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Functional Sidearm Promoted Electron-Transfer Reactions: A New Route to Metallacarboranes Incorporating the η^7-*arachno*-Carboranyl Ligands

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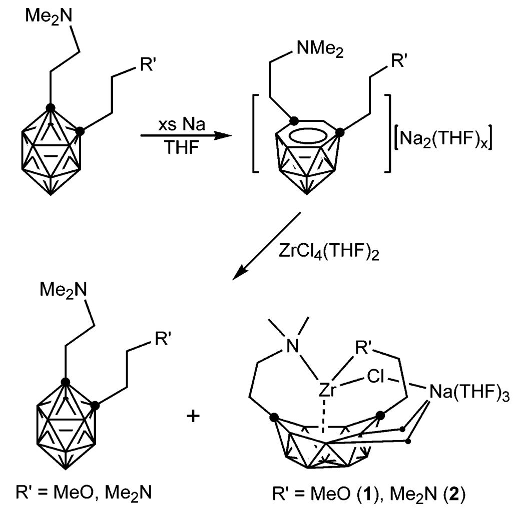
Summary: Reactions of [nido-($Me_2NCH_2CH_2$)$RC_2B_{10}H_{10}$]Na_2 (R = H, $MeOCH_2CH_2$, $Me_2NCH_2CH_2$) with $ZrCl_4(THF)_2$ or $SmI_2(THF)_x$ gave unprecedentedly metallacarboranes with η^7-arachno-carboranyl ligands, in which the heteroatom-containing pendant sidearms are both electronically and entropically necessary for the formation of such complexes with the central metal ions in the highest oxidation state.

ortho-Carboranes (*closo*-$R_2C_2B_{10}H_{10}$) are a class of versatile molecules that can be converted into *nido*-$R_2C_2B_9H_9^{2-}$, *nido*-$R_2C_2B_{10}H_{10}^{2-}$, and *arachno*-$R_2C_2B_{10}H_{10}^{4-}$ anions, respectively, under proper reaction conditions.[1] Among them, *nido*-$R_2C_2B_{10}H_{10}^{2-}$ anions have been proved to be very strong reducing agents, which can reduce M(IV) to M(II) (M = group 4 metals)[2−4] and Ln(III) to Ln(II) (Ln = Sm, Eu, Yb).[5,6] Therefore, conventional salt metathesis between *nido*-$R_2C_2B_{10}H_{10}^{2-}$ and MCl_4 often results in the formation of divalent sandwich group 4 metallacarboranes [(η^6-$R_2C_2B_{10}H_{10})_2M]^{2-}$ (R_2 = H_2, Me_2, $C_6H_4(CH_2)_2$).[2,3] Reaction of [*nido*-$R_2C_2B_{10}H_{10}$]Na_2 with $LnCl_3$ (Ln = Sm, Eu, Yb) leads to the preparation of divalent lanthanacarboranes, for example, europacarborane [(η^6-$C_2B_{10}H_{12})_2Eu]^{2-}$,[5] ytterbacarborane [$\eta^2$-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$Yb(DME)_3$,[6b] [$\eta^6$-{[*o*-$C_6H_4(CH_2)_2$]$C_2B_{10}H_{10}$}$Yb(NC_5H_5)_3${$Na(NC_5H_5)_2$}$_{0.5}$]$_2$($\mu$-Cl),[6c] or mixed-valent samaracarborane cluster {{[η^6-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]Sm}{[$\eta^6$-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]Na}}$_2$Na.[6b] These divalent metallacarboranes are thermodynamically stable, in which no electron transfer from the divalent metal ion to the *nido*-$R_2C_2B_{10}H_{10}^{2-}$ ligands has ever been reported in the literature. During the course of our study on the effects of functional sidearms on the reactivity of metallacarboranes, we have unprecedentedly discovered that reaction of [*nido*-($Me_2NCH_2CH_2$)$RC_2B_{10}H_{10}$]Na_2 with $ZrCl_4(THF)_2$ or $SmI_2(THF)_x$ gave directly metallacarboranes with η^7-*arachno*-carboranyl ligands. This new finding is reported in this communication.

