Synthesis, Structural Characterization, and Reactivity of Group 4 Metal Complexes Derived from 1-Indenyl-1,2-carborane

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Treatment of 1-indenyl-1,2-carborane with 1 equiv of $M(NMe_2)_4$ (M = Zr, Hf) in toluene gave [η^5-$(C_2B_{10}H_{11})C_9H_6$]$M(NMe_2)_3$ (**2**), which were converted to [η^5-$(C_9H_7)C_2B_9H_{10}$]$M(NMe_2)_2(HNMe_2)$ (**3**) in the presence of $HNMe_2$. Complexes **3** were also prepared from an equimolar reaction of [Me_3NH][7-C_9H_7-7,8-$C_2B_9H_{11}$] (**4**) with $M(NMe_2)_4$. Dissolving **2** or **3** in polar solvents led to the isolation of structurally unique complexes [σ:η^5-$(C_9H_6)C_2B_9H_{10}$]$M(NMe_2)(L)_n$ (M = Ti, L = DME, n = 1 (**5a**); M = Zr, L = DME, n = 1 (**5b**), L = Py, n = 2 (**5b′**), L = THF, n = 2 (**5b″**)). Interaction of **3** with 1 or 2 equiv of diisopropylcarbodiimide yielded the monoguanidinate complex [η^5-$(C_9H_7)C_2B_9H_{10}$]$Zr(NMe_2)$[η^2-$(Pr^iN)_2C(NMe_2)$] (**9**) or diguanidinate complex [η^5-$(C_9H_7)C_2B_9H_{10}$]Zr[η^2-$(Pr^iN)_2C(NMe_2)$]$_2$ (**10**). Heating **9** in toluene gave a C−N bond cleavage product, [η^1:σ:η^5-{[2-C═NPr^i($NHPr^i$)]C_9H_5}$C_2B_9H_{10}$]Zr[η^2-$(Pr^iN)_2C(NMe_2)$] (**11a**). Triguanidinate complexes [{η^2-$(Pr^iN)_2C(NR_2)$}$_3$M][$(C_9H_7)C_2B_9H_{11}$] (**8**) (M = Ti, Zr, Hf; NR_2 = NMe_2, NEt_2, $N(CH_2)_4$) were prepared from reactions of **3** or **5b** with 3 equiv of guanidines in refluxing THF. Treatment of **5b** with 1 equiv of diphenylketene generated [σ:η^5-{[3-C(═CPh_2)-O]C_9H_6}$C_2B_9H_{10}$]$Zr(NMe_2)(THF)_2$ (**14**). These complexes were fully characterized by various spectroscopic techniques and elemental analyses. Some were further confirmed by single-crystal X-ray analyses.

Introduction

Ligands impose a dominant control over both chemical and physical properties of the resulting metal complexes. Ligand design has thus become a central theme in the development of the chemistry of organometallic compounds.[1] It is expected that incorporation of a carboranyl fragment into the ligand framework would provide new metal/charge combinations, which would have an impact on the properties of metal complexes. In this connection, a series of single-atom-bridged cyclopentadienyl-, indenyl-, and fluorenyl-carboranyl ligands $A(C_5H_5)(C_2B_{10}H_{11})$ (A = Me_2C,[2] Me_2Si[3]), $A'(C_9H_7)(C_2B_{10}H_{11})$ (A′ = Me_2C,[4] Me_2Si,[5] Pr^i_2NB,[6] Pr^i_2NP[7]), and $A''(C_{13}H_9)(C_2B_{10}H_{11})$ (A″ = H_2C,[8] Me_2Si[9]) have been developed. These ligands are finding many applications in organometallic chemistry, and the results show that the bridging atom significantly influences properties of the resulting organometallic complexes.[1g–j,2–9]

It is anticipated that the interactions between a cyclic organic moiety and a carboranyl group would be largely enhanced if there is no linkage in between. A recently reported compound, 1-indenyl-1,2-carborane, exhibits an interesting property.[10] Its trianion [7-C_9H_6-7,9-$C_2B_{10}H_{11}$]$^{3-}$ and penta-anion [7-C_9H_6-7,10-$C_2B_{10}H_{11}$]$^{5-}$ have demonstrated a very similar coordination mode to that of [$C_6H_5(C_5H_4)$]$^-$ in lanthanide chemistry, which favors the formation of "metal-bridged" complexes.[10] One would expect that reaction of group 4 metal amides $M(NMe_2)_4$ with 1-indenyl-1,2-carborane or 7-indenyl-7,8-dicarbollide would most likely afford the same type of "metal-bridged" dinuclear amide complexes. To our surprise, the dicarbollide derivative [7-C_9H_6-7,8-$C_2B_9H_{10}$]$^{3-}$ is able to form an unprecedented highly constrained-geometry metal complex [σ:η^5-$(C_9H_6)C_2B_9H_{10}$]-

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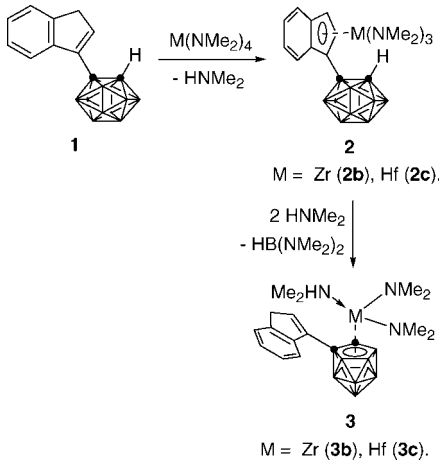
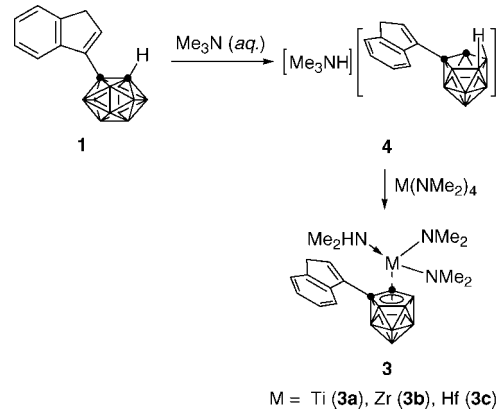
Scheme 1



Scheme 2



$Zr(NMe_2)(DME)$, which exhibits unique chemical properties.[11] We then extended our research to include the Ti and Hf chemistry. This article reports a full account on the reactions of $M(NMe_2)_4$ with 1-indenyl-1,2-carborane and 7-indenyl-7,8-dicarbollide, the interconversions among different types of amide complexes, and their reactivities.

Results and Discussion

Synthesis of Amide Complexes. Our previous work showed that interaction of group 4 metal amides $M(NMe_2)_4$ (M = Ti, Zr, Hf) with $A(C_5H_5)(C_2B_{10}H_{11})$ (A = Me_2C, Me_2Si)[2c] or $A'(C_9H_7)(C_2B_{10}H_{11})$ (A′ = Me_2C,[2c] Me_2Si,[2c] Pr^i_2NB,[6b] Pr^i_2NP[7b]) led to the clean formation of the corresponding constrained-geometry metal complexes $[\eta^5{:}\sigma\text{-}A(C_5H_4)C_2B_{10}H_{10}]M(NMe_2)_2$ or $[\eta^5{:}\sigma\text{-}A'(C_9H_6)C_2B_{10}H_{10}]M(NMe_2)_2$, respectively.[1i] It is anticipated that the two acidic protons in 1-C_9H_7-1,2-$C_2B_{10}H_{11}$ (**1**) would allow similar amine elimination reaction to occur. However, treatment of **1** with 1 equiv of $Zr(NMe_2)_4$ in toluene at room temperature produced only the monodeprotonated complex $[\eta^5\text{-}(C_2B_{10}H_{11})C_9H_6]Zr(NMe_2)_3$ (**2b**) in quantitative yield. On the other hand, reaction of **1** with $Hf(NMe_2)_4$ at room temperature gave a mixture of products. Complex $[\eta^5\text{-}(C_2B_{10}H_{11})C_9H_6]Hf(NMe_2)_3$ (**2c**) was finally isolated in quantitative yield from an equimolar reaction of **1** with $Hf(NMe_2)_4$ in toluene at −30 °C (Scheme 1). It is noted that the $HNMe_2$ generated in the reactions must be immediately removed; otherwise, a mixture of products would be formed. Under similar reaction conditions, reaction of **1** with $Ti(NMe_2)_4$ did not lead to the isolation of any pure products. The ^{1}H NMR experiments indicated that only about 20% of **1** was consumed, even after the reaction mixture of $Ti(NMe_2)_4$ and 1 equiv of **1** in benzene-d_6 stood at room temperature for 4 weeks. Its ^{1}H NMR spectrum became very complicated upon heating. Such reactivity differences among group 4 metal complexes were reported in the literature and is probably due to the size effect.[12]

The ^{1}H NMR spectrum of **2b** in benzene-d_6 showed two doublets at 6.47 and 5.99 ppm with J = 3.6 Hz assignable to the C_5 ring protons of the indenyl, a broad singlet at 3.29 ppm attributable to the cage C*H* proton, and a singlet at 2.58 ppm corresponding to the $N(CH_3)_2$ group, in addition to the aromatic protons in the range 7.9–6.8 ppm. One singlet at 43.7 ppm assignable to the $Zr(N(CH_3)_2)_3$ unit was observed in the ^{13}C NMR spectrum besides the indenyl and cage carbon signals. Its ^{11}B NMR exhibited a 1:1:4:4 pattern. Similar spectroscopic features were also observed in the NMR spectra of **2c**. The compositions of **2b**,**c** were further confirmed by elemental analyses.

Complexes **2b**,**c** are very stable in toluene, and no amine elimination was observed even at refluxing temperature. Prolonged reaction of **1** with 1 equiv of $Zr(NMe_2)_4$ in a sealed NMR tube, however, led to the formation of a 1:1 mixture of **2b** and an unidentified species as indicated by ^{1}H NMR. The ^{11}B NMR showed a characteristic resonance at 29 ppm assignable to $HB(NMe_2)_2$,[13a,b] suggesting that a deboration reaction occurred. It was assumed that this new species might be formed from the reaction of **2b** with $HNMe_2$ generated *in situ* in the reaction mixture.[13c–j] In fact, treatment of **2b** or **2c** with 2.2 equiv of $HNMe_2$ in toluene yielded almost quantitatively complexes $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]M(NMe_2)_2(HNMe_2)$ (M = Zr (**3b**), Hf (**3c**)) (Scheme 1).

The above results clearly showed that amines can serve as deboration agents. Therefore, an aqueous solution of Me_3N (45%) was then used as the reagent to convert **1** to $[Me_3NH][7\text{-}C_9H_7\text{-}7,8\text{-}C_2B_9H_{11}]$ (**4**) in 99% yield in refluxing methanol. An equimolar reaction of **4** with $M(NMe_2)_4$ (M = Ti, Zr, Hf) in toluene at room temperature afforded $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]\text{-}Ti(NMe_2)_2(HNMe_2)$ (**3a**) in 62% yield or **3b**,**c** in >95% yields (Scheme 2). Complex **3b** is barely soluble in toluene, while **3c** is insoluble. Both are slightly soluble in DME and soluble in THF and pyridine, whereas complexes **2b**,**c** are soluble in most organic solvents, which facilitates the purification of **3b**,**c**. Complex **3a** is slightly soluble in toluene and soluble in THF, DME, and pyridine.

The ^{1}H NMR spectrum of **3b** in benzene-d_6 displayed two doublets at 1.99 and 1.73 ppm with J = 6.0 Hz corresponding to the coordinated dimethyl amine, two singlets at 2.55 and 2.06 ppm attributable to the $Zr(N(CH_3)_2)_2$ protons, a singlet of indenyl

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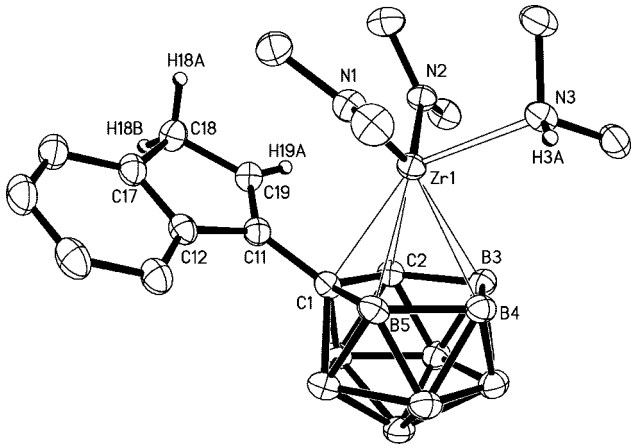

Figure 1. Molecular structure of $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Zr(NMe_2)_2(HNMe_2)$ (**3b**) (thermal ellipsoids drawn at the 30% probability level).

