Organometallics **2004,** *23,* 4301−4307

Substituent Effects. Synthesis and Structural Characterization of Group 4 Metallacarboranes Containing $(C_6H_5CH_2)_2C_2B_9H_9^{2-}$ and $[o\text{-}C_6H_4(CH_2)_2]C_2B_9H_9^{2-}$ Ligands

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Received May 25, 2004

Substituents on the carborane cage carbons affect not only bonding interactions between the group 4 metal ion and the carboranyl of the C_2B_9 system but also the reactivity pattern of the resulting metal complexes. Treatment of $MCl_4(THF)_2$ with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ in THF at room temperature gave the bis(carboranyl) complexes $\{\eta^4{:}\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2MCl(THF)\}\{Na(THF)_3\}$ (M = Zr (**1**), Hf (**2**)). Under the same reaction conditions, interaction of $TiCl_4(THF)_2$ with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ led to the isolation of a small amount of $TiCl_3(THF)_3$ and B-substituted zwitterionic compound $(C_6H_5CH_2)_2C_2B_9H_9(THF)$ (**4**). Reaction of **1** with 1 equiv of $Li[N(SiMe_3)_2]$ resulted in the replacement of a Na^+ by a Li^+, giving the ionic complex $[\eta^3{:}\eta^2\text{-}\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)][Li(THF)_4]$ (**3**). $ClZr[N(SiMe_3)_2]_3$ was isolated from the reaction of **1** with excess $Li[N(SiMe_3)_2]$. An equimolar reaction between $M(NEt_2)_4$ and $(C_6H_5CH_2)_2C_2B_9H_{11}$ afforded the monocarboranyl complexes $[\eta^2\text{-}(C_6H_5CH_2)_2C_2B_9H_9]M(NEt_2)_2(NHEt_2)$ (M = Ti (**5**), Zr (**6**)). It is believed that the additional $N(p_\pi)\rightarrow M(d_\pi)$ interactions stabilize this type of complex. Treatment of $MCl_4(THF)_2$ with 1 equiv of less bulky yet rigid $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_x$ generated a bent-metallocene type of complex, $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]_2M(THF)_2$ (M = Zr (**7**), Hf (**8**)). These metallacarboranes were all fully characterized by various spectroscopic techniques and elemental analyses. Molecular structures of **1** and **3**−**5** were confirmed by single-crystal X-ray analyses.

Introduction

Group 4 metallacarboranes have been extensively studied.[1] A series of full- and half-sandwich metallacarboranes of the C_2B_4 systems have been prepared and structurally characterized, in which group 4 metals are always η^5-bound to the open C_2B_3 five-membered ring.[2] The reaction chemistry of these metallacarboranes is, however, very limited, probably because of steric hindrance of the carboranyl ligands and/or low stability of their alkyl derivatives.[2a,c,d,f]

Many group 4 metallacarboranes of the C_2B_9 systems are also known.[3] In contrast to the C_2B_4 system, their alkyl derivatives are isolable and show a rich reaction chemistry. For example, $[Cp^*(C_2B_9H_{11})]MCH_3$ ($Cp^* = C_5Me_5$) exhibits a variety of ligand exchange, insertion (alkenes, alkynes, etc.), and ligand C−H activation reactions characteristic of electrophilic metal alkyls.[3b,d−f,h] It is noted that the solid-state structures and reactivity patterns of these complexes are dependent upon the size

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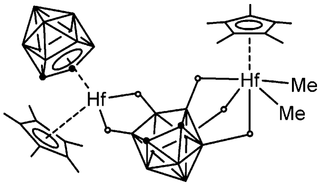
10.1021/om049629r CCC: $27.50 © 2004 American Chemical Society
Publication on Web 08/07/2004

Chart 1



of the group 4 metals. One of the Hf complexes, shown in Chart 1, draws our attention, in which the bridging $C_2B_9H_{11}^{2-}$ ligand bonds to two metals in η^2- and η^3-fashion, respectively.[3c] Interestingly, it resembles "[Cp*-($C_2B_9H_{11}$)]HfCH_3" species in reactivity.

We are interested in the bonding interactions between group 4 metal ions and $R_2C_2B_9H_9^{2-}$ ligands and the effects of such bonding on reactivity. Our previous work shows that introduction of two benzyl groups into the cage carbon atoms of the C_2B_9 system can force the lanthanide ion to move away from the top of the C_2B_3 five-membered ring to the side of the cage, resulting in the formation of *exo-nido*-lanthanacarboranes.[4] With this in mind, we introduced $(C_6H_5CH_2)_2C_2B_9H_9^{2-}$ and $[o\text{-}C_6H_4(CH_2)_2]C_2B_9H_9^{2-}$ ligands into group 4 metal chemistry to study the effects of cage carbon substituents on bonding interactions between the carboranyl and metal ion and on reactivity of the resulting metallacarboranes. These results are reported in this article.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$,[4] $[o\text{-}C_6H_4(CH_2)_2]C_2B_{10}H_{10}$,[5] $M(NEt_2)_4$ (M = Ti, Zr),[6] and $MCl_4(THF)_2$ (M = Ti, Zr, Hf)[6] were prepared according to literature methods. All 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. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 MHz. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., U.K.