Scheme 1



Treatment of [($Me_2NCH_2CH_2$)($R'CH_2CH_2$)$C_2B_{10}H_{10}$]$Na_2(THF)_x$ with 1 equiv of $ZrCl_4(THF)_2$ in THF gave high-valent zirconacarboranes [η^1:η^1:η^7-($Me_2NCH_2CH_2$)($R'CH_2CH_2$)$C_2B_{10}H_{10}$]Zr(μ-Cl)Na$(THF)_3$ (R′ = MeO (**1**) (45%), Me_2N (**2**) (42%)) and 1-$Me_2NCH_2CH_2$-2-$R'CH_2CH_2$-1,2-$C_2B_{10}H_{10}$ (R′ = MeO (47%), Me_2N (48%)) (Scheme 1).[7] The molar ratio of metallacarborane to *o*-carborane was about 1:1 according to the ^{11}B NMR spectra of the reaction solutions. They were easily separated, as *o*-carboranes were soluble in *n*-hexane whereas **1** and **2** were insoluble. Both **1** and **2** were fully characterized by various spectroscopic techniques and elemental analyses.[7]

The solid-state structures of **1** and **2** were further confirmed by single-crystal X-ray analyses[8] and are

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(4) It was reported that treatment of [$Me_2Si(NR)(C_2B_{10}H_{11})$]$Na_3$ with an equimolar amount of MCl_4 in THF produced [η^1:η^6-$Me_2Si(NR)(C_2B_{10}H_{11})$]$MCl(THF)_n$ (R = 2,6-$^iPr_2C_6H_3$; M = Ti, *n* = 0; M = Zr, *n* = 1). Their structures have not been subjected to X-ray analyses yet. See: Wang, J.; Zhu, Y.; Li, S.; Zheng, C.; Maguire, J. A.; Hosmane, N. S. *J. Organomet, Chem.* 2003, ***680***, 173.

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10.1021/om050454a CCC: $30.25

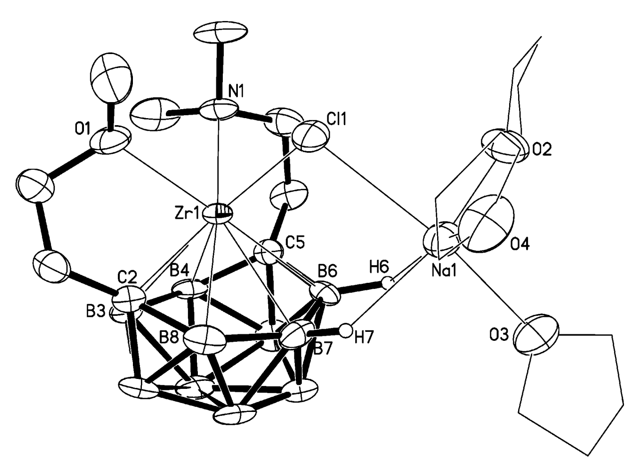

Figure 1. Molecular structure of $[\eta^1{:}\eta^1{:}\eta^7\text{-}(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_{10}H_{10}}]\mathrm{Zr}(\mu\text{-}\mathrm{Cl})\mathrm{Na(THF)_3}$ (**1**). Selected bond distances (Å): Zr(1)−C(2) = 2.226(10), Zr(1)−B(3) = 2.543(10), Zr(1)−B(4) = 2.545(11), Zr(1)−C(5) = 2.238(10), Zr(1)−B(6) = 2.562(14), Zr(1)−B(7) = 2.575(13), Zr(1)−B(8) = 2.570(13), Zr(1)−O(1) = 2.389(7), Zr(1)−N(1) = 2.451(8), Zr(1)−Cl(1) = 2.505(3).

