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Highly Electrophilic Half-Sandwich Group 4 Metallacarborane Alkyls. C−H/C−O Activation and Alkyne Insertion Reactions at Neutral Metal Complexes

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Summary: Treatment of 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ *with* $M(CH_2SiMe_3)_4$ *in toluene gave the C−H activation products* [η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]$M(CH_2SiMe_3)(THF)$ (M = Zr (**1**), Hf (**2**)). *Insertion of diphenylacetylene into the azametallacyclopropane in* **2** *and subsequent elimination of* $SiMe_4$ *afforded a new metallacyclic complex,* [σ:σ:η^1:η^5-{$(CH_2)[(CH_2)PhC{=}CPh]N(CH_2CH_2)C_2B_9H_{10}$}]Hf(THF) (**3**). *Reaction of* $Zr(CH_2Ph)_4$ *with* 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ *in DME generated a C−H/C−O activation product,* [{η^1:σ:η^5-[$MeN(CH_2)CH_2CH_2$]$C_2B_9H_{10}$}Zr(μ:η^1-$OCH_2CH_2OCH_3$)]$_2$ (**4**). *These results demonstrated that neutral half-sandwich metallacarborane alkyls have characteristics of electrophilic metal alkyls.*

Dicarbollide ion ($C_2B_9H_{11}^{2-}$) is an isolobal inorganic analogue of $C_5H_5^-$. Replacement of a uninegative $C_5H_5^-$ ligand of [$(C_5H_5)_2MR$]$^+$ (M = group 4 metals) by the dinegative ligand $C_2B_9H_{11}^{2-}$ leads to the formation of mixed sandwich complexes [$(C_5H_5)(C_2B_9H_{11})$]MR. These neutral complexes show a variety of ligand exchange, insertion, and ligand C−H activation reactions characteristic of electrophilic metal alkyls.[1] We wondered whether this approach could be applied to constrained-geometry catalyst systems [η^5:σ-$Me_2Si(C_5H_4)(NR')$]MCl_2/MAO[2] and whether there would be an analogy between the active species [{η^5:σ-$Me_2Si(C_5H_4)(NR')$}MR]$^+$ and neutral complexes [η^1:η^5-$(Me_2NCH_2CH_2)C_2B_9H_{10}$]$MR_2$.

A half-sandwich group 4 metallacarborane alkyl of the C_2B_{10} system [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]$Hf(CH_2SiMe_3)_2$ was recently prepared in our laboratory[3] that indicated that the tethered amido sidearm is necessary to stabilize this class of complexes.[4] Unfortunately, the high reducing power of the [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ ligand makes the reactivity study on [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]$Hf(CH_2SiMe_3)_2$ unfeasible. In this regard, we turned our attention to the C_2B_9 system and discovered that C−H/C−O activation reactions proceeded at the electrophilic metal center during the preparation of metallacarborane alkyls. These interesting results are reported in this communication.

Half-sandwich group 4 metallacarborane amides and chlorides have been well-known.[4c,d,5] Their alkyl derivatives incorporating a dicarbollide ion have not been reported. Treatment of $M(CH_2SiMe_3)_4$ with 1 equiv of the zwitterionic salt 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ in toluene at room temperature gave, after recrystallization from toluene/THF, half-sandwich metallacarborane alkyls of the general formula [η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]$M(CH_2SiMe_3)(THF)$ (M = Zr (**1**), Hf (**2**)) (Scheme 1).[6] The expected dialkyl complexes [η^1:η^5-$(Me_2NCH_2CH_2)C_2B_9H_{10}$]$M(CH_2SiMe_3)_2$ were not isolated. But they may serve as the intermediates and subsequently eliminate a $SiMe_4$ molecule via the rupture of a C−H bond at one of the N-methyl groups to give the final products. Such an internal C−H activation is normally observed at methylzirconocene cations[7] or [$(C_5Me_5)(C_2B_9H_{11})$]$TiCH_3$,[1b,g] rather than neutral metallocene alkyls. Both complexes **1** and **2** were fully characterized by various spectroscopic techniques and elemental analyses.[6]