Preparation of {η^4:η^2-[$(C_6H_5CH_2)_2C_2B_9H_9$]$_2$ZrCl(THF)}{Na(THF)$_3$} (1). To a THF (20 mL) solution of $ZrCl_4(THF)_2$ (0.37 g, 0.98 mmol) was slowly added a THF (15 mL) solution of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ (prepared in situ from $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$ (0.37 g, 1.00 mmol) and NaH (0.12 g, 5.00 mmol)[4]) at room temperature, and the mixture was stirred overnight. After removal of the solvent, the sticky residue was extracted with toluene (2 × 15 mL). The toluene solutions were combined and concentrated to about 15 mL, to which was added *n*-hexane (2 mL). **1** was isolated as orange crystals after this solution stood at room temperature for a week (0.38 g, 72% based on carboranyl salt). ^1H NMR (CD_2Cl_2): δ 7.35–7.16 (m, 20H) (aryl *H*), 3.63 (d, J = 15 Hz, 4H) ($C_6H_5CH_2$), 3.54 (d, J = 15 Hz, 4H) ($C_6H_5CH_2$), 3.66 (m, 16H) (THF), 1.85 (m, 16H) (THF). ^{13}C NMR (CD_2Cl_2): δ 138.09, 129.31, 127.93, 126.52 (aryl *C*), 68.05 (THF), 41.34 ($C_6H_5CH_2$), 25.25 (THF), the cage carbons were not observed. ^{11}B NMR (CD_2Cl_2): δ −2.48 (2), −15.97 (4), −19.73 (4), −25.57 (4), −34.26 (4). IR (KBr, cm^{-1}): ν_{BH} 2532 (s), 2321 (w). Anal. Calcd for $C_{44}H_{70}B_{18}ClNaO_3Zr$ (**1** − THF): C, 53.31; H, 7.12. Found: C, 53.60; H, 7.35.

Preparation of {η^4:η^2-[$(C_6H_5CH_2)_2C_2B_9H_9$]$_2$HfCl(THF)}{Na(THF)$_3$} (2). This complex was prepared as yellow crystals from $HfCl_4(THF)_2$ (0.46 g, 1.00 mmol) and $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ (1.00 mmol) in THF (35 mL) using the procedure identical to that reported for **1**: yield 0.35 g (61%). ^1H NMR (CD_2Cl_2): δ 7.38–7.12 (m, 20H) (aryl *H*), 3.81 (d, J = 15 Hz, 4H) ($C_6H_5CH_2$), 3.64 (d, J = 15 Hz, 4H) ($C_6H_5CH_2$), 3.55 (m, 16H) (THF), 1.77 (m, 16H) (THF). ^{13}C NMR (CD_2Cl_2): δ 142.25, 131.35, 129.27, 127.76 (aryl *C*), 68.66 (THF), 40.15 ($C_6H_5CH_2$), 25.46 (THF), the cage carbons were not observed. ^{11}B NMR (CD_2Cl_2): δ −2.18 (2), −15.70 (4), −19.62 (4), −25.32 (4), −33.86 (4). IR (KBr, cm^{-1}): ν_{BH} 2556 (s), 2355 (w). Anal. Calcd for $C_{48}H_{78}B_{18}ClNaO_4Hf$: C, 50.10; H, 6.83. Found: C, 50.50; H, 7.15.

Preparation of [η^3:η^2-{$(C_6H_5CH_2)_2C_2B_9H_9$}$_2$ZrCl(THF)][Li(THF)$_4$] (3). To a toluene (20 mL) solution of **1** (0.38 g, 0.36 mmol) was slowly added a toluene (15 mL) solution of $LiN(SiMe_3)_2$ (0.061 g, 0.36 mmol) at room temperature, and the reaction mixture was stirred for 2 days. After removal of the solvent, the residue was extracted with THF/toluene (1:5, 3 × 10 mL). The clear solutions were combined and concentrated to about 15 mL. **3** was isolated as orange crystals after this solution stood at room temperature for 5 days (0.25 g, 62%). ^1H NMR (CD_2Cl_2): δ 7.33–7.10 (m, 20H) (aryl *H*), 3.77 (br s, 20H) (THF), 3.19 (d, J = 15.0 Hz, 4H) ($C_6H_5CH_2$), 3.03 (d, J = 15 Hz, 4H) ($C_6H_5CH_2$), 1.91 (br s, 20H) (THF). ^{13}C NMR (CD_2Cl_2): δ 141.80, 129.39, 127.24, 125.09 (aryl *C*), 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 −8.37 (2), −11.88 (4), −19.49 (6), −26.60 (2), −37.10 (4). IR (KBr, cm^{-1}): ν_{BH} 2529 (s), 2318 (w). 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.

Reaction of 1 with Excess LiN(SiMe$_3$)$_2$. Isolation of ClZr[N(SiMe$_3$)$_2$]$_3$. To a toluene (20 mL) solution of **1** (0.38 g, 0.36 mmol) was slowly added a toluene (20 mL) solution of $LiN(SiMe_3)_2$ (0.24 g, 1.44 mmol) at room temperature, and the reaction mixture was stirred for 2 days. After removal of the solvent, the residue was extracted with toluene (3 × 10 mL). The clear solutions were combined and concentrated to about 10 mL. $ClZr[N(SiMe_3)_2]_3$ was isolated as colorless crystals after this solution stood at room temperature for 4 days (0.12 g, 55%). ^1H NMR (CD_2Cl_2): δ 0.22 (s). Its solid-state structure was confirmed by a single-crystal X-ray analysis.

Reaction of TiCl$_4$(THF)$_2$ with [$(C_6H_5CH_2)_2C_2B_9H_9$]Na$_2$(THF)$_x$. Isolation of TiCl$_3$(THF)$_3$ and $(C_6H_5CH_2)_2C_2B_9H_9$(THF)·2($C_6H_5CH_3$) (4·2($C_6H_5CH_3$)). To a THF (20 mL) solution of $TiCl_4(THF)_2$ (0.33 g, 1.00 mmol) was slowly added a THF (15 mL) solution of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ (prepared in situ from $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$ (0.37 g, 1.00 mmol) and NaH (0.12 g, 5.00 mmol)[4]) at room temperature, and the mixture was stirred overnight. The color of the solution turned gradually to dark green. After removal of the solvent, the solid was extracted with THF/toluene (1:5, 2 × 15 mL). The clear solutions were combined and concentrated to about 15 mL. A small amount of dark green crystals and a few pale yellow ones were obtained after this solution stood at room temperature for 3 days. The dark green crystals were identified as $TiCl_3(THF)_3$, and the pale yellow ones were characterized to be **4**·2($C_6H_5CH_3$) by single-crystal X-ray analyses, respectively. It was not possible to take the spectroscopic data for **4**·2($C_6H_5CH_3$) due to an insufficient amount of crystals obtained.