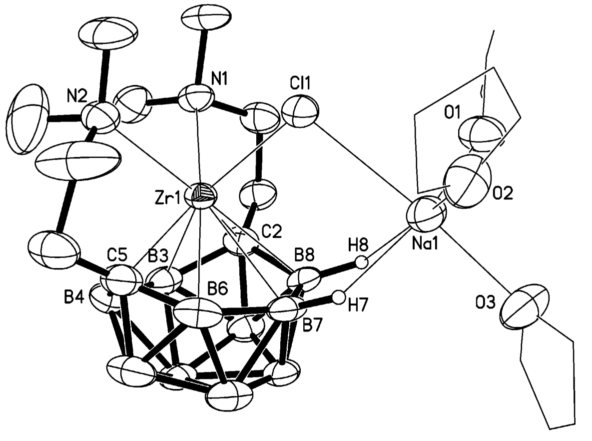

Figure 2. Molecular structure of $[\eta^1{:}\eta^1{:}\eta^7\text{-}(\mathrm{Me_2NCH_2CH_2})_2\mathrm{C_2B_{10}H_{10}}]\mathrm{Zr}(\mu\text{-}\mathrm{Cl})\mathrm{Na(THF)_3}$ (**2**). Selected bond distances (Å): Zr(1)−C(2) = 2.249(7), Zr(1)−B(3) = 2.537(9), Zr(1)−B(4) = 2.522(9), Zr(1)−C(5) = 2.203(8), Zr(1)−B(6) = 2.535(10), Zr(1)−B(7) = 2.527(8), Zr(1)−B(8) = 2.606(9), Zr(1)−N(1) = 2.506(7), Zr(1)−N(2) = 2.547(6), Zr(1)−Cl(1) = 2.483(2).

shown in Figures 1 and 2, respectively. The Zr metal is η^7-bound to an *arachno*-carboranyl ligand, σ-bound to a bridging Cl atom, and coordinated to the functional sidearms via two nitrogen atoms in **2** or one nitrogen and one oxygen atom in **1** in a three-legged piano stool geometry. They are 16-electron complexes.[9] The Zr−C, Zr−B, Zr−N, and Zr−Cl distances in **1** and **2** are very similar, which are close to the corresponding values found in $[\{(\mu\text{-}\eta^5){:}\eta^7\text{-}\mathrm{Me_2Si(C_5H_4)(C_2B_{10}H_{11})}\}\mathrm{Zr(NEt_2)_2}\{\mathrm{Na_3(THF)_4}\}]_n$ prepared from the reaction of $[\eta^5{:}\sigma\text{-}\mathrm{Me_2Si(C_5H_4)(C_2B_{10}H_{10})}]\mathrm{Zr(NEt_2)_2}$ with excess Na in THF.[10]

The most interesting feature in the observation of products **1** and **2** is the mechanism by which they are formed since the only method presently known to prepare *arachno*-carboranyl tetraanions from *closo*-carborane is to use group 1 metals as reducing agents.[9−12] In view of the strong reducing power of *nido*-$\mathrm{R_2C_2B_{10}H_{10}}^{2-}$,[2,3,5,6] the following reaction mechanism is proposed: reaction of $[(\mathrm{Me_2NCH_2CH_2})(\mathrm{R'CH_2CH_2})\mathrm{C_2B_{10}H_{10}}]\mathrm{Na_2(THF)}_x$ with $\mathrm{ZrCl_4(THF)_2}$ gives the divalent zirconacarborane $[\eta^1{:}\eta^1{:}\eta^6\text{-}(\mathrm{Me_2NCH_2CH_2})(\mathrm{R'CH_2CH_2})\mathrm{C_2B_{10}H_{10}}]\mathrm{Zr^{II}}$ (**A**) intermediate and *o*-carborane 1-$\mathrm{Me_2NCH_2CH_2}$-2-$\mathrm{R'CH_2CH_2}$-1,2-$\mathrm{C_2B_{10}H_{10}}$,[2,3] followed by intramolecular electron transfer from the Zr(II) center to the *nido*-carborane in **A**, affording the final