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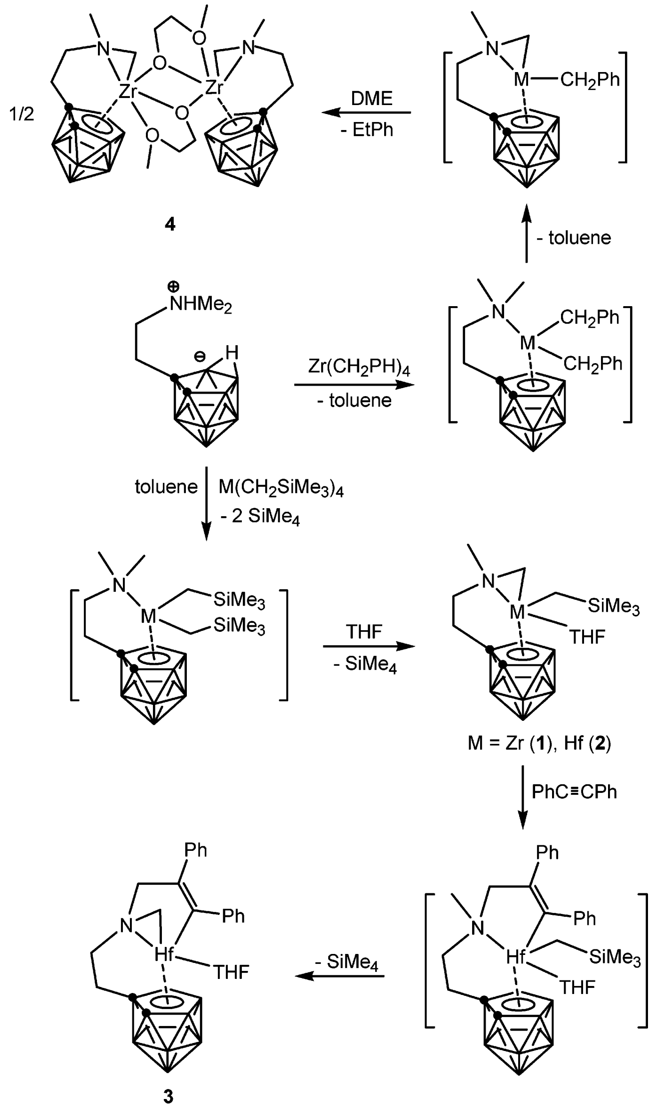
Scheme 1



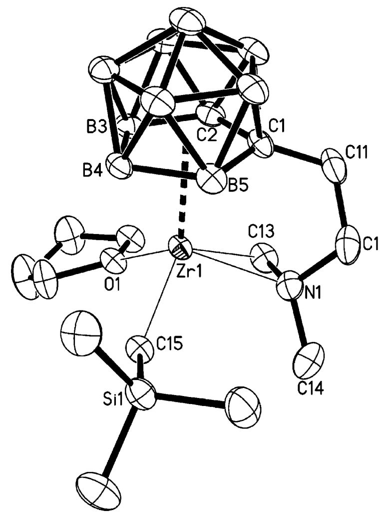


Figure 1. Molecular structure of $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$ (**1**).