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Preparation of $(C_6H_5CH_2)_2C_2B_9H_{11}$. To a suspension of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ (prepared from $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$ (1.25 g, 3.35 mmol) and NaH (0.36 g, 15.00 mmol)[4]) in toluene (25 mL) was added 85% H_3PO_4 (10.20 g, 88.5 mmol). The resulting two-phase mixture was vigorously stirred at room temperature overnight. The toluene layer was decanted, and the H_3PO_4 layer was extracted with toluene (2 × 15 mL). The toluene solutions were combined and dried over $MgSO_4$. After removal of toluene under vacuum, the pale yellow solid was recrystallized from toluene/*n*-hexane to give $(C_6H_5CH_2)_2C_2B_9H_{11}$ as a white solid (0.76 g, 72%). ^1H NMR (CD_2Cl_2): δ 7.35−7.16 (m, 10H) (aryl *H*), 3.64 (d, $J = 15$ Hz, 2H) ($C_6H_5CH_2$), 3.54 (d, $J = 15$ Hz, 2H) ($C_6H_5CH_2$). ^{13}C NMR (CD_2Cl_2): δ 137.94, 129.29, 128.04, 126.60 (aryl *C*), 86.91 (cage *C*), 41.34 ($C_6H_5CH_2$). ^{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_{BH} 2552 (s). Anal. Calcd for $C_{16}H_{25}B_9$: C, 61.07; H, 8.01. Found: C, 61.25; H, 7.96.

Preparation of $[\eta^2\text{-}(C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2)\cdot CH_2Cl_2$ ($5\cdot CH_2Cl_2$). A toluene (15 mL) solution of $(C_6H_5CH_2)_2C_2B_9H_{11}$ (0.79 g, 2.51 mmol) was added dropwise to a toluene (10 mL) solution of $Ti(NEt_2)_4$ (0.84 g, 2.50 mmol) with vigorous stirring at room temperature, and the reaction mixture was stirred overnight. After removal of the solvent, the red solid was recrystallized from a CH_2Cl_2 solution, affording **5**·CH_2Cl_2 as red crystals (1.37 g, 83%). ^1H NMR (CD_2Cl_2): δ 7.20 (m, 10H) (aryl *H*), 5.31 (s, 2H) (CH_2Cl_2), 3.18 (d, $J = 15$ Hz, 2H) ($C_6H_5CH_2$), 3.03 (d, $J = 15$ Hz, 2H) ($C_6H_5CH_2$), 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 (aryl *C*), 42.85 (NCH_2CH_3), 40.87 ($C_6H_5CH_2$), 13.08 (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_{BH} 2524 (s), 2393 (m). Anal. Calcd for $C_{28}H_{54}B_9N_3Ti$ (**5**): C, 58.20; H, 9.42; N, 7.27. Found: C, 58.56; H, 9.32; N, 6.97.

Preparation of $[\eta^2\text{-}(C_6H_5CH_2)_2C_2B_9H_9]Zr(NEt_2)_2(NHEt_2)$ (6). This complex was prepared as yellow crystals from $(C_6H_5CH_2)_2C_2B_9H_{11}$ (0.31 g, 1.00 mmol) and $Zr(NEt_2)_4$ (0.38 g, 1.00 mmol) in toluene (30 mL) using the procedure identical to that reported for **5**: yield 0.49 g (78%). ^1H NMR (CD_2Cl_2): δ 7.21 (m, 10H) (aryl *H*), 3.19 (d, $J = 15$ Hz, 2H) ($C_6H_5CH_2$), 3.01 (d, $J = 15$ Hz, 2H) ($C_6H_5CH_2$), 2.70 (q, $J = 7.2$ Hz, 12H) (NCH_2CH_3), 1.15 (t, $J = 7.2$ Hz, 18H) (NCH_2CH_3). ^{13}C NMR (CD_2Cl_2): δ 141.91, 130.75, 127.18, 125.01 (aryl *C*), 44.62 (NCH_2CH_3), 40.79 ($CH_2C_6H_5$), 13.54 (NCH_2CH_3), the cage carbons were not observed. ^{11}B NMR (CD_2Cl_2): δ 0.24 (3), −8.41 (4), −24.56 (1), −27.14 (1). IR (KBr, cm^{-1}): ν_{BH} 2518 (s), 2354 (w). Anal. Calcd for $C_{28}H_{54}B_9N_3Zr$: C, 54.13; H, 8.76; N, 6.76. Found: C, 54.34; H, 8.75; N, 6.55.

Preparation of $[Me_3NH][\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_{10}]$. To a mixture of 1,2-$[o\text{-}C_6H_4(CH_2)_2]$-1,2-$C_2B_{10}H_{10}$ (0.62 g, 2.52 mmol) and KOH (0.56 g, 10.7 mmol) was added freshly distilled CH_3OH (40 mL) with stirring at 0 °C. The reaction mixture was allowed to warm to room temperature within 30 min and was refluxed for 2 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 white precipitate. The product was collected by filtration, washed with water (3 × 10 mL), and dried in a vacuum to give a white powder (0.53 g, 71%). ^1H NMR (acetone-d_6): δ 7.01 (m, 4H) (aryl *H*), 3.20 (s, 9H) ($HN(CH_3)_3$), 3.08 (d, $J = 15$ Hz, 2H) ($C_6H_4(CH_2)_2$), 2.86 (d, $J = 15$ Hz, 2H) ($C_6H_4(CH_2)_2$). ^{13}C NMR (acetone-d_6): δ 144.28, 132.17, 130.83 (aryl *C*), 50.68 ($HN(CH_3)_3$), 44.90 ($C_6H_4(CH_2)_2$), the cage carbons were not observed. ^{11}B NMR (acetone-d_6): δ −11.19 (2), −12.43 (1), −20.87 (2), −21.79 (2), −35.88 (1), −38.16 (1). IR (KBr, cm^{-1}): ν_{BH} 2576 (s). Anal. Calcd for $C_{13}H_{28}B_9N$: C, 52.81; H, 9.55; N, 4.74. Found: C, 52.59; H, 9.69; N, 4.50.