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(7) Preparation of **1**: To a THF (10 mL) solution of 1-$\mathrm{Me_2NCH_2CH_2}$-2-$\mathrm{MeOCH_2CH_2}$-1,2-$\mathrm{C_2B_{10}H_{10}}$[14] (273 mg, 1.00 mmol) was added finely cut Na metal (230 mg, 10.0 mmol), and the mixture was stirred at room temperature for 2 days. After removal of excess Na metal by filtration, the resulting $[(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_{10}H_{10}}]\mathrm{Na_2(THF)}_x$ solution was slowly added to a THF solution of $\mathrm{ZrCl_4(THF)_2}$ (377 mg, 1.00 mmol) at room temperature. The reaction mixture was then stirred at room temperature overnight. The color of the solution changed from pale yellow to brown and finally to orange. The precipitate was filtered off and washed with THF (5 mL × 3). Removal of the solvent gave an orange solid, which was washed with *n*-hexane (5 mL × 4). Concentration of the *n*-hexane solution afforded 1-$\mathrm{Me_2NCH_2CH_2}$-2-$\mathrm{MeOCH_2CH_2}$-1,2-$\mathrm{C_2B_{10}H_{10}}$ (129 mg, 0.47 mmol, 47%). The residue was recrystallized from THF/toluene to give **1** as orange crystals (285 mg, 0.45 mmol, 45%). ^{1}H NMR (pyridine-d_5): δ 4.40 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2OCH_3}$), 4.05 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{OCH_3}$), 3.85 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2N(CH_3)_2}$), 3.64 (m, 12H, THF), 3.30 (s, 3H, $\mathrm{CH_2CH_2OC}H_3$), 3.19 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{N(CH_3)_2}$), 2.20 (s, 6H, $\mathrm{CH_2CH_2N(C}H_3)_2$), 1.58 (m, 12H, THF). ^{13}C NMR (pyridine-d_5): δ 76.8, 76.6 (cage *C*), 67.1 (THF), 65.1 ($C\mathrm{H_2CH_2OCH_3}$), 64.5 ($\mathrm{CH_2}C\mathrm{H_2O}C\mathrm{H_3}$), 58.6 ($C\mathrm{H_2CH_2N(CH_3)_2}$), 45.9 ($\mathrm{CH_2}C\mathrm{H_2N(CH_3)_2}$), 43.2 ($\mathrm{CH_2CH_2N(}C\mathrm{H_3)_2}$), 24.6 (THF). ^{11}B NMR (pyridine-d_5): δ 4.0 (2B), −0.4 (1B), −5.1 (4B), −13.7 (2B), −29.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2509 (vs), 2451 (vs). Anal. Calcd for $\mathrm{C_{17}H_{43}B_{10}ClNNaO_3Zr}$ (**1** − THF): C, 35.96; H, 7.64; N, 2.47. Found: C, 35.69; H, 7.63; N, 2.22. **2**: This complex was prepared from 1,2-$(\mathrm{Me_2NCH_2CH_2})_2$-1,2-$\mathrm{C_2B_{10}H_{10}}$[14] (286 mg, 1.00 mmol), Na metal (230 mg, 10.0 mmol). and $\mathrm{ZrCl_4(THF)_2}$ (377 mg, 1.00 mmol) in THF using the same procedure reported for **1**: yield **2** (273 mg, 0.42 mmol, 42%) and 1,2-$(\mathrm{Me_2NCH_2CH_2})_2$-1,2-$\mathrm{C_2B_{10}H_{10}}$ (138 mg, 0.48 mmol, 48%). For **2**: ^{1}H NMR (pyridine-d_5): δ 3.77 (m, 4H, $\mathrm{C}H_2\mathrm{CH_2N(CH_3)_2}$), 3.63 (m, 12H, THF), 3.05 (m, 4H, $\mathrm{CH_2C}H_2\mathrm{N(CH_3)_2}$), 2.32 (s, 12H, $\mathrm{CH_2CH_2N(C}H_3)_2$), 1.58 (m, 12H, THF). ^{13}C NMR (pyridine-d_5): δ 76.0, 74.0 (cage *C*), 67.1 (THF), 60.1 ($C\mathrm{H_2CH_2N(CH_3)_2}$), 44.8 ($\mathrm{CH_2}C\mathrm{H_2N(CH_3)_2}$), 43.1 ($\mathrm{CH_2CH_2N(}C\mathrm{H_3)_2}$), 25.1 (THF). ^{11}B NMR (pyridine-d_5): δ 3.6 (2B), −0.7 (1B), −5.4 (4B), −14.0 (2B), −30.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2499 (vs), 2450 (vs). Anal. Calcd for $\mathrm{C_{20}H_{50}B_{10}ClN_2NaO_{2.5}Zr}$ (**2** − 0.5THF): C, 38.93; H, 8.18; N, 4.54. Found: C, 38.85; H, 8.26; N, 4.31. **3**: To a THF (10 mL) solution of 1-$\mathrm{Me_2NCH_2CH_2}$-1,2-$\mathrm{C_2B_{10}H_{11}}$[14] (215 mg, 1.00 mmol) was added finely cut Na metal (230 mg, 10.0 mmol), and the mixture was stirred at room temperature for 2 days. After removal of excess Na metal by filtration, the resulting $[(\mathrm{Me_2NCH_2CH_2})\mathrm{C_2B_{10}H_{11}}]\mathrm{Na_2(THF)}_x$ solution was slowly added to a THF solution of $\mathrm{SmI_2(THF)}_x$ (38.0 mL of 0.053 M, 2.01 mmol) at room temperature. The reaction mixture was then stirred at room temperature overnight. The color of the solution changed from dark green to dark brown. The precipitate was filtered off and washed with THF (5 mL × 3). The resulting solutions were combined and concentrated to about 10 mL, to which was added toluene (7 mL). Complex **3** was isolated as dark brown crystals after this solution stood at room temperature for 4 days (107 mg, 20%). ^{1}H NMR (pyridine-d_5): δ 3.66, 1.60 (br s, THF), and other broad, unresolved peaks. ^{11}B NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν_{BH} 2497 (vs), 2355(s). Anal. Calcd for $\mathrm{C_{36}H_{108}B_{40}N_4NaO_3Sm_5}$ (**3** − 5THF): C, 23.13; H, 5.83; N, 3.00. Found: C, 23.13; H, 6.06; N, 3.27.