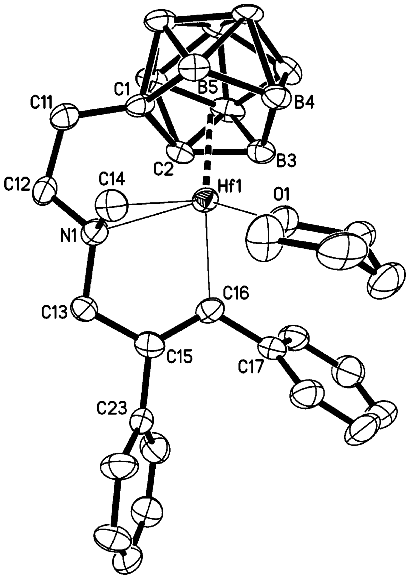


Figure 2. Molecular structure of $[\sigma:\sigma:\eta^1:\eta^5\text{-}\{(CH_2)[(CH_2)PhC{=}CPh]N(CH_2CH_2)C_2B_9H_{10}\}]Hf(THF)$ (**3**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1−4

	1 (M = Zr)	**2** (M = Hf)	**3** (M = Hf)	**4** (M = Zr)
M−C(1)	2.611(5)	2.589(10)	2.536(8)	2.629(4)
M−C(2)	2.660(5)	2.643(10)	2.475(8)	2.566(4)
M−B(3)	2.534(7)	2.538(12)	2.462(10)	2.492(5)
M−B(4)	2.439(6)	2.415(12)	2.498(10)	2.512(6)
M−B(5)	2.475(6)	2.461(11)	2.542(10)	2.562(5)
av M−cage atom	2.544(7)	2.529(12)	2.503(10)	2.552(6)
M−C(N)	2.233(6)	2.226(11)	2.194(9)	2.209(6)
M−C(TMS)	2.242(6)	2.226(10)		
M−C(sp^2)			2.251(9)	
M−N	2.244(5)	2.221(9)	2.207(7)	2.300(4)
M−O(THF)	2.224(4)	2.190(7)	2.182(6)	
M−O(1)				2.167(3)
M−O(2)				2.370(4)
N−C−M	71.3(3)	70.7(6)	70.6(4)	75.4(3)
C−M−N	38.2(2)	38.3(4)	39.8(3)	36.3(2)

Single-crystal X-ray diffraction studies revealed that **1** and **2** are isostructural and isomorphous.[8] Figure 1 shows their representative structure of **1**. The metal atom is η^5-bound to a pentagonal bonding face of the dicarbollide ion, σ-bound to two carbon atoms from CH_2SiMe_3 and NCH_2 groups, and coordinated to the nitrogen atom of the sidearm and a THF molecule in a four-legged piano stool geometry. As shown in Table 1, the differences in bond distances between **1** and **2** are within 0.02 Å, which is consistent with the difference between Shannon's ionic radii of Zr(IV) and Hf(IV).[9] The Zr−C(13) distance of 2.237(6) Å is very close to the Zr−C(15) distance of 2.242(6) Å, which compare well with the 2.246(3) Å found in $^{tol}[NCN]Zr(CH_2SiMe_3)_2$,[10] 2.273(3) Å in $(\eta^5\text{-}C_5Me_5)_2Zr[CH_2N(Me)CH_2N(Me)CH_2]$,[11] and 2.272(7) Å in $[(\eta^5\text{-}C_5H_5)\{\eta^5:\sigma:\sigma\text{-}(C_5H_4)C(Me)_2N(Me)\text{-}$

