4)
C(16)	-622(6)	5528(6)	2047(4)	140(3)
C(17)	-1151(4)	6004(5)	2599(3)	106(2)
C(21)	-6793(2)	6830(2)	618(2)	45(1)
C(22)	-6078(2)	7697(2)	269(2)	46(1)
C(31)	-5208(3)	5676(3)	3585(2)	69(1)
C(32)	-6449(4)	5499(3)	3765(2)	68(1)
C(33)	-6907(5)	5428(3)	4429(2)	92(1)
C(34)	-8037(7)	5256(4)	4586(4)	127(2)
C(35)	-8771(6)	5178(4)	4085(5)	133(3)
C(36)	-8343(5)	5223(4)	3421(4)	117(2)
C(37)	-7188(4)	5382(3)	3260(2)	85(1)
C(41)	-6407(3)	5774(2)	416(2)	53(1)
C(42)	-7257(3)	5004(3)	588(2)	63(1)
C(43)	-7208(4)	4417(3)	1176(3)	90(1)
C(44)	-7952(7)	3663(5)	1309(4)	142(3)
C(45)	-8743(7)	3507(5)	853(6)	150(4)
C(46)	-8829(5)	4085(5)	277(4)	132(3)
C(47)	-8078(4)	4828(4)	132(3)	93(2)
C(51)	-4970(3)	7443(3)	-192(2)	54(1)
C(52)	-4974(3)	7723(2)	-929(2)	51(1)
C(53)	-5320(3)	7096(4)	-1386(2)	78(1)
C(54)	-5287(5)	7366(7)	-2062(3)	132(3)
C(55)	-4901(7)	8215(8)	-2307(3)	155(4)
C(56)	-4520(6)	8865(5)	-1862(4)	142(3)
C(57)	-4550(4)	8612(3)	-1175(2)	87(1)
C(61)	-3172(3)	8784(3)	956(3)	82(1)
C(62)	-1968(4)	8553(5)	667(3)	126(2)
C(63)	-1578(4)	7693(4)	1002(4)	118(2)
C(64)	-2614(3)	7092(3)	1157(3)	85(1)
B(3)	-5595(3)	7502(3)	2954(2)	50(1)
B(4)	-4646(3)	8351(3)	2594(2)	52(1)
B(5)	-3315(4)	7940(3)	2908(2)	64(1)
B(7)	-5815(4)	7687(3)	3839(2)	66(1)
B(8)	-5625(4)	8716(3)	3273(2)	60(1)
B(9)	-4122(4)	8986(4)	3245(2)	72(1)
B(10)	-3449(4)	8126(4)	3787(2)	79(1)
B(11)	-4453(4)	7322(4)	4147(2)	75(1)
B(12)	-4861(5)	8582(4)	4028(2)	78(1)
B(23)	-6141(3)	8642(3)	775(2)	47(1)
B(24)	-7044(3)	8368(3)	1487(2)	46(1)
B(25)	-7350(3)	7148(3)	1381(2)	44(1)
B(27)	-6970(3)	8707(3)	58(2)	54(1)
B(28)	-7613(3)	9140(3)	838(2)	53(1)
B(29)	-8415(3)	8151(3)	1238(2)	50(1)
B(30)	-8252(3)	7165(3)	694(2)	51(1)

B(31)	-7400(3)	7512(3)	-39(2)	52(1)
B(32)	-8392(3)	8390(3)	347(2)	55(1)
O(2)	-10503(3)	1166(3)	2633(2)	104(1)
O(3)	-9860(3)	-462(2)	3673(2)	98(1)
O(4)	-8795(3)	1575(2)	3762(2)	104(1)
O(5)	-11517(3)	1453(2)	4093(2)	91(1)
Li(1)	-10174(7)	936(5)	3562(4)	81(2)
C(65)	-11594(6)	991(7)	2394(3)	166(3)
C(66)	-11452(9)	934(9)	1697(4)	225(5)
C(67)	-10358(8)	1168(8)	1479(3)	197(5)
C(68)	-9776(7)	1368(7)	2080(3)	168(3)
C(71)	-9568(9)	-1082(5)	3119(4)	178(4)
C(72)	-9158(7)	-2008(5)	3361(4)	137(2)
C(73)	-9596(7)	-2089(5)	4059(4)	144(3)
C(74)	-9899(8)	-1076(5)	4262(3)	160(3)
C(81)	-12526(5)	934(5)	4316(3)	119(2)
C(82)	-13545(6)	1559(6)	4133(3)	129(2)
C(83)	-13187(7)	2537(6)	4071(4)	151(3)
C(84)	-11881(6)	2471(5)	4068(4)	132(2)
C(91)	-8575(9)	2519(5)	3766(7)	286(8)
C(92)	-7364(8)	2601(6)	3952(7)	237(6)
C(93)	-6925(6)	1675(7)	4101(4)	159(3)
C(94)	-7789(7)	1056(6)	3939(7)	240(6)

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atom	x	y	z	U(eq)
Zr	4017(1)	2500(1)	4776(1)	26(1)
Si(11)	3647(1)	4254(1)	4586(1)	37(1)
Si(12)	5555(1)	3852(1)	4794(1)	35(1)
Si(21)	5469(1)	1062(1)	4960(1)	35(1)
Si(22)	4614(1)	1713(1)	2656(1)	37(1)
Si(31)	2859(1)	1534(1)	6162(1)	37(1)
Si(32)	4117(1)	2582(1)	7668(2)	34(1)
Cl	2616(1)	2500(1)	3372(2)	52(1)
N(2)	4776(2)	1733(2)	4170(3)	28(1)
N(3)	3708(2)	2193(2)	6290(4)	30(1)
N(1)	4466(3)	3561(2)	4772(4)	31(1)
C(111)	4094(5)	5156(3)	5252(7)	57(2)
C(112)	2757(4)	3998(4)	5292(7)	54(1)
C(113)	3137(5)	4433(4)	3027(7)	62(2)
C(121)	5579(5)	4408(5)	3496(7)	61(2)
C(122)	6104(4)	4412(4)	6066(7)	58(2)
C(123)	6305(4)	3062(4)	4830(8)	58(2)
C(211)	5099(5)	127(3)	4417(8)	62(2)
C(212)	5482(5)	1104(5)	6517(6)	61(2)
C(213)	6674(4)	1146(4)	4964(7)	55(2)
C(221)	3673(5)	1086(4)	1962(7)	62(2)
C(222)	5608(5)	1390(4)	2190(6)	56(2)
C(223)	4370(5)	2653(5)	2002(7)	57(2)
C(311)	1734(4)	1962(4)	5838(8)	63(2)
C(312)	2889(5)	867(4)	5008(6)	53(1)
C(313)	2955(5)	973(4)	7492(7)	58(2)
C(321)	4751(5)	1944(4)	8784(6)	53(1)
C(322)	3198(5)	2956(5)	8248(7)	60(2)
C(323)	4917(5)	3344(4)	7623(7)	62(2)

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atom	x	y	z	U(eq)
Ti(1)	3500(1)	7150(1)	6868(1)	35(1)
Cl(1)	14036(4)	9246(5)	10771(3)	134(2)
Cl(2)	11872(8)	8256(6)	10888(4)	170(2)
C(3)	12348(5)	9561(5)	11016(3)	111(2)
C(10)	315(3)	5665(3)	8567(2)	50(1)
C(11)	-618(3)	6323(3)	9213(2)	51(1)
C(12)	-1962(4)	6328(4)	9312(2)	66(1)
C(13)	-2814(4)	6898(4)	9916(2)	84(1)
C(14)	-2316(5)	7445(4)	10429(2)	86(1)
C(15)	-1004(5)	7448(4)	10338(2)	82(1)
C(16)	-140(4)	6878(4)	9738(2)	67(1)
C(20)	1711(3)	4339(2)	7152(2)	43(1)
C(21)	1014(3)	3517(2)	6875(1)	38(1)
C(22)	1035(4)	3307(3)	6122(2)	61(1)
C(23)	447(5)	2512(3)	5870(2)	75(1)
C(24)	-154(4)	1904(3)	6367(2)	65(1)
C(25)	-179(3)	2092(3)	7112(2)	59(1)
C(26)	399(3)	2888(3)	7364(2)	49(1)
C(31)	3937(3)	5429(3)	8145(2)	49(1)
C(32)	4722(5)	5303(4)	8881(2)	81(1)
C(33)	6027(3)	4536(3)	7306(2)	56(1)
C(34)	5812(4)	3408(4)	7029(3)	87(1)
C(35)	3832(4)	9778(3)	6882(2)	58(1)
C(36)	4506(4)	10642(3)	7112(2)	72(1)
C(38)	3326(12)	8941(8)	8106(5)	73(2)
C(39)	5812(3)	6862(3)	5822(2)	55(1)
C(40)	6570(4)	5688(4)	5369(2)	86(1)
C(41)	3437(4)	7690(3)	5206(2)	60(1)
C(42)	3402(6)	8929(5)	4839(3)	107(2)
B(3)	1502(3)	6706(3)	6596(2)	37(1)
B(4)	1068(3)	8154(2)	7012(2)	36(1)
B(5)	267(3)	7937(3)	7860(2)	37(1)
B(6)	-965(3)	6468(3)	7169(2)	43(1)
B(7)	-111(3)	6622(3)	6313(2)	43(1)
B(8)	-14(3)	8148(3)	6254(2)	42(1)
B(9)	-830(3)	8932(3)	7093(2)	40(1)
B(10)	-1405(3)	7895(3)	7637(2)	42(1)
B(11)	-1562(3)	7990(3)	6641(2)	46(1)
N(1)	4215(3)	8541(2)	7346(1)	50(1)
N(2)	4649(2)	5636(2)	7455(1)	43(1)
N(3)	4264(2)	7245(2)	5910(1)	44(1)
C(1)	180(2)	6543(2)	7843(1)	37(1)
C(2)	872(2)	5820(2)	7111(1)	36(1)
C(37)	2825(10)	9349(11)	8474(5)	102(4)
Cl(1')	14047(6)	8532(5)	11117(4)	197(3)
Cl(2')	11375(8)	9020(7)	10536(5)	211(3)
C(38')	4397(8)	8567(7)	8152(3)	53(1)
C(37')	4311(16)	9007(12)	8669(9)	150(6)

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atom	x	y	z	U(eq)
Zr	0	0	10000	47(1)
C(1)	1799(3)	-833(3)	8955(3)	46(1)
C(2)	2259(3)	-172(3)	9448(3)	45(1)
C(3)	2432(3)	-2219(3)	9417(3)	53(1)
C(4)	4721(4)	-3329(4)	9189(4)	72(1)
C(5)	6013(5)	-3593(4)	9355(5)	85(2)
C(6)	6433(4)	-3017(5)	9854(5)	81(1)
C(7)	5560(4)	-2163(4)	10174(4)	66(1)
C(8)	4272(3)	-1896(3)	10015(3)	53(1)
C(9)	3850(4)	-2499(3)	9531(3)	54(1)
C(10)	3285(3)	-991(4)	10367(3)	51(1)
O(1)	3192(4)	-4188(4)	14135(4)	101(1)
C(11)	2904(8)	-5291(7)	14382(9)	150(3)
C(12)	3618(14)	-5717(12)	13517(11)	226(7)
C(13)	4496(12)	-5004(9)	12947(10)	192(5)
C(14)	4259(8)	-4043(8)	13331(8)	135(3)
B(3)	1689(4)	1255(4)	9171(4)	49(1)
B(4)	228(4)	2088(4)	8397(4)	52(1)
B(5)	-312(4)	1297(4)	7807(4)	52(1)
B(6)	659(4)	-217(4)	8061(4)	50(1)
B(7)	2850(4)	877(4)	8114(4)	55(1)
B(8)	1725(5)	2376(4)	7668(4)	60(1)
B(9)	539(5)	2459(5)	6845(4)	63(1)
B(10)	816(5)	1098(5)	6695(4)	59(1)
B(11)	2251(4)	15(5)	7445(4)	56(1)
B(12)	2145(5)	1612(5)	6733(4)	62(1)
Na	1621(2)	-2652(2)	14415(1)	76(1)
O(2)	965(4)	-3470(4)	16366(3)	92(1)
C(21)	1468(11)	-3559(14)	17327(7)	214(6)
C(22)	562(11)	-3873(11)	18332(6)	177(4)
C(23)	-225(11)	-4388(10)	18079(7)	161(4)
C(24)	-75(7)	-4037(6)	16802(5)	106(2)
O(3)	2693(4)	-1271(4)	14196(4)	107(1)
C(31)	3737(15)	-1016(16)	13630(19)	363(15)
C(32)	3944(12)	45(13)	13643(16)	266(9)
C(33)	2830(12)	661(10)	13844(13)	210(6)
C(34)	2104(12)	-317(13)	14446(15)	280(10)

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atom	x	y	z	U(eq)
Zr	5000	1644(1)	2500	48(1)
C(1)	3342(3)	1812(2)	1520(3)	54(1)
C(2)	3257(3)	1466(2)	2176(3)	52(1)
C(3)	3044(3)	1564(2)	725(3)	65(1)
C(4)	1600(4)	1241(3)	-5(3)	84(2)
C(5)	874(5)	918(4)	-58(4)	109(3)
C(6)	790(4)	583(3)	572(5)	102(2)
C(7)	1424(4)	574(3)	1234(4)	76(2)
C(8)	2161(3)	893(2)	1272(3)	63(1)
C(9)	2250(3)	1225(2)	653(3)	62(1)
C(10)	2871(3)	898(2)	1987(3)	62(1)
O(1)	5420(3)	2099(2)	-513(3)	103(1)
C(11)	4844(6)	2557(5)	-533(6)	196(6)
C(12)	4908(7)	2910(5)	-1138(7)	185(5)
C(13)	5690(7)	2776(6)	-1350(9)	239(8)
C(14)	6032(6)	2291(5)	-888(7)	185(5)
O(2)	4396(4)	899(2)	-660(3)	117(2)
C(21)	3993(7)	401(4)	-613(6)	166(4)
C(22)	3338(14)	287(9)	-1210(13)	139(7)
C(23)	3385(11)	648(7)	-1686(7)	250(9)
C(24)	3896(10)	1128(6)	-1335(7)	296(11)
O(3)	6638(3)	930(2)	-152(3)	118(2)
C(31)	6652(8)	691(5)	-891(6)	178(5)
C(32)	7465(8)	776(5)	-1046(7)	174(4)
C(33)	8038(7)	880(6)	-324(7)	205(6)
C(34)	7510(6)	1054(6)	200(6)	183(5)
O(4)	0	-570(12)	2500	387(13)
C(41)	593(16)	-3(12)	3006(11)	317(13)
C(42)	400(20)	573(10)	2832(12)	400(30)
B(3)	3504(3)	1640(3)	3058(3)	55(1)
B(4)	4219(4)	2207(2)	3339(3)	54(1)
B(5)	4401(3)	2586(2)	2514(3)	56(2)
B(6)	3830(4)	2388(2)	1572(3)	56(1)
B(7)	2732(4)	2424(3)	1647(4)	66(2)
B(8)	2664(4)	2685(3)	2548(4)	69(2)
B(9)	3140(4)	2288(3)	3357(4)	65(2)
B(10)	3706(4)	2854(3)	3094(4)	64(2)
B(11)	3460(4)	2933(3)	2059(4)	65(2)
B(12)	2521(4)	1959(3)	2482(4)	65(2)
Cl	4848(1)	868(1)	1511(1)	61(1)
Na	5479(2)	1324(1)	262(1)	81(1)

Appendix III. Bond Distances (Å) and Angles (°).