Preparation of $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]_2Zr(THF)_2$ (7). To a suspension of NaH (0.08 g, 3.33 mmol) in THF (10 mL) was slowly added a THF solution (10 mL) of $[Me_3NH][\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_{10}]$ (0.22 g, 0.74 mmol) at room temperature, and the mixture was refluxed overnight. After removal of excess NaH and a half amount of THF, the resulting $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_x$ was slowly added to a THF solution (10 mL) of $ZrCl_4(THF)_2$ (0.28 g, 0.74 mmol) at room temperature. The reaction mixture was then stirred overnight. After removal of the precipitate and the solvent, the residue was extracted with hot toluene (3 × 10 mL). The toluene solutions were combined and concentrated to about 15 mL, to which was added *n*-hexane (2 mL). **7** was isolated as a white crystalline solid after this solution stood at room temperature for 2 days (0.17 g, 65%, based on carboranyl salt). ^1H NMR (pyridine-d_5): δ 6.95 (m, 8H) (aryl *H*), 3.63 (m, 8H) (THF), 3.40 (d, $J = 15$ Hz, 4H) ($C_6H_4(CH_2)_2$), 3.29 (d, $J = 15$ Hz, 4H) ($C_6H_4(CH_2)_2$), 1.59 (m, 8H, THF). ^{13}C NMR (pyridine-d_5): δ 139.30, 128.0, 126.95 (aryl *C*), 67.14 (THF), 39.71 ($C_6H_4(CH_2)_2$), 25.13 (THF), cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ −5.86 (6), −9.50 (8), −12.06 (2), −32.51 (2). IR (KBr, cm^{-1}): ν_{BH} 2526 (s). Anal. Calcd for $C_{28}H_{50}B_{18}O_2Zr$: C, 47.73; H, 7.15. Found: C, 47.36; H, 7.35.

Preparation of $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]_2Hf(THF)_2$ (8). This complex was prepared as a yellow solid from $HfCl_4(THF)_2$ (0.34 g, 0.73 mmol) and $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_x$ (prepared in situ from $[Me_3NH][\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_{10}]$ (0.22 g, 0.74 mmol) and NaH (0.08 g, 3.33 mmol) in THF) in THF (30 mL) using the procedure identical to that reported for **7**: yield 0.18 g (61% based on the carboranyl salt). ^1H NMR (pyridine-d_5): δ 6.97 (m, 8H) (aryl *H*), 3.63 (m, 8H, THF), 3.42 (d, $J = 15$ Hz, 4H) ($C_6H_4(CH_2)_2$), 3.27 (d, $J = 15$ Hz, 4H) ($C_6H_4(CH_2)_2$), 1.59 (m, 8H, THF). ^{13}C NMR (pyridine-d_5): δ 139.79, 127.61, 125.50 (aryl *C*), 70.75 (cage *C*), 67.84 (THF), 40.38 ($C_6H_4(CH_2)_2$), 25.81 (THF). ^{11}B NMR (pyridine-d_5): δ −5.71 (6), −9.43 (8), −12.00 (2), −32.23 (2). IR (KBr, cm^{-1}): ν_{BH} 2551 (s). Anal. Calcd for $C_{28}H_{50}B_{18}O_2Hf$: C, 42.47; H, 6.37. Found: C, 42.36; H, 5.99.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[7] 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.[8] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1. Selected bond lengths are compiled in Table 2. Further details are included in the Supporting Information.

Results and Discussion

Reaction of $MCl_4(THF)_2$ with $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2$. Treatment of $MCl_4(THF)_2$ with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ in THF at room temperature gave, after recrystallization from a toluene/*n*-hexane solution, the bis(carboranyl) complexes $\{\eta^4\text{:}\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2MCl(THF)\}\{Na(THF)_3\}$ (M = Zr (**1**), Hf (**2**)) in good yields (Scheme 1). Expected half-sandwich complexes were not isolated, but they might serve as intermediates which reacted further with another equivalent of carboranyl salt to give the thermodynamically stable products. This result differs significantly from

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(7) Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

(8) *SHELXTL V 5.03* Program Package; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995.

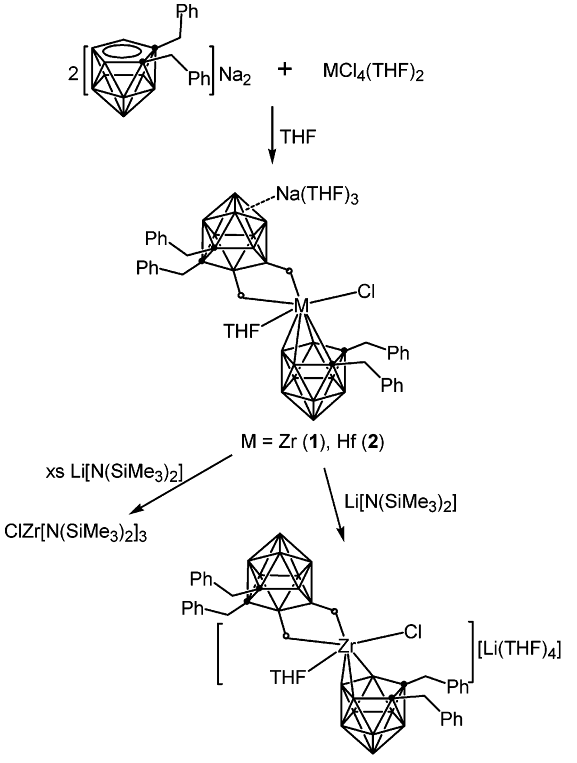
Table 1. Crystal Data and Summary of Data Collection and Refinement for 1 and 3−5

