

Unexpected Intramolecular Oxidative Addition: Novel Synthetic Route to High-Valent Group 4 Metallocarboranes Bearing a η^6 - or η^7 -Carboranyl Ligand

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Summary: The first high-valent zirconacarboranes bearing a η^6 - or η^7 -carboranyl ligand have been prepared and structurally characterized by an unexpected oxidative-addition reaction between Zr(II) and the carborane cage. The bridging ligand $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})]^{3-}$ can provide a much more open coordination environment at the metal center, probably offering a model complex for catalysis study.

Group 4 metallocarboranes have received much attention, since they exhibit interesting catalytic properties in olefin polymerization.¹ Most of these works have focused on the C_2B_9 ^{1,2} and C_2B_4 systems.³ The only known group 4 metallocarborane with the C_2B_{10} system is the divalent species $[(\eta^6\text{-R}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2\text{M}]^{2-}$ (R = H, Me), prepared from the reaction of *nido*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}^{2-}$ with MCl_4 , in which the group 4 metal ions are reduced from +4 to +2 by the *nido*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}^{2-}$ anion during the reaction.⁴ It is very clear that the high-valent Zr(IV) metallocarboranes bearing a $\text{C}_2\text{B}_{10}\text{H}_{12}^{2-}$ ligand cannot be prepared by the conventional metathesis methods.

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We have reported that treatment of $\text{SmI}_2(\text{THF})_x$ with $[\text{Me}_2\text{A}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}$ (A = C,⁵ Si⁶) leads to the isolation of the trivalent samaracarboranes $[\eta^5:\eta^6\text{-Me}_2\text{A}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$, in which the Sm(II) serves as the reductant and *o*-carborane is the oxidant. $\text{SmI}_2(\text{THF})_x$ can also mediate the reduction and coupling of the carborane in a tandem manner.⁷ Our recent results show that *o*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ can be further reduced by group 1 metals in the presence of UCl_4 and MCl_3 (M = lanthanides, Y) to $[\text{arachno-R}_2\text{C}_2\text{B}_{10}\text{H}_{10}]^{4-}$ tetraanions which are capable of being η^7 -bound to the transition-metal ions: for example, the mixed-sandwich metallocarborane $[\{(\eta^7\text{-C}_2\text{B}_{10}\text{H}_{12})(\eta^6\text{-C}_2\text{B}_{10}\text{H}_{12})\text{U}\}\{\text{K}_2(\text{THF})_5\}]_2^{8}$ and the half-sandwich lanthanacarboranes $[\eta^7\text{-(C}_6\text{H}_5\text{-CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Ln}(\text{THF})_2\{\text{Na}(\text{THF})_3\}_2$ (Ln = Dy, Er, Y).⁹ The 13-vertex *closo*-metallocarboranes of the type $[\eta^6\text{-(C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{MCl}(\text{THF})_x$ are believed to serve as intermediates which accept two more electrons from Na metal to form the final product.⁹ This methodology is, however, not suitable for the preparation of the high-valent group 4 metallocarboranes, since M(IV) can be reduced to M(II) in the presence of group 1 metals or $[\text{nido-R}_2\text{C}_2\text{B}_{10}\text{H}_{10}]^{2-}$ ions.^{4,10} Therefore, a new method is definitely desirable. We report herein a novel synthetic route to the high-valent Zr(IV) carboranyl complexes via intramolecular electron-transfer reactions.

Treatment of $[\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{ZrCl}(\text{NMe}_2)$ with 1 equiv of *n*-BuLi in THF/pyridine gave, after work-up, the unprecedented complex $[\eta^5:\eta^6:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10}\text{CH}_2\text{NMe})]\text{Zr}(\text{NC}_5\text{H}_5)$ (**1**) as yellow crystals in 56% isolated yield.¹¹ Interaction of **1** with excess Na did not afford X-ray-quality crystals, but the reaction did proceed well on the basis of ¹¹B NMR spectroscopic analyses. After many attempts, a Zr(IV) metallocarborane bearing a η^7 -carboranyl ligand, $[\{(\mu\text{-}\eta^5):\eta^7\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})\}\text{Zr}(\text{NEt}_2)_2\{\text{Na}_3(\text{THF})_4\}]_n$ (**2**), was successfully prepared in 33% isolated yield by direct