2			
Zr(1)-O(5)	2.186(4)	Zr(1)-B(24)	2.328(6)
Zr(1)-Cl(1)	2.3936(16)	Zr(1)-B(4)	2.408(5)
Zr(1)-B(5)	2.451(5)	Zr(1)-B(3)	2.634(5)
Zr(1)-B(23)	2.642(6)	Zr(1)-C(1)	2.774(4)
Na(1)-O(6)	2.261(5)	Na(1)-O(7)	2.322(5)
Na(1)-O(8)	2.331(4)	Na(1)-B(28)	2.868(6)
Na(1)-B(31)	2.955(6)	Na(1)-B(29)	3.037(6)
O(5)-C(54)	1.460(7)	O(5)-C(51)	1.497(5)
O(6)-C(64)	1.364(8)	O(6)-C(61)	1.379(9)
O(7)-C(71')	1.377(10)	O(7)-C(71)	1.426(12)
O(7)-C(74)	1.447(9)	O(7)-C(74')	1.471(12)
O(8)-C(81)	1.401(7)	O(8)-C(84)	1.428(6)
C(1)-C(11)	1.565(7)	C(1)-C(2)	1.606(7)
C(1)-B(5)	1.692(8)	C(1)-B(6)	1.745(6)
C(1)-B(10)	1.767(7)	C(2)-C(21)	1.559(7)
C(2)-B(3)	1.663(8)	C(2)-B(6)	1.717(7)
C(2)-B(7)	1.732(6)	C(3)-C(31)	1.541(6)
C(3)-C(4)	1.561(6)	C(3)-B(25)	1.644(7)
C(3)-B(26)	1.708(8)	C(3)-B(30)	1.712(7)
C(4)-C(41)	1.551(6)	C(4)-B(23)	1.634(6)
C(4)-B(26)	1.703(7)	C(4)-B(27)	1.746(7)
C(11)-C(12)	1.503(7)	C(12)-C(17)	1.364(7)
C(12)-C(13)	1.377(7)	C(13)-C(14)	1.401(8)
C(14)-C(15)	1.328(9)	C(15)-C(16)	1.369(9)
C(16)-C(17)	1.381(8)	C(21)-C(22)	1.490(7)
C(22)-C(23)	1.380(7)	C(22)-C(27)	1.383(6)
C(23)-C(24)	1.367(9)	C(24)-C(25)	1.391(8)
C(25)-C(26)	1.381(9)	C(26)-C(27)	1.357(9)
C(31)-C(32)	1.489(7)	C(32)-C(37)	1.397(8)
C(32)-C(33)	1.398(6)	C(33)-C(34)	1.367(8)
C(34)-C(35)	1.371(10)	C(35)-C(36)	1.341(9)
C(36)-C(37)	1.389(8)	C(41)-C(42)	1.496(7)
C(42)-C(47)	1.371(7)	C(42)-C(43)	1.395(8)
C(43)-C(44)	1.388(9)	C(44)-C(45)	1.397(8)
C(45)-C(46)	1.376(10)	C(46)-C(47)	1.383(8)
C(51)-C(52)	1.526(9)	C(52)-C(53)	1.435(8)
C(53)-C(54)	1.501(9)	C(61)-C(62)	1.308(12)
C(62)-C(63)	1.483(12)	C(63)-C(64)	1.398(11)
C(71)-C(72)	1.502(12)	C(72)-C(73)	1.447(10)
C(73)-C(74)	1.480(12)	C(71')-C(72')	1.387(16)
C(72')-C(73')	1.326(18)	C(73')-C(74')	1.390(19)
C(81)-C(82)	1.490(9)	C(82)-C(83)	1.489(9)
C(83)-C(84)	1.510(8)	B(3)-B(7)	1.780(7)
B(3)-B(4)	1.792(8)	B(3)-B(8)	1.825(7)
B(4)-B(9)	1.724(7)	B(4)-B(5)	1.746(9)
B(4)-B(8)	1.775(7)	B(5)-B(10)	1.767(7)
B(5)-B(9)	1.782(7)	B(6)-B(11)	1.733(9)
B(6)-B(7)	1.746(10)	B(6)-B(10)	1.770(9)
B(7)-B(11)	1.743(9)	B(7)-B(8)	1.757(9)
B(8)-B(9)	1.762(9)	B(8)-B(11)	1.772(9)
B(9)-B(11)	1.772(8)	B(9)-B(10)	1.772(9)
B(10)-B(11)	1.768(9)	B(23)-B(24)	1.711(9)

B(23)-B(28)	1.799(8)	B(23)-B(27)	1.808(8)
B(24)-B(25)	1.732(7)	B(24)-B(28)	1.769(9)
B(24)-B(29)	1.782(7)	B(25)-B(29)	1.792(8)
B(25)-B(30)	1.799(8)	B(26)-B(30)	1.759(9)
B(26)-B(27)	1.760(7)	B(26)-B(31)	1.765(8)
B(27)-B(31)	1.763(8)	B(27)-B(28)	1.773(8)
B(28)-B(29)	1.788(8)	B(28)-B(31)	1.789(7)
B(29)-B(30)	1.727(6)	B(29)-B(31)	1.799(9)
B(30)-B(31)	1.753(8)	O(5)-Zr(1)-B(24)	92.56(18)
O(5)-Zr(1)-Cl(1)	88.76(10)	B(24)-Zr(1)-Cl(1)	111.82(13)
O(5)-Zr(1)-B(4)	91.56(17)	B(24)-Zr(1)-B(4)	103.86(18)
Cl(1)-Zr(1)-B(4)	144.27(14)	O(5)-Zr(1)-B(5)	133.67(16)
B(24)-Zr(1)-B(5)	97.82(19)	Cl(1)-Zr(1)-B(5)	127.32(15)
B(4)-Zr(1)-B(5)	42.1(2)	O(5)-Zr(1)-B(3)	78.33(15)
B(24)-Zr(1)-B(3)	142.56(18)	Cl(1)-Zr(1)-B(3)	104.28(12)
B(4)-Zr(1)-B(3)	41.32(18)	B(5)-Zr(1)-B(3)	66.23(18)
O(5)-Zr(1)-B(23)	122.94(14)	B(24)-Zr(1)-B(23)	39.6(2)
Cl(1)-Zr(1)-B(23)	86.15(12)	B(4)-Zr(1)-B(23)	122.48(18)
B(5)-Zr(1)-B(23)	91.10(17)	B(3)-Zr(1)-B(23)	157.03(17)
O(5)-Zr(1)-C(1)	136.34(13)	B(24)-Zr(1)-C(1)	126.98(18)
Cl(1)-Zr(1)-C(1)	91.88(11)	B(4)-Zr(1)-C(1)	64.11(17)
B(5)-Zr(1)-C(1)	37.15(17)	B(3)-Zr(1)-C(1)	59.25(16)
B(23)-Zr(1)-C(1)	100.65(16)	O(6)-Na(1)-O(7)	95.01(19)
O(6)-Na(1)-O(8)	105.42(18)	O(7)-Na(1)-O(8)	131.72(15)
O(6)-Na(1)-B(28)	131.23(17)	O(7)-Na(1)-B(28)	105.2(2)
O(8)-Na(1)-B(28)	93.39(16)	O(6)-Na(1)-B(31)	99.25(16)
O(7)-Na(1)-B(31)	96.33(18)	O(8)-Na(1)-B(31)	121.92(17)
B(28)-Na(1)-B(31)	35.74(14)	O(6)-Na(1)-B(29)	99.63(17)
O(7)-Na(1)-B(29)	130.63(17)	O(8)-Na(1)-B(29)	88.88(15)
B(28)-Na(1)-B(29)	35.11(16)	B(31)-Na(1)-B(29)	34.92(16)
C(54)-O(5)-C(51)	108.5(4)	C(54)-O(5)-Zr(1)	126.8(3)
C(51)-O(5)-Zr(1)	124.1(3)	C(64)-O(6)-C(61)	105.4(6)
C(64)-O(6)-Na(1)	129.3(5)	C(61)-O(6)-Na(1)	125.2(4)
C(71')-O(7)-C(71)	38.0(7)	C(71')-O(7)-C(74)	110.3(6)
C(71)-O(7)-C(74)	105.5(6)	C(71')-O(7)-C(74')	98.7(7)
C(71)-O(7)-C(74')	117.7(7)	C(74)-O(7)-C(74')	35.8(7)
C(71')-O(7)-Na(1)	133.0(4)	C(71)-O(7)-Na(1)	114.3(6)
C(74)-O(7)-Na(1)	114.8(5)	C(74')-O(7)-Na(1)	125.6(5)
C(81)-O(8)-C(84)	106.3(4)	C(81)-O(8)-Na(1)	115.2(3)
C(84)-O(8)-Na(1)	131.5(3)	C(11)-C(1)-C(2)	121.1(4)
C(11)-C(1)-B(5)	121.2(4)	C(2)-C(1)-B(5)	111.1(4)
C(11)-C(1)-B(6)	116.2(4)	C(2)-C(1)-B(6)	61.5(3)
B(5)-C(1)-B(6)	111.1(4)	C(11)-C(1)-B(10)	117.1(4)
C(2)-C(1)-B(10)	110.2(3)	B(5)-C(1)-B(10)	61.4(3)
B(6)-C(1)-B(10)	60.5(3)	C(11)-C(1)-Zr(1)	103.6(2)
C(2)-C(1)-Zr(1)	78.7(2)	B(5)-C(1)-Zr(1)	61.0(2)
B(6)-C(1)-Zr(1)	133.7(3)	B(10)-C(1)-Zr(1)	120.7(3)
C(21)-C(2)-C(1)	118.6(4)	C(21)-C(2)-B(3)	125.0(4)
C(1)-C(2)-B(3)	109.8(4)	C(21)-C(2)-B(6)	111.1(4)
C(1)-C(2)-B(6)	63.3(3)	B(3)-C(2)-B(6)	113.0(4)
C(21)-C(2)-B(7)	116.2(4)	C(1)-C(2)-B(7)	111.4(4)
B(3)-C(2)-B(7)	63.2(3)	B(6)-C(2)-B(7)	60.8(3)
C(31)-C(3)-C(4)	116.4(4)	C(31)-C(3)-B(25)	121.1(4)
C(4)-C(3)-B(25)	111.2(3)	C(31)-C(3)-B(26)	115.3(3)
C(4)-C(3)-B(26)	62.6(3)	B(25)-C(3)-B(26)	116.2(4)
C(31)-C(3)-B(30)	121.4(3)	C(4)-C(3)-B(30)	111.6(4)
B(25)-C(3)-B(30)	64.8(3)	B(26)-C(3)-B(30)	61.9(3)
C(41)-C(4)-C(3)	117.0(3)	C(41)-C(4)-B(23)	123.5(4)