	1	**3**	**4**·2($C_6H_5CH_3$)	**5**·CH_2Cl_2
formula	$C_{48}H_{78}B_{18}ClNaO_4Zr$	$C_{52}H_{86}B_{18}ClLiO_5Zr$	$C_{34}H_{47}B_9O$	$C_{29}H_{56}B_9Cl_2N_3Ti$
cryst size (mm)	0.35 × 0.35 × 0.25	0.60 × 0.45 × 0.25	0.50 × 0.25 × 0.20	0.60 × 0.50 × 0.30
fw	1063.3	1119.4	569.0	662.9
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	14.287(7)	11.572(1)	10.616(2)	10.249(1)
b, Å	15.103(7)	13.575(1)	10.968(2)	11.374(1)
c, Å	15.133(8)	19.779(1)	28.299(5)	17.818(2)
α, deg	63.36(1)	87.14(1)	90	85.43(1)
β, deg	86.49(1)	85.83(1)	100.48(1)	88.30(1)
γ, deg	83.52(1)	86.25(1)	90	65.13(1)
V, $Å^3$	2900(2)	3088.9(4)	3240.2(9)	1878.6(4)
Z	2	2	4	2
D_{calcd}, Mg/m^3	1.218	1.204	1.166	1.172
radiation (*λ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	3.0 to 50.0	3.5 to 50.0	3.9 to 50.0	4.0 to 52.0
μ, mm^{-1}	0.284	0.264	0.063	0.394
F(000)	1112	1176	1216	704
no. of obsd reflns	7567	10809	4247	4890
no. of params refnd	719	703	379	436
goodness of fit	0.960	1.007	0.998	1.092
R1	0.078	0.056	0.095	0.059
wR2	0.176	0.143	0.265	0.177

Table 2. Selected Bond Lengths (Å) for 1 and 3

	1	**3**
Zr−C1	2.774(4)	3.054(4)
Zr−C2	2.918(4)	3.017(4)
Zr−B3	2.637(5)	2.528(4)
Zr−B4	2.408(5)	2.310(4)
Zr−B5	2.451(5)	2.575(3)
Zr−B23	2.643(6)	2.482(4)
Zr−B24	2.329(6)	2.353(4)
Zr−Cl1	2.395(2)	2.388(1)
Zr−O5	2.185(4)	2.226(2)

Scheme 1

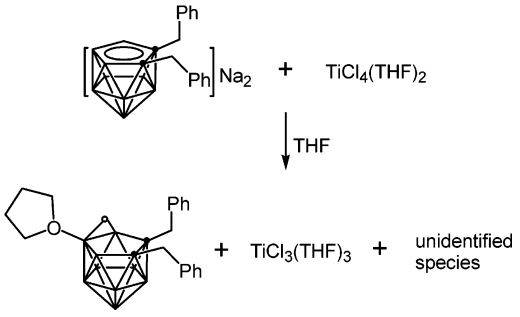


3

that of the C_2B_4 system, in which half-sandwich metallacarboranes were isolable.[2d,j]

Under the same reaction conditions, interaction of $TiCl_4(THF)_2$ with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ in THF at room temperature led to the isolation of a small amount of dark green crystals and a few colorless ones (Scheme 2). The ^{11}B NMR of the mother liquor was very complicated. The dark green crystals did not contain any boron atom, as indicated by the ^{11}B NMR, and were identified as the known trivalent Ti(III) chloride complex $TiCl_3(THF)_3$ by a single-crystal X-ray analysis.[9] The spectroscopic data of the colorless crystals were unable to be taken due to an insufficient amount of materials, but its structure was confirmed by a single-crystal X-ray analysis to be a B-substituted zwitterionic compound, $(C_6H_5CH_2)_2C_2B_9H_9(THF)\cdot 2(C_6H_5CH_3)$ (**4**·2($C_6H_5CH_3$)), as shown in Figure 1. The formation of **4** may be mediated by titanium chloride.[10] Dark green color also appeared if the above reaction was carried out in dry toluene, indicating the presence of trivalent Ti(III) species generated in the reaction. It is noteworthy that reaction of Cp_2TiCl_2 with $[(Me_3Si)_2C_2B_4H_4]Li_2$ in dry benzene gave a trivalent complex, $[Cp\{(Me_3Si)_2C_2B_4H_4\}Ti]_2$.[11] No pure product was isolated from the reaction of $TiCl_3(THF)_3$ with 1 equiv of $[(C_6H_5CH_2)_2C_2B_9H_9]Na_2(THF)_x$ in THF.

Scheme 2



4

Substitution of the chloro group in **1** was attempted. Treatment of **1** with 1 equiv of $Li[N(SiMe_3)_2]$ in toluene

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[9] The molecular structure of $TiCl_3(THF)_3$ was reported, see: Handlovič, M.; Mikloš, D.; Zikmund, M. *Acta Crystallogr.* **1981**, *B37*, 811.

[10] Lewis acid-promoted substitution reactions of the cage B−H bond were reported, see: Kang, H. C.; Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2024, and references therein.

[11] Hosmane, N. S.; Wang, Y.; Zhang, H.; Maguire, J. A.; Waldhör, E.; Kaim, W.; Binder, H.; Kremer, R. K.*Organometallics* **1994**, *13*, 4156.

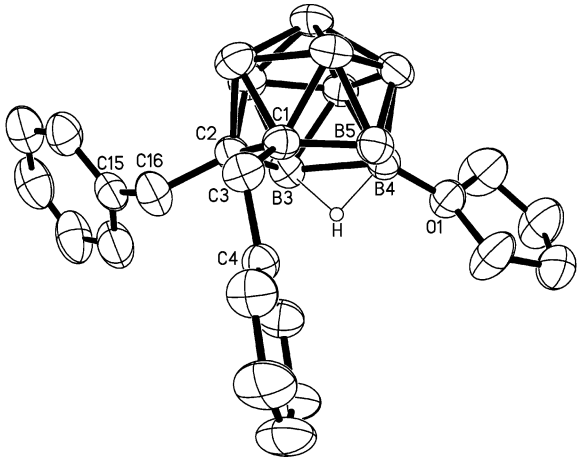

Figure 1. Molecular structure of $(C_6H_5CH_2)_2C_2B_9H_9(THF)$ (**4**) (the two solvated toluene molecules are not shown). Selected bond distances (Å): C1−C3 = 1.537(5), C1−C2 = 1.583(5), C1−B5 = 1.602(5), C2−B3 = 1.613(5), C2−C16 = 1.543(5), B3−B4 = 1.853(6), B4−B5 = 1.767(6), B4−O1 = 1.499(5).