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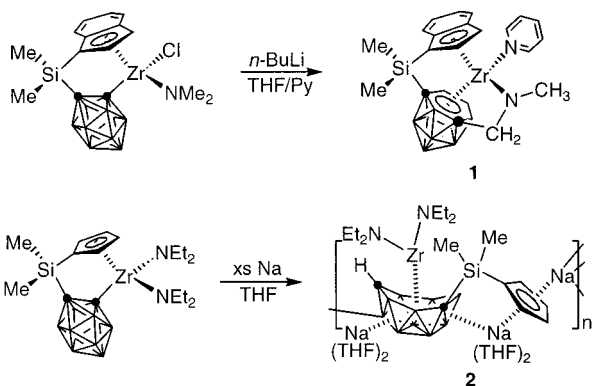
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Scheme 1



reaction of $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NEt}_2)_2$ with excess Na in THF.¹² The synthetic routes are summarized in Scheme 1.

Both **1** and **2** are extremely air- and moisture-sensitive but remain stable for months at room temperature under an inert atmosphere. They are soluble in polar solvents such as THF and pyridine and sparingly soluble in toluene but are insoluble in hexane. They are fully characterized by various spectroscopic data, elemental analyses, and single-crystal X-ray diffraction studies.¹³

The solid-state structures of **1** and **2** are shown in Figures 1 and 2, respectively. In **1**, the Zr atom is η^5 -bound to the C₅ ring of the indenyl group, η^6 -bound to the open hexagonal C₂B₄ bonding face of the *nido*-C₂B₁₀ moiety, and σ -bound to two N atoms from the appended amido group and coordinated pyridine in a distorted-tetrahedral geometry. The average Zr–C(C₅

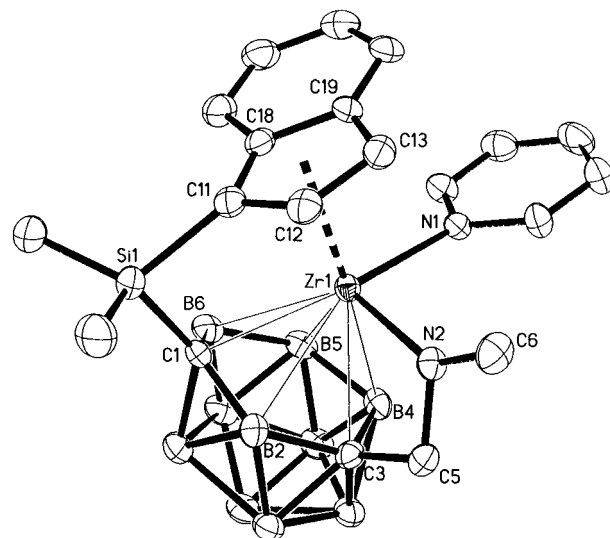


Figure 1. Molecular structure of **1**. Selected distances (Å) and angles (deg): Zr1–C1, 2.491(5) [2.485(5)]; Zr1–C3, 2.567(5) [2.579(6)]; Zr1–B2, 2.620(7) [2.614(7)]; Zr1–B4, 2.535(6) [2.527(7)]; Zr1–B5, 2.753(6) [2.736(7)]; Zr1–B6, 2.789(6) [2.784(6)]; Zr1–N1, 2.354(5) [2.342(5)]; Zr1–N2, 2.054(4) [2.050(5)]; average Zr1–C₅ ring, 2.571(5) [2.583(6)]; N1–Zr1–N2, 95.88(17) [92.95(19)]; ring centroid–Zr1–ring centroid, 133.5 [133.5]. Distances and angles in brackets are those of a second molecule.