CH_2 at 2.77 ppm,[14] a broad singlet of cage C*H* at 3.20 ppm, a singlet of the olefinic proton at 5.62 ppm,[14] and the multiplets of aromatic protons in the range 7.0–8.3 ppm. In addition to the indenyl carbon resonances, four signals assignable to the coordinated dimethyl amine and dimethyl amido carbons at 39.2, 41.7, 47.7, and 49.6 ppm were observed in the ^{13}C NMR spectrum of **3b**, which was significantly different from that of **2b**. The ^{11}B NMR of **3b** exhibited a 1:1:4:2:1 pattern. Similar spectroscopic features were also observed in the NMR spectra of **3a**. Due to the very poor solubility of **3c** in benzene-d_6 and CD_2Cl_2, its NMR spectra had to be recorded in pyridine-d_5. The compositions of **3a**,**b**,**c** were confirmed by elemental analyses.

Single-crystal X-ray analyses revealed that **3b**,**c** are isostructural and adopt monomeric three-legged piano stool geometry containing an η^5-dicarbollyl ligand with two amido and one amine ligand in the basal positions, a structure that is similar to $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(HNEt_2)$,[15] $[\eta^5\text{-}(Me_2NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2(HNMe_2)$,[16] and $[\eta^5\text{-}(Bn_2NCH_2CH_2)C_2B_9H_{10}]Zr(NMe_2)_2(HNMe_2)$ (Bn = $C_6H_5CH_2$).[17] The representative structure of **3b** is shown in Figure 1. For easy comparison, key structural parameters are compiled in Table 1. The short Zr−N(1)/N(2) distances of 2.027(3)/2.032(3) Å and the planar geometry around the N(1) and N(2) atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in $N(p_\pi)\rightarrow Zr(d_\pi)$ interactions.[18] As expected, the Zr−N(3) distance of 2.345(3) Å is much longer than the Zr−N(amido) distances and the N(3) adopts a pyramidal geometry. The average Zr−cage atom distance is 2.530(4) Å. These structural data are very close to those found in $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(HNEt_2)$,[15] $[\eta^5\text{-}(Me_2NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2(HNMe_2)$,[16] and $[\eta^5\text{-}(Bn_2NCH_2CH_2)C_2B_9H_{10}]Zr(NMe_2)_2(HNMe_2)$.[17]

Amine elimination reactions between metal amides and ligands bearing acidic protons are a useful method for the preparation of organometallic amide complexes.[1i,19] It is very interesting to note that both complexes **2** and **3** are very stable in toluene even at refluxing temperature, although they contain both basic M−NMe_2 and acidic cage C−H or indenyl CH_2. However, treatment of **4** with $Ti(NMe_2)_4$ in polar solvent DME (dimethoxyethane) or directly dissolving **3a** in DME resulted in the isolation of $[\sigma:\eta^5\text{-}(C_9H_6)C_2B_9H_{10}]Ti(NMe_2)(DME)$ (**5a**) in 26% yield. In a similar manner, directly dissolving **3b** in pyridine (Py) led to the isolation of $[\sigma:\eta^5\text{-}(C_9H_6)C_2B_9H_{10}]Zr(NMe_2)(Py)_2$ (**5b′**) in 86% yield (Scheme 3), whereas **3c** is stable in pyridine. On the other hand, complex **3b** is stable in DME and THF at room temperature, but decomposes under refluxing conditions.

Directly dissolving **2b** in polar solvents did not offer the expected product $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Zr(NMe_2)_2$; instead, $[\sigma:\eta^5\text{-}(C_9H_6)C_2B_9H_{10}]Zr(NMe_2)(L)_n$ (L = DME, n = 1 (**5b**); L = Py, n = 2 (**5b′**); L = THF, n = 2 (**5b″**)) were isolated respectively from DME, pyridine, and THF solution at room temperature (Scheme 4). Considering the stability of **3b** in DME or THF at room temperature, the formation of **5** from **2b** should not be via **3b**. Therefore, a possible reaction pathway is proposed in Scheme 4. Intramolecular amine elimination of **2b** affords the intermediate $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Zr(NMe_2)_2$ (**A**), followed by nucleophilic attack of amine generated *in situ* on the cage boron atom to give the final product and release $HB(NMe_2)_2$.[13c–j] A doublet at 29 ppm observed in the proton-coupled ^{11}B NMR spectrum of the reaction mixture supported the formation of $HB(NMe_2)_2$.[13a,b]

The ^1H NMR spectra of **5** in pyridine-d_5 displayed two doublets at ∼6.1 and ∼6.4 ppm with $J \approx 4.5$ Hz corresponding to the olefinic protons and a singlet at ∼3.2 ppm assignable to $N(CH_3)_2$ with an integral ratio of 1:1:6, in addition to the aromatic, cage, and coordinated solvent peaks. Their ^{13}C NMR spectra showed a characteristic Ti−*C*(indenyl) resonance at 92.6 ppm or Zr−*C*(indenyl) resonance at ∼85 ppm as well as dimethyl amido signals in the range 42–46 ppm, besides the aromatic and coordinated solvent carbon signals. A 2:2:2:3 pattern was observed in the ^{11}B NMR spectra.

Single-crystal X-ray analyses confirmed the molecular structures of **5a**, **5b**, and **5b″**. The representative structures of **5a** and **5b″** are shown in Figures 2 and 3. The central metal atom is η^5-bound to the dicarbollyl, η^1-bound to the indenyl, σ-bound to the dimethyl amino group, and coordinated by one DME or two THF molecules, respectively. The C(11)−C(19)/C(18)−C(19) distances of 1.461(4)/1.345(5) Å in **5a**, 1.465(9)/1.36(1) Å in **5b**, and 1.442(9)/1.325(9) Å in **5b″** indicate a single and a double bond, respectively. The Ti(1)−C(11) distance of 2.425(3) Å is significantly longer than the typical Ti−C σ-bond distances, for example, 2.128(5) Å in $(\eta^5\text{-}C_5Me_5)Ti(Me)_2[ONMe(Bu^t)]$,[20] 2.132(4) Å in $[\sigma:\eta^1:\sigma\text{-}(2\text{-}O\text{-}3,5\text{-}Bu^t_2\text{-}C_6H_2)(C_5H_3N)\{3,5\text{-}(CF_3)_2\text{-}C_6H_2\}]Ti(CH_2Ph)_2$,[21] 2.165(4) Å in $[\eta^5:\eta^1\text{-}(C_9H_6)(CH_2CH_2$-

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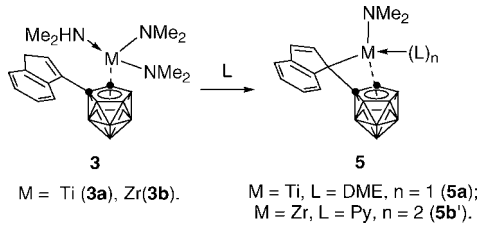
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3b, 3c, 5a, 5b, 5b″, and 6

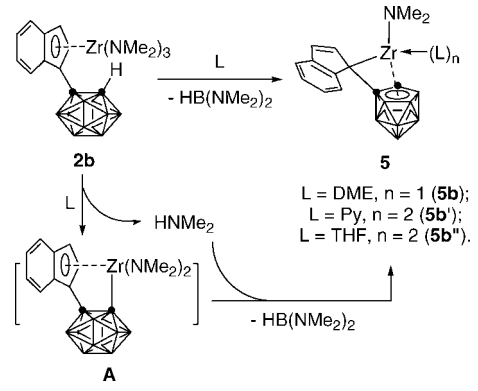
	3b	3c	5a	5b[a]	5b″	6
(M)	(Zr)	(Hf)	(Ti)	(Zr)	(Zr)	(Hf)
av M−cage atom	2.530(4)	2.56(1)	2.350(4)	2.469(8)	2.464(8)	2.565(8)
av M−N(amido)	2.030(3)	2.077(9)	1.891(3)	2.010(6)	2.003(5)	2.005(5)
M−N(amine)	2.345(3)	2.361(8)				
M−C(11)			2.425(3)	2.477(6)	2.487(6)	
M−C(11)−C(1)			62.6(1)	65.7(3)	65.7(3)	
M−C(1)−C(11)	89.3(2)	91.5(5)	80.9(2)	78.7(4)	78.8(3)	107.9(4)

[a] See ref 11.

Scheme 3



Scheme 4



OMe)]TiMeCl$_2$,[22] 1.97(2) and 2.232(9) Å in [η^5:σ-Me$_2$C-(C_5H_4)($C_2B_{10}H_{10}$)]Ti(CH_2Ph)(NMe_2),[23] 2.160(2) Å in (η^5-$C_2B_9H_{11}$)(η^5-C_5Me_5)TiMe, and 2.294(3) Å in (η^5-$C_2B_9H_{11}$)Ti($C_5Me_4CH_2$).[24] The Ti−N(1) distance of 1.891(3) Å is well comparable to those reported in the literature, 1.900(2) Å in (η^5-$C_2B_9H_{11}$)Ti(NMe_2)$_2$($HNMe_2$),[6b] 1.862(3) Å in [σ:η^1:η^5-(OCH_2)(Me_2NCH_2)$C_2B_9H_9$]Ti(NMe_2),[12c] 1.868(3) Å in [σ:η^1:η^5-(OCH_2)(Et_2NCH_2)$C_2B_9H_9$]Ti(NEt_2),[12c] 1.892(3) Å in [η^5:σ-Pr$^i_2$NP(C_9H_6)$C_2B_{10}H_{10}$]Ti(NMe_2)$_2$,[7b] and 1.900(4) Å in [(η^5-

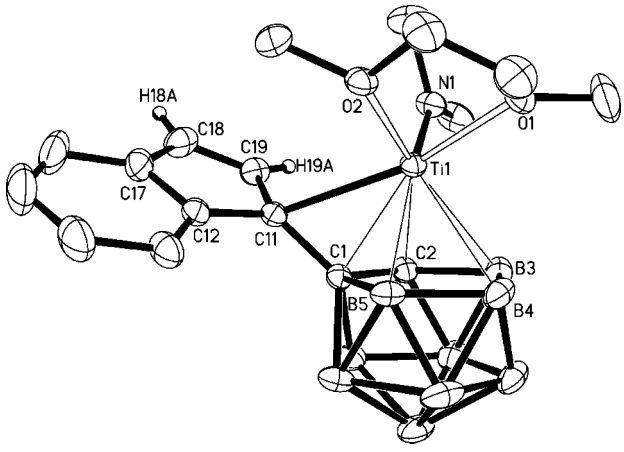


Figure 2. Molecular structure of [σ:η^5-(C_9H_6)$C_2B_9H_{10}$]-Ti(NMe_2)(DME) (**5a**) (thermal ellipsoids drawn at the 30% probability level).

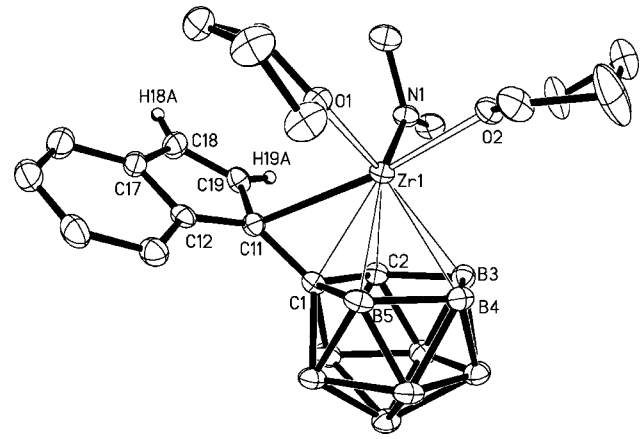


Figure 3. Molecular structure of [σ:η^5-(C_9H_6)$C_2B_9H_{10}$]-Zr(NMe_2)(THF)$_2$ (**5b″**) (thermal ellipsoids drawn at the 30% probability level).

$C_2B_9H_{10}$)(CH_2)$_2$(η^1-NBn_2)]Ti(NMe_2)$_2$.[17] The Zr−N(1) distances of 2.003(5) Å in **5b″** and 2.010(6) Å in **5b** are close to those reported in the literature, 2.005(7) Å in (μ-O)[Zr(NMe_2)(O-Ar)$_2$]$_2$ (Ar = 2,6-Bu$^t_2$-4-Me-3,5-N_2C_4),[25] 2.029(4) Å in [η^5:σ-Me_2Si(C_9H_6)$C_2B_{10}H_{10}$]Zr(NEt_2)$_2$,[2c] 2.026(2) Å in [η^5:σ-Pr$^i_2$NB(C_9H_6)$C_2B_{10}H_{10}$]Zr(NMe_2)$_2$,[6b] and 2.030(3) Å in **3b**. The Zr−C(11) distance of 2.491(6) Å in **5b″** and 2.477(6) Å in **5b** are much longer than the Zr−C σ-bond distances of 2.272(3) Å in [σ:η^1:σ-(2-O-3,5-Bu$^t_2$-C_6H_2)(C_5H_3N){3,5-(CF_3)$_2$-C_6H_2}]-Zr(CH_2Ph)$_2$,[21] 2.312(6) Å in [(η^5-C_5H_4)$SiMe_2$(η^5-2-Me-$C_{13}H_7$)]-Zr(CH_2Ph)$_2$,[26] 2.290(2) Å in (CBC)Zr(CH_2TMS)$_2$ (CBC = {1,4,811-tetraazabicyclo[6.6.2]hexadecane}$^{2-}$),[27] 2.242(6) Å in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(CH_2TMS)(THF),[28] and Zr−C(cage) distance of 2.345(2) Å in [η^5:σ-Pr$^i_2$NB(C_9H_6)$C_2B_{10}H_{10}$]Zr(NMe_2)$_2$.[6b] To the best of our knowledge, the measured M−C(indenyl) distances in **5** represent the longest group 4 metal–carbon σ-bond length reported thus far.