resulted in the replacement of a Na^+ by a Li^+, giving the ionic complex $[\eta^3{:}\eta^2\text{-}\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)][Li(THF)_4]$ (**3**) in 62% yield. The major alteration is that a group 1 ion complex no longer coordinates to the cage in **3**. Reaction of **1** with excess $Li[N(SiMe_3)_2]$ led to the isolation of $ClZr[N(SiMe_3)_2]_3$ in 55% yield. Its solid-state structure was confirmed by single-crystal X-ray analyses and is the same as the reported one.[12] Surprisingly, the carboranyl ligands rather than the chloro group were replaced by the amido moieties.[13] There were no reactions between **1** and Me_3SiCH_2MgCl or CpNa since **1** was recovered and no changes were observed in the ^{11}B NMR. On the other hand, **1** did react with MeLi or $LiC{\equiv}CPh$, leading to brown solutions with complicated ^{11}B NMR spectra, suggesting that the resulting metal alkyl complexes may be unstable. No pure products were isolated from these reactions. These results also indicate that the coordinated chloro group in **1** is probably protected by the surrounding ligands to some extent, which inhibits the attacks by large nucleophiles. This reactivity pattern resembles that exhibited by full-sandwich zirconacarborane chloride complexes of the C_2B_4 system.[2a,c,d]

Complexes **1**−**3** were characterized by various spectroscopic techniques. The ^1H NMR spectra showed that the methylene protons of the benzyl groups in all three complexes are nonequivalent with the coupling constant $J = 15$ Hz and indicated the molar ratio of two THF molecules per cage in **1** and **2** and two and a half THF molecules per cage in **3**, respectively. Their ^{13}C NMR spectra exhibited four aromatic carbon signals in the range 142−125 ppm, one methylene carbon resonance at about 40 ppm, and two peaks attributable to THF. The cage carbons were not observed in the ^{13}C NMR spectra. The ^{11}B NMR spectra of **1** and **2** were very similar, displaying a 1:2:2:2:2 splitting pattern, whereas that of **3** showed a 1:2:3:1:2 splitting pattern. The solid-state IR spectra of **1**−**3** displayed a characteristic doublet centered around 2530 cm^{-1} and a shoulder at about 2330 cm^{-1} attributable to a M−H−B stretching mode.[14]

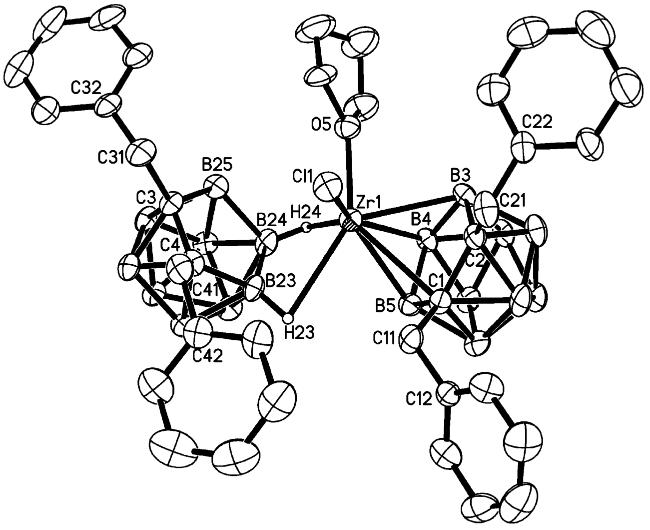

Figure 2. Molecular structure of the anion $[\eta^4{:}\eta^2\text{-}\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)]^-$ in **1** (the coordinated $Na(THF)_3{}^+$ complex cation is removed for clarity).

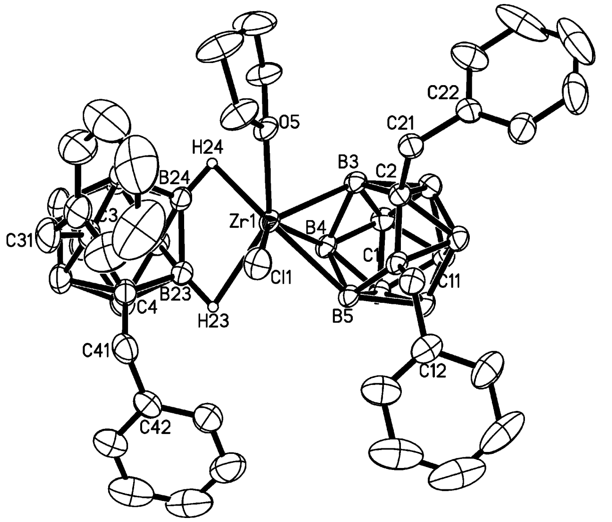

Figure 3. Molecular structure of the anion $[\eta^3{:}\eta^2\text{-}\{(C_6H_5CH_2)_2C_2B_9H_9\}_2ZrCl(THF)]^-$ in **3** (the separated $[Li(THF)_4]^+$ complex cation is removed for clarity).

Molecular structures of **1** and **3** derived from single-crystal X-ray analyses are shown in Figures 2 and 3, respectively. The $Na(THF)_3{}^+$ complex cation binds to the Zr atom via three sets of B−H−Na interactions in **1**, while **3** consists of well-separated, alternating layers of discrete tetrahedral cations $[Li(THF)_4]^+$ and anions. The coordination environments of the Zr atom in both **1** and **3** are similar, but the coordination details and the orientations of four benzyl moieties are different in both complexes. Table 2 lists some bond distances around the Zr atom for comparison. The Zr−Cl and Zr−O distances are all shorter than the corresponding values of 2.467(2) and 2.273(5) Å observed in $[\{\eta^5\text{-}(Me_3Si)RC_2B_4H_4\}_2ZrCl(THF)]^-$ (R = H, Me, Me_3Si).[2a] Steric effects im-

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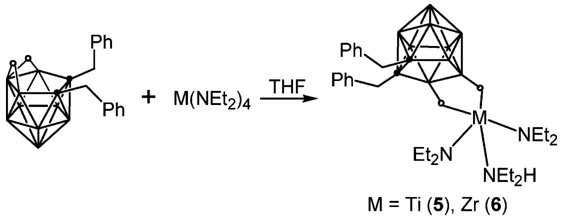
(12) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

(13) It was reported that $ClZr[N(SiMe_3)_2]_3$ did not react with excess $Li[N(SiMe_3)_2]$; see ref 12.