C(3)-C(4)-B(23)	110.2(4)	C(41)-C(4)-B(26)	113.3(3)
C(3)-C(4)-B(26)	62.9(3)	B(23)-C(4)-B(26)	114.8(4)
C(41)-C(4)-B(27)	119.2(4)	C(3)-C(4)-B(27)	111.6(4)
B(23)-C(4)-B(27)	64.6(3)	B(26)-C(4)-B(27)	61.4(3)
C(12)-C(11)-C(1)	119.8(3)	C(17)-C(12)-C(13)	116.9(5)
C(17)-C(12)-C(11)	122.3(5)	C(13)-C(12)-C(11)	120.7(4)
C(12)-C(13)-C(14)	120.4(5)	C(15)-C(14)-C(13)	120.4(6)
C(14)-C(15)-C(16)	121.1(6)	C(15)-C(16)-C(17)	118.0(6)
C(12)-C(17)-C(16)	123.2(6)	C(22)-C(21)-C(2)	116.1(4)
C(23)-C(22)-C(27)	116.6(5)	C(23)-C(22)-C(21)	121.3(4)
C(27)-C(22)-C(21)	122.1(5)	C(24)-C(23)-C(22)	120.6(5)
C(23)-C(24)-C(25)	121.7(6)	C(26)-C(25)-C(24)	118.1(6)
C(27)-C(26)-C(25)	119.0(6)	C(26)-C(27)-C(22)	123.9(6)
C(32)-C(31)-C(3)	115.5(4)	C(37)-C(32)-C(33)	116.9(5)
C(37)-C(32)-C(31)	122.1(4)	C(33)-C(32)-C(31)	121.0(5)
C(34)-C(33)-C(32)	120.4(6)	C(33)-C(34)-C(35)	122.1(6)
C(36)-C(35)-C(34)	118.2(6)	C(35)-C(36)-C(37)	121.9(7)
C(36)-C(37)-C(32)	120.3(5)	C(42)-C(41)-C(4)	117.0(4)
C(47)-C(42)-C(43)	119.0(5)	C(47)-C(42)-C(41)	120.2(5)
C(43)-C(42)-C(41)	120.7(4)	C(44)-C(43)-C(42)	120.6(5)
C(43)-C(44)-C(45)	119.6(7)	C(46)-C(45)-C(44)	119.3(6)
C(45)-C(46)-C(47)	120.6(6)	C(42)-C(47)-C(46)	120.8(6)
O(5)-C(51)-C(52)	102.7(5)	C(53)-C(52)-C(51)	106.4(5)
C(52)-C(53)-C(54)	103.2(6)	O(5)-C(54)-C(53)	105.5(5)
C(62)-C(61)-O(6)	113.9(8)	C(61)-C(62)-C(63)	105.2(8)
C(64)-C(63)-C(62)	104.5(7)	O(6)-C(64)-C(63)	110.0(7)
O(7)-C(71)-C(72)	105.7(8)	C(73)-C(72)-C(71)	104.5(7)
C(72)-C(73)-C(74)	106.8(6)	O(7)-C(74)-C(73)	107.5(7)
O(7)-C(71')-C(72')	111.1(8)	C(73')-C(72')-C(71')	104.6(13)
C(72')-C(73')-C(74')	110.4(13)	C(73')-C(74')-O(7)	104.6(10)
O(8)-C(81)-C(82)	107.5(5)	C(83)-C(82)-C(81)	107.1(6)
C(82)-C(83)-C(84)	102.0(5)	O(8)-C(84)-C(83)	106.7(5)
C(2)-B(3)-B(7)	60.3(3)	C(2)-B(3)-B(4)	107.8(4)
B(7)-B(3)-B(4)	106.3(4)	C(2)-B(3)-B(8)	106.2(4)
B(7)-B(3)-B(8)	58.3(3)	B(4)-B(3)-B(8)	58.8(3)
C(2)-B(3)-Zr(1)	82.2(2)	B(7)-B(3)-Zr(1)	136.4(4)
B(4)-B(3)-Zr(1)	62.6(2)	B(8)-B(3)-Zr(1)	120.5(3)
B(9)-B(4)-B(5)	61.8(3)	B(9)-B(4)-B(8)	60.4(3)
B(5)-B(4)-B(8)	108.8(4)	B(9)-B(4)-B(3)	108.1(4)
B(5)-B(4)-B(3)	103.7(4)	B(8)-B(4)-B(3)	61.5(3)
B(9)-B(4)-Zr(1)	131.6(4)	B(5)-B(4)-Zr(1)	70.2(2)
B(8)-B(4)-Zr(1)	136.4(4)	B(3)-B(4)-Zr(1)	76.1(2)
C(1)-B(5)-B(4)	107.2(4)	C(1)-B(5)-B(10)	61.4(3)
B(4)-B(5)-B(10)	108.1(4)	C(1)-B(5)-B(9)	107.0(4)
B(4)-B(5)-B(9)	58.5(3)	B(10)-B(5)-B(9)	59.9(3)
C(1)-B(5)-Zr(1)	81.9(2)	B(4)-B(5)-Zr(1)	67.6(2)
B(10)-B(5)-Zr(1)	140.5(4)	B(9)-B(5)-Zr(1)	125.7(4)
C(2)-B(6)-B(11)	106.5(5)	C(2)-B(6)-C(1)	55.3(3)
B(11)-B(6)-C(1)	106.6(4)	C(2)-B(6)-B(7)	60.0(3)
B(11)-B(6)-B(7)	60.1(4)	C(1)-B(6)-B(7)	104.4(4)
C(2)-B(6)-B(10)	105.1(4)	B(11)-B(6)-B(10)	60.6(4)
C(1)-B(6)-B(10)	60.4(3)	B(7)-B(6)-B(10)	108.4(5)
C(2)-B(7)-B(11)	105.5(4)	C(2)-B(7)-B(6)	59.2(3)
B(11)-B(7)-B(6)	59.6(4)	C(2)-B(7)-B(8)	106.3(4)
B(11)-B(7)-B(8)	60.8(4)	B(6)-B(7)-B(8)	108.8(5)
C(2)-B(7)-B(3)	56.5(3)	B(11)-B(7)-B(3)	108.7(4)
B(6)-B(7)-B(3)	106.1(4)	B(8)-B(7)-B(3)	62.1(3)
B(7)-B(8)-B(9)	107.3(5)	B(7)-B(8)-B(11)	59.2(4)

B(9)-B(8)-B(11)	60.2(4)	B(7)-B(8)-B(4)	108.1(4)
B(9)-B(8)-B(4)	58.3(3)	B(11)-B(8)-B(4)	106.8(4)
B(7)-B(8)-B(3)	59.6(3)	B(9)-B(8)-B(3)	105.1(4)
B(11)-B(8)-B(3)	105.5(4)	B(4)-B(8)-B(3)	59.7(3)
B(4)-B(9)-B(8)	61.2(3)	B(4)-B(9)-B(11)	109.1(4)
B(8)-B(9)-B(11)	60.2(4)	B(4)-B(9)-B(10)	108.9(4)
B(8)-B(9)-B(10)	108.7(4)	B(11)-B(9)-B(10)	59.8(4)
B(4)-B(9)-B(5)	59.7(3)	B(8)-B(9)-B(5)	107.8(4)
B(11)-B(9)-B(5)	106.8(4)	B(10)-B(9)-B(5)	59.6(3)
B(11)-B(10)-C(1)	104.2(4)	B(11)-B(10)-B(5)	107.6(5)
C(1)-B(10)-B(5)	57.2(3)	B(11)-B(10)-B(6)	58.7(4)
C(1)-B(10)-B(6)	59.1(3)	B(5)-B(10)-B(6)	106.5(4)
B(11)-B(10)-B(9)	60.1(4)	C(1)-B(10)-B(9)	104.2(4)
B(5)-B(10)-B(9)	60.5(3)	B(6)-B(10)-B(9)	106.8(5)
B(6)-B(11)-B(7)	60.3(4)	B(6)-B(11)-B(10)	60.7(4)
B(7)-B(11)-B(10)	108.6(4)	B(6)-B(11)-B(9)	108.4(4)
B(7)-B(11)-B(9)	107.4(4)	B(10)-B(11)-B(9)	60.1(3)
B(6)-B(11)-B(8)	108.7(4)	B(7)-B(11)-B(8)	60.0(4)
B(10)-B(11)-B(8)	108.4(4)	B(9)-B(11)-B(8)	59.6(4)
C(4)-B(23)-B(24)	107.7(4)	C(4)-B(23)-B(28)	106.2(3)
B(24)-B(23)-B(28)	60.5(4)	C(4)-B(23)-B(27)	60.7(3)
B(24)-B(23)-B(27)	109.0(4)	B(28)-B(23)-B(27)	58.9(3)
C(4)-B(23)-Zr(1)	118.0(3)	B(24)-B(23)-Zr(1)	60.2(3)
B(28)-B(23)-Zr(1)	113.5(3)	B(27)-B(23)-Zr(1)	168.9(4)
B(23)-B(24)-B(25)	104.4(4)	B(23)-B(24)-B(28)	62.2(4)
B(25)-B(24)-B(28)	109.0(4)	B(23)-B(24)-B(29)	108.6(4)
B(25)-B(24)-B(29)	61.3(3)	B(28)-B(24)-B(29)	60.5(3)
B(23)-B(24)-Zr(1)	80.1(3)	B(25)-B(24)-Zr(1)	109.2(3)
B(28)-B(24)-Zr(1)	131.5(4)	B(29)-B(24)-Zr(1)	168.0(4)
C(3)-B(25)-B(24)	106.1(4)	C(3)-B(25)-B(29)	104.5(4)
B(24)-B(25)-B(29)	60.7(3)	C(3)-B(25)-B(30)	59.4(3)
B(24)-B(25)-B(30)	106.8(4)	B(29)-B(25)-B(30)	57.5(3)
C(4)-B(26)-C(3)	54.5(3)	C(4)-B(26)-B(30)	103.0(4)
C(3)-B(26)-B(30)	59.2(3)	C(4)-B(26)-B(27)	60.5(3)
C(3)-B(26)-B(27)	104.2(3)	B(30)-B(26)-B(27)	107.4(4)
C(4)-B(26)-B(31)	105.6(3)	C(3)-B(26)-B(31)	105.0(4)
B(30)-B(26)-B(31)	59.7(3)	B(27)-B(26)-B(31)	60.0(3)
C(4)-B(27)-B(26)	58.1(3)	C(4)-B(27)-B(31)	103.9(4)
B(26)-B(27)-B(31)	60.1(3)	C(4)-B(27)-B(28)	102.6(4)
B(26)-B(27)-B(28)	107.9(4)	B(31)-B(27)-B(28)	60.8(3)
C(4)-B(27)-B(23)	54.7(3)	B(26)-B(27)-B(23)	104.0(4)
B(31)-B(27)-B(23)	107.1(4)	B(28)-B(27)-B(23)	60.3(3)
B(24)-B(28)-B(27)	108.0(4)	B(24)-B(28)-B(29)	60.1(3)
B(27)-B(28)-B(29)	107.6(3)	B(24)-B(28)-B(31)	108.5(4)
B(27)-B(28)-B(31)	59.3(3)	B(29)-B(28)-B(31)	60.4(3)
B(24)-B(28)-B(23)	57.3(3)	B(27)-B(28)-B(23)	60.8(3)
B(29)-B(28)-B(23)	104.5(4)	B(31)-B(28)-B(23)	106.4(3)
B(24)-B(28)-Na(1)	124.2(4)	B(27)-B(28)-Na(1)	118.9(3)
B(29)-B(28)-Na(1)	77.6(3)	B(31)-B(28)-Na(1)	74.8(3)
B(23)-B(28)-Na(1)	177.8(4)	B(30)-B(29)-B(24)	107.8(4)
B(30)-B(29)-B(28)	107.2(4)	B(24)-B(29)-B(28)	59.4(3)
B(30)-B(29)-B(25)	61.5(3)	B(24)-B(29)-B(25)	58.0(3)
B(28)-B(29)-B(25)	105.5(4)	B(30)-B(29)-B(31)	59.6(3)
B(24)-B(29)-B(31)	107.5(4)	B(28)-B(29)-B(31)	59.8(3)
B(25)-B(29)-B(31)	107.8(4)	B(30)-B(29)-Na(1)	120.9(3)
B(24)-B(29)-Na(1)	115.5(3)	B(28)-B(29)-Na(1)	67.3(3)
B(25)-B(29)-Na(1)	172.7(3)	B(31)-B(29)-Na(1)	70.1(3)
C(3)-B(30)-B(29)	104.5(3)	C(3)-B(30)-B(31)	105.4(4)

B(29)-B(30)-B(31)	62.3(3)	C(3)-B(30)-B(26)	58.9(3)
B(29)-B(30)-B(26)	109.9(4)	B(31)-B(30)-B(26)	60.4(3)
C(3)-B(30)-B(25)	55.8(3)	B(29)-B(30)-B(25)	61.0(3)
B(31)-B(30)-B(25)	109.5(3)	B(26)-B(30)-B(25)	106.2(4)
B(30)-B(31)-B(27)	107.5(4)	B(30)-B(31)-B(26)	60.0(3)
B(27)-B(31)-B(26)	59.8(3)	B(30)-B(31)-B(28)	106.1(4)
B(27)-B(31)-B(28)	59.9(3)	B(26)-B(31)-B(28)	107.0(4)
B(30)-B(31)-B(29)	58.1(3)	B(27)-B(31)-B(29)	107.6(4)
B(26)-B(31)-B(29)	106.4(4)	B(28)-B(31)-B(29)	59.8(3)
B(30)-B(31)-Na(1)	123.9(4)	B(27)-B(31)-Na(1)	115.3(3)
B(26)-B(31)-Na(1)	175.1(3)	B(28)-B(31)-Na(1)	69.5(2)
B(29)-B(31)-Na(1)	75.0(2)		