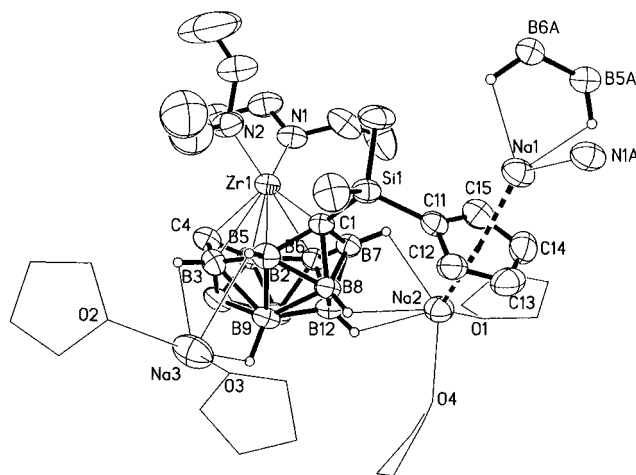


Figure 2. Molecular structure of **2** showing a portion of the infinite polymeric chain. Selected distances (Å): Zr1–C1, 2.271(3); Zr1–C4, 2.266(3); Zr1–B2, 2.568(4); Zr1–B3, 2.565(4); Zr1–B5, 2.660(4); Zr1–B6, 2.693(4); Zr1–B7, 2.634(4); Zr1–N1, 2.116(3); Zr1–N2, 2.099(3); average Na1···B, 2.793(4); average Na2···B, 3.010(4); average Na3···B, 3.019(4); average Na1–C(C₅ ring), 2.705(4); average Na2–C(C₅ ring), 2.775(4).

ring) distance of 2.577(5) Å is close to the corresponding values of 2.541(5) Å in $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$ ¹⁴ and 2.619(2) Å in *rac*- $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)_2]\text{Zr}(\text{NMe}_2)_2$.¹⁵ The Zr–cage atom distances range from 2.485(5) to 2.789(6) Å with an average value of 2.623(5) Å. Such a large variation in bond lengths is perhaps due to the strong interaction between the Zr atom and the appended amido group (MeRN[−]), leading to a

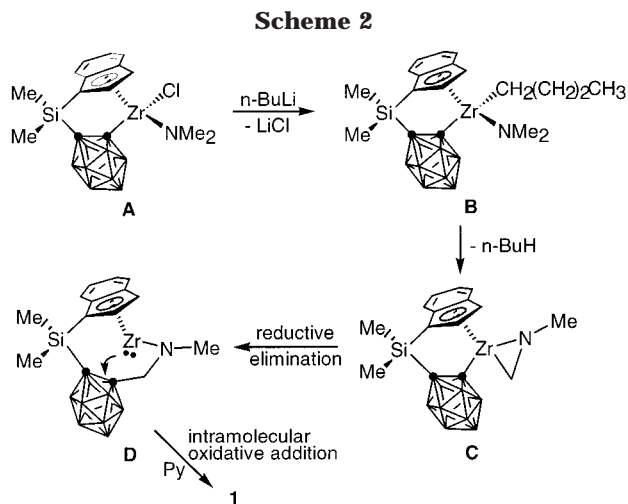
(11) To a THF solution (20 mL) of $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{ZrCl}(\text{NMe}_2)$ ¹⁹ (243 mg, 0.50 mmol) was slowly added a 0.16 M solution of *n*-BuLi in hexane (3.20 mL, 0.51 mmol) at -78°C with stirring. The mixture was warmed to room temperature and stirred at 40°C overnight, resulting in a dark brown solution. Removal of the solvent and recrystallization from THF/*n*-hexane/pyridine at room temperature gave **1** as yellow crystals (148 mg, 56%). ¹H NMR (pyridine-*d*₅, 300 MHz, TMS): δ 8.25 (d, *J* = 6.9 Hz, 1H), 7.41 (t, *J* = 6.9 Hz, 1H), 7.24 (t, *J* = 6.9 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 6.9 Hz, 1H) (C₉H₆), 4.80 (s, 2H) (NCH₂), 4.37 (s, 3H) (NCH₃), 2.28 (s, 3H), 2.10 (s, 3H) ((CH₃)₂Si). ¹³C NMR (pyridine-*d*₅, 75 MHz, TMS): δ 137.86, 134.28, 128.71, 128.09, 127.97, 126.59, 125.06, 122.06, 106.15 (C₉H₆), 93.29, 73.23 (C₂B₁₀H₁₀), 50.11 (NCH₂), 31.00 (NCH₃), 0.69, −2.30 ((CH₃)₂Si). ¹¹B NMR (pyridine-*d*₅, 128 MHz, BF₃·OEt₂): δ 10.6 (1), 7.0 (1), 2.0 (1), 0.4 (2), −3.8 (3), −13.5 (1), −21.1 (1). IR (KBr, cm^{−1}): ν_{BH} 2521 (vs), 2469 (s). Anal. Calcd for C₂₀H₃₂B₁₀N₂SiZr: C, 45.51; H, 6.11; N, 5.31. Found: C, 45.85; H, 6.22; N, 5.15.