(14) (a) Xie, Z.; Yan, C.; Yang, Q.; Mak, T. C. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1761. (b) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W.-H.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2000**, *122*, 5758. (c) Wang, S.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 3842.

Scheme 3



posed by the benzyl groups lead to much longer Zr−C(cage) distances, with the shortest one being 2.774(4) Å. If the reported longest Zr−cage atom distance of 2.789(6) Å found in [η^5:η^6:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10}CH_2$-NMe)]$Zr(NC_5H_5)$[15] is taken as a cutoff point, the Zr atom is then bound to one of the $(C_6H_5CH_2)_2C_2B_9H_9^{2-}$ lignads in η^4- and η^3-fashion in **1** and **3**, respectively. The large variations in bond lengths within the complex are perhaps due to the steric effects generated by the substituents. The differences in bond lengths between **1** and **3** may result from packing forces.[16]

The above results show that substituent effects are very obvious, which cause slip distortion of the Zr atom from the center of the C_2B_3 bonding face of the carboranyl ligand. As a result, mono(carboranyl) species are unstable, which would react further with another equivalent of carborane dianion to produce the thermodynamically more stable bis(carboranyl) complexes.

Reaction of $M(NEt_2)_4$ with $(C_6H_5CH_2)_2C_2B_9H_{11}$. To stabilize the half-sandwich species, it is necessary to fulfill either steric or electronic requirements of the central metal ions. The amido group can donate lone-pair electrons to a d^0 metal ion in addition to a normal σ bond to meet the electronic requirements, which may lead to the isolation of half-sandwich complexes.[3j,17] An equimolar reaction between $M(NEt_2)_4$ and $(C_6H_5$-$CH_2)_2C_2B_9H_{11}$ in toluene at room temperature gave, after recrystallization from CH_2Cl_2, the monocarboranyl complexes [η^2-$(C_6H_5CH_2)_2C_2B_9H_9$]$M(NEt_2)_2(NHEt_2)$ (M = Ti (**5**), Zr (**6**)) in good yields (Scheme 3). $(C_6H_5$-$CH_2)_2C_2B_9H_{11}$ was prepared in 72% yield by treatment of [$(C_6H_5CH_2)_2C_2B_9H_9$]Na_2 with 85% H_3PO_4 in toluene at room temperature according to the literature method for the preparation of $C_2B_9H_{13}$.[3j] This reaction was closely monitored by ^{11}B NMR since [$(C_6H_5CH_2)_2C_2B_9H_9$]-Na_2 and $(C_6H_5CH_2)_2C_2B_9H_{11}$ showed different splitting patterns in the ^{11}B NMR spectra. Alkane elimination reactions were also examined. To our surprise, there were no reactions at all between $(C_6H_5CH_2)_2C_2B_9H_{11}$ and $M(CH_2Ph)_4$ (M = Ti, Zr) or $Zr(CH_2SiMe_3)_4$ in toluene at 0−50 °C. As the temperature was increased to >50 °C, the color of the mixture changed from pale yellow to dark blue with complicated ^{11}B NMR spectra, suggesting that decomposition reactions proceeded at temperatures > 50 °C. These results imply that the acidity/basicity is not the sole factor to control these elimination reactions; steric factors must also be taken into account.

Ligand substitution and protonolysis reactions were attempted. **5** did not react with THF. It did react with 2 equiv of Et_3NHCl and Me_3SiCl to give a mixture of complexes as suggested by very complicated ^{11}B NMR spectra.

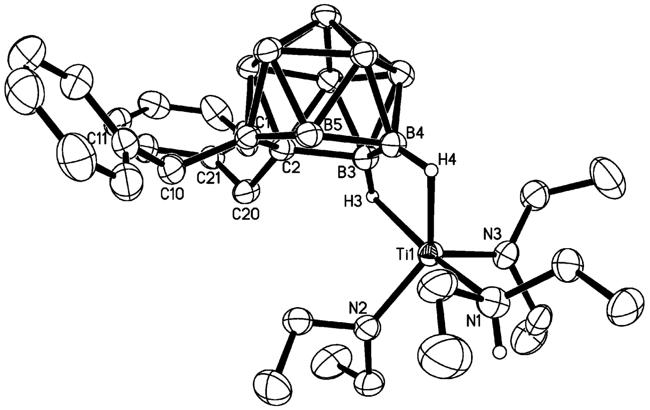


Figure 4. Molecular structure of [η^2-$(C_6H_5CH_2)_2C_2B_9H_9$]-$Ti(NEt_2)_2(NHEt_2)$ (**5**) (the solvated dichloromethane molecule is not shown). Selected bond distances (Å): Ti1−B3 = 2.379(3), Ti1−B4 = 2.283(3), Ti1−N1 = 2.225(2), Ti1−N2 = 1.879(2), Ti1−N3 = 1.867(2).

The ^{11}B NMR spectra of both **5** and **6** showed a 3:4:1:1 splitting pattern which differs significantly from that of $(C_6H_5CH_2)_2C_2B_9H_{11}$. Their ^{1}H NMR spectra exhibited one multiplet of aromatic protons, two doublets of benzyl methylene protons, and only one set of Et protons, suggesting there are possible exchanges of the N-H proton between M-NEt_2 groups.