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Cl(1)-Zr(1)	2.3883(9)	Zr(1)-O(1)	2.226(2)
Zr(1)-B(24)	2.308(3)	Zr(1)-B(4)	2.353(3)
Zr(1)-B(3)	2.483(4)	Zr(1)-B(23)	2.529(3)
Zr(1)-B(25)	2.576(3)	O(1)-C(61)	1.465(4)
O(1)-C(64)	1.468(4)	C(1)-C(11)	1.549(5)
C(1)-C(2)	1.575(5)	C(1)-B(5)	1.612(6)
C(1)-B(10)	1.718(6)	C(1)-B(11)	1.724(6)
C(2)-C(31)	1.541(5)	C(2)-B(3)	1.598(5)
C(2)-B(11)	1.717(5)	C(2)-B(7)	1.740(6)
C(11)-C(12)	1.505(6)	C(12)-C(17)	1.362(6)
C(12)-C(13)	1.382(7)	C(13)-C(14)	1.367(10)
C(14)-C(15)	1.309(11)	C(15)-C(16)	1.366(10)
C(16)-C(17)	1.380(9)	C(21)-C(41)	1.536(4)
C(21)-C(22)	1.584(4)	C(21)-B(25)	1.663(4)
C(21)-B(30)	1.717(4)	C(21)-B(31)	1.722(5)
C(22)-C(51)	1.549(4)	C(22)-B(23)	1.660(5)
C(22)-B(27)	1.714(5)	C(22)-B(31)	1.724(4)
C(31)-C(32)	1.486(5)	C(32)-C(33)	1.380(6)
C(32)-C(37)	1.384(6)	C(33)-C(34)	1.354(8)
C(34)-C(35)	1.363(9)	C(35)-C(36)	1.370(9)
C(36)-C(37)	1.380(7)	C(41)-C(42)	1.492(5)
C(42)-C(43)	1.379(6)	C(42)-C(47)	1.395(6)
C(43)-C(44)	1.384(7)	C(44)-C(45)	1.363(11)
C(45)-C(46)	1.357(10)	C(46)-C(47)	1.380(8)
C(51)-C(52)	1.489(4)	C(52)-C(53)	1.369(5)
C(52)-C(57)	1.385(5)	C(53)-C(54)	1.368(7)
C(54)-C(55)	1.321(10)	C(55)-C(56)	1.390(11)
C(56)-C(57)	1.384(8)	C(61)-C(62)	1.488(6)
C(62)-C(63)	1.380(7)	C(63)-C(64)	1.498(6)
B(3)-B(4)	1.734(5)	B(3)-B(7)	1.778(5)
B(3)-B(8)	1.790(5)	B(4)-B(5)	1.750(5)
B(4)-B(9)	1.749(5)	B(4)-B(8)	1.761(6)
B(5)-B(10)	1.764(6)	B(5)-B(9)	1.779(7)
B(7)-B(8)	1.761(6)	B(7)-B(11)	1.763(6)
B(7)-B(12)	1.765(6)	B(8)-B(12)	1.785(6)
B(8)-B(9)	1.797(6)	B(9)-B(10)	1.731(7)
B(9)-B(12)	1.792(7)	B(10)-B(11)	1.736(7)
B(10)-B(12)	1.750(7)	B(11)-B(12)	1.753(7)
B(23)-B(24)	1.732(5)	B(23)-B(27)	1.764(5)
B(23)-B(28)	1.789(5)	B(24)-B(29)	1.742(5)
B(24)-B(25)	1.742(5)	B(24)-B(28)	1.755(5)
B(25)-B(30)	1.771(5)	B(25)-B(29)	1.801(5)
B(27)-B(31)	1.751(6)	B(27)-B(28)	1.773(6)
B(27)-B(32)	1.774(5)	B(28)-B(32)	1.771(5)
B(28)-B(29)	1.800(6)	B(29)-B(30)	1.751(5)
B(29)-B(32)	1.774(5)	B(30)-B(31)	1.755(5)
B(30)-B(32)	1.769(6)	B(31)-B(32)	1.762(5)
O(2)-C(68)	1.358(7)	O(2)-C(65)	1.418(6)
O(2)-Li(1)	1.910(8)	O(3)-C(74)	1.399(7)
O(3)-C(71)	1.422(7)	O(3)-Li(1)	1.913(8)
O(4)-C(91)	1.323(7)	O(4)-C(94)	1.379(8)
O(4)-Li(1)	1.940(8)	O(5)-C(84)	1.418(7)
O(5)-C(81)	1.434(6)	O(5)-Li(1)	1.924(9)
C(65)-C(66)	1.382(9)	C(66)-C(67)	1.360(10)
C(67)-C(68)	1.454(8)	C(71)-C(72)	1.388(8)
C(72)-C(73)	1.437(9)	C(73)-C(74)	1.466(8)

C(81)-C(82)	1.464(8)	C(82)-C(83)	1.413(8)
C(83)-C(84)	1.507(9)	C(91)-C(92)	1.487(10)
C(92)-C(93)	1.352(10)	C(93)-C(94)	1.410(9)
O(1)-Zr(1)-B(24)	124.13(11)	O(1)-Zr(1)-B(4)	86.31(11)
B(24)-Zr(1)-B(4)	103.32(13)	O(1)-Zr(1)-Cl(1)	88.98(6)
B(24)-Zr(1)-Cl(1)	132.46(9)	B(4)-Zr(1)-Cl(1)	112.79(10)
O(1)-Zr(1)-B(3)	122.53(10)	B(24)-Zr(1)-B(3)	96.14(13)
B(4)-Zr(1)-B(3)	41.92(13)	Cl(1)-Zr(1)-B(3)	91.11(9)
O(1)-Zr(1)-B(23)	83.83(10)	B(24)-Zr(1)-B(23)	41.64(12)
B(4)-Zr(1)-B(23)	114.04(13)	Cl(1)-Zr(1)-B(23)	131.94(9)
B(3)-Zr(1)-B(23)	132.08(12)	O(1)-Zr(1)-B(25)	136.47(9)
B(24)-Zr(1)-B(25)	41.33(12)	B(4)-Zr(1)-B(25)	132.60(12)
Cl(1)-Zr(1)-B(25)	91.15(8)	B(3)-Zr(1)-B(25)	100.99(12)
B(23)-Zr(1)-B(25)	64.37(11)	C(61)-O(1)-C(64)	107.7(3)
C(61)-O(1)-Zr(1)	126.7(2)	C(64)-O(1)-Zr(1)	121.5(2)
C(11)-C(1)-C(2)	119.1(3)	C(11)-C(1)-B(5)	121.0(3)
C(2)-C(1)-B(5)	113.2(3)	C(11)-C(1)-B(10)	116.0(3)
C(2)-C(1)-B(10)	111.1(3)	B(5)-C(1)-B(10)	63.9(3)
C(11)-C(1)-B(11)	112.1(3)	C(2)-C(1)-B(11)	62.6(2)
B(5)-C(1)-B(11)	114.9(3)	B(10)-C(1)-B(11)	60.6(3)
C(31)-C(2)-C(1)	118.8(3)	C(31)-C(2)-B(3)	121.9(3)
C(1)-C(2)-B(3)	109.2(3)	C(31)-C(2)-B(11)	115.9(3)
C(1)-C(2)-B(11)	63.0(2)	B(3)-C(2)-B(11)	113.9(3)
C(31)-C(2)-B(7)	119.3(3)	C(1)-C(2)-B(7)	111.6(3)
B(3)-C(2)-B(7)	64.2(2)	B(11)-C(2)-B(7)	61.3(2)
C(12)-C(11)-C(1)	116.6(3)	C(17)-C(12)-C(13)	114.6(5)
C(17)-C(12)-C(11)	122.6(5)	C(13)-C(12)-C(11)	122.8(5)
C(14)-C(13)-C(12)	123.1(7)	C(15)-C(14)-C(13)	119.7(8)
C(14)-C(15)-C(16)	121.1(9)	C(15)-C(16)-C(17)	118.3(8)
C(12)-C(17)-C(16)	123.0(6)	C(41)-C(21)-C(22)	117.0(3)
C(41)-C(21)-B(25)	125.5(3)	C(22)-C(21)-B(25)	109.8(2)
C(41)-C(21)-B(30)	118.5(2)	C(22)-C(21)-B(30)	111.2(2)
B(25)-C(21)-B(30)	63.15(19)	C(41)-C(21)-B(31)	111.7(2)
C(22)-C(21)-B(31)	62.7(2)	B(25)-C(21)-B(31)	113.5(2)
B(30)-C(21)-B(31)	61.4(2)	C(51)-C(22)-C(21)	119.4(3)
C(51)-C(22)-B(23)	120.7(3)	C(21)-C(22)-B(23)	110.1(2)
C(51)-C(22)-B(27)	119.4(3)	C(21)-C(22)-B(27)	111.6(2)
B(23)-C(22)-B(27)	63.0(2)	C(51)-C(22)-B(31)	117.7(3)
C(21)-C(22)-B(31)	62.6(2)	B(23)-C(22)-B(31)	112.8(2)
B(27)-C(22)-B(31)	61.2(2)	C(32)-C(31)-C(2)	116.4(3)
C(33)-C(32)-C(37)	117.5(4)	C(33)-C(32)-C(31)	122.5(4)
C(37)-C(32)-C(31)	120.0(4)	C(34)-C(33)-C(32)	121.8(6)
C(33)-C(34)-C(35)	120.5(7)	C(34)-C(35)-C(36)	119.4(6)
C(35)-C(36)-C(37)	120.2(6)	C(36)-C(37)-C(32)	120.6(5)
C(42)-C(41)-C(21)	116.5(3)	C(43)-C(42)-C(47)	118.7(4)
C(43)-C(42)-C(41)	121.1(4)	C(47)-C(42)-C(41)	120.1(4)
C(42)-C(43)-C(44)	120.6(6)	C(45)-C(44)-C(43)	119.3(7)
C(46)-C(45)-C(44)	121.4(7)	C(45)-C(46)-C(47)	119.8(7)
C(46)-C(47)-C(42)	120.1(6)	C(52)-C(51)-C(22)	118.4(3)
C(53)-C(52)-C(57)	118.1(4)	C(53)-C(52)-C(51)	121.8(3)
C(57)-C(52)-C(51)	119.9(3)	C(52)-C(53)-C(54)	120.4(5)
C(55)-C(54)-C(53)	122.4(6)	C(54)-C(55)-C(56)	119.0(6)
C(57)-C(56)-C(55)	119.6(6)	C(56)-C(57)-C(52)	120.3(5)
O(1)-C(61)-C(62)	104.0(4)	C(63)-C(62)-C(61)	106.2(4)
C(62)-C(63)-C(64)	106.6(4)	O(1)-C(64)-C(63)	104.7(4)
C(2)-B(3)-B(4)	108.5(3)	C(2)-B(3)-B(7)	61.8(2)
B(4)-B(3)-B(7)	108.8(3)	C(2)-B(3)-B(8)	107.8(3)
B(4)-B(3)-B(8)	59.9(2)	B(7)-B(3)-B(8)	59.1(2)

C(2)-B(3)-Zr(1)	124.8(2)	B(4)-B(3)-Zr(1)	65.01(17)
B(7)-B(3)-Zr(1)	171.6(3)	B(8)-B(3)-Zr(1)	112.5(2)
B(3)-B(4)-B(5)	103.5(3)	B(3)-B(4)-B(9)	108.6(3)
B(5)-B(4)-B(9)	61.1(3)	B(3)-B(4)-B(8)	61.6(2)
B(5)-B(4)-B(8)	109.3(3)	B(9)-B(4)-B(8)	61.6(2)
B(3)-B(4)-Zr(1)	73.07(17)	B(5)-B(4)-Zr(1)	118.2(2)
B(9)-B(4)-Zr(1)	178.3(3)	B(8)-B(4)-Zr(1)	119.9(2)
C(1)-B(5)-B(4)	105.3(3)	C(1)-B(5)-B(10)	61.0(3)
B(4)-B(5)-B(10)	106.5(3)	C(1)-B(5)-B(9)	106.0(3)
B(4)-B(5)-B(9)	59.4(2)	B(10)-B(5)-B(9)	58.5(3)
C(2)-B(7)-B(8)	103.0(3)	C(2)-B(7)-B(11)	58.7(2)
B(8)-B(7)-B(11)	107.6(3)	C(2)-B(7)-B(12)	104.2(3)
B(8)-B(7)-B(12)	60.8(3)	B(11)-B(7)-B(12)	59.6(3)
C(2)-B(7)-B(3)	54.0(2)	B(8)-B(7)-B(3)	60.8(2)
B(11)-B(7)-B(3)	103.5(3)	B(12)-B(7)-B(3)	107.0(3)
B(7)-B(8)-B(4)	108.4(3)	B(7)-B(8)-B(12)	59.7(3)
B(4)-B(8)-B(12)	107.4(3)	B(7)-B(8)-B(3)	60.1(2)
B(4)-B(8)-B(3)	58.5(2)	B(12)-B(8)-B(3)	105.6(3)
B(7)-B(8)-B(9)	107.5(3)	B(4)-B(8)-B(9)	58.9(2)
B(12)-B(8)-B(9)	60.0(3)	B(3)-B(8)-B(9)	104.1(3)
B(10)-B(9)-B(4)	108.0(3)	B(10)-B(9)-B(5)	60.3(3)
B(4)-B(9)-B(5)	59.5(2)	B(10)-B(9)-B(12)	59.5(3)
B(4)-B(9)-B(12)	107.6(3)	B(5)-B(9)-B(12)	107.3(4)
B(10)-B(9)-B(8)	107.0(3)	B(4)-B(9)-B(8)	59.5(2)
B(5)-B(9)-B(8)	106.4(3)	B(12)-B(9)-B(8)	59.7(3)
C(1)-B(10)-B(9)	103.6(3)	C(1)-B(10)-B(11)	59.9(3)
B(9)-B(10)-B(11)	109.8(3)	C(1)-B(10)-B(12)	105.6(3)
B(9)-B(10)-B(12)	62.0(3)	B(11)-B(10)-B(12)	60.4(3)
C(1)-B(10)-B(5)	55.1(2)	B(9)-B(10)-B(5)	61.2(3)
B(11)-B(10)-B(5)	107.0(3)	B(12)-B(10)-B(5)	109.9(3)
C(2)-B(11)-C(1)	54.5(2)	C(2)-B(11)-B(10)	103.7(3)
C(1)-B(11)-B(10)	59.5(3)	C(2)-B(11)-B(12)	105.7(3)
C(1)-B(11)-B(12)	105.2(3)	B(10)-B(11)-B(12)	60.2(3)
C(2)-B(11)-B(7)	60.0(2)	C(1)-B(11)-B(7)	103.7(3)
B(10)-B(11)-B(7)	108.1(4)	B(12)-B(11)-B(7)	60.3(3)
B(10)-B(12)-B(11)	59.4(3)	B(10)-B(12)-B(7)	107.4(3)
B(11)-B(12)-B(7)	60.2(3)	B(10)-B(12)-B(8)	106.7(3)
B(11)-B(12)-B(8)	107.0(3)	B(7)-B(12)-B(8)	59.5(2)
B(10)-B(12)-B(9)	58.5(3)	B(11)-B(12)-B(9)	106.2(4)
B(7)-B(12)-B(9)	107.6(3)	B(8)-B(12)-B(9)	60.3(2)
C(22)-B(23)-B(24)	108.4(3)	C(22)-B(23)-B(27)	60.0(2)
B(24)-B(23)-B(27)	108.5(3)	C(22)-B(23)-B(28)	107.4(2)
B(24)-B(23)-B(28)	59.8(2)	B(27)-B(23)-B(28)	59.9(2)
C(22)-B(23)-Zr(1)	89.68(17)	B(24)-B(23)-Zr(1)	62.33(15)
B(27)-B(23)-Zr(1)	145.0(2)	B(28)-B(23)-Zr(1)	122.1(2)
B(23)-B(24)-B(29)	109.3(3)	B(23)-B(24)-B(25)	103.1(3)
B(29)-B(24)-B(25)	62.2(2)	B(23)-B(24)-B(28)	61.7(2)
B(29)-B(24)-B(28)	62.0(2)	B(25)-B(24)-B(28)	110.0(3)
B(23)-B(24)-Zr(1)	76.02(17)	B(29)-B(24)-Zr(1)	139.8(2)
B(25)-B(24)-Zr(1)	77.60(17)	B(28)-B(24)-Zr(1)	137.7(2)
C(21)-B(25)-B(24)	108.1(3)	C(21)-B(25)-B(30)	59.93(19)
B(24)-B(25)-B(30)	106.9(3)	C(21)-B(25)-B(29)	106.3(2)
B(24)-B(25)-B(29)	58.90(19)	B(30)-B(25)-B(29)	58.7(2)
C(21)-B(25)-Zr(1)	89.47(17)	B(24)-B(25)-Zr(1)	61.07(14)
B(30)-B(25)-Zr(1)	143.2(2)	B(29)-B(25)-Zr(1)	119.9(2)
C(22)-B(27)-B(31)	59.7(2)	C(22)-B(27)-B(23)	57.01(19)
B(31)-B(27)-B(23)	106.6(3)	C(22)-B(27)-B(28)	105.7(3)
B(31)-B(27)-B(28)	108.7(3)	B(23)-B(27)-B(28)	60.8(2)