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(8) Crystal data for **1** ($C_{14}H_{38}B_9NOSiZr$; fw, 453.1): monoclinic, space group *C*2/*c*, *a* = 27.357(2) Å, *b* = 10.728(1) Å, *c* = 18.613(1) Å, β = 95.84(1)°, *V* = 5434.4(6) Å^3, *T* = 293 K, *Z* = 8, d_{calcd} = 1.107 g/cm^3, R1 = 0.067 ($I > 2\sigma(I)$), wR2(F^2) = 0.204. For **2** ($C_{14}H_{38}B_9HfNOSi$; fw, 540.3): monoclinic, space group *C*2/*c*, *a* = 27.501(2) Å, *b* = 10.683(1) Å, *c* = 18.551(1) Å, β = 96.03(1)°, *V* = 5420.3(5) Å^3, *T* = 293 K, *Z* = 8, d_{calcd} = 1.321 g/cm^3, R1 = 0.054 ($I > 2\sigma(I)$), wR2(F^2) = 0.154. For **3** ($C_{24}H_{36}B_9HfNO$; fw, 630.3): monoclinic, space group $P2_1/n$, *a* = 9.648(1) Å, *b* = 12.703(1) Å, *c* = 24.763(1) Å, β = 98.53(1)°, *V* = 3001.2(2) Å^3, *T* = 293 K, *Z* = 4, d_{calcd} = 1.395 g/cm^3, R1 = 0.048 ($I > 2\sigma(I)$), wR2(F^2) = 0.161. For **4** ($C_{20}H_{56}B_{18}Cl_4N_2O_4Zr_2$; fw, 907.5): triclinic, space group $P\bar{1}$, *a* = 9.841(1) Å, *b* = 10.331(1) Å, *c* = 11.121(1) Å, α = 69.97(1)°, β = 98.53(1)°, γ = 69.97(1)°, *V* = 1009.6(2) Å^3, *T* = 293 K, *Z* = 1, d_{calcd} = 1.493 g/cm^3, R1 = 0.050 ($I > 2\sigma(I)$), wR2(F^2) = 0.121.

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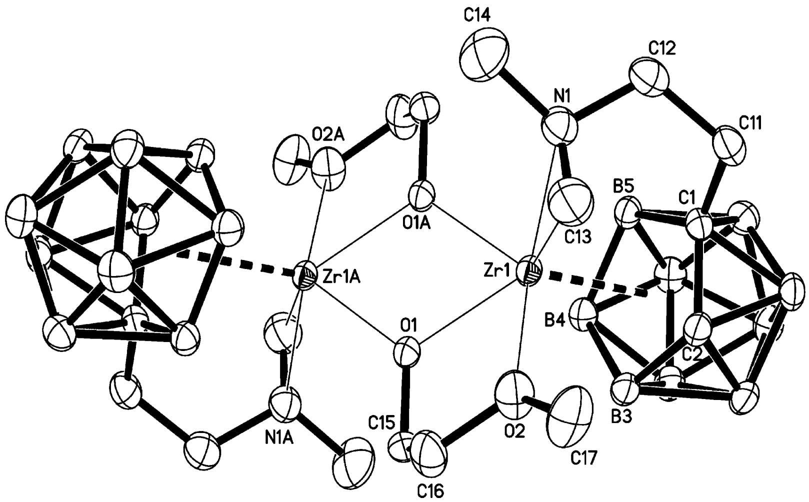

Figure 3. Molecular structure of $[\{\eta^1{:}\sigma{:}\eta^5\text{-}[MeN(CH_2)CH_2CH_2]C_2B_9H_{10}\}Zr(\mu{:}\eta^1\text{-}OCH_2CH_2OCH_3)]_2$ (**4**).

$CH_2\}Zr(Bu^tNC)][MeB(C_6F_5)_3]$.[7a] The average Zr−cage atom distance of 2.544(6) Å is close to that of 2.564(5) Å found in $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(HNEt_2)$.[5a] The Hf−C(13) distance of 2.226(10) Å is the same as that of Hf−C(15), which compare with the average Hf−C distance of 2.168(5) Å in $[\eta^1{:}\eta^6\text{-}(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Hf(CH_2SiMe_3)_2$,[3] 2.261(12) Å in $(C_{23}H_{28}N_4\text{-}4,5)Hf(CH_2SiMe_3)_2$,[12a] 2.316(8) Å in $(\eta^5\text{-}C_5H_5)_2Hf(CH_2CMe_2)(PMe_3)$,[12b] and 2.255(1) Å in $(\eta^5\text{-}C_5H_5)_2Hf(CH_2CH_2CPh{=}CPh)$.[12c] The average Hf−cage atom distance of 2.529(11) Å is close to that of 2.516(10) Å found in $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5{:}\eta^1\text{-}C_2B_9H_{10})Hf(\eta^5\text{-}C_5Me_5)(H)$.[1d]