(12) To a THF solution (15 mL) of $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NEt}_2)_2$ ¹⁴ (158 mg, 0.32 mmol) was added finely cut Na metal (350 mg, 1.50 mmol), and the mixture was stirred at room temperature for 5 days, leading to a dark brown solution. After removal of excess Na, the resulting clear solution was concentrated to about 5 mL, to which was added 1 mL of toluene. **2** was isolated as yellow crystals after this solution stood at room temperature for several days (90 mg, 33%). ¹H NMR (pyridine-*d*₅, 300 MHz, TMS): δ 6.64 (m, 4H) (C₅H₄), 3.64 (m, 16H) (THF), 3.34 (q, *J* = 6.9 Hz, 8H) (N(CH₂CH₃)₂), 1.60 (m, 16H) (THF), 1.11 (t, *J* = 6.9 Hz, 12H) (N(CH₂CH₃)₂), 0.78 (s, 6H) ((CH₃)₂Si). ¹³C NMR (pyridine-*d*₅, 75 MHz, TMS): δ 128.72, 127.98, 125.07 (C₅H₄), 103.75 (C₂B₁₀H₁₀), 67.15, 25.13 (THF), 31.03, 14.84 (NEt₂), 0.74 ((CH₃)₂Si). ¹¹B NMR (pyridine-*d*₅, 128 MHz, BF₃·OEt₂): δ −2.9 (3), −9.3 (4), −20.4 (2), −37.3 (1). IR (KBr, cm^{−1}): ν_{BH} 2426 (vs), 2314 (m). Anal. Calcd for C₂₁H₄₉B₁₀N₂Na₃OSiZr (**2**–3THF): C, 39.29; H, 7.69; N, 4.36. Found: C, 39.40; H, 7.32; N, 4.31.

(13) Crystal data for **1** (C₂₀H₃₂B₁₀N₂SiZr; fw, 527.89): triclinic, space group *P*1, *a* = 10.241(1) Å, *b* = 16.265(1) Å, *c* = 16.660(1) Å, α = 66.59(1)°, β = 84.54(1)°, γ = 85.24(1)°, *V* = 2532.0(3) Å³, *T* = 293 K, *Z* = 4, *d*_{calcd} = 1.385 g/cm³, *R*₁ = 0.052 (*I* > 2.0 σ (*I*)), *wR*₂(*F*²) = 0.128. Crystal data for **2** (C₃₃H₇₃B₁₀N₂Na₃O₄SiZr; fw, 858.31): monoclinic, space group *P*2₁/*n*, *a* = 14.983(1) Å, *b* = 17.212(1) Å, *c* = 21.420(1) Å, β = 93.21(1)°, *V* = 5514.9(4) Å³, *T* = 293 K, *Z* = 4, *d*_{calcd} = 1.034 g/cm³, *R*₁ = 0.085 (*I* > 2.0 σ (*I*)), *wR*₂(*F*²) = 0.233.