C(22)-B(27)-B(32)	105.4(3)	B(31)-B(27)-B(32)	60.0(2)
B(23)-B(27)-B(32)	106.9(3)	B(28)-B(27)-B(32)	59.9(2)
B(24)-B(28)-B(32)	106.8(3)	B(24)-B(28)-B(27)	107.0(3)
B(32)-B(28)-B(27)	60.1(2)	B(24)-B(28)-B(23)	58.5(2)
B(32)-B(28)-B(23)	106.0(3)	B(27)-B(28)-B(23)	59.4(2)
B(24)-B(28)-B(29)	58.7(2)	B(32)-B(28)-B(29)	59.6(2)
B(27)-B(28)-B(29)	106.8(3)	B(23)-B(28)-B(29)	104.3(2)
B(24)-B(29)-B(30)	107.7(3)	B(24)-B(29)-B(32)	107.2(3)
B(30)-B(29)-B(32)	60.2(2)	B(24)-B(29)-B(28)	59.4(2)
B(30)-B(29)-B(28)	107.3(3)	B(32)-B(29)-B(28)	59.4(2)
B(24)-B(29)-B(25)	58.86(19)	B(30)-B(29)-B(25)	59.8(2)
B(32)-B(29)-B(25)	106.6(3)	B(28)-B(29)-B(25)	105.4(2)
C(21)-B(30)-B(29)	106.1(2)	C(21)-B(30)-B(31)	59.5(2)
B(29)-B(30)-B(31)	109.2(3)	C(21)-B(30)-B(32)	105.6(3)
B(29)-B(30)-B(32)	60.5(2)	B(31)-B(30)-B(32)	60.0(2)
C(21)-B(30)-B(25)	56.92(18)	B(29)-B(30)-B(25)	61.5(2)
B(31)-B(30)-B(25)	106.8(2)	B(32)-B(30)-B(25)	108.2(3)
C(21)-B(31)-C(22)	54.73(18)	C(21)-B(31)-B(27)	103.6(2)
C(22)-B(31)-B(27)	59.1(2)	C(21)-B(31)-B(30)	59.2(2)
C(22)-B(31)-B(30)	103.1(2)	B(27)-B(31)-B(30)	107.9(3)
C(21)-B(31)-B(32)	105.7(3)	C(22)-B(31)-B(32)	105.5(3)
B(27)-B(31)-B(32)	60.7(2)	B(30)-B(31)-B(32)	60.4(2)
B(31)-B(32)-B(30)	59.6(2)	B(31)-B(32)-B(28)	108.3(2)
B(30)-B(32)-B(28)	107.8(2)	B(31)-B(32)-B(29)	107.8(3)
B(30)-B(32)-B(29)	59.2(2)	B(28)-B(32)-B(29)	61.0(2)
B(31)-B(32)-B(27)	59.3(2)	B(30)-B(32)-B(27)	106.3(3)
B(28)-B(32)-B(27)	60.0(2)	B(29)-B(32)-B(27)	107.9(2)
C(68)-O(2)-C(65)	107.1(4)	C(68)-O(2)-Li(1)	129.8(4)
C(65)-O(2)-Li(1)	122.4(4)	C(74)-O(3)-C(71)	106.9(5)
C(74)-O(3)-Li(1)	129.9(4)	C(71)-O(3)-Li(1)	123.2(4)
C(91)-O(4)-C(94)	105.5(5)	C(91)-O(4)-Li(1)	131.6(5)
C(94)-O(4)-Li(1)	122.9(5)	C(84)-O(5)-C(81)	106.2(5)
C(84)-O(5)-Li(1)	122.3(4)	C(81)-O(5)-Li(1)	126.4(4)
O(2)-Li(1)-O(3)	105.2(4)	O(2)-Li(1)-O(5)	106.4(4)
O(3)-Li(1)-O(5)	114.8(4)	O(2)-Li(1)-O(4)	111.3(4)
O(3)-Li(1)-O(4)	108.1(4)	O(5)-Li(1)-O(4)	110.9(4)
C(66)-C(65)-O(2)	108.0(6)	C(67)-C(66)-C(65)	109.3(6)
C(66)-C(67)-C(68)	106.5(6)	O(2)-C(68)-C(67)	108.1(6)
C(72)-C(71)-O(3)	109.7(6)	C(71)-C(72)-C(73)	105.6(6)
C(72)-C(73)-C(74)	106.0(6)	O(3)-C(74)-C(73)	107.4(6)
O(5)-C(81)-C(82)	107.6(5)	C(83)-C(82)-C(81)	106.1(6)
C(82)-C(83)-C(84)	107.0(6)	O(5)-C(84)-C(83)	107.1(6)
O(4)-C(91)-C(92)	109.4(7)	C(93)-C(92)-C(91)	107.1(6)
C(92)-C(93)-C(94)	104.6(7)	O(4)-C(94)-C(93)	113.0(7)

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Zr-N(1)	2.067(4)	Zr-N(3)	2.074(4)
Zr-N(2)	2.082(4)	Zr-Cl	2.3974(18)
Si(11)-N(1)	1.773(4)	Si(11)-C(112)	1.857(7)
Si(11)-C(113)	1.871(7)	Si(11)-C(111)	1.891(7)
Si(12)-N(1)	1.771(4)	Si(12)-C(123)	1.854(7)
Si(12)-C(122)	1.861(7)	Si(12)-C(121)	1.872(7)
Si(21)-N(2)	1.750(4)	Si(21)-C(212)	1.868(7)
Si(21)-C(211)	1.873(7)	Si(21)-C(213)	1.881(6)
Si(22)-N(2)	1.775(4)	Si(22)-C(222)	1.869(7)
Si(22)-C(221)	1.884(7)	Si(22)-C(223)	1.892(9)
Si(31)-N(3)	1.769(4)	Si(31)-C(312)	1.859(7)
Si(31)-C(311)	1.868(6)	Si(31)-C(313)	1.876(7)
Si(32)-N(3)	1.769(4)	Si(32)-C(321)	1.863(7)
Si(32)-C(322)	1.872(7)	Si(32)-C(323)	1.880(7)
N(1)-Zr-N(3)	114.22(16)	N(1)-Zr-N(2)	114.39(16)
N(3)-Zr-N(2)	113.63(16)	N(1)-Zr-Cl	104.27(12)
N(3)-Zr-Cl	104.31(12)	N(2)-Zr-Cl	104.43(12)
N(1)-Si(11)-C(112)	110.9(3)	N(1)-Si(11)-C(113)	111.2(3)
C(112)-Si(11)-C(113)	109.0(3)	N(1)-Si(11)-C(111)	113.4(3)
C(112)-Si(11)-C(111)	105.3(4)	C(113)-Si(11)-C(111)	106.8(4)
N(1)-Si(12)-C(123)	111.0(2)	N(1)-Si(12)-C(122)	114.7(3)
C(123)-Si(12)-C(122)	104.8(3)	N(1)-Si(12)-C(121)	111.8(3)
C(123)-Si(12)-C(121)	107.5(4)	C(122)-Si(12)-C(121)	106.5(4)
N(2)-Si(21)-C(212)	111.4(3)	N(2)-Si(21)-C(211)	111.2(3)
C(212)-Si(21)-C(211)	108.2(4)	N(2)-Si(21)-C(213)	114.9(3)
C(212)-Si(21)-C(213)	103.6(3)	C(211)-Si(21)-C(213)	107.1(4)
N(2)-Si(22)-C(222)	113.5(3)	N(2)-Si(22)-C(221)	111.1(3)
C(222)-Si(22)-C(221)	106.5(4)	N(2)-Si(22)-C(223)	111.6(3)
C(222)-Si(22)-C(223)	105.0(4)	C(221)-Si(22)-C(223)	108.7(4)
N(3)-Si(31)-C(312)	110.9(3)	N(3)-Si(31)-C(311)	111.8(3)
C(312)-Si(31)-C(311)	108.6(4)	N(3)-Si(31)-C(313)	113.8(3)
C(312)-Si(31)-C(313)	105.3(3)	C(311)-Si(31)-C(313)	106.1(4)
N(3)-Si(32)-C(321)	114.9(3)	N(3)-Si(32)-C(322)	111.6(3)
C(321)-Si(32)-C(322)	106.1(4)	N(3)-Si(32)-C(323)	110.9(3)
C(321)-Si(32)-C(323)	104.7(4)	C(322)-Si(32)-C(323)	108.2(4)
Si(21)-N(2)-Si(22)	116.8(2)	Si(21)-N(2)-Zr	127.7(2)
Si(22)-N(2)-Zr	115.2(2)	Si(31)-N(3)-Si(32)	116.2(2)
Si(31)-N(3)-Zr	116.2(2)	Si(32)-N(3)-Zr	127.2(2)
Si(12)-N(1)-Si(11)	116.1(2)	Si(12)-N(1)-Zr	127.3(2)
Si(11)-N(1)-Zr	116.2(2)		