Reaction of Amide Complexes 3. As described previously, attempts to prepare the constrained-geometry Hf complex by directly dissolving **3c** in polar solvents failed. On the other hand, a C−O bond cleavage product, [{η^5-(C_9H_7)$C_2B_9H_{10}$}Hf(NMe_2)(μ:η^1-$OCH_2CH_2OCH_3$)]$_2$ (**6**), was isolated in 12% yield at room temperature from a DME solution of **3c**. A possible reaction

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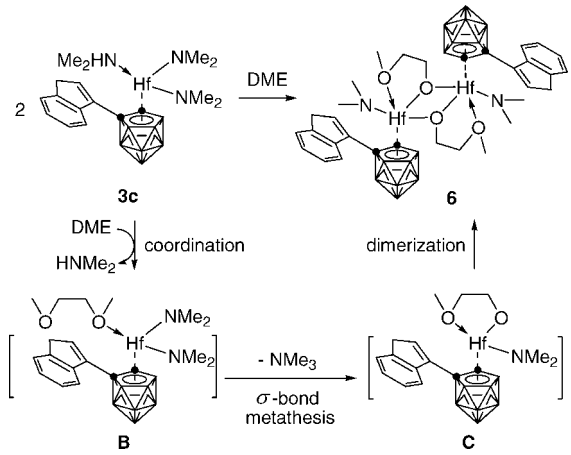
Scheme 5



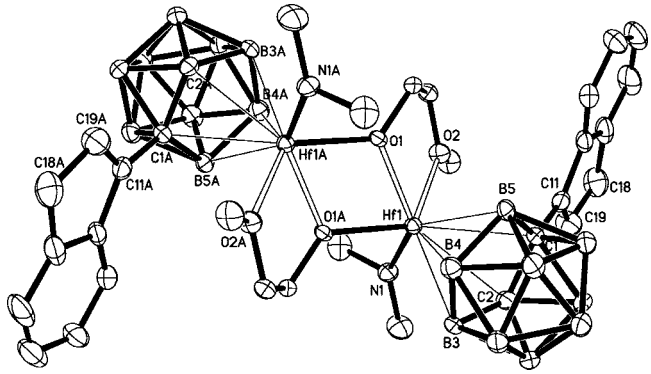


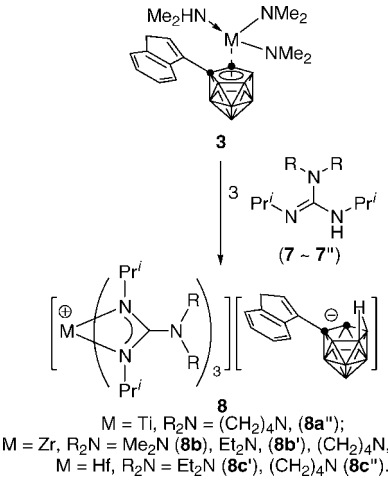
Figure 4. Molecular structure of $[\{\eta^5\text{-}(C_9H_7)C_2B_9H_{10}\}Hf(NMe_2)(\mu\text{:}\eta^1\text{-}OCH_2CH_2OCH_3)]_2$ (**6**) (thermal ellipsoids drawn at the 30% probability level).

pathway is shown in Scheme 5. Replacement of Me_2NH by DME, followed by σ-bond metathesis and dimerization, gives **6**.[29]

The ^{1}H NMR spectrum of **6** showed two doublets at 8.17 and 7.15 ppm with $J = 7.5$ Hz, two triplets at 7.33 and 7.26 ppm with $J = 7.5$ Hz, and two singlets at 6.41 and 3.24 ppm assignable to the indenyl group, in addition to a singlet at 3.25 ppm attributable to the $N(CH_3)_2$ and resonances at 3.49, 3.17, and 3.06 ppm corresponding to $OCH_2CH_2OCH_3$. Its ^{11}B NMR displayed a 2:2:2:2:2:2:2:2:2 pattern, which is significantly different from the parent complex **3c**.

An X-ray analysis revealed that **6** is a dimer and showed two THF of solvation. Each Hf atom is σ-bound to a dimethylamino group and two doubly bridging O atoms, η^5-bound to a dicarbollyl ligand and coordinated to an O atom in a typical four-legged piano stool geometry (Figure 4). The Hf(1)−cage atom distance of 2.565(8) Å in **6** is close to 2.56(1) Å in **3c** and 2.63(1) Å in $[\eta^1\text{:}\eta^5\text{-}(Pr^i_2C_6H_3N{=}CH)C_2B_9H_{10}]Hf(NMe_2)_2(NHMe_2)$.[13d] The Hf(1)−N(1) distance of 2.005(5) Å in **6** is comparable with 2.077(9) Å in **3c**, 2.067(4) Å in $(\eta^5\text{-}C_5Me_5)\{\sigma\text{:}\eta^2\text{-}[OC\text{-}C(Ph)NC(NMe_2)NPh]\}Hf(NMe_2)$,[30] 2.059(7) Å in $[\eta^1\text{:}\eta^5\text{-}(Pr^i_2C_6H_3N{=}CH)C_2B_9H_{10}]Hf(NMe_2)_2(NHMe_2)$,[13d] 2.004(12) Å in $[\eta^5\text{:}\sigma\text{-}Pr^i_2NP(C_9H_6)(C_2B_{10}H_{10})]Hf(NMe_2)_2$,[7b] and 1.991(1) Å in $[\sigma\text{:}\sigma\text{-}Pr^i_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]Hf(NEt_2)_2(THF)$.[31] The Hf(1)−O(1)/Hf(1)−O(1A) distances of 2.162(4)/2.101(4) Å in **6** are longer than 2.075(1) Å in $[\sigma\text{:}\sigma\text{-}Pr^i_2NP(O)(C_9H_6)\text{-}(C_2B_{10}H_{10})]Hf(NEt_2)_2(THF)$,[31] 1.999(3) Å in $(\eta^5\text{-}C_5Me_5)\{\sigma\text{:}\eta^2\text{-}[OC\text{-}C(Ph)NC(NMe_2)NPh]\}Hf(NMe_2)$,[30] and 2.021(3) Å in $(\eta^5\text{-}C_5Me_5)[\sigma\text{:}\eta^1\text{-}(O\text{-}C_6H_2\text{-}2,4\text{-}Me_2\text{-}6\text{-}C_3H_4ON)]HfCl_2$.[32]

Scheme 6



M = Ti, $R_2N = (CH_2)_4N$, (**8a"**);
M = Zr, $R_2N = Me_2N$ (**8b**), Et_2N, (**8b'**), $(CH_2)_4N$, (**8b"**);
M = Hf, $R_2N = Et_2N$ (**8c'**), $(CH_2)_4N$ (**8c"**).

In view of the wide applications of guanidine derivatives as electronically and sterically flexible ligands in organometallic chemistry,[19g,33] we would like to incorporate guanidines into metallacarboranes to study the effects of metal/charge combinations on the reactivity of group 4 metal complexes. Treatment of **3** with 1 or 2 equiv of guanidines always gave a mixture of inseparable products. In the presence of 3 or more equiv of guanidines $Pr^iN{=}C(NR_2)\text{-}NHPr^i$ ($NR_2 = NMe_2$ (**7**), NEt_2 (**7′**), $N(CH_2)_4$ (**7″**)), ionic complexes $[\{\eta^2\text{-}(Pr^iN)_2C(NR_2)\}_3M][(C_9H_7)\text{-}C_2B_9H_{11}]$ (M = Ti, $NR_2 = N(CH_2)_4$ (**8a″**); M = Zr, $NR_2 = NMe_2$ (**8b**), NEt_2 (**8b′**), $N(CH_2)_4$ (**8b″**); M = Hf, $NR_2 = NEt_2$ (**8c′**), $N(CH_2)_4$ (**8c″**)) were isolated in 57%−91% yields (Scheme 6). It is clear that the high acidity of guanidines ($pK_a \approx 13.6$)[33a] drives the protonation reactions to completion.

The ^{1}H NMR spectra of **8** exhibited a broad singlet in the range −1.0 to −1.3 ppm corresponding to the bridging B*H*B proton in addition to the resonances of the indenyl and guanidinate protons. The characteristic guanidinate carbon (N_3C) resonance at ∼170 ppm was observed in their ^{13}C NMR spectra. Their ^{11}B NMR spectra displayed a 1:1:1:1:1:1:1:1:1 pattern, which is similar to that of **4**.

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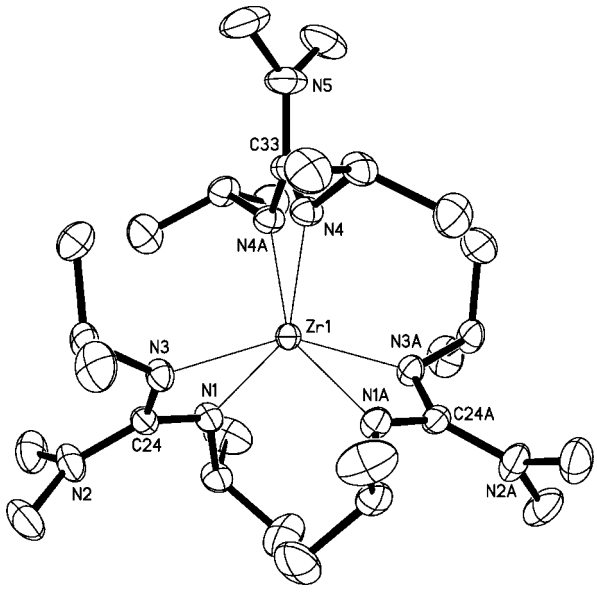


Figure 5. Molecular structure of the cation in $[\{\eta^2\text{-}(Pr^iN)_2C(NMe_2)\}_3Zr][(C_9H_7)C_2B_9H_{11}]$ (**8b**) (thermal ellipsoids drawn at the 30% probability level).

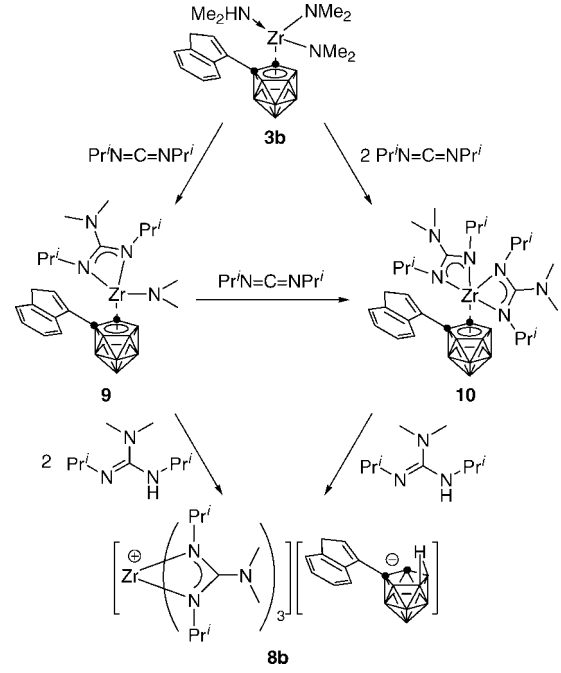
Single-crystal X-ray diffraction studies confirmed that **8** are ionic complexes, consisting of well-separated cations $[\{\eta^2\text{-}(Pr^iN)_2C(NR_2)\}_3M]^+$ and monoanions $[(C_9H_7)C_2B_9H_{11}]^-$. Different from $[\eta^5\text{-}(Et)C_5Me_4]_2ZrMe(C_2B_9H_{12})$,[34] no Zr−H−B bonding interaction is observed in complexes **8**. In the cation, the metal is η^2-bound to three guanidinates with an average Zr−N distance of ∼2.2 Å. Figure 5 shows the representative structure of the cation in **8b**.

Although the controlled syntheses of mono- and diguanidinate complexes from the reactions of **3** with 1 or 2 equiv of guanidines were unsuccessful, they were achieved by stepwise insertion of carbodiimide into the M−N bonds in **3**. Treatment of **3b** with 1 or 2 equiv of diisopropylcarbodiimide in THF at room temperature afforded, after recrystallization from toluene, monoguanidinate complex $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Zr(NMe_2)[\eta^2\text{-}(Pr^iN)_2C(NMe_2)]\cdot 0.5C_7H_8$ (**9**·0.5C_7H_8) or diguanidinate complex $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Zr[\eta^2\text{-}(Pr^iN)_2C(NMe_2)]_2$ (**10**) in 6% or 90% isolated yields, respectively. It is noted that the former reaction also generated **10**, leading to the rather low isolated yield of **9**. Reaction of **9** with an equimolar amount of diisopropylcarbodiimide afforded **10**. Both complexes reacted further with guanidine **7** in refluxing THF to produce complex **8b** (Scheme 7).