Preliminary results showed that alkyne can insert into the M−C bond in both **1** and **2**. Complex **1** reacted readily with excess diphenylacetylene in toluene at room temperature to give a mixture of products as suggested by both ^1H and ^{11}B NMR spectra. Complex **2** showed no reactivity toward diphenylacetylene at room temperature probably due to the less reactive Hf−C σ bond. This reaction, however, proceeded at 60 °C to afford the spiro metallacarborane alkyl $[\sigma{:}\sigma{:}\eta^1{:}\eta^5\text{-}\{(CH_2)[(CH_2)PhC{=}CPh]N(CH_2CH_2)C_2B_9H_{10}\}]Hf(THF)$ (**3**).[6] It did not react further with the second equivalent of diphenylacetylene (Scheme 1). The formation of complex **3** may undergo insertion of the C≡C triple bond into the Hf−C σ bond of the constrained three-membered ring, followed by the elimination of $SiMe_4$. Both the insertion and C−H activation reactions were promoted by heating. The molecular structure of **3** is shown in Figure 2. The Hf coordination geometry is four-legged piano stool, which is similar to its parent complex **2**. The bond distances between the Hf atom and the ligand atoms are generally shorter than the corresponding values observed in **2** (Table 1). The Hf−C(16) distance of 2.251(9) Å is longer than the Hf−C(14) distance of 2.194(9) Å, but is very close to the corresponding value of 2.268(4) Å observed in $(\eta^5\text{-}C_5H_5)_2Hf(CH_2CH_2CPh{=}CPh)$.[12c] The C(13)−C(15) distance of 1.477(13) Å and the C(15)−C(16) distance of 1.363(13) Å clearly reveal the presence of localized multiple bonding between C(15) and C(16). The four ring atoms (N(1), C(13), C(15), and C(16)) are nearly coplanar, and the Hf atom is displaced 0.40 Å from this plane.

Under similar reaction conditions, $Zr(CH_2Ph)_4$ did not react with the zwitterionic salt $7\text{-}Me_2N(H)CH_2CH_2\text{-}7,8\text{-}C_2B_9H_{11}$.[13] Reflux of this mixture in toluene led to the decomposition of the product. Reflux in DME afforded a C−H/C−O activation product $[\{\eta^1{:}\sigma{:}\eta^5\text{-}[MeN(CH_2)CH_2CH_2]C_2B_9H_{10}\}Zr(\mu{:}\eta^1\text{-}OCH_2CH_2OCH_3)]_2$ (**4**)[6] with the formation of toluene and ethylbenzene as identified by GC-MS. The proposed reaction pathway is illustrated in Scheme 1. Protonolysis and internal C−H activation give $[\eta^1{:}\sigma{:}\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]ZrCH_2Ph$, an anologue of **1**. Coordination of DME and subsequent methyl abstract reaction via the C−O activation afford the final product **4**. It is noted that the C−O activation often occurs at metallocene cations.[13] This result further demonstrates the highly electrophilic nature of this class of half-sandwich metallacarborane alkyls.

The molecular structure of **4** was confirmed by single-crystal X-ray analyses,[8] shown in Figure 3. It is a centrosymmetric dimer. Each Zr atom is η^5-bound to a dicarbollyl ligand, σ-bound to a methylene carbon, and coordinated to one nitrogen and three oxygen atoms in a five-legged piano stool geometry. As indicated in Table 1, the Zr−C(13), Zr−N(1), and Zr−cage atom distances are very comparable to the corresponding values observed in **1**.

In summary, alkane elimination reactions are a very useful method for the preparation of highly electrophilic half-sandwich metallacarborane alkyls. A Lewis base functionalized sidearm is crucial to stabilize this class of complexes. They can undergo C−H/C−O activation reactions and react with alkyne to give the insertion products, which are characteristic of metallocene alkyl cations.

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Supporting Information Available: Detailed experimental procedures and complete characterization data, tables of crystallographic data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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