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Ti(1)-N(3)	1.871(2)	Ti(1)-N(2)	1.879(2)
Ti(1)-N(1)	2.235(2)	Ti(1)-B(4)	2.280(3)
Ti(1)-B(3)	2.376(3)	Cl(1)-Cl(1')	0.977(7)
Cl(1)-C(3)	1.665(6)	Cl(2)-Cl(2')	0.984(8)
Cl(2)-C(3)	1.778(8)	Cl(2)-Cl(1')	2.428(9)
C(10)-C(11)	1.508(4)	C(10)-C(1)	1.539(4)
C(11)-C(16)	1.375(5)	C(11)-C(12)	1.380(4)
C(12)-C(13)	1.386(5)	C(13)-C(14)	1.367(6)
C(14)-C(15)	1.351(6)	C(15)-C(16)	1.385(5)
C(20)-C(21)	1.512(3)	C(20)-C(2)	1.533(3)
C(21)-C(22)	1.381(4)	C(21)-C(26)	1.384(4)
C(22)-C(23)	1.386(5)	C(23)-C(24)	1.368(5)
C(24)-C(25)	1.359(5)	C(25)-C(26)	1.380(4)
C(31)-N(2)	1.464(4)	C(31)-C(32)	1.524(4)
C(33)-N(2)	1.475(3)	C(33)-C(34)	1.511(5)
C(35)-N(1)	1.480(4)	C(35)-C(36)	1.505(4)
C(38)-C(37)	0.858(8)	C(38)-N(1)	1.596(9)
C(39)-N(3)	1.465(4)	C(39)-C(40)	1.517(5)
C(41)-N(3)	1.466(4)	C(41)-C(42)	1.493(5)
B(3)-C(2)	1.624(3)	B(3)-B(4)	1.737(4)
B(3)-B(7)	1.786(4)	B(3)-B(8)	1.797(4)
B(4)-B(5)	1.748(4)	B(4)-B(9)	1.773(4)
B(4)-B(8)	1.775(4)	B(5)-C(1)	1.627(3)
B(5)-B(9)	1.786(4)	B(5)-B(10)	1.792(4)
B(6)-C(2)	1.712(3)	B(6)-C(1)	1.736(4)
B(6)-B(10)	1.763(4)	B(6)-B(7)	1.769(4)
B(6)-B(11)	1.772(4)	B(7)-C(2)	1.724(4)
B(7)-B(11)	1.767(4)	B(7)-B(8)	1.775(4)
B(8)-B(11)	1.784(4)	B(8)-B(9)	1.799(4)
B(9)-B(10)	1.745(4)	B(9)-B(11)	1.791(4)
B(10)-C(1)	1.728(3)	B(10)-B(11)	1.777(5)
C(1)-C(2)	1.583(3)	C(38')-C(37')	1.067(14)
N(3)-Ti(1)-N(2)	112.69(10)	N(3)-Ti(1)-N(1)	95.22(9)
N(2)-Ti(1)-N(1)	98.86(9)	N(3)-Ti(1)-B(4)	118.36(10)
N(2)-Ti(1)-B(4)	122.04(10)	N(1)-Ti(1)-B(4)	101.92(9)
N(3)-Ti(1)-B(3)	102.15(10)	N(2)-Ti(1)-B(3)	101.29(9)
N(1)-Ti(1)-B(3)	145.68(9)	B(4)-Ti(1)-B(3)	43.76(9)
Cl(1')-Cl(1)-C(3)	71.7(5)	Cl(2')-Cl(2)-C(3)	66.8(5)
Cl(2')-Cl(2)-Cl(1')	99.8(7)	C(3)-Cl(2)-Cl(1')	42.6(2)
Cl(1)-C(3)-Cl(2)	113.2(4)	C(11)-C(10)-C(1)	115.6(2)
C(16)-C(11)-C(12)	118.2(3)	C(16)-C(11)-C(10)	121.5(3)
C(12)-C(11)-C(10)	120.2(3)	C(11)-C(12)-C(13)	120.8(4)
C(14)-C(13)-C(12)	119.9(4)	C(15)-C(14)-C(13)	119.8(4)
C(14)-C(15)-C(16)	120.8(4)	C(11)-C(16)-C(15)	120.5(4)
C(21)-C(20)-C(2)	119.5(2)	C(22)-C(21)-C(26)	117.1(2)
C(22)-C(21)-C(20)	120.8(2)	C(26)-C(21)-C(20)	122.0(2)
C(21)-C(22)-C(23)	121.0(3)	C(24)-C(23)-C(22)	120.5(3)
C(25)-C(24)-C(23)	119.4(3)	C(24)-C(25)-C(26)	120.2(3)
C(25)-C(26)-C(21)	121.8(3)	N(2)-C(31)-C(32)	116.2(3)
N(2)-C(33)-C(34)	112.0(2)	N(1)-C(35)-C(36)	116.1(3)
C(37)-C(38)-N(1)	165.4(11)	N(3)-C(39)-C(40)	114.2(3)
N(3)-C(41)-C(42)	114.4(3)	C(2)-B(3)-B(4)	109.0(2)
C(2)-B(3)-B(7)	60.53(15)	B(4)-B(3)-B(7)	109.29(19)
C(2)-B(3)-B(8)	107.06(19)	B(4)-B(3)-B(8)	60.26(15)
B(7)-B(3)-B(8)	59.40(15)	C(2)-B(3)-Ti(1)	127.46(17)
B(4)-B(3)-Ti(1)	65.18(12)	B(7)-B(3)-Ti(1)	170.89(17)

B(8)-B(3)-Ti(1)	111.82(15)	B(3)-B(4)-B(5)	103.37(18)
B(3)-B(4)-B(9)	107.81(18)	B(5)-B(4)-B(9)	60.95(16)
B(3)-B(4)-B(8)	61.53(15)	B(5)-B(4)-B(8)	108.86(19)
B(9)-B(4)-B(8)	60.95(17)	B(3)-B(4)-Ti(1)	71.06(13)
B(5)-B(4)-Ti(1)	120.65(16)	B(9)-B(4)-Ti(1)	178.12(19)
B(8)-B(4)-Ti(1)	117.20(17)	C(1)-B(5)-B(4)	105.94(19)
C(1)-B(5)-B(9)	105.36(19)	B(4)-B(5)-B(9)	60.21(16)
C(1)-B(5)-B(10)	60.46(15)	B(4)-B(5)-B(10)	107.6(2)
B(9)-B(5)-B(10)	58.39(15)	C(2)-B(6)-C(1)	54.66(14)
C(2)-B(6)-B(10)	103.82(18)	C(1)-B(6)-B(10)	59.16(15)
C(2)-B(6)-B(7)	59.36(15)	C(1)-B(6)-B(7)	102.94(18)
B(10)-B(6)-B(7)	107.9(2)	C(2)-B(6)-B(11)	104.90(19)
C(1)-B(6)-B(11)	104.36(18)	B(10)-B(6)-B(11)	60.33(17)
B(7)-B(6)-B(11)	59.86(17)	C(2)-B(7)-B(11)	104.6(2)
C(2)-B(7)-B(6)	58.68(15)	B(11)-B(7)-B(6)	60.17(17)
C(2)-B(7)-B(8)	103.77(19)	B(11)-B(7)-B(8)	60.47(17)
B(6)-B(7)-B(8)	108.1(2)	C(2)-B(7)-B(3)	55.10(14)
B(11)-B(7)-B(3)	106.95(19)	B(6)-B(7)-B(3)	104.39(19)
B(8)-B(7)-B(3)	60.61(15)	B(4)-B(8)-B(7)	108.10(19)
B(4)-B(8)-B(11)	108.0(2)	B(7)-B(8)-B(11)	59.55(16)
B(4)-B(8)-B(3)	58.22(15)	B(7)-B(8)-B(3)	59.99(15)
B(11)-B(8)-B(3)	105.76(19)	B(4)-B(8)-B(9)	59.48(16)
B(7)-B(8)-B(9)	107.1(2)	B(11)-B(8)-B(9)	59.97(17)
B(3)-B(8)-B(9)	104.2(2)	B(10)-B(9)-B(4)	108.56(19)
B(10)-B(9)-B(5)	60.99(16)	B(4)-B(9)-B(5)	58.83(15)
B(10)-B(9)-B(11)	60.31(17)	B(4)-B(9)-B(11)	107.8(2)
B(5)-B(9)-B(11)	107.93(19)	B(10)-B(9)-B(8)	107.8(2)
B(4)-B(9)-B(8)	59.57(15)	B(5)-B(9)-B(8)	106.11(19)
B(11)-B(9)-B(8)	59.58(17)	C(1)-B(10)-B(9)	102.91(18)
C(1)-B(10)-B(6)	59.63(15)	B(9)-B(10)-B(6)	108.9(2)
C(1)-B(10)-B(11)	104.5(2)	B(9)-B(10)-B(11)	61.11(17)
B(6)-B(10)-B(11)	60.09(17)	C(1)-B(10)-B(5)	55.04(14)
B(9)-B(10)-B(5)	60.63(15)	B(6)-B(10)-B(5)	106.34(19)
B(11)-B(10)-B(5)	108.3(2)	B(7)-B(11)-B(6)	59.97(17)
B(7)-B(11)-B(10)	107.4(2)	B(6)-B(11)-B(10)	59.58(17)
B(7)-B(11)-B(8)	59.98(17)	B(6)-B(11)-B(8)	107.6(2)
B(10)-B(11)-B(8)	107.16(19)	B(7)-B(11)-B(9)	107.83(19)
B(6)-B(11)-B(9)	106.5(2)	B(10)-B(11)-B(9)	58.58(16)
B(8)-B(11)-B(9)	60.45(16)	C(35)-N(1)-C(38)	104.9(4)
C(35)-N(1)-Ti(1)	114.46(18)	C(38)-N(1)-Ti(1)	105.4(3)
C(31)-N(2)-C(33)	114.0(2)	C(31)-N(2)-Ti(1)	113.01(17)
C(33)-N(2)-Ti(1)	132.29(19)	C(39)-N(3)-C(41)	114.6(2)
C(39)-N(3)-Ti(1)	119.85(18)	C(41)-N(3)-Ti(1)	125.52(19)
C(10)-C(1)-C(2)	116.0(2)	C(10)-C(1)-B(5)	121.6(2)
C(2)-C(1)-B(5)	113.04(19)	C(10)-C(1)-B(10)	120.2(2)
C(2)-C(1)-B(10)	111.3(2)	B(5)-C(1)-B(10)	64.50(16)
C(10)-C(1)-B(6)	114.3(2)	C(2)-C(1)-B(6)	61.90(15)
B(5)-C(1)-B(6)	115.56(19)	B(10)-C(1)-B(6)	61.21(16)
C(20)-C(2)-C(1)	120.7(2)	C(20)-C(2)-B(3)	118.7(2)
C(1)-C(2)-B(3)	108.44(18)	C(20)-C(2)-B(6)	118.79(18)
C(1)-C(2)-B(6)	63.44(16)	B(3)-C(2)-B(6)	114.62(19)
C(20)-C(2)-B(7)	119.6(2)	C(1)-C(2)-B(7)	111.92(19)
B(3)-C(2)-B(7)	64.37(16)	B(6)-C(2)-B(7)	61.97(17)
Cl(1)-Cl(1')-Cl(2)	107.3(6)		

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Zr-C(2)#1	2.431(3)	Zr-C(2)	2.431(3)
Zr-C(1)	2.442(3)	Zr-C(1)#1	2.442(3)
Zr-B(4)	2.510(4)	Zr-B(4)#1	2.510(4)
Zr-B(5)	2.511(4)	Zr-B(5)#1	2.511(4)
Zr-B(3)#1	2.558(4)	Zr-B(3)	2.558(4)
Zr-B(6)	2.578(4)	Zr-B(6)#1	2.578(4)
C(1)-C(2)	1.490(4)	C(1)-C(3)	1.531(5)
C(1)-B(6)	1.602(5)	C(1)-B(11)	1.770(5)
C(2)-C(10)	1.531(5)	C(2)-B(3)	1.605(5)
C(2)-B(7)	1.749(5)	C(3)-C(9)	1.509(5)
C(4)-C(9)	1.379(6)	C(4)-C(5)	1.389(7)
C(5)-C(6)	1.379(7)	C(6)-C(7)	1.385(6)
C(7)-C(8)	1.383(5)	C(8)-C(9)	1.393(5)
C(8)-C(10)	1.506(5)	O(1)-C(11)	1.398(8)
O(1)-C(14)	1.409(8)	O(1)-Na	2.309(4)
C(11)-C(12)	1.463(12)	C(12)-C(13)	1.385(12)
C(13)-C(14)	1.456(11)	B(3)-B(8)	1.767(6)
B(3)-B(4)	1.799(6)	B(3)-B(7)	1.824(6)
B(4)-B(5)	1.777(6)	B(4)-B(8)	1.787(6)
B(4)-B(9)	1.801(6)	B(5)-B(10)	1.776(6)
B(5)-B(6)	1.796(6)	B(5)-B(9)	1.799(6)
B(5)-Na#1	2.905(5)	B(6)-B(10)	1.775(6)
B(6)-B(11)	1.834(6)	B(7)-B(12)	1.756(7)
B(7)-B(8)	1.810(7)	B(7)-B(11)	1.970(6)
B(8)-B(9)	1.767(7)	B(8)-B(12)	1.795(7)
B(9)-B(10)	1.753(7)	B(9)-B(12)	1.793(7)
B(9)-Na#1	2.990(6)	B(10)-B(12)	1.782(7)
B(10)-B(11)	1.812(7)	B(10)-Na#1	2.936(5)
B(11)-B(12)	1.752(7)	Na-O(3)	2.271(4)
Na-O(2)	2.273(4)	Na-B(5)#1	2.905(5)
Na-B(10)#1	2.936(5)	Na-B(9)#1	2.990(6)
O(2)-C(21)	1.380(8)	O(2)-C(24)	1.419(7)
C(21)-C(22)	1.447(12)	C(22)-C(23)	1.384(10)
C(23)-C(24)	1.467(9)	O(3)-C(31)	1.283(11)
O(3)-C(34)	1.345(11)	C(31)-C(32)	1.435(13)
C(32)-C(33)	1.297(14)	C(33)-C(34)	1.491(14)
C(2)#1-Zr-C(2)	180.0	C(2)#1-Zr-C(1)	144.40(11)
C(2)-Zr-C(1)	35.60(10)	C(2)#1-Zr-C(1)#1	35.60(10)
C(2)-Zr-C(1)#1	144.40(11)	C(1)-Zr-C(1)#1	180.0
C(2)#1-Zr-B(4)	107.34(13)	C(2)-Zr-B(4)	72.66(13)
C(1)-Zr-B(4)	85.34(13)	C(1)#1-Zr-B(4)	94.66(13)
C(2)#1-Zr-B(4)#1	72.66(13)	C(2)-Zr-B(4)#1	107.34(13)
C(1)-Zr-B(4)#1	94.66(13)	C(1)#1-Zr-B(4)#1	85.34(13)
B(4)-Zr-B(4)#1	180.00(17)	C(2)#1-Zr-B(5)	95.17(13)
C(2)-Zr-B(5)	84.83(13)	C(1)-Zr-B(5)	72.19(13)
C(1)#1-Zr-B(5)	107.81(13)	B(4)-Zr-B(5)	41.46(14)
B(4)#1-Zr-B(5)	138.54(14)	C(2)#1-Zr-B(5)#1	84.83(13)
C(2)-Zr-B(5)#1	95.17(13)	C(1)-Zr-B(5)#1	107.81(13)
C(1)#1-Zr-B(5)#1	72.19(13)	B(4)-Zr-B(5)#1	138.54(14)
B(4)#1-Zr-B(5)#1	41.46(14)	B(5)-Zr-B(5)#1	180.000(1)
C(2)#1-Zr-B(3)#1	37.42(12)	C(2)-Zr-B(3)#1	142.58(12)
C(1)-Zr-B(3)#1	113.32(12)	C(1)#1-Zr-B(3)#1	66.68(12)
B(4)-Zr-B(3)#1	138.44(14)	B(4)#1-Zr-B(3)#1	41.56(14)
B(5)-Zr-B(3)#1	106.97(14)	B(5)#1-Zr-B(3)#1	73.03(14)
C(2)#1-Zr-B(3)	142.58(12)	C(2)-Zr-B(3)	37.42(12)
C(1)-Zr-B(3)	66.69(12)	C(1)#1-Zr-B(3)	113.32(12)