In addition to the resonances of indenyl and cage protons, the ^{1}H NMR spectrum of **9** exhibited a singlet at 3.03 ppm assignable to Zr−N(CH_3)$_2$, two multiplets at 3.83 and 2.51 ppm, and two broad peaks at 1.13 and 0.79 ppm attributable to guanidinate, whereas a multiplet at 3.84 ppm and two peaks at 2.57 and 1.21 ppm corresponding to guanidinates were observed in the ^{1}H NMR spectrum of **10**. The characteristic guanidinate carbon (*C*N$_3$) resonances at 173.1 and 172.0 were also observed in the ^{13}C NMR spectra of **9** and **10**, respectively. Their ^{11}B NMR showed 1:1:1:4:1:1 and 1:1:4:2:1 patterns, which are different from those of **3b** and **8**.

The solid-state structure of **9** was confirmed by a single-crystal X-ray diffraction study. The Zr atom in **9** is coordinated by one N atom, an η^2-guanidinate, and an η^5-dicarbollyl ligand,

Scheme 7



as shown in Figure 6. The average Zr−cage atom distance of 2.532(4) Å in **9** is almost the same as that of 2.530(4) Å in **3b**. For easy comparison, key structural parameters are compiled in Tables 1 and 2.

It was communicated earlier that heating **10** in toluene caused an unexpected C−N bond cleavage process to produce **11a**.[11] Under the same reaction conditions, **11a** was isolated in 28% yield from a refluxing toluene solution of **9**. A possible reaction pathway is illustrated in Scheme 8. Intramolecular amine elimination of **9** gives the intermediate **D/D′**, which undergoes C−N bond cleavage upon heating to generate carbodiimide and metallacarborane amide **E**. Interaction between **D/D′** and *in situ* generated carbodiimide affords **F**. 1,5-Sigmatropic rearrangement[35] over the indenyl ring followed by an intramolecular proton shift gives the final product **11a**.[36]

Reaction of Amide Complex 5b. Complex **5b** reacted with 2 equiv of guanidines $Pr^iNH\text{-}C(NR_2)$═NPr^i in refluxing toluene

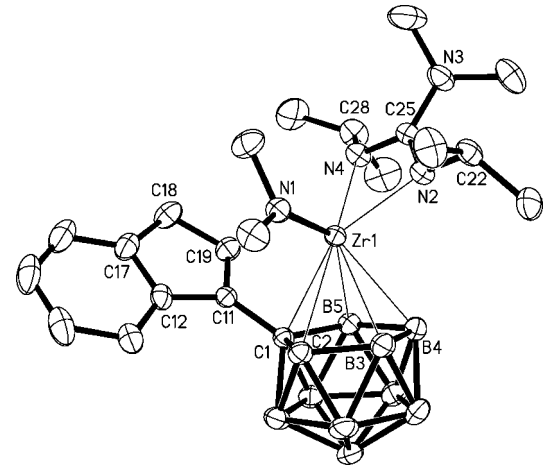


Figure 6. Molecular structure of $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Zr(NMe_2)[\eta^2\text{-}(Pr^iN)_2C(NMe_2)]$ (**9**) (thermal ellipsoids drawn at the 30% probability level).

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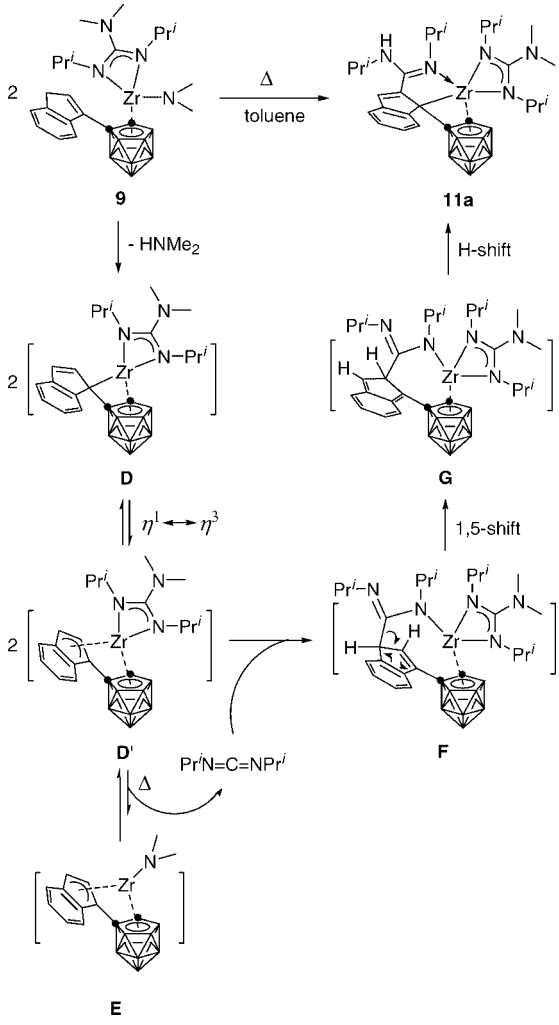
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 9, 10, 11a, 11b, 11c, 13a, 13c, and 14

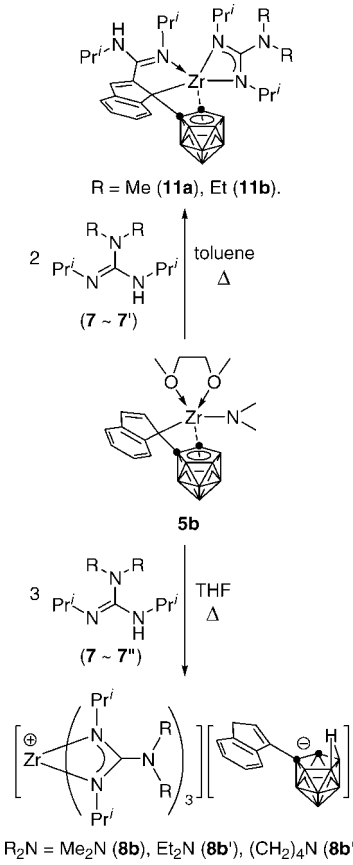
	9	**10**[ab]	**11a**[a]	**11b**[ab]	**11c**[a]	**13a**[a]	**13c**[a]	**14**
av Zr−cage atom	2.532(4)	2.61(2)	2.481(5)	2.494(2)	2.492(5)	2.552(6)	2.554(4)	2.603(6)
av Zr−N(guanidinate)	2.213(3)	2.210(8)	2.196(3)	2.18(1)	2.195(3)	2.186(4)	2.189(3)	
Zr−N(amido)	2.018(3)					2.082(4)	2.081(2)	2.006(4)
Zr−N(imine)			2.223(3)	2.24(1)	2.242(3)			
Zr−C(indenyl)			2.499(4)[c]	2.51(1)[c]	2.488(4)[c]	2.716(5)[c]	2.700(3)[c]	
						2.603(5)[d]	2.618(3)[d]	
Zr−C(11)−C(1)			65.8(2)	65.3(5)	65.8(2)	66.3(3)	65.9(2)	
Zr−C(1)−C(11)	85.1(2)	108.5(5)	78.4(2)	78.6(6)	78.4(2)	81.3(3)	81.4(2)	88.1(3)
N−Zr−N(guanidinate)	60.3(1)	60.3(3)	61.1(1)	61.4(4)	61.1(1)	61.8(2)	61.6(1)	

[a] See ref 11. [b] Average values of two crystallographically independent molecules in the unit cell. [c] Zr−C(11). [d] Zr−C(19).

Scheme 8



Scheme 9



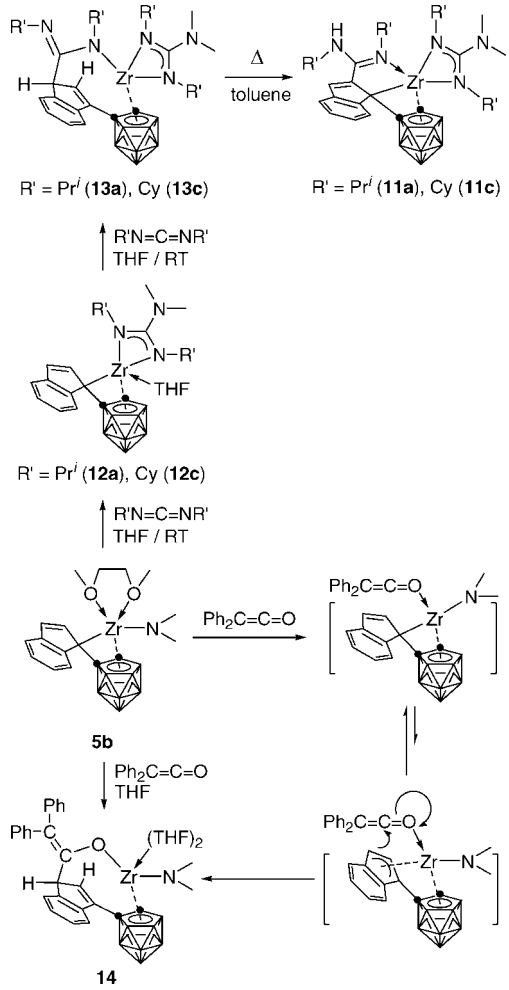
to give unprecedented zirconacarboranes $[\eta^1{:}\sigma{:}\eta^5$-{[2-{C═NPr^i(NHPr^i)}]$C_9H_5$}$C_2B_9H_{10}$]Zr[$\eta^2$-(Pr^{i}N)$_2$C(NR$_2$)] (R = Me (**11a**), Et (**11b**)) in 30–47% yields.[11] These complexes were also isolated from equimolar reactions in a much lower yield. On the other hand, interaction of **5b** with 3 equiv of guanidines in refluxing THF afforded **8b**−**8b″** in 33–60% isolated yields (Scheme 9). These results suggested that the solvents and reaction temperature may play a role in the formation of the final products.

To understand the above reaction pathway, reaction of **5b** with carbodiimides was attempted, as the insertion of R′N═C═NR′ into the M−N bond gives the M-guanidinates.[37] Treatment of **5b** with 1 equiv of R′N═C═NR′ (R′ = Pr^i, Cy) in THF at room temperature gave the Zr−N insertion products $[\sigma{:}\eta^5$-(C_9H_6)$C_2B_9H_{10}$]Zr[η^2-(R′N)$_2$C(NMe$_2$)](THF) (R′ = Pr^i (**12a**), Cy (**12c**)) in 71–74% isolated yields. Complexes **12a**,**c** reacted further with another equivalent of R′N═C═NR′ to generate the Zr−C insertion species $[\sigma{:}\eta^5$-{3-[C(═NR′)NR′]-1-C_9H_6}-$C_2B_9H_{10}$]Zr[η^2-(R′N)$_2$C(NMe$_2$)] (R′ = Pr^i (**13a**), Cy (**13c**)) in quantitative yields.[11] They were cleanly converted to $[\eta^1{:}\sigma{:}\eta^5$-{2-[C═NR′(NHR′)]$C_9H_5$}$C_2B_9H_{10}$]Zr[$\eta^2$-(R′N)$_2$C(NMe$_2$)] (R′ = Pr^i (**11a**), Cy (**11c**)) upon refluxing in toluene. A possible reaction mechanism was discussed in the preliminary communication.[11] In sharp contrast, reaction of **5b** with an equimolar amount of diphenylketene in THF at room temperature afforded, after recrystallization from THF, $[\sigma{:}\eta^5$-{[3-C(═CPh$_2$)-O]-C_9H_6}$C_2B_9H_{10}$]Zr(NMe$_2$)(THF)$_2$ (**14**) in 64% isolated yield. These transformations are outlined in Scheme 10. The formation

(35) For 1,5-sigmatropic rearrangement in indene derivatives, see: (a) Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219–221*, 311. (b) Christopher, J. N.; Jordan, R. F.; Peterson, J. L., Jr.; Young, V. G. *Organometallics* **1997**, *16*, 3044. (c) Dolbier, W. R., Jr.; McCullagh, L.; Rolison, D.; Anapolle, K. E. *J. Am. Chem. Soc.* **1975**, *97*, 934. (d) Stradiotto, M.; Hazendonk, P.; Bain, A. D.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **2000**, *19*, 590.

(36) A similar reaction pathway was proposed for the conversion of **10** to **11a**, see ref 11.

Scheme 10



of **14** may involve the coordination of ketene to the Zr atom, followed by the nucleophilic attack of the indenyl on ketene (Scheme 10). Complex **14** is stable in THF and does not react further with another equivalent of ketene presumably due to steric reasons. It is not clear at this stage why **5b** shows a different chemoselectivity toward ketene and carbodiimide. Insertion of the C═O unit in $R_2C{=}C{=}O$ into the M−C[38] and M−N[39] bonds has been documented, but the preference in reactivity is not clearly addressed yet.