(8) Crystal data for **1** ($\mathrm{C_{21}H_{51}B_{10}ClNNaO_4Zr}$; fw, 639.4): orthorhombic, space group $P2_12_12_1$, a = 9.890(1) Å, b = 15.119(1) Å, c = 22.728(2) Å, V = 3398.4(5) Å^3, T = 293 K, Z = 4, d_{calcd} = 1.250 g/cm^3, R1 = 0.060 ($I > 2\sigma(I)$), wR2(F^2) = 0.142. For **2** ($\mathrm{C_{22}H_{54}B_{10}ClN_2NaO_3Zr}$; fw, 652.4): monoclinic, space group $P2_1/n$, a = 9.939(2) Å, b = 22.339(5) Å, c = 15.553(3) Å, β = 90.00(3)°, V = 3453.3(12) Å^3, T = 293 K, Z = 4, d_{calcd} = 1.255 g/cm^3, R1 = 0.082 ($I > 2\sigma(I)$), wR2(F^2) = 0.223. For **3** ($\mathrm{C_{56}H_{148}B_{40}N_4NaO_8Sm_5}$; fw, 2212.9): tetragonal, space group $I4_1/a$, a = b = 29.949(1) Å, c = 13.724(1) Å, V = 12309.6(11) Å^3, T = 293 K, Z = 4, d_{calcd} = 1.194 g/cm^3, R1 = 0.109 ($I > 2\sigma(I)$), wR2(F^2) = 0.264.

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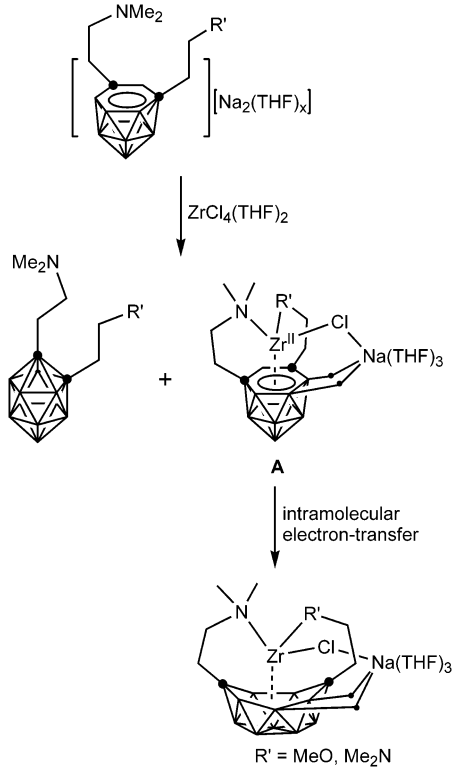
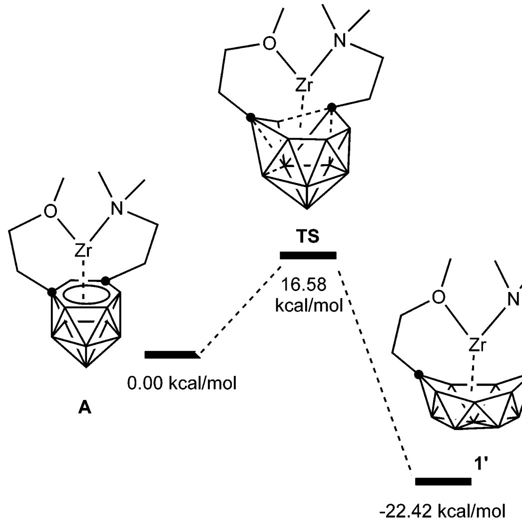
Scheme 2