B(4)-Zr-B(3)	41.56(14)	B(4)#1-Zr-B(3)	138.44(14)
B(5)-Zr-B(3)	73.03(14)	B(5)#1-Zr-B(3)	106.97(14)
B(3)#1-Zr-B(3)	180.0(2)	C(2)#1-Zr-B(6)	113.72(12)
C(2)-Zr-B(6)	66.28(12)	C(1)-Zr-B(6)	37.09(12)
C(1)#1-Zr-B(6)	142.91(12)	B(4)-Zr-B(6)	73.25(14)
B(4)#1-Zr-B(6)	106.75(14)	B(5)-Zr-B(6)	41.31(14)
B(5)#1-Zr-B(6)	138.69(14)	B(3)#1-Zr-B(6)	99.02(13)
B(3)-Zr-B(6)	80.98(13)	C(2)#1-Zr-B(6)#1	66.28(12)
C(2)-Zr-B(6)#1	113.72(12)	C(1)-Zr-B(6)#1	142.91(12)
C(1)#1-Zr-B(6)#1	37.09(12)	B(4)-Zr-B(6)#1	106.75(14)
B(4)#1-Zr-B(6)#1	73.25(14)	B(5)-Zr-B(6)#1	138.69(14)
B(5)#1-Zr-B(6)#1	41.31(14)	B(3)#1-Zr-B(6)#1	80.98(13)
B(3)-Zr-B(6)#1	99.02(13)	B(6)-Zr-B(6)#1	180.0
C(2)-C(1)-C(3)	115.8(3)	C(2)-C(1)-B(6)	124.9(3)
C(3)-C(1)-B(6)	119.2(3)	C(2)-C(1)-B(11)	97.7(3)
C(3)-C(1)-B(11)	111.3(3)	B(6)-C(1)-B(11)	65.7(2)
C(2)-C(1)-Zr	71.79(18)	C(3)-C(1)-Zr	123.2(2)
B(6)-C(1)-Zr	76.1(2)	B(11)-C(1)-Zr	123.7(2)
C(1)-C(2)-C(10)	114.9(3)	C(1)-C(2)-B(3)	125.4(3)
C(10)-C(2)-B(3)	119.5(3)	C(1)-C(2)-B(7)	98.0(3)
C(10)-C(2)-B(7)	112.5(3)	B(3)-C(2)-B(7)	65.7(2)
C(1)-C(2)-Zr	72.61(18)	C(10)-C(2)-Zr	121.8(2)
B(3)-C(2)-Zr	75.59(19)	B(7)-C(2)-Zr	123.8(2)
C(9)-C(3)-C(1)	112.0(3)	C(9)-C(4)-C(5)	120.4(4)
C(6)-C(5)-C(4)	120.1(4)	C(5)-C(6)-C(7)	119.5(4)
C(8)-C(7)-C(6)	120.7(4)	C(7)-C(8)-C(9)	119.5(4)
C(7)-C(8)-C(10)	122.7(3)	C(9)-C(8)-C(10)	117.8(3)
C(4)-C(9)-C(8)	119.7(4)	C(4)-C(9)-C(3)	122.5(4)
C(8)-C(9)-C(3)	117.8(3)	C(8)-C(10)-C(2)	112.4(3)
C(11)-O(1)-C(14)	108.4(5)	C(11)-O(1)-Na	119.3(4)
C(14)-O(1)-Na	127.5(4)	O(1)-C(11)-C(12)	108.3(7)
C(13)-C(12)-C(11)	105.8(8)	C(12)-C(13)-C(14)	109.5(8)
O(1)-C(14)-C(13)	106.4(7)	C(2)-B(3)-B(8)	117.1(3)
C(2)-B(3)-B(4)	118.6(3)	B(8)-B(3)-B(4)	60.2(3)
C(2)-B(3)-B(7)	61.0(2)	B(8)-B(3)-B(7)	60.5(2)
B(4)-B(3)-B(7)	105.5(3)	C(2)-B(3)-Zr	66.99(17)
B(8)-B(3)-Zr	121.4(3)	B(4)-B(3)-Zr	67.79(18)
B(7)-B(3)-Zr	114.2(2)	B(5)-B(4)-B(8)	108.4(3)
B(5)-B(4)-B(3)	115.0(3)	B(8)-B(4)-B(3)	59.0(2)
B(5)-B(4)-B(9)	60.4(3)	B(8)-B(4)-B(9)	59.0(3)
B(3)-B(4)-B(9)	109.6(3)	B(5)-B(4)-Zr	69.30(19)
B(8)-B(4)-Zr	122.9(3)	B(3)-B(4)-Zr	70.65(19)
B(9)-B(4)-Zr	124.0(3)	B(10)-B(5)-B(4)	108.8(3)
B(10)-B(5)-B(6)	59.6(2)	B(4)-B(5)-B(6)	116.3(3)
B(10)-B(5)-B(9)	58.7(3)	B(4)-B(5)-B(9)	60.5(3)
B(6)-B(5)-B(9)	110.2(3)	B(10)-B(5)-Zr	123.8(3)
B(4)-B(5)-Zr	69.24(19)	B(6)-B(5)-Zr	71.35(19)
B(9)-B(5)-Zr	124.1(3)	B(10)-B(5)-Na#1	73.2(2)
B(4)-B(5)-Na#1	120.8(2)	B(6)-B(5)-Na#1	114.2(2)
B(9)-B(5)-Na#1	74.8(2)	Zr-B(5)-Na#1	158.49(19)
C(1)-B(6)-B(10)	117.2(3)	C(1)-B(6)-B(5)	118.3(3)
B(10)-B(6)-B(5)	59.6(2)	C(1)-B(6)-B(11)	61.6(2)
B(10)-B(6)-B(11)	60.3(3)	B(5)-B(6)-B(11)	105.1(3)
C(1)-B(6)-Zr	66.84(18)	B(10)-B(6)-Zr	120.3(3)
B(5)-B(6)-Zr	67.34(18)	B(11)-B(6)-Zr	114.3(2)
C(2)-B(7)-B(12)	125.4(3)	C(2)-B(7)-B(8)	107.9(3)
B(12)-B(7)-B(8)	60.4(3)	C(2)-B(7)-B(3)	53.3(2)
B(12)-B(7)-B(3)	108.4(3)	B(8)-B(7)-B(3)	58.2(2)

C(2)-B(7)-B(11)	82.7(2)	B(12)-B(7)-B(11)	55.8(3)
B(8)-B(7)-B(11)	105.6(3)	B(3)-B(7)-B(11)	112.6(3)
B(3)-B(8)-B(9)	112.7(3)	B(3)-B(8)-B(4)	60.8(2)
B(9)-B(8)-B(4)	60.9(3)	B(3)-B(8)-B(12)	109.2(3)
B(9)-B(8)-B(12)	60.4(3)	B(4)-B(8)-B(12)	106.2(3)
B(3)-B(8)-B(7)	61.3(2)	B(9)-B(8)-B(7)	108.6(3)
B(4)-B(8)-B(7)	106.5(3)	B(12)-B(8)-B(7)	58.3(3)
B(10)-B(9)-B(8)	111.7(4)	B(10)-B(9)-B(12)	60.3(3)
B(8)-B(9)-B(12)	60.6(3)	B(10)-B(9)-B(5)	60.0(3)
B(8)-B(9)-B(5)	108.3(3)	B(12)-B(9)-B(5)	105.2(3)
B(10)-B(9)-B(4)	108.7(3)	B(8)-B(9)-B(4)	60.1(3)
B(12)-B(9)-B(4)	105.7(3)	B(5)-B(9)-B(4)	59.2(2)
B(10)-B(9)-Na#1	71.1(2)	B(8)-B(9)-Na#1	175.5(3)
B(12)-B(9)-Na#1	123.7(3)	B(5)-B(9)-Na#1	69.7(2)
B(4)-B(9)-Na#1	115.9(3)	B(9)-B(10)-B(6)	113.4(3)
B(9)-B(10)-B(5)	61.3(3)	B(6)-B(10)-B(5)	60.8(2)
B(9)-B(10)-B(12)	60.9(3)	B(6)-B(10)-B(12)	109.4(3)
B(5)-B(10)-B(12)	106.6(3)	B(9)-B(10)-B(11)	109.5(3)
B(6)-B(10)-B(11)	61.5(2)	B(5)-B(10)-B(11)	106.9(3)
B(12)-B(10)-B(11)	58.3(3)	B(9)-B(10)-Na#1	74.5(2)
B(6)-B(10)-Na#1	113.7(3)	B(5)-B(10)-Na#1	71.4(2)
B(12)-B(10)-Na#1	127.1(3)	B(11)-B(10)-Na#1	174.5(3)
B(12)-B(11)-C(1)	124.7(3)	B(12)-B(11)-B(10)	60.0(3)
C(1)-B(11)-B(10)	107.1(3)	B(12)-B(11)-B(6)	108.1(3)
C(1)-B(11)-B(6)	52.7(2)	B(10)-B(11)-B(6)	58.2(2)
B(12)-B(11)-B(7)	55.9(3)	C(1)-B(11)-B(7)	81.7(2)
B(10)-B(11)-B(7)	104.6(3)	B(6)-B(11)-B(7)	111.2(3)
B(11)-B(12)-B(7)	68.3(3)	B(11)-B(12)-B(10)	61.7(3)
B(7)-B(12)-B(10)	115.6(3)	B(11)-B(12)-B(9)	110.5(3)
B(7)-B(12)-B(9)	109.9(3)	B(10)-B(12)-B(9)	58.7(3)
B(11)-B(12)-B(8)	116.2(3)	B(7)-B(12)-B(8)	61.3(3)
B(10)-B(12)-B(8)	109.0(3)	B(9)-B(12)-B(8)	59.0(3)
O(3)-Na-O(2)	104.82(16)	O(3)-Na-O(1)	103.73(17)
O(2)-Na-O(1)	107.34(17)	O(3)-Na-B(5)#1	100.19(16)
O(2)-Na-B(5)#1	134.10(15)	O(1)-Na-B(5)#1	103.16(15)
O(3)-Na-B(10)#1	104.20(17)	O(2)-Na-B(10)#1	100.50(15)
O(1)-Na-B(10)#1	133.46(16)	B(5)#1-Na-B(10)#1	35.39(12)
O(3)-Na-B(9)#1	133.32(17)	O(2)-Na-B(9)#1	104.07(14)
O(1)-Na-B(9)#1	101.62(16)	B(5)#1-Na-B(9)#1	35.49(12)
B(10)#1-Na-B(9)#1	34.40(14)	C(21)-O(2)-C(24)	107.6(5)
C(21)-O(2)-Na	129.4(4)	C(24)-O(2)-Na	123.0(3)
O(2)-C(21)-C(22)	109.0(7)	C(23)-C(22)-C(21)	105.1(7)
C(22)-C(23)-C(24)	108.2(6)	O(2)-C(24)-C(23)	106.1(5)
C(31)-O(3)-C(34)	105.2(8)	C(31)-O(3)-Na	132.6(6)
C(34)-O(3)-Na	120.4(5)	O(3)-C(31)-C(32)	111.6(9)
C(33)-C(32)-C(31)	106.0(10)	C(32)-C(33)-C(34)	102.2(10)
O(3)-C(34)-C(33)	109.2(9)		