The ^{1}H NMR spectrum of **14** displayed two characteristic doublets at 6.19 and 5.03 ppm with J = 1.8 Hz assignable to the olefinic and the benzylic C*H*, a singlet at 2.57 ppm for the $N(CH_3)_2$ group, a singlet at 3.77 ppm attributable to the cage C*H*, several multiplets in the range 7.0 to 7.9 ppm corresponding to the aromatic protons, and THF resonances at 1.59 and 3.63 ppm, respectively. Its ^{11}B NMR exhibited a 1:1:4:2:1 pattern.

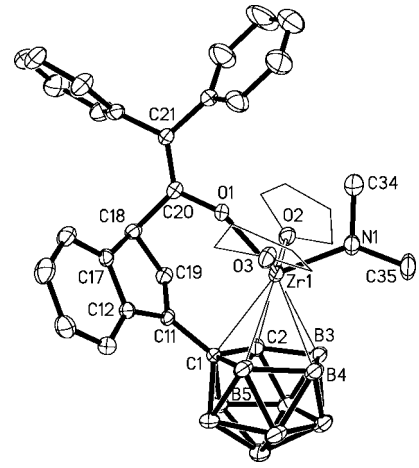


Figure 7. Molecular structure of $[\sigma{:}\eta^5$-{[3-C(═CPh_2)-O]-C_9H_6}$C_2B_9H_{10}$]Zr(NMe_2)$(THF)_2$ (**14**) (thermal ellipsoids drawn at the 30% probability level).

The molecular structure of **14** was confirmed by single-crystal X-ray analyses and is shown in Figure 7. The Zr atom is σ-bound to the N and O atoms, η^5-bound to the dicarbollyl, and coordinated to two THF molecules. The Zr−N(1) distance of 2.006(4) Å is close to that observed in **3b**, **5b**, **5b″**, and **9**. The Zr−O distance of 2.034(3) Å is very comparable to 1.996(4) Å in (CBC)Zr(O-2,6-$C_6H_3Me_2$)$_2$ (CBC = {1,4,811-tetraazabicyclo[6.6.2]hexadecane}$^{2-}$),[27] 1.957(6) Å in (μ-O)[Zr(NMe_2)(O-Ar)$_2$]$_2$ (Ar = 2,6-Bu^t_2-4-Me-3,5-N_2C_4),[25] and 1.952(2) Å in $[\sigma{:}\eta^1{:}\sigma$-(2-O-3,5-$Bu^t_2$-$C_6H_2$)($C_5H_3N$){3,5-$(CF_3)_2$-$C_6H_2$}]Zr($CH_2Ph$)$_2$.[21] The C(20)−C(21) distance of 1.353(7) Å and the planar geometry around them indicate the double-bond character.

Conclusion

Several group 4 metal amides derived from 1-indenyl-1,2-carborane (**1**) and [Me_3NH][7-C_9H_7-7,8-$C_2B_9H_{11}$] (**4**) were synthesized and structurally characterized. Interconversions among $[\eta^5$-($C_2B_{10}H_{11}$)C_9H_6]M(NMe_2)$_3$ (**2**), $[\eta^5$-(C_9H_7)$C_2B_9H_{10}$]-M(NMe_2)$_2$($HNMe_2$) (**3**), and $[\sigma{:}\eta^5$-(C_9H_6)$C_2B_9H_{10}$]M(NMe_2)-$(L)_n$ (**5**) were studied, which showed that the nature of solvents and metals played a very important role in these transformations.

Stepwise insertion of diisopropylcarbodiimide into the Zr−N bond in **3b** gave the monoguanidinate complex $[\eta^5$-(C_9H_7)-$C_2B_9H_{10}$]Zr(NMe_2)$[\eta^2$-(Pr^iN)$_2$C(NMe_2)] (**9**) and diguanidinate complex $[\eta^5$-(C_9H_7)$C_2B_9H_{10}$]Zr$[\eta^2$-(Pr^iN)$_2$C(NMe_2)$]_2$ (**10**), respectively. They were not obtained from the reaction of **3b** with the corresponding guanidine, which only afforded triguanidinate complexes [{η^2-(Pr^iN)$_2$C(NR_2)}$_3$M][(C_9H_7)$C_2B_9H_{11}$] (**8**) (M = Ti, Zr, Hf; NR_2 = NMe_2, NEt_2, $N(CH_2)_4$). Heating **9** or **10** in toluene gave the same C−N bond cleavage product $[\eta^1{:}\sigma{:}\eta^5$-{[2-C═$NPr^i$($NHPr^i$)]$C_9H_5$}$C_2B_9H_{10}$]Zr$[\eta^2$-($Pr^iN$)$_2CNMe_2$] (**11a**). A possible mechanism for the formation of **11a** was proposed, which was supported by experimental results. This work showed that guanidinate ligands are not always inert. Under certain circumstances, guanidinates can undergo C−N bond cleavage to generate amides and carbodiimides.

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 were freshly distilled from sodium

(37) Selected examples, see: (a) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. A* **1970**, 2550. (b) Thomas, E. W.; Nishizawa, E. E.; Zimmermann, D. C.; Williams, D. J. *J. Med. Chem.* **1989**, *32*, 228. (c) Montilla, F.; Pastor, A.; Galindo, A. *J. Organomet. Chem.* **2004**, *689*, 993. (d) Ong, T.-G.; O'Brien, J. S.; Korobkov, I.; Richeson, D. S. *Organometallics* **2006**, *25*, 4728. (e) Montilla, F.; del Río, D.; Pastor, A.; Galindo, A. *Organometallics* **2006**, *25*, 4996.

(38) Selected examples, see: (a) Beckhaus, R.; Wagner, T.; Zimmermann, C.; Herdtweck, E. *J. Organomet. Chem.* **1993**, *460*, 181. (b) Moloy, K. G.; Fangan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56. (c) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *24*, 654. (d) Himbert, G.; Henn, L.; Hoge, R. *J. Organomet. Chem.* **1980**, *184*, 317.

(39) Selected examples, see ref 12c and: (a) Liu, R.; Zhang, C.; Zhu, Z.; Luo, J.; Zhou, X.; Weng, L. *Chem.−Eur. J.* **2006**, *12*, 6940. (b) Ando, F.; Kohmura, Y.; Koketsu, J. *Bull. Chem. Soc. Jpn.* **1987**, *69*, 1564.

benzophenone ketyl immediately prior to use. Diphenylketene,[40] Pr^iNH-C(NMe_2)=NPr^i (**7**),[41] Pr^iNH-C(NEt_2)=NPr^i (**7′**),[42] Pr^iNH-C[$N(CH_2)_4$]=NPr^i (**7″**),[42] and 1-indenyl-1,2-carborane (**1**)[10] were prepared according to literature methods. $M(NMe_2)_4$ (M = Ti, Zr, Hf) and other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.0 MHz. ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 75.5 MHz or a Varian Inova 400 spectrometer at 100.7 MHz. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.0 MHz. All chemical shifts were reported in δ units with reference to the residual protons and carbons of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., U.K., or Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of [η^5-($C_2B_{10}H_{11}$)C_9H_6]Zr(NMe_2)$_3$ (2b). A toluene solution (3 mL) of $Zr(NMe_2)_4$ (133 mg, 0.5 mmol) was added to a toluene solution (3 mL) of **1** (129 mg, 0.5 mmol), and the mixture was stirred at room temperature for 5 min. After removal of the solvent, the residue was dried under vacuum at room temperature for 12 h to give **2b** as a yellow oil (240 mg, 100%). ^{1}H NMR (benzene-d_6): δ 7.89 (m, 1H), 7.30 (m, 1H), 6.86 (m, 2H) (aromatic), 6.47 (d,J = 3.6 Hz, 1H), 5.99 (d,J = 3.6 Hz, 1H) (olefinic), 3.29 (s, 1H) (cage *H*), 2.58 (s, 18H) (CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 126.3, 125.6, 124.3, 123.3, 123.0, 122.2, 120.5, 105.4, 97.8 (indenyl), 76.0, 66.7 (cage *C*), 43.7 (CH_3). ^{11}B{^{1}H} NMR (benzene-d_6): δ −1.7 (1B), −4.0 (1B), −9.3 (4B), −12.6 (4B). IR (KBr, cm^{-1}): υ_{B-H} 2578 (vs). Anal. Calcd for $C_{17}H_{35}B_{10}N_3Zr$ (**2b**): C, 42.47; H, 7.34; N, 8.74. Found: C, 42.96; H, 7.46; N, 8.45.

Preparation of [η^5-($C_2B_{10}H_{11}$)C_9H_6]Hf(NMe_2)$_3$ (2c). This complex was prepared as a pale yellow oil from $Hf(NMe_2)_4$ (177 mg, 0.5 mmol) and **1** (129 mg, 0.5 mmol) in toluene (6 mL) at −30 °C, using the identical procedures reported for **2b**: yield 284 mg (100%). ^{1}H NMR (benzene-d_6): δ 7.89 (d, J = 8.1 Hz, 1H), 7.29 (dd, J = 6.9 Hz, 2.4 Hz, 1H), 6.85 (m, 2H) (aromatic), 6.42 (d, J = 3.9 Hz, 1H), 5.96 (d, J = 3.9 Hz, 1H) (olefinic), 3.33 (s, 1H) (cage *H*), 2.65 (s, 18H) (CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ 126.4, 125.4, 124.6, 123.5, 123.3, 122.5, 120.6, 105.1, 97.7 (indenyl), 75.6, 66.5 (cage *C*), 43.4 (CH_3). ^{11}B{^{1}H} NMR (benzene-d_6): δ −1.7 (1B), −3.9 (1B), −9.3 (4B), −12.6 (4B). IR (KBr, cm^{-1}): υ_{B-H} 2580 (vs). Anal. Calcd for $C_{17}H_{35}B_{10}HfN_3$ (**2c**): C, 35.94; H, 6.21; N, 7.40. Found: C, 36.43; H, 6.46; N, 7.01.

Preparation of [Me_3NH][7-C_9H_7-7,8-$C_2B_9H_{11}$] (4). An aqueous solution of trimethylamine (45%, 10 mL) was added to a methanol solution (30 mL) of **1** (1.29 g, 5.0 mmol) at room temperature, and the pale yellow solution was heated to reflux for 8 h. After removal of the volatile chemicals, the residue was dried in vacuum at room temperature for 6 h to afford **4** as a pale orange solid (1.53 g, 99%). ^{1}H NMR (acetone-d_6): δ 7.55 (d, J = 7.5 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H) (aromatic), 6.00 (t, J = 1.8 Hz, 1H) (olefinic), 3.17 (d, J = 1.8 Hz, 2H) (CH_2), 3.15 (s, 9H) ($N(CH_3)_3$), 1.95 (s, 1H) (cage C*H*), −2.15 (bs, 1H) (B*H*B). ^{13}C{^{1}H} NMR (acetone-d_6): δ 149.3, 148.1, 144.7, 126.4, 125.9, 124.7, 124.0, 121.6 (indenyl), 46.0 ($N(CH_3)_3$), 37.5 (CH_2), the cage carbons were not observed. ^{11}B{^{1}H} NMR (acetone-d_6): δ −9.5 (1B), −10.4 (1B), −13.5 (1B), −16.6 (1B), −17.3 (1B), −19.9 (1B), −21.9 (1B), −33.2 (1B), −37.0 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2525 (vs). Anal. Calcd for $C_{14}H_{28}B_9N$ (**4**): C, 54.65; H, 9.17; N, 4.55. Found: C, 54.33; H, 9.13; N, 4.48.

Preparation of [η^5-(C_9H_7)$C_2B_9H_{10}$]Ti(NMe_2)$_2$($HNMe_2$) (3a). Compound **4** (154 mg, 0.5 mmol) was added to a toluene solution (10 mL) of $Ti(NMe_2)_4$ (112 mg, 0.5 mmol) at room temperature, and the mixture was stirred for 12 h. After filtration, the deep red filtrate was concentrated to ca. 3 mL. Complex **3a** was obtained as a red crystalline solid after this solution stood at room temperature for 2 days (133 mg, 62%). ^{1}H NMR (benzene-d_6): δ 8.25 (d,J = 7.5 Hz, 1H), 7.07 (m, 3H) (aromatic), 5.60 (s, 1H) (olefinic), 3.90 (s, 1H) (cage C*H*), 2.79 (s, 2H) (CH_2), 2.87 (s, 6H) ($N(CH_3)_2$), 2.33 (s, 6H) ($N(CH_3)_2$), 2.09 (d, J = 6.0 Hz, 3H) ($HN(CH_3)_2$), 1.86 (d, J = 6.0 Hz, 3H) ($HN(CH_3)_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 144.8, 143.6, 143.5, 127.0, 126.2, 125.3, 124.0, 123.9 (aromatic and olefinic), 51.4 ($N(CH_3)_2$), 47.0 ($N(CH_3)_2$), 44.2 ($HN(CH_3)_2$), 43.5 ($HN(CH_3)_2$), 37.3 (CH_2), the cage carbons were not observed. ^{11}B{^{1}H} NMR (benzene-d_6): δ 6.8 (1B), −1.4 (1B), −2.9 (1B), −4.2 (3B), −10.7 (1B), −13.3 (1B), −17.3 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2528 (vs). Anal. Calcd for $C_{17}H_{36}B_9N_3Ti$ (**3a**): C, 47.74; H, 8.48; N, 9.83. Found: C, 47.84; H, 8.17; N, 9.74.