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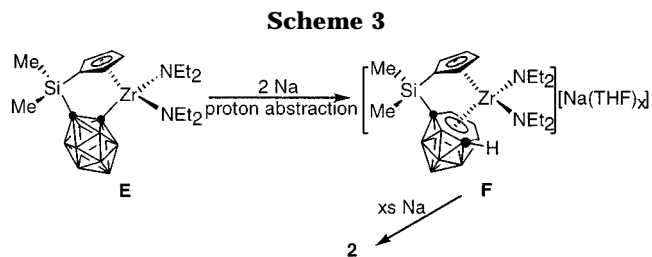


highly asymmetric η^6 bonding. The average Zr–ring centroid (C_2B_4) distance of 2.045 Å is very close to the 2.038 Å in $[(\eta^5-C_5Me_5)(\eta^5-C_2B_9H_{11})]Zr\{C(Me)=CMe_2\}$.^{1a} The average ring centroid (C_5)–Zr–ring centroid (C_2B_4) angle of 133.5° is significantly smaller than the corresponding value of 141.3° in the nonbridged zirconocene $[(\eta^5-C_5Me_5)(\eta^5-C_2B_9H_{11})]Zr\{C(Me)=CMe_2\}$, indicating that the bridging ligand can indeed offer a much more open coordination environment around the metal center.

As shown in Figure 2, the Zr atom is η^7 -bound to the open C_2B_5 bonding face of the *arachno*-carboranyl tetraanion and σ -bound to two N atoms of the Et_2N moieties. The cyclopentadienyl is bound to both Na(1) and Na(2) ions in a η^5 -fashion. The Na(1) ion is then coordinated to two B–H bonds and N(1) from the neighboring molecule resulting in an infinite polymeric chain. The average Zr–N distance of 2.108(3) Å and Zr–cage C distance of 2.269(3) Å compare to the values of 2.031(2) and 2.384(2) Å in its parent complex $[\eta^5-\sigma-Me_2Si(C_5H_4)(C_2B_{10}H_{10})]Zr(NEt_2)_2$,¹⁴ respectively. The average Zr–cage B distance of 2.624(4) Å is identical with that of 2.623(5) Å in **1**.

Complexes **1** and **2** represent the first examples of the high-valent group 4 metallocarboranes bearing an η^6 - or η^7 -carboranyl ligand, respectively.¹⁶ Obviously, the formation of **1** involves sp^3 C–H bond activation and cage reduction. The proposed mechanism is shown in Scheme 2. Reaction of **A** with 1 equiv of *n*-BuLi followed by butane elimination gives the metallacyclic complex **C**.¹⁷ Reductive elimination affords the Zr(II) species **D**.¹⁰

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An intramolecular oxidative-addition/electron-transfer reaction generates the final product **1**.^{10,18} The possible pathway for the formation of **2** is shown in Scheme 3. Reduction of **E** with 2 equiv of Na and proton abstraction from the solvent give the zirconocene(IV) complex ion **F**.¹⁰ Reduction of **F** by excess Na affords the final product **2**, in which Zr(IV) is stabilized by an *arachno*-carboranyl ligand and two amido groups via $N(p\pi)$ –Zr($d\pi$) interactions.⁸ Since *arachno*- $C_2B_{10}H_{12}^{4-}$ is a $10e^-$ π -ligand,⁹ as expected, no bent zirconocene is isolated due to the 18-electron rule.

In summary, high-valent zirconacarboranes bearing a η^6 - or η^7 -carboranyl ligand have been prepared and structurally characterized for the first time. An intramolecular oxidative-addition/electron-transfer reaction offers a novel synthetic route to the high-valent group 4 metallocarboranes that cannot be prepared by the conventional metathesis methods. The bridging ligand $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]^{3-}$ can indeed provide a much more open coordination environment at the Zr center, probably offering a model complex for catalysis study. This work also shows that the *arachno*- $C_2B_{10}H_{12}^{4-}$ tetraanion can effectively stabilize high oxidation states of the group 4 metals.

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Supporting Information Available: Tables giving X-ray diffraction results for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) This compound was prepared by treatment of $[\eta^5-\sigma-Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ with an equimolar amount of Me_3SiCl in toluene.¹⁴