Figure 4 shows the molecular structure of **5**. Its crystal lattice contains one CH_2Cl_2 of solvation. Unlike (η^5-$C_2B_9H_{11}$)$Zr(NEt_2)_2(NHEt_2)$[3j] and (η^5-$C_2B_9H_{11}$)Ti-$(NMe_2)_2(NHMe_2)$,[17] the Ti atom in **5** is bound to $(C_6H_5CH_2)_2C_2B_9H_9^{2-}$ in η^2-fashion via B−H−Ti interactions. Again, this example illustrates the importance of the cage carbon substituents in bonding interactions between the dicarbollide and a group 4 metal ion. The Ti−B distances are 2.379(3) and 2.283(3) Å, with an average value of 2.331(3) Å. This measured value is well comparable to the average Ti−cage atom distance of 2.375(6) Å in (η^5-$Et_2C_2B_4H_4$)$TiCl_2(PMe_3)_2$,[2j] but significantly shorter than the average Ti−cage atom distances of 2.423(2) Å in (η^5-$C_2B_9H_{11}$)$Ti(NMe_2)_2(NHMe_2)$,[17] 2.463(3) Å in [(η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)TiMe]$_n$,[3g] and 2.407(6) Å in [(η^5-C_5H_5){η^5-$(Me_3Si)_2C_2B_4H_4$}TiCl(THF),[2f] presumably due to the differences in coordination number of the Ti(IV) ion.[18] The short Ti−N(2) and Ti−N(3) bond distances (1.879(2) and 1.867(2) Å) and the planar geometry around the N(2) and N(3) nitrogen atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in $N(p_\pi)\rightarrow Ti(d_\pi)$ interactions. The Ti−N(1)-(amine) distance of 2.225(2) Å is much longer than the Ti−N(amido) ones, and the N(1) adopts a pyramidal geometry. These distances are comparable to the corresponding values observed in (η^5-$C_2B_9H_{11}$)$Ti(NMe_2)_2$-$(NHMe_2)$.[17]

The isolation of **5** and **6** implies that the additional $N(p_\pi)\rightarrow Ti(d_\pi)$ interactions can make compensation for the losses of electrons from the carboranyl ligand, thus stabilizing the half-sandwich complexes.

Reaction of $MCl_4(THF)_2$ with [{o-$C_6H_4(CH_2)_2$}-$C_2B_9H_9$]Na_2. The above examples clearly demonstrate

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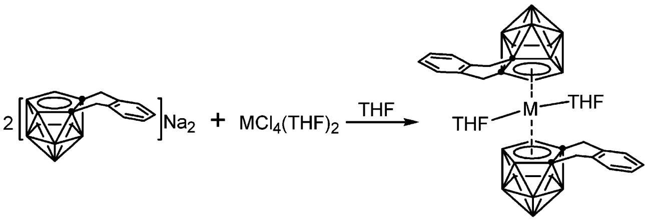
Scheme 4



M = Zr (**7**), Hf (**8**)

that benzyl substituents on the open C_2B_3 five-membered ring of the C_2B_9 system can change the bonding modes between the cage and group 4 metal ion, leading to the formation of *exo-nido*-metallacarboranes. If the two benzyl groups are replaced by a less bulky yet rigid moiety of *o*-xylylene, what would be the bonding mode between the carboranyl ligand and group 4 metal ion?

Using the conventional method for the synthesis of dicarbollide,[19] $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2$ was easily prepared from μ-1,2-$[o\text{-}C_6H_4(CH_2)_2]$-1,2-$C_2B_{10}H_{10}$. Treatment of $MCl_4(THF)_2$ with 1 equiv of $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]Na_2(THF)_x$ in THF at room temperature afforded, after recrystallization from a toluene solution, $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]_2M(THF)_2$ (M = Zr (**7**), Hf (**8**)) in good yields (Scheme 4). Many attempts were made to grow X-ray-quality crystals, but all failed.

The ^{1}H NMR spectra of both **7** and **8** showed one multiplet of aromatic protons, two doublets of *o*-xylylene methylene protons, and two multiplets of THF protons and supported the molar ratio of one THF molecule per cage. Such a low THF-to-cage molar ratio suggests that complexes **7** and **8** may not contain any complex cation $Na(THF)_x$. Their ^{13}C NMR spectra exhibited three aromatic carbon signals in the range 139−126 ppm, one methylene carbon resonance at about 40 ppm, and two peaks attributable to THF. The ^{11}B NMR spectra of **7** and **8** were very similar, displaying a 3:4:1:1 splitting pattern. Their solid-state IR spectra displayed a characteristic terminal B−H absorption around 2530 cm^{-1}, indicating there are no B−H−M interactions.[14] Elemental analyses are consistent with the formula of $[\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9]_2M(THF)_2$. On the basis of these results, **7** and **8** may be best described as a full-sandwich type of structure, in which the metal ion is η^5-bound to each of the two carboranyl ligands and coordinated to two THF molecules.

Conclusion

Unlike the unsubstituted $C_2B_9H_{11}^{2-}$, which is usually η^5-bound to group 4 metal ions,[3] the dibenzyl-substituted one, $(C_6H_5CH_2)_2C_2B_9H_9^{2-}$, is a more versatile ligand and can bond to the metal ions in η^2-, η^3-, or η^4-fashion, resulting in the formation of the ‘slipped’ or *exo-nido* metallacarboranes. The less bulky yet rigid *o*-xylylene-substituted carboranyl ligand, $\{o\text{-}C_6H_4(CH_2)_2\}C_2B_9H_9^{2-}$, prefers to be η^5-bound to group 4 metal ions. Effects of substituents on the bonding interactions between the group 4 metal ion and the carboranyl of the C_2B_9 system are very obvious.

Only bis(carboranyl) group 4 metal complexes were isolated from 1:1 stoichiometric reactions of $MCl_4(THF)_2$ with the sodium salts of carborane dianions. Mono(carboranyl) group 4 metal complexes were prepared via amine elimination reactions of $M(NEt_2)_4$ and neutral carborane acids, presumably the additional $N(p_\pi)\rightarrow M(d_\pi)$ interactions stabilizing this type of complexes. Ligand substitution reactions of the above complexes were attempted but not very successful. For example, the chloro group in **1** was found to be inert in the presence of $(Me_3Si)_2NLi$, Me_3SiCH_2MgCl, or CpNa, most likely due to the very crowded environments around the Cl atom.

Acknowledgment. This work was supported by grants from the Research Grants Council of the Hong Kong Special Administration Region (Project No. 403103) and National Natural Science Foundation of China through the Outstanding Young Investigator Award Fund (Project No. 20129002). Z.X. acknowledges the Croucher Foundation for a Senior Research Fellowship Award.

Supporting Information Available: Crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **1**, **3**, **4**·$2(C_6H_5CH_3)$, and **5**·CH_2Cl_2 as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049629R

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