Preparation of [η^5-(C_9H_7)$C_2B_9H_{10}$]Zr(NMe_2)$_2$($HNMe_2$) (3b). Compound **4** (154 mg, 0.5 mmol) was added to a toluene solution (10 mL) of $Zr(NMe_2)_4$ (134 mg, 0.5 mmol) at room temperature, and the mixture was stirred for 5 min until a clear solution was formed. After filtration, the filtrate was concentrated to ca. 3 mL. Complex **3b** was obtained as yellow crystals after the solution stood at room temperature for 12 h (226 mg, 96%). ^{1}H NMR (benzene-d_6): δ 8.23 (d,J = 7.8 Hz, 1H), 7.07 (m, 3H) (aromatic), 5.62 (s, 1H) (olefinic), 3.20 (s, 1H) (cage C*H*), 2.77 (s, 2H) (CH_2), 2.55 (s, 6H) ($N(CH_3)_2$), 2.06 (s, 6H) ($N(CH_3)_2$), 1.99 (d, J = 6.0 Hz, 3H) ($HN(CH_3)_2$), 1.73 (d, J = 6.0 Hz, 3H) ($HN(CH_3)_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 145.2, 142.1, 140.4, 127.7, 126.3, 125.9, 124.4, 123.6 (aromatic and olefinic), 49.6 ($N(CH_3)_2$), 47.7 ($N(CH_3)_2$), 41.7 ($HN(CH_3)_2$), 39.2 ($HN(CH_3)_2$), 37.9 (CH_2), the cage carbons were not observed. ^{11}B{^{1}H} NMR (benzene-d_6): δ −1.3 (1B), −2.7 (1B), −6.5 (4B), −13.8 (2B), −19.7 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2542 (vs). Anal. Calcd for $C_{17}H_{36}B_9N_3Zr$ (**3b**): C, 43.35; H, 7.70; N, 8.92. Found: C, 43.80; H, 7.61; N, 8.54.

Alternate Method. Complex **2b** (240 mg, 0.5 mmol) was added to a toluene solution (5 mL) of $NHMe_2$ (50 mg, 1.1 mmol) at −30 °C. The Schlenk flask was closed and stirred at room temperature for 12 h. Removal of the volatile chemicals afforded a pale yellow solid identified as **3b** (231 mg, 98%).

Preparation of [η^5-(C_9H_7)$C_2B_9H_{10}$]Hf(NMe_2)$_2$($HNMe_2$) (3c). This complex was prepared as pale yellow crystals from $Hf(NMe_2)_4$ (177 mg, 0.5 mmol) and **4** (154 mg, 0.5 mmol) in toluene (10 mL) using the identical procedures reported for **3b**: yield 274 mg (98%). ^{1}H NMR (pyridine-d_5): δ 8.00 (m, 1H), 7.28 (m, 1H), 7.12 (m, 2H) (aromatic), 6.19 (s, 1H) (olefinic), 3.29 (s, 1H) (cage C*H*), 3.16 (s, 1H) (*H*$N(CH_3)_2$), 3.09 (s, 2H) (CH_2), 2.95 (s, 12H) ($N(CH_3)_2$), 2.37 (s, 6H) ($HN(CH_3)_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 144.5, 142.9, 141.0, 128.7, 128.0, 125.8, 125.0, 124.1 (aromatic and olefinic), 43.7 ($N(CH_3)_2$), 38.4 ($HN(CH_3)_2$), 36.5 (CH_2), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.2 (2B), −5.9 (2B), −10.3 (2B), −16.0 (2B), −26.8 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2548 (vs). Anal. Calcd for $C_{17}H_{36}B_9HfN_3$ (**3c**): C, 36.57; H, 6.50; N, 7.53. Found: C, 37.03; H, 6.61; N, 7.29.

Alternate Method. Complex **2c** (284 mg, 0.5 mmol) was added to a toluene solution (5 mL) of $NHMe_2$ (50 mg, 1.1 mmol) at −30 °C. The Schlenk flask was closed and stirred at room temperature for 6 h. Removal of the volatile chemicals afforded a pale yellow solid identified as **3c** (273 mg, 98%).

Preparation of [σ:η^5-(C_9H_6)$C_2B_9H_{10}$]Ti(NMe_2)(DME) (5a). A DME solution (5 mL) of **3a** (214 mg, 0.5 mmol) was stirred at room temperature for 6 h. After filtration, the resulting clear solution was concentrated to 2 mL. Complex **5a** was obtained as deep red crystals after this solution stood at room temperature for 48 h (56 mg, 26%). ^{1}H NMR (pyridine-d_5): δ 7.40 (d, J = 7.5 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 7.5 Hz, 1H) (aromatic), 6.45

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(41) Coles, M. P.; Hitchcock, P. B. *Eur. J. Inorg. Chem.* **2004**, 2662.
(42) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2006**, *25*, 5515.

(d, $J = 4.8$ Hz, 1H) (olefinic), 6.40 (t, $J = 7.5$ Hz, 1H) (aromatic), 6.13 (d, $J = 4.8$ Hz, 1H) (olefinic), 3.47 (s, 4H) (DME), 3.25 (s, 6H) (DME), 3.29 (s, 6H) (N(CH_3)$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 143.5, 140.4, 128.7, 128.0, 121.7, 120.7, 118.1, 115.9 (aromatic and olefinic), 92.6 (Ti-*C*), 71.4 (DME), 57.9 (DME), 46.0 (N(*C*H$_3$)$_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 12.0 (2B), −2.7 (2B), −4.1 (2B), −11.1 (3B). IR (KBr, cm^{-1}): υ_{B-H} 2516 (vs). Anal. Calcd for $C_{15}H_{27}B_9NOTi$ (**5a** − 0.5DME): C, 47.10; H, 7.11; N, 3.66. Found: C, 47.17; H, 7.43; N, 3.28.

Preparation of [σ:η^5-(C_9H_6)$C_2B_9H_{10}$]Zr(NMe$_2$)(DME) (5b). Complex **2b** (240 mg, 0.5 mmol) was dissolved in DME (2 mL) at room temperature to give **5b** as red crystals after the solution stood at room temperature for 2 weeks (195 mg, 83%). ^{1}H NMR (pyridine-d_5): δ 7.51 (d, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 6.79 (t, $J = 7.8$ Hz, 1H), 6.58 (t, $J = 7.8$ Hz, 1H) (aromatic), 6.42 (d, $J = 4.5$ Hz, 1H), 6.06 (d, $J = 4.5$ Hz, 1H) (olefinic), 3.48 (s, 4H) (DME), 3.25 (s, 6H) (DME), 3.11 (s, 6H) (N(CH_3)$_2$), 3.07 (s, 1H) (cage C*H*). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 140.9, 139.1, 120.1, 119.6, 119.4 110.1 (aromatic and olefinic), 85.5 (cage *C*), 84.9 (Zr-*C*), 71.4 (DME), 58.3 (cage *C*), 57.9 (DME), 42.7 (N(*C*H$_3$)$_2$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.0 (2B), −4.5 (2B), −6.2 (2B), −14.4 (3B). IR (KBr, cm^{-1}): υ_{B-H} 2513 (vs). These data are identical with those reported in the literature.[11]

Preparation of [σ:η^5-(C_9H_6)$C_2B_9H_{10}$]Zr(NMe$_2$)(Py)$_2$ (5b′). A pyridine solution (5 mL) of **3b** (236 mg, 0.5 mmol) was stirred at room temperature for 6 h. The resulting deep red solution was concentrated to ca. 2 mL, to which was added *n*-hexane (5 mL). The red precipitate was collected by filtration and dried in vacuum for 1 h to afford **5b′** as a red powder (232 mg, 86%). ^{1}H NMR (pyridine-d_5): δ 8.71 (m, 4H), 7.56 (m, 2H), 7.19 (m, 4H) (pyridine), 7.51 (d, $J = 7.2$ Hz, 1H), 7.23 (d, $J = 7.2$ Hz, 1H), 6.80 (t, $J = 7.2$ Hz, 1H), 6.58 (t, $J = 7.2$ Hz, 1H) (aromatic), 6.42 (d, $J = 4.2$ Hz, 1H), 6.07 (d, $J = 4.2$ Hz, 1H) (olefinic), 3.11 (s, 6H) (N(CH_3)$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 149.6, 135.3, 123.3 (pyridine), 140.8, 139.1, 128.7, 128.0, 120.1, 119.6, 119.4 110.1 (aromatic and olefinic), 85.5 (cage *C*), 84.8 (Zr-*C*), 58.3 (cage *C*), 42.6 (N(*C*H$_3$)$_2$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.0 (2B), −4.5 (2B), −6.0 (2B), −14.3 (3B). IR (KBr, cm^{-1}): υ_{B-H} 2528 (vs). Anal. Calcd for $C_{23}H_{32}B_9N_3Zr$ (**5b′**): C, 51.25; H, 5.98; N, 7.80. Found: C, 51.66; H, 6.53; N, 7.73.

Preparation of [σ:η^5-(C_9H_6)$C_2B_9H_{10}$]Zr(NMe$_2$)(THF)$_2$·THF (5b″·THF). This complex was prepared as orange-red crystals from **2b** (240 mg, 0.5 mmol) and THF (2 mL) using the identical procedures reported for **5b**: yield 107 mg (36%). ^{1}H NMR (pyridine-d_5): δ 7.50 (d, $J = 7.5$ Hz, 1H), 7.20 (d, $J = 7.5$ Hz, 1H), 6.79 (t, $J = 7.5$ Hz, 1H), 6.58 (t, $J = 7.5$ Hz, 1H) (aromatic), 6.41 (d, $J = 4.5$ Hz, 1H), 6.06 (d, $J = 4.5$ Hz, 1H) (olefinic), 3.64 (m, 8H) (THF), 3.10 (s, 6H) (N(CH_3)$_2$), 1.60 (m, 8H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 140.9, 139.1, 128.7, 125.8, 120.1, 119.6, 119.5, 110.1 (aromatic and olefinic), 85.6 (cage *C*), 84.9 (Zr-*C*), 67.2 (THF), 58.3 (cage *C*), 42.6 (N(*C*H$_3$)$_2$), 25.1 (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.3 (2B), −4.3 (2B), −6.0 (2B), −14.1 (3B). IR (KBr, cm^{-1}): υ_{B-H} 2526 (vs). Anal. Calcd for $C_{19}H_{34}B_9NO_{1.5}Zr$ (**5b″** − 0.5THF): C, 46.67; H, 7.01; N, 2.86. Found: C, 46.19; H, 6.99; N, 2.49.

Alternate Method. A suspension of **5b** (235 mg, 0.5 mmol) in THF (5 mL) was heated to reflux for 4 h. Removal of the volatile chemicals afforded an orange solid identified as **5b″** (262 mg, 99%).

Preparation of [{η^5-(C_9H_7)$C_2B_9H_{10}$}Hf(NMe$_2$)(μ:η^1-OCH$_2$CH$_2$OCH$_3$)]$_2$·2THF (6·2THF). A DME solution (10 mL) of **3c** (279 mg, 0.5 mmol) stood at room temperature for 5 days to give **6**·2THF as orange crystals (37 mg, 12%). ^{1}H NMR (pyridine-d_5): δ 8.17 (d, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.26 (t, $J = 7.5$ Hz, 2H), 7.15 (d, $J = 7.5$ Hz, 2H) (aromatic), 6.41 (s, 2H) (olefinic), 3.63 (m, 8H) (THF), 3.49 (s, 6H) (OCH_3), 3.25 (s, 12H) (N(CH_3)$_2$), 3.24 (s, 4H) (CH_2), 3.17 (m, 4H) (OCH_2), 3.06 (m, 4H) (OCH_2), 1.59 (m, 8H) (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.6 (2B), −9.5 (2B), −12.5 (2B), −15.6 (2B), −16.4 (2B), −19.0 (2B), −20.8 (2B), −32.2 (2B), −36.0 (2B). IR (KBr, cm^{-1}): υ_{B-H} 2526 (vs). Anal. Calcd for $C_{34}H_{64}B_{18}Hf_2N_2O_{4.5}$ (**6** + 0.5THF): C, 36.32; H, 5.74; N, 2.49. Found: C, 36.44; H, 5.77; N, 2.56.