Scheme 3

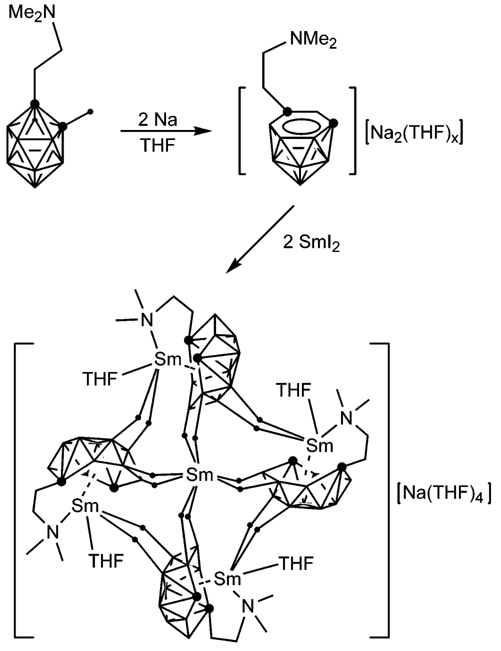


product **1** or **2**, shown in Scheme 2. This proposal is supported by theoretical studies with the aid of B3LYP density functional theory calculations.[13]

Scheme 3 shows the potential energy profile calculated for the conversion of complex **A** to **1′**, a model complex of **1**. The activation energy is calculated to be only 16.58 kcal/mol, indicating that this process can occur readily. Such a conversion involves intramolecular electron transfer in which the Zr(II) center in **A** formally loses two d electrons to the *nido*-carborane ligand, leading to the formation of the *arachno*-carborane ligand in **1**.

The calculated reaction energy indicates that the intramolecular electron-transfer process is thermodynamically very favorable. The large exothermicity calculated for **A** → **1′** suggests that there is a strong thermodynamic driving force for the formation of **1′**. It is expected that the two pendant sidearms, which are classified as hard ligands in inorganic chemistry, contribute significantly to the driving force because these two hard ligands tend to stabilize a Zr(IV) metal center instead of a Zr(II). The d^0 Zr(IV) center fulfills the bonding requirement with an η^7-*arachno*-carboranyl ligand.[9] The argument here explains why the heteroatoms in the pendant groups are required for the formation of **1**, as Zr(II) is found to be stable in anionic metallacarboranes $[(\eta^6\text{-}R_2C_2B_{10}H_{10})_2Zr]^{2-}$ in which the two R groups do not have heteroatoms.[2,3]

Scheme 4



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The two pendant groups not only provide the hard ligands to facilitate the formation of **1** but also are entropically important. If the hard ligands were not associated with the two pendant groups, we expect that the formation of **A** is entropically very unfavorable because the reaction of $[R_2C_2B_{10}H_{10}]Na_2$ with $ZrCl_4(THF)_2$ might give stable $[(nido\text{-}R_2C_2B_{10}H_{10})_2Zr]^{2-}$ as reported in the literature.[2,3]

This mechanism is further supported by the following experiment. Reaction of $[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Na_2$ with 2 equiv of SmI_2 in THF afforded $[\{\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Sm(THF)\}_4Sm][Na(THF)_4]$ (**3**) as dark brown crystals in 20% yield (Scheme 4).[7] Unlike previous reactions, no *closo*-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$ was isolated. Complex **3** is a paramagnetic species, which does not offer useful NMR information. Its structure was established by single-crystal X-ray diffraction studies.[8]