Zr-B(5)	2.467(6)	Zr-B(5)#1	2.467(6)
Zr-B(4)	2.520(5)	Zr-B(4)#1	2.520(5)
Zr-Cl	2.5339(13)	Zr-Cl#1	2.5339(13)
Zr-C(2)#1	2.751(4)	Zr-C(2)	2.751(4)
Zr-B(3)#1	2.761(5)	Zr-B(3)	2.761(5)
Zr-B(6)	2.848(6)	Zr-B(6)#1	2.848(6)
C(1)-C(2)	1.457(7)	C(1)-C(3)	1.508(7)
C(1)-B(6)	1.584(7)	C(1)-B(7)	1.805(8)
C(2)-C(10)	1.509(7)	C(2)-B(3)	1.580(7)
C(2)-B(12)	1.827(8)	C(3)-C(9)	1.489(7)
C(4)-C(9)	1.387(7)	C(4)-C(5)	1.382(9)
C(5)-C(6)	1.401(11)	C(6)-C(7)	1.378(9)
C(7)-C(8)	1.394(7)	C(8)-C(9)	1.385(7)
C(8)-C(10)	1.510(7)	O(1)-C(14)	1.367(8)
O(1)-C(11)	1.431(10)	O(1)-Na	2.305(5)
C(11)-C(12)	1.386(11)	C(12)-C(13)	1.411(12)
C(13)-C(14)	1.465(12)	O(2)-C(24)	1.402(11)
O(2)-C(21)	1.372(9)	O(2)-Na	2.349(5)
C(21)-C(22)	1.349(18)	C(22)-C(23)	1.22(2)
C(23)-C(24)	1.475(15)	O(3)-C(34)	1.431(10)
O(3)-C(31)	1.430(9)	O(3)-Na	2.325(5)
C(31)-C(32)	1.394(13)	C(32)-C(33)	1.428(14)
C(33)-C(34)	1.438(12)	O(4)-C(41)	1.79(3)
O(4)-C(41)#2	1.79(3)	C(41)-C(42)	1.44(4)
C(42)-C(42)#2	1.55(7)	B(3)-B(4)	1.782(8)
B(3)-B(9)	1.783(9)	B(3)-B(12)	1.848(8)
B(3)-Na#1	3.164(6)	B(4)-B(9)	1.737(8)
B(4)-B(10)	1.773(8)	B(4)-B(5)	1.792(8)
B(5)-B(10)	1.777(8)	B(5)-B(11)	1.758(8)
B(5)-B(6)	1.788(8)	B(5)-B(5)#1	1.921(10)
B(6)-B(11)	1.739(8)	B(6)-B(7)	1.783(8)
B(7)-B(8)	1.735(9)	B(7)-B(11)	1.741(10)
B(7)-B(12)	1.936(9)	B(8)-B(9)	1.756(9)
B(8)-B(12)	1.766(10)	B(8)-B(11)	1.780(9)
B(8)-B(10)	1.787(10)	B(9)-B(10)	1.752(9)
B(9)-B(12)	1.833(9)	B(10)-B(11)	1.797(9)
Cl-Na	2.829(3)	Na-B(3)#1	3.164(6)
B(5)-Zr-B(5)#1	45.8(2)	B(5)-Zr-B(4)	42.11(18)
B(5)#1-Zr-B(4)	75.45(18)	B(5)-Zr-B(4)#1	75.45(18)
B(5)#1-Zr-B(4)#1	42.11(18)	B(4)-Zr-B(4)#1	114.8(3)
B(5)-Zr-Cl	134.77(15)	B(5)#1-Zr-Cl	130.87(13)
B(4)-Zr-Cl	144.46(14)	B(4)#1-Zr-Cl	88.93(13)
B(5)-Zr-Cl#1	130.87(13)	B(5)#1-Zr-Cl#1	134.77(15)
B(4)-Zr-Cl#1	88.93(13)	B(4)#1-Zr-Cl#1	144.46(14)
Cl-Zr-Cl#1	84.97(6)	B(5)-Zr-C(2)#1	121.16(16)
B(5)#1-Zr-C(2)#1	76.65(16)	B(4)-Zr-C(2)#1	124.21(17)
B(4)#1-Zr-C(2)#1	66.77(17)	Cl-Zr-C(2)#1	88.67(10)
Cl#1-Zr-C(2)#1	78.09(11)	B(5)-Zr-C(2)	76.65(16)
B(5)#1-Zr-C(2)	121.17(16)	B(4)-Zr-C(2)	66.77(17)
B(4)#1-Zr-C(2)	124.21(17)	Cl-Zr-C(2)	78.09(11)
Cl#1-Zr-C(2)	88.67(10)	C(2)#1-Zr-C(2)	162.1(2)
B(5)-Zr-B(3)#1	111.77(18)	B(5)#1-Zr-B(3)#1	68.55(17)
B(4)-Zr-B(3)#1	141.16(18)	B(4)#1-Zr-B(3)#1	39.12(18)
Cl-Zr-B(3)#1	73.69(12)	Cl#1-Zr-B(3)#1	106.07(13)
C(2)#1-Zr-B(3)#1	33.32(16)	C(2)-Zr-B(3)#1	146.59(15)
B(5)-Zr-B(3)	68.55(17)	B(5)#1-Zr-B(3)	111.77(18)

B(4)-Zr-B(3)	39.12(18)	B(4)#1-Zr-B(3)	141.16(18)
Cl-Zr-B(3)	106.07(13)	Cl#1-Zr-B(3)	73.69(13)
C(2)#1-Zr-B(3)	146.59(15)	C(2)-Zr-B(3)	33.32(16)
B(3)#1-Zr-B(3)	179.7(3)	B(5)-Zr-B(6)	38.47(18)
B(5)#1-Zr-B(6)	67.83(19)	B(4)-Zr-B(6)	69.78(18)
B(4)#1-Zr-B(6)	70.53(18)	Cl-Zr-B(6)	96.34(12)
Cl#1-Zr-B(6)	144.94(12)	C(2)#1-Zr-B(6)	136.88(16)
C(2)-Zr-B(6)	57.73(15)	B(3)#1-Zr-B(6)	107.90(17)
B(3)-Zr-B(6)	72.31(16)	B(5)-Zr-B(6)#1	67.83(19)
B(5)#1-Zr-B(6)#1	38.47(18)	B(4)-Zr-B(6)#1	70.53(18)
B(4)#1-Zr-B(6)#1	69.78(18)	Cl-Zr-B(6)#1	144.94(12)
Cl#1-Zr-B(6)#1	96.34(12)	C(2)#1-Zr-B(6)#1	57.73(15)
C(2)-Zr-B(6)#1	136.88(16)	B(3)#1-Zr-B(6)#1	72.31(16)
B(3)-Zr-B(6)#1	107.90(17)	B(6)-Zr-B(6)#1	101.9(2)
C(2)-C(1)-C(3)	116.7(4)	C(2)-C(1)-B(6)	125.5(4)
C(3)-C(1)-B(6)	117.2(4)	C(2)-C(1)-B(7)	103.2(4)
C(3)-C(1)-B(7)	111.4(4)	B(6)-C(1)-B(7)	63.1(3)
C(1)-C(2)-C(10)	116.3(4)	C(1)-C(2)-B(3)	125.8(5)
C(10)-C(2)-B(3)	117.8(4)	C(1)-C(2)-B(12)	91.9(4)
C(10)-C(2)-B(12)	113.4(4)	B(3)-C(2)-B(12)	65.2(3)
C(1)-C(2)-Zr	79.6(3)	C(10)-C(2)-Zr	122.3(3)
B(3)-C(2)-Zr	73.7(3)	B(12)-C(2)-Zr	121.3(3)
C(9)-C(3)-C(1)	113.3(4)	C(9)-C(4)-C(5)	120.6(7)
C(4)-C(5)-C(6)	119.2(6)	C(7)-C(6)-C(5)	120.6(6)
C(6)-C(7)-C(8)	119.5(6)	C(9)-C(8)-C(7)	120.3(5)
C(9)-C(8)-C(10)	118.2(5)	C(7)-C(8)-C(10)	121.5(5)
C(8)-C(9)-C(4)	119.7(5)	C(8)-C(9)-C(3)	118.3(5)
C(4)-C(9)-C(3)	122.0(5)	C(8)-C(10)-C(2)	113.2(4)
C(14)-O(1)-C(11)	104.2(7)	C(14)-O(1)-Na	128.0(5)
C(11)-O(1)-Na	125.9(5)	C(12)-C(11)-O(1)	110.1(7)
C(13)-C(12)-C(11)	105.8(8)	C(12)-C(13)-C(14)	106.4(9)
O(1)-C(14)-C(13)	108.6(7)	C(24)-O(2)-C(21)	101.9(8)
C(24)-O(2)-Na	128.5(6)	C(21)-O(2)-Na	128.7(5)
C(22)-C(21)-O(2)	115.2(13)	C(23)-C(22)-C(21)	104.2(17)
C(22)-C(23)-C(24)	112.1(14)	O(2)-C(24)-C(23)	102.4(10)
C(34)-O(3)-C(31)	106.5(7)	C(34)-O(3)-Na	122.7(5)
C(31)-O(3)-Na	127.9(6)	C(32)-C(31)-O(3)	108.1(9)
C(31)-C(32)-C(33)	107.4(10)	C(32)-C(33)-C(34)	105.9(10)
O(3)-C(34)-C(33)	107.7(9)	C(41)-O(4)-C(41)#2	81(2)
C(42)-C(41)-O(4)	124(3)	C(41)-C(42)-C(42)#2	106(2)
C(2)-B(3)-B(4)	119.5(4)	C(2)-B(3)-B(9)	119.7(4)
B(4)-B(3)-B(9)	58.3(3)	C(2)-B(3)-B(12)	63.8(3)
B(4)-B(3)-B(12)	104.8(4)	B(9)-B(3)-B(12)	60.6(3)
C(2)-B(3)-Zr	73.0(2)	B(4)-B(3)-Zr	63.1(2)
B(9)-B(3)-Zr	117.4(3)	B(12)-B(3)-Zr	119.9(3)
C(2)-B(3)-Na#1	146.4(4)	B(4)-B(3)-Na#1	75.5(3)
B(9)-B(3)-Na#1	93.9(3)	B(12)-B(3)-Na#1	145.8(3)
Zr-B(3)-Na#1	91.28(16)	B(9)-B(4)-B(10)	59.9(3)
B(9)-B(4)-B(5)	106.5(4)	B(10)-B(4)-B(5)	59.8(3)
B(9)-B(4)-B(3)	60.9(3)	B(10)-B(4)-B(3)	111.8(4)
B(5)-B(4)-B(3)	111.5(4)	B(9)-B(4)-Zr	133.0(4)
B(10)-B(4)-Zr	126.1(3)	B(5)-B(4)-Zr	67.4(2)
B(3)-B(4)-Zr	77.8(3)	B(4)-B(5)-B(10)	59.6(3)
B(4)-B(5)-B(11)	110.4(4)	B(10)-B(5)-B(11)	61.1(3)
B(4)-B(5)-B(6)	118.8(4)	B(10)-B(5)-B(6)	112.1(4)
B(11)-B(5)-B(6)	58.7(3)	B(4)-B(5)-B(5)#1	110.5(4)
B(10)-B(5)-B(5)#1	139.1(5)	B(11)-B(5)-B(5)#1	138.2(4)
B(6)-B(5)-B(5)#1	107.0(5)	B(4)-B(5)-Zr	70.5(3)

B(10)-B(5)-Zr	129.0(3)	B(11)-B(5)-Zr	136.7(4)
B(6)-B(5)-Zr	82.4(3)	B(5)#1-B(5)-Zr	67.09(12)
C(1)-B(6)-B(11)	118.6(4)	C(1)-B(6)-B(7)	64.5(3)
B(11)-B(6)-B(7)	59.2(4)	C(1)-B(6)-B(5)	115.9(4)
B(11)-B(6)-B(5)	59.8(3)	B(7)-B(6)-B(5)	103.6(4)
C(1)-B(6)-Zr	74.7(3)	B(11)-B(6)-Zr	116.1(3)
B(7)-B(6)-Zr	121.6(3)	B(5)-B(6)-Zr	59.2(2)
B(8)-B(7)-B(11)	61.6(4)	B(8)-B(7)-B(6)	109.5(5)
B(11)-B(7)-B(6)	59.1(3)	B(8)-B(7)-C(1)	123.2(4)
B(11)-B(7)-C(1)	107.4(4)	B(6)-B(7)-C(1)	52.4(3)
B(8)-B(7)-B(12)	57.2(3)	B(11)-B(7)-B(12)	107.2(4)
B(6)-B(7)-B(12)	110.8(4)	C(1)-B(7)-B(12)	78.7(3)
B(7)-B(8)-B(9)	116.7(5)	B(7)-B(8)-B(12)	67.1(4)
B(9)-B(8)-B(12)	62.7(4)	B(7)-B(8)-B(11)	59.4(4)
B(9)-B(8)-B(11)	110.2(5)	B(12)-B(8)-B(11)	113.3(4)
B(7)-B(8)-B(10)	110.4(4)	B(9)-B(8)-B(10)	59.3(4)
B(12)-B(8)-B(10)	110.8(4)	B(11)-B(8)-B(10)	60.5(4)
B(8)-B(9)-B(4)	108.0(4)	B(8)-B(9)-B(10)	61.3(4)
B(4)-B(9)-B(10)	61.1(3)	B(8)-B(9)-B(3)	110.4(4)
B(4)-B(9)-B(3)	60.8(3)	B(10)-B(9)-B(3)	112.7(4)
B(8)-B(9)-B(12)	58.9(4)	B(4)-B(9)-B(12)	107.3(4)
B(10)-B(9)-B(12)	109.3(4)	B(3)-B(9)-B(12)	61.4(3)
B(9)-B(10)-B(4)	59.1(3)	B(9)-B(10)-B(5)	106.6(4)
B(4)-B(10)-B(5)	60.7(3)	B(9)-B(10)-B(11)	109.6(5)
B(4)-B(10)-B(11)	109.5(4)	B(5)-B(10)-B(11)	58.9(3)
B(9)-B(10)-B(8)	59.5(4)	B(4)-B(10)-B(8)	105.1(4)
B(5)-B(10)-B(8)	103.1(4)	B(11)-B(10)-B(8)	59.6(4)
B(7)-B(11)-B(6)	61.6(4)	B(7)-B(11)-B(8)	59.0(4)
B(6)-B(11)-B(8)	109.5(5)	B(7)-B(11)-B(5)	106.7(4)
B(6)-B(11)-B(5)	61.5(3)	B(8)-B(11)-B(5)	104.1(4)
B(7)-B(11)-B(10)	109.7(5)	B(6)-B(11)-B(10)	113.4(4)
B(8)-B(11)-B(10)	59.9(4)	B(5)-B(11)-B(10)	60.0(3)
B(8)-B(12)-C(2)	125.6(4)	B(8)-B(12)-B(9)	58.4(4)
C(2)-B(12)-B(9)	105.3(4)	B(8)-B(12)-B(3)	107.0(5)
C(2)-B(12)-B(3)	50.9(3)	B(9)-B(12)-B(3)	58.0(3)
B(8)-B(12)-B(7)	55.7(3)	C(2)-B(12)-B(7)	85.9(3)
B(9)-B(12)-B(7)	104.1(5)	B(3)-B(12)-B(7)	113.5(4)
Zr-Cl-Na	104.56(7)	O(1)-Na-O(3)	94.7(2)
O(1)-Na-O(2)	90.5(2)	O(3)-Na-O(2)	97.0(2)
O(1)-Na-Cl	143.13(16)	O(3)-Na-Cl	121.31(17)
O(2)-Na-Cl	92.37(15)	O(1)-Na-B(3)#1	108.11(19)
O(3)-Na-B(3)#1	96.13(18)	O(2)-Na-B(3)#1	156.19(18)
Cl-Na-B(3)#1	63.82(11)		

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