Preparation of [{η^2-(Pr^{i}N)$_2$C−N(CH$_2$)$_4$}$_3$Ti][(C_9H_7)$C_2B_9H_{11}$] (8a″). Compound **7″** (394 mg, 2.0 mmol) was added to a THF solution (10 mL) of **3a** (214 mg, 0.5 mmol), and this mixture was heated to reflux for 12 h. The resulting filtrate was concentrated to 3 mL after filtration. Complex **8a″** was obtained as deep red crystals after this solution stood at room temperature for 3 days (252 mg, 57%). ^{1}H NMR (pyridine-d_5): δ 8.19 (d, $J = 7.5$ Hz, 1H), 7.34 (m, 2H), 7.16 (d, $J = 7.5$ Hz, 1H) (aromatic), 6.43 (s, 1H) (olefinic), 3.74 (m, 6H) (NC*H*Me$_2$), 3.40 (m, 12H) (NCH_2CH$_2$), 3.16 (s, 2H) (CH_2), 2.76 (s, 1H) (cage C*H*), 1.87 (m, 6H) (NCH$_2$CH_2), 1.66 (m, 6H) (NCH$_2$CH_2), 1.31 (d, $J = 6.3$ Hz, 18H) (CH_3), 1.09 (d, $J = 6.3$ Hz, 18H) (CH_3), −1.19 (br, 1H) (B*H*B). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 170.7 (*C*N$_3$), 147.4, 143.9, 125.8, 125.6, 123.9, 121.1 (aromatic and olefinic), 49.5, 49.0 (N*C*HMe$_2$), 48.2, 46.5 (NCH$_2$CH$_2$), 36.8 (*C*H$_2$), 25.0 (CH(*C*H$_3$)$_2$), 24.7, 23.6 (NCH$_2$*C*H$_2$), 23.2 (CH(*C*H$_3$)$_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.3 (1B), −9.3 (1B), −12.5 (1B), −15.4 (2B), −18.8 (1B), −20.7 (1B), −32.0 (1B), −35.8 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2520 (vs). Anal. Calcd for $C_{44}H_{84}B_9N_9Ti$ (**8a″**): C, 59.76; H, 9.57; N, 14.25. Found: C, 58.99; H, 9.39; N, 13.61.

Preparation of [{η^2-(Pr^{i}N)$_2$C(NMe$_2$)}$_3$Zr][(C_9H_7)$C_2B_9H_{11}$] (8b). This complex was prepared as pale yellow crystals from **3b** (236 mg, 0.5 mmol) and **7** (342 mg, 2.0 mmol) in THF (10 mL) using the identical procedures reported for **8a″**: yield 335 mg (79%). ^{1}H NMR (pyridine-d_5): δ 8.18 (d, $J = 7.2$ Hz, 1H), 7.34 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 1H) (aromatic), 6.43 (s, 1H) (olefinic), 3.60 (m, 6H) (NC*H*Me$_2$), 3.17 (s, 2H) (CH_2), 2.75 (s, 1H) (cage C*H*), 2.72 (s, 18H) (N(CH_3)$_2$), 1.24 (d, $J = 6.6$ Hz, 18H) (CH_3), 1.04 (d, $J = 6.3$ Hz, 18H) (CH_3), −1.27 (br, 1H) (B*H*B). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 173.5 (*C*N$_3$), 148.7, 147.4, 143.9, 125.8, 125.6, 123.9, 121.1 (aromatic and olefinic), 47.0 (N*C*HMe$_2$), 39.1 (N(*C*H$_3$)$_2$), 36.8 (*C*H$_2$), 25.2, 24.3 (*C*H$_3$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.5 (1B), −9.3 (1B), −12.5 (1B), −15.5 (1B), −16.1, (1B), −18.9 (1B), −20.8 (1B), −32.1 (1B), −35.9 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2520 (vs). Anal. Calcd for $C_{38}H_{78}B_9N_9Zr$ (**8b**): C, 53.72; H, 9.25; N, 14.84. Found: C, 54.24; H, 9.29; N, 14.56.

Alternate Method. This complex was also prepared from **5b** (235 mg, 0.5 mmol) and **7** (257 mg, 1.5 mmol), or **9** (276 mg, 0.5 mmol) and **7** (172 mg, 1.0 mmol), or **10** (339 mg, 0.5 mmol) and **7** (86 mg, 0.5 mmol) in refluxing THF (10 mL). Complex **8b** was collected as pale yellow crystals after workup in 33% (140 mg), or 57% (242 mg), or 73% (310 mg) yield, respectively.

Preparation of [{η^2-(Pr^{i}N)$_2$C(NEt$_2$)}$_3$Zr][(C_9H_7)$C_2B_9H_{11}$] (8b′). This complex was prepared as pale yellow crystals from **3b** (236 mg, 0.5 mmol) and **7′** (398 mg, 2.0 mmol) in THF (10 mL) using the identical procedures reported for **8a″**: yield 387 mg (83%). ^{1}H NMR (pyridine-d_5): δ 8.20 (d, $J = 7.2$ Hz, 1H), 7.34 (m, 2H), 7.15 (d, $J = 7.2$ Hz, 1H) (aromatic), 6.43 (s, 1H) (olefinic), 3.53 (m, 6H) (NC*H*Me$_2$), 3.16 (s, 2H) (CH_2), 3.15 (q, $J = 6.9$ Hz, 6H) (CH_2CH$_3$), 2.94 (q, $J = 6.9$ Hz, 6H) (CH_2CH$_3$), 2.74 (s, 1H) (cage C*H*), 1.29 (d, $J = 6.0$ Hz, 18H) (CH_3), 1.08 (d, $J = 6.3$ Hz, 18H) (CH_3), 1.01 (t, $J = 6.9$ Hz, 18H) (CH$_2$CH_3), −1.09 (br, 1H) (B*H*B). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 175.2 (*C*N$_3$), 147.4, 143.9, 125.8, 125.6, 123.9, 121.1 (aromatic and olefinic), 47.6, 47.4 (N*C*HMe$_2$), 41.7, 39.2 (*C*H$_2$CH$_3$), 36.8 (*C*H$_2$), 25.0, 24.2 (CH(*C*H$_3$)$_2$), 13.0 (CH$_2$*C*H$_3$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.5 (1B), −9.4 (1B), −12.7 (1B), −15.6 (1B), −16.1, (1B), −18.9 (1B), −20.9 (1B), −32.1 (1B), −35.8 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2522 (vs). Anal. Calcd for $C_{44}H_{90}B_9N_9Zr$ (**8b′**): C, 56.60; H, 9.71; N, 13.50. Found: C, 56.75; H, 9.29; N, 13.24.

Table 3. Crystal Data and Summary of Data Collection and Refinement for 3b, 3c, 5a, 5b″·THF and 6·2THF

	3b	**3c**	**5a**	**5b"·THF**	**6·2THF**
formula	$C_{17}H_{36}B_9N_3Zr$	$C_{17}H_{36}B_9HfN_3$	$C_{17}H_{32}B_9NO_2Ti$	$C_{25}H_{46}B_9NO_3Zr$	$C_{40}H_{76}B_{18}Hf_2N_2O_6$
cryst size (mm)	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.30	0.40 × 0.40 × 0.30	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.20
fw	471.00	558.27	427.63	597.14	1232.59
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	15.196(3)	15.551(3)	9.786(1)	9.487(2)	9.448(1)
b, Å	9.917(2)	10.170(2)	13.942(1)	13.100(3)	14.743(2)
c, Å	16.573(3)	19.253(4)	17.754(1)	13.729(3)	18.820(2)
α, deg	90	90	90	94.24(3)	90
β, deg	107.43(3)	122.79(3)	105.44(1)	105.41(3)	97.71(1)
γ, deg	90	90	90	108.92(3)	90
V, Å^3	2382.9(8)	2559.9(9)	2335.0(3)	1531.7(5)	2597.7(5)
Z	4	4	4	2	2
D_{calcd}, Mg/m^3	1.313	1.449	1.216	1.295	1.576
radiation (*λ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	3.2 to 50.0	4.7 to 50.0	3.8 to 54.0	4.2 to 50.0	3.5 to 52.0
μ, mm^{-1}	0.471	4.084	0.380	0.387	4.039
F(000)	976	1104	896	624	1224
no. of obsd reflns	3767	4382	5088	5395	5124
no. of params refnd	272	271	271	352	307
goodness of fit	1.067	1.120	0.939	1.068	1.100
R1	0.046	0.083	0.060	0.065	0.033
wR2	0.130	0.208	0.149	0.166	0.072

Table 4. Crystal Data and Summary of Data Collection and Refinement for 8b, 8b″, 8c″, 9·0.5C$_7$H$_8$, and 14·THF

	8b	**8b″**	**8c″**	**9·0.5C$_7$H$_8$**	**14·THF**
formula	$C_{38}H_{78}B_9N_9Zr$	$C_{44}H_{84}B_9N_9Zr$	$C_{44}H_{84}B_9HfN_9$	$C_{25.5}H_{47}B_9N_4Zr$	$C_{39}H_{56}B_9NO_4Zr$
cryst size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.10	0.50 × 0.40 × 0.30	0.30 × 0.20 × 0.10
fw	849.60	927.71	1014.98	598.18	791.36
cryst syst	orthorhombic	orthorhombic	orthorhombic	triclinic	triclinic
space group	*Pnna*	*Pnna*	*Pnna*	$P\bar{1}$	$P\bar{1}$
a, Å	17.773(2)	17.786(1)	17.749(1)	10.156(2)	9.627(1)
b, Å	22.528(3)	22.652(2)	22.514(2)	10.811(2)	11.510(1)
c, Å	12.737(1)	13.190(1)	13.119(1)	16.456(2)	18.669(2)
α, deg	90	90	90	78.11(1)	86.48(1)
β, deg	90	90	90	73.68(1)	86.61(1)
γ, deg	90	90	90	69.56(1)	81.02(1)
V, Å^3	5100(1)	5313.8(7)	5242.2(7)	1613.1(4)	2036.8(3)
Z	4	4	4	2	2
D_{calcd}, Mg/m^3	1.107	1.160	1.286	1.232	1.290
radiation (*λ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	3.6 to 50.0	3.6 to 55.7	3.6 to 55.7	2.6 to 50.0	2.2 to 50.0
μ, mm^{-1}	0.250	0.246	2.029	0.363	0.311
F(000)	1816	1984	2112	626	828
no. of obsd reflns	4500	6314	6245	5646	7154
no. of params refnd	287	318	318	370	487
goodness of fit	1.088	0.997	1.042	1.043	1.017
R1	0.062	0.066	0.041	0.046	0.062
wR2	0.172	0.201	0.117	0.116	0.137

Alternate Method. This complex was also prepared from **5b** (235 mg, 0.5 mmol) and **7′** (300 mg, 1.5 mmol) in refluxing THF. Complex **8b′** was collected as pale yellow crystals (205 mg, 44%).

Preparation of [{η^2-(Pr^{i}N)$_2$C−N(CH$_2$)$_4$}$_3$Zr][(C$_9$H$_7$)C$_2$B$_9$H$_{11}$] (8b″). This complex was prepared as pale yellow crystals from **3b** (236 mg, 0.5 mmol) and **7″** (394 mg, 2.0 mmol) in THF (10 mL) using the identical procedures reported for **8a″**: yield 417 mg (90%). ^{1}H NMR (pyridine-d_5): δ 8.19 (d, J = 7.2 Hz, 1H), 7.35 (m, 2H), 7.16 (d, J = 7.2 Hz, 1H) (aromatic), 6.43 (s, 1H) (olefinic), 3.65 (m, 6H) (NC*H*Me$_2$), 3.36 (m, 6H) (NC*H*$_2$), 3.17 (s, 2H) (C*H*$_2$), 3.10 (m, 6H) (NC*H*$_2$), 2.74 (s, 1H) (cage C*H*), 1.88 (br, 6H) (NCH$_2$C*H*$_2$), 1.63 (br, 6H) (NCH$_2$C*H*$_2$), 1.28 (d, J = 6.3 Hz, 18H) (C*H*$_3$), 1.04 (d, J = 6.0 Hz, 18H) (C*H*$_3$), −1.24 (br, 1H) (B*H*B). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 169.5 (*C*N$_3$), 147.4, 143.9, 125.8, 125.6, 123.9, 121.1 (aromatic and olefinic), 49.4 (N*C*HMe$_2$), 46.8 (N*C*H$_2$CH$_2$), 46.5 (N*C*HMe$_2$), 39.0 (N*C*H$_2$CH$_2$), 36.8 (*C*H$_2$), 25.3 (NCH$_2$*C*H$_2$), 25.1 (CH(*C*H$_3$)$_2$), 25.0 (NCH$_2$*C*H$_2$), 23.7 (CH(*C*H$_3$)$_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.4 (1B), −9.4 (1B), −12.5 (1B), −15.6 (2B), −19.0 (1B), −20.9 (1B), −32.1 (1B), −35.9 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2522 (vs). Anal. Calcd for C$_{44}$H$_{84}$B$_9$N$_9$Zr (**8b″**): C, 56.97; H, 9.13; N, 13.59. Found: C, 56.58; H, 9.26; N, 13.26.

Alternate Method. This complex was also prepared from **5b** (235 mg, 0.5 mmol) and **7″** (297 mg, 1.5 mmol) in refluxing THF. Complex **8b″** was collected as pale yellow crystals (278 mg, 60%).