Figure 3 shows the molecular structure of a novel pentanuclear cluster anion, in which the central Sm atom is bonded to four identical $[\{\eta^1{:}\eta^7\text{-}(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Sm(THF)]^-$ units through Sm−H−B interactions. It is very clear that the *nido*-carborane receives two electrons from the Sm(II) ions to form *arachno*-carborane, and at the same time the Sm(II) is oxidized to the Sm(III) during the reaction. Since *nido*-carborane acts only as an oxidizing agent in this reaction, no *closo*-

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[13] See Supporting Information for details.

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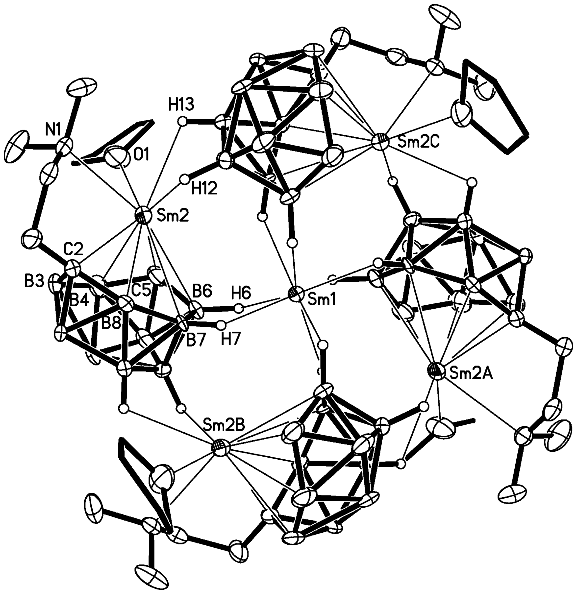

Figure 3. Molecular structure of the anion $[\{\eta^1{:}\eta^7\text{-}(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Sm(THF)]_4Sm^-$ in **3**. Selected bond distances (Å): Sm(2)−C(2) = 2.48(3), Sm(2)−B(3) = 2.76(9), Sm(2)−B(4) = 2.72(4), Sm(2)−C(5) = 2.43(3), Sm(2)−B(6) = 2.88(3), Sm(2)−B(7) = 2.91(3), Sm(2)−B(8) = 2.80(3), Sm(2)−N(1) = 2.74(2), Sm(2)−O(1) = 2.56(2), Sm(1)−B(6) = 2.90(3), Sm(1)−B(7) = 2.89(2), Sm(1)−H(6) = 2.23(2), Sm(1)−H(7) = 2.17(2).

carborane is generated, which is consistent with the experimental results. We, therefore, suggest that complex $[\eta^1{:}\eta^6\text{-}(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Sm^{II}(THF)_x$ may serve as an intermediate in the reaction. It is noteworthy that in the absence of a $Me_2NCH_2CH_2$ group, the divalent samaracarboranes of $(\eta^6\text{-}C_2B_{10}H_{12})Sm(THF)_4$[5b] and $\{[\eta^5{:}\eta^6\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]Sm(THF)_2\}\{K(THF)_2\}$[6a] are thermodynamically stable. These results further illustrate the importance of the functional sidearms in these redox reactions.

In summary, a new synthetic route to high-valent metallacarboranes bearing an *arachno*-carboranyl ligand is described. The heteroatom-containing pendant sidearms on the carborane cage are both electronically and entropically necessary for the formation of such complexes. Thus, controlled syntheses of divalent metallacarboranes of the type $[(nido\text{-}R_2C_2B_{10}H_{10})_2M]^{2-}$ (M = group 4 metals) or $(nido\text{-}R_2C_2B_{10}H_{10})Ln$ (Ln = Sm, Eu, Yb) or high-valent metallacarboranes of the type $(arachno\text{-}R_2C_2B_{10}H_{10})M$ or $[(arachno\text{-}R_2C_2B_{10}H_{10})Ln]^-$ can be achieved by changing the nature of the substituents R.

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Supporting Information Available: Tables of crystallographic data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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