Preparation of [{η^2-(Pr^{i}N)$_2$C(NEt$_2$)}$_3$Hf][(C$_9$H$_7$)C$_2$B$_9$H$_{11}$] (8c′). This complex was prepared as pale yellow crystals from **3c** (279 mg, 0.5 mmol) and **7′** (398 mg, 2.0 mmol) in THF (10 mL) using the identical procedures reported for **8a″**: yield 444 mg (87%). ^{1}H NMR (pyridine-d_5): δ 8.21 (d, J = 7.2 Hz, 1H), 7.34 (m, 2H), 7.15 (d, J = 7.2 Hz, 1H) (aromatic), 6.43 (s, 1H) (olefinic), 3.73 (m, 6H) (NC*H*Me$_2$), 3.19 (q, J = 6.9 Hz, 6H) (C*H*$_2$CH$_3$), 3.16 (s, 2H) (C*H*$_2$), 2.96 (q, J = 6.9 Hz, 6H) (C*H*$_2$CH$_3$), 2.77 (s, 1H) (cage C*H*), 1.26 (d, J = 5.4 Hz, 18H) (C*H*$_3$), 1.06 (d, J = 6.3 Hz, 18H) (C*H*$_3$), 1.01 (t, J = 6.9 Hz, 18H) (CH$_2$C*H*$_3$), −1.10 (br, 1H) (B*H*B). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 174.3 (*C*N$_3$), 147.4, 143.9, 125.8, 125.7, 123.9, 121.1 (aromatic and olefinic), 49.2, 49.1 (N*C*HMe$_2$), 41.6, 39.2 (*C*H$_2$CH$_3$), 36.8 (*C*H$_2$), 25.0, 24.1 (CH(*C*H$_3$)$_2$), 13.1 (CH$_2$*C*H$_3$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.3 (1B), −9.2 (1B), −12.4 (1B), −15.3 (2B), −18.7 (1B), −20.6 (1B), −32.0 (1B), −35.6 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2522 (vs). Anal. Calcd for C$_{44}$H$_{90}$B$_9$HfN$_9$ (**8c′**): C, 51.76; H, 8.88; N, 12.35. Found: C, 51.88; H, 8.99; N, 12.45.

Preparation of [{η^2-(Pr^{i}N)$_2$C-N(CH$_2$)$_4$}$_3$Hf][(C$_9$H$_7$)C$_2$B$_9$H$_{11}$] (8c″). This complex was prepared as pale yellow crystals from **3c** (279 mg, 0.5 mmol) and **7″** (394 mg, 2.0 mmol) in THF (10 mL) using the identical procedures reported for **8a″**: yield 462 mg (91%). ^{1}H NMR (pyridine-d_5): δ 8.19 (d, J = 7.2 Hz, 1H), 7.34 (m, 2H), 7.16 (d, J = 7.2 Hz, 1H) (aromatic), 6.43 (s, 1H) (olefinic), 3.79 (m, 6H) (NC*H*Me$_2$), 3.41 (m, 6H) (NC*H*$_2$), 3.15 (s, 2H) (C*H*$_2$), 3.12 (m, 6H) (NC*H*$_2$), 2.76 (s, 1H) (cage C*H*), 1.87 (m, 6H) (NCH$_2$C*H*$_2$), 1.62 (m, 6H) (NCH$_2$C*H*$_2$), 1.27 (d, J = 6.3 Hz, 18H) (C*H*$_3$), 1.05 (d, J = 5.7 Hz, 18H) (C*H*$_3$), −1.19 (br, 1H) (B*H*B). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 168.8 (*C*N$_3$), 147.4, 143.9, 125.8, 125.6, 123.9, 121.1 (aromatic and olefinic), 49.4 (N*C*HMe$_2$), 46.5 (NCH$_2$CH$_2$), 46.3 (N*C*HMe$_2$), 39.0 (NCH$_2$CH$_2$), 36.8 (*C*H$_2$), 25.4 (NCH$_2$*C*H$_2$), 25.1 (CH(*C*H$_3$)$_2$), 24.0 (NCH$_2$*C*H$_2$), 23.8 (CH(*C*H$_3$)$_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.5 (1B), −9.2 (1B), −12.4 (1B), −15.5 (2B), −18.8 (1B), −20.8 (1B), −32.0 (1B), −35.8 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2522 (vs). Anal. Calcd for C$_{44}$H$_{84}$B$_9$HfN$_9$ (**8c″**): C, 52.07; H, 8.34; N, 12.42. Found: C, 51.85; H, 8.47; N, 12.43.

Preparation of [η^5-(C$_9$H$_7$)C$_2$B$_9$H$_{10}$]Zr(NMe$_2$)[η^2-(Pr^{i}N)$_2$-C(NMe$_2$)]·0.5C$_7$H$_8$ (9·0.5C$_7$H$_8$). Diisopropylcarbodiimide (63 mg, 0.5 mmol) was slowly added to a THF solution (10 mL) of **3b** (236 mg, 0.5mmol) at room temperature, and the mixture was stirred at room temperature for 1 h. Removal of the solvent and recrystallization from toluene afforded **9**·0.5C$_7$H$_8$ as yellow crystals (18 mg, 6%). ^{1}H NMR (pyridine-d_5): δ 8.20 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.24 (m, 2H) (aromatic), 7.19 (m, 2.5H) (toluene), 6.35 (s, 1H) (olefinic), 3.83 (m, 2H) (NC*H*Me$_2$), 3.13 (s, 2H) (C*H*$_2$), 3.03 (s, 6H) (Zr−N(C*H*$_3$)$_2$), 2.51 (s, 6H) (C−N(C*H*$_3$)$_2$), 2.20 (s, 1.5H) (toluene), 1.13 (br, 6H), 0.79 (br, 6H) (NCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 173.1 (*C*N$_3$), 144.4, 143.9, 128.7, 128.0, 125.8, 125.1, 123.9 121.1 (aromatic, olefinic and toluene), 47.9 (Zr−N(*C*H$_3$)$_2$), 47.0 (N*C*HMe$_2$), 39.4 (C−N(*C*H$_3$)$_2$), 36.4 (*C*H$_2$), 24.1, 23.1 (NCH(*C*H$_3$)$_2$), 21.9 (toluene *C*H$_3$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 3.5 (1B), −3.6 (1B), −6.0 (1B), −11.4 (4B), −16.0 (1B), −26.6 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2541 (vs). Anal. Calcd for C$_{25.5}$H$_{47}$B$_9$N$_4$Zr (**9** + 0.5C$_7$H$_8$): C, 51.20; H, 7.92; N, 9.37. Found: C, 51.08; H, 8.17; N, 9.02.

Preparation of [η^5-(C$_9$H$_7$)C$_2$B$_9$H$_{10}$]Zr[η^2-(Pr^{i}N)$_2$C(NMe$_2$)]$_2$ (10). Diisopropylcarbodiimide (126 mg, 1.0 mmol) was added to a THF solution (10 mL) of **3b** (236 mg, 0.5 mmol), and the mixture was stirred for 2 h at room temperature. The resulting solution was concentrated to ca. 2 mL, to which was added *n*-hexane (10 mL). Complex **10** was collected as a yellow solid after this solution stood at room temperature for 2 h (305 mg, 90%). ^{1}H NMR (pyridine-d_5): δ 8.41 (d, J = 7.2 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H) (aromatic), 6.33 (s, 1H) (olefinic), 3.84 (m, 4H) (Me$_2$C*H*N), 3.47 (s, 1H) (cage C*H*), 3.20 (s, 2H) (C*H*$_2$), 2.57 (s, 12H) (N(C*H*$_3$)$_2$), 1.21 (br, 24H) (NCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 172.0 (*C*N$_3$), 144.4, 144.1, 125.2, 124.8, 123.8 123.6 (aromatic and olefinic), 48.3 (N*C*HMe$_2$), 39.4 (N(*C*H$_3$)$_2$), 36.4 (*C*H$_2$), 23.3, 22.9 (NCH(*C*H$_3$)$_2$), the cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.4 (1B), −6.1 (1B), −8.7 (4B), −16.3 (2B), −29.3 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2540 (vs). These data are identical with those reported in the literature.[11]

Preparation of [η^1:σ:η^5-{[2-C=NPr^i(NHPr^i)]C$_9$H$_5$}C$_2$B$_9$H$_{10}$]Zr[η^2-(Pr^{i}N)$_2$C(NMe$_2$)] (11a). A toluene suspension of **9** (276 mg, 0.5 mmol) was heated to reflux for 12 h. After filtration of the hot solution, the resulting clear red filtrate was concentrated to ca. 3 mL, from which **11a** was collected as red crystals (89 mg, 28%). ^{1}H NMR (pyridine-d_5): δ 8.45 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.24 (m, 2H) (aromatic), 6.85 (s, 1H) (olefinic), 4.63 (m, 1H) (NC*H*Me$_2$), 4.37 (m, 1H) (NC*H*Me$_2$), 4.19 (m, 1H) (NC*H*Me$_2$), 3.10 (m, 1H) (NC*H*Me$_2$), 2.69 (s, 6H) (N(C*H*$_3$)$_2$), 1.87 (br, 3H) (C*H*$_3$), 1.42 (br, 3H) (C*H*$_3$), 1.35 (d, J = 6.0 Hz, 3H) (C*H*$_3$), 1.29 (d, J = 6.6 Hz, 3H) (C*H*$_3$), 1.18 (d, J = 6.6 Hz, 3H) (C*H*$_3$), 1.06 (d, J = 6.3 Hz, 3H) (C*H*$_3$), 0.30 (br, 3H) (C*H*$_3$), 0.16 (br, 3H) (C*H*$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 173.8 (*C*N$_3$), 165.7 (*C*N$_2$), 143.2, 138.1, 128.7, 128.0, 125.1, 121.9, 121.3, 116.3 (aromatic and olefinic), 86.1 (Zr-*C* and cage *C*), 59.3 (cage *C*), 49.6, 48.9, 46.6 (N-*C*H), 39.6 (N(*C*H$_3$)$_2$), 39.1 (N-*C*H), 24.3, 23.7, 23.4, 23.0, 22.5, 22.1, 21.8, 20.6 (*C*H$_3$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 6.2 (1B), 3.1 (1B), −2.7 (1B), −5.2 (1B), −6.5 (1B), −12.9 (3B), −16.3 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2523 (vs). These data are identical with those reported in the literature.[11]

Preparation of [σ:η^5-{[3-C(=CPh$_2$)-O]C$_9$H$_6$}C$_2$B$_9$H$_{10}$]Zr-(NMe$_2$)(THF)$_2$·THF (14·THF). Complex **5b** (236 mg, 0.5 mmol) was slowly added to a THF solution (5 mL) of diphenylketene (97 mg, 0.5 mmol), and the mixture was stirred at room temperature for 2 h. After filtration, the clear filtrate was concentrated to 2 mL. Complex **14**·THF was obtained as yellowish-green crystals after this solution stood at room temperature for 24 h (253 mg, 64%). ^{1}H NMR (pyridine-d_5): δ 7.87 (d, J = 7.8 Hz, 1H), 7.50 (m, 4H), 7.34 (m, 2H), 7.14 (m, 4H), 7.03 (m, 3H) (aromatic), 6.19 (d, J = 1.8 Hz, 1H) (olefinic), 5.03 (d, J = 1.8 Hz, 1H) (benzylic C*H*), 3.77 (s, 1H) (cage C*H*), 3.63 (m, 12H) (THF), 2.57 (s, 6H) (N(C*H*$_3$)$_2$), 1.59 (m, 12H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 150.6, 146.5, 143.8, 141.8, 141.6, 131.7, 131.2, 129.8, 128.6, 128.0, 127.4, 126.4, 126.2, 125.4, 125.1, 124.5, 122.3, 116.8 (aromatic and olefinic), 67.1 (THF), 52.6 (benzylic *C*H), 36.8 (N(*C*H$_3$)$_2$), 25.1 (THF), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.2 (1B), −3.5 (1B), −6.1 (4B), −15.0 (2B), −18.7 (1B). IR (KBr, cm^{-1}): υ_{B-H} 2543 (vs). Anal. Calcd for C$_{31}$H$_{40}$B$_9$NO$_2$Zr (**14** − THF): C, 57.53; H, 6.23; N, 2.16. Found: C, 57.52; H, 6.64; N, 1.92.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[43] 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 on F^2 using the SHELXTL program package.[44] All hydrogen atoms except for those of the disordered anions in **8b**, **8b″**, and **8c″** were geometrically fixed using the riding model. Complexes **5b″**, **6**, **9**, and **14** showed the solvation of one THF, two THF, half toluene, and one THF molecule, respectively. The anion [7-C$_9$H$_7$-7,8-C$_2$B$_9$H$_{11}$]$^-$ in **8b**, **8b″**, and **8c″** was positionally disordered with 0.5:0.5 occupancies. Crystal data and details of data collection and structure refinements are given in Tables 3 and 4. Further details are included in the Supporting Information.

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Supporting Information Available: Crystallographic data in CIF format for **3b**, **3c**, **5a**, **5b″**·THF, **6**·2THF, **8b**, **8b″**, **8c″**, **9**·0.5C$_7$H$_8$, and **14**·THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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