Synthesis, Structural Characterization, and Reactivity of Rare Earth Complexes Incorporating Lewis Base Appended *nido*-Carborane Anions of the C_2B_9 and C_2B_{10} Systems

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Reaction of 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1**) with excess Na metal in THF, followed by treatment with 1 equiv of YCl_3, afforded [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_{10}H_{11}$]YCl$(THF)_3$ (**2**), which contains a terminal Y−Cl bond. Recrystallization of **2** from MeCN/toluene gave [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_{10}H_{11}$]YCl$(MeCN)_3$·MeCN (**3·MeCN**). Treatment of **2** with 1 equiv of Cp″Li in THF gave [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_{10}H_{11}$]YCp″(μ-Cl)Li$(THF)_2$ (**4**). Interaction of **2** with $AgBPh_4$ or potassium phthalimide gave neutral carborane **1** and other unidentified species. Amine elimination reaction is an effective method for the production of half-sandwich lanthanacarborans. Treatment of 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (**5**) with Ln[N$(SiHMe_2)_2$]$_3$-$(THF)_2$ or ClY[N$(SiHMe_2)_2$]$_2$$(THF)_x$ afforded [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Ln[N$(SiHMe_2)_2$]-$(THF)_2$ (Ln = Sm (**6**), Er (**7**)) or [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]YCl$(THF)_2$ (**8**), respectively. Complex **8** was also prepared from an equimolar reaction of K_2[$Me_2NCH_2CH_2C_2B_9H_{10}$] with YCl_3 in THF. [η^1:η^1:η^5-($Me_2NCH_2CH_2$)($MeOCH_2CH_2$)$C_2B_9H_9$]Y(μ-Cl)$_2$K$(THF)_2$ (**10**) was prepared in a similar manner from the reaction of K_2[($Me_2NCH_2CH_2$)($MeOCH_2CH_2$)$C_2B_9H_9$] with YCl_3. Complex **10** underwent partial hydrolysis to produce [$YCl_2(THF)_5$][*nido*-($Me_2NCH_2CH_2$)($MeOCH_2CH_2$)$C_2B_9H_{10}$]·THF (**11·THF**). On the other hand, treatment of K_2[($Me_2NCH_2CH_2$)($MeOCH_2CH_2$)$C_2B_9H_9$] with 1 equiv of Cp″$_2$LnI in THF afforded mixed-sandwich lanthanacarboranes [η^1:η^1:η^5-($Me_2NCH_2CH_2$)($MeOCH_2CH_2$)$C_2B_9H_9$]LnCp″ (Ln = Y (**12**), Er (**13**)). Complex **12** was also prepared from an equimolar reaction of **10** with Cp″Li in THF. All complexes were fully characterized by various spectroscopic techniques and elemental analyses. Complexes **3**, **4**, **6**−**8**, and **11**−**13** were further confirmed by single-crystal X-ray analyses.

Introduction

Although the chemistry of organolanthanide chloride complexes of the type Cp_2LnCl (Cp = C_5H_5 or its derivatives) has been extensively investigated,[1] the parallel studies on its isolobal carboranyl ligand systems are very limited.[2] Only few examples of half-sandwich lanthanacarboranes containing the C_2B_{10},[3] C_2B_9,[4] and C_2B_4[5] ligand systems are known, and their alkyl derivatives remain elusive probably due to the decomposition of unstable (CB)LnR (CB = carboranyl, R = alkyl) complexes. One of the commonly used methods to stabilize Cp-based organolanthanide complexes is to incorporate the functional sidearms into the cyclic π ligands since the tethered donors can coordinate to the lanthanide ions to fulfill the electronic and steric requirements.[1,6,7] Our recent work shows that the Lewis base functionalized sidearms on the five-membered ring of the indenyl unit in linked carboranyl-indenyl hybrid ligands have significant effects on the stability of organolanthanide complexes.[8] In view of the role of functional sidearms in stabilizing organolanthanide chloride complexes, we have introduced Lewis base appended carboranyl ligands into rare earths in the hope that these ligands can prevent half-sandwich lanthanacarboranes from ligand redistribution reactions. In this article, we report the synthesis, structural

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characterization, and reactivity of half-sandwich lanthanacarboranes involving *nido*-$Me_2NCH_2CH_2C_2B_{10}H_{11}^{2-}$, *nido*-$Me_2NCH_2CH_2C_2B_9H_{10}^{2-}$, and *nido*-$(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9^{2-}$ ligands.

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 (except MeCN) were freshly distilled from sodium benzophenone ketyl immediately prior to use. MeCN was freshly distilled from CaH_2 immediately prior to use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Compounds 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1**),[9] 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (**5**),[9] 7-$Me_2NHCH_2CH_2$-8-$MeOCH_2CH_2$-7,8-$C_2B_9H_{10}$ (**9**),[9] Cp″Li[10] (Cp″ = $(Me_3Si)_2C_5H_3$), $Ln[N(SiHMe_2)]_3(THF)_2$,[11] $Li[N(SiHMe_2)_2]$,[12] $YCl_3(THF)_{3.5}$,[13] and $Cp''_2LnI(THF)$[14] were prepared according to literature methods. 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 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts are reported in δ units with references 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., Middlesex, U.K.

Preparation of [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]YCl(THF)$_3$ (2). To a THF (25 mL) solution of 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1**; 215 mg, 1.0 mmol) was added finely cut Na metal (230 mg, 10.0 mmol), and the mixture was stirred at room temperature for 3 days. After removal of excess Na and addition of YCl_3 (195 mg, 1.0 mmol), the reaction mixture was stirred at room temperature for 1 day. The precipitate was filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated to about 10 mL, to which was added toluene (about 8 mL). Complex **2** was isolated as colorless crystals after this solution stood at room temperature for 4 days (373 mg, 67%). ^1H NMR (pyridine-d_5): δ 3.64 (m, 12H, THF), 3.06 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.60 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.27 (s, 6H, $CH_2CH_2N(CH_3)_2$), 1.62 (m, 12H, THF). ^{13}C NMR (pyridine-d_5): δ 87.6 (cage *C*), 67.2 (THF), 62.4 ($CH_2CH_2N(CH_3)_2$), 48.6 ($CH_2CH_2N(CH_3)_2$), 45.3 ($CH_2CH_2N(CH_3)_2$), 25.1 (THF). ^{11}B NMR (pyridine-d_5): δ 16.2 (1B), 10.6 (1B), 0.3 (1B), −7.7 (2B), −12.4 (2B), −20.4 (2B), −29.5 (1B). IR (KBr, cm^{-1}): ν 2524 (vs) (BH). Anal. Calcd for $C_{14}H_{37}B_{10}ClNO_2Y$ (**2**−THF): C, 34.75; H, 7.71; N, 2.89. Found: C, 34.47; H, 7.95; N, 2.80.

Preparation of [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]YCl(MeCN)$_3$·MeCN (3·MeCN). Recrystallization of [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]YCl(THF)$_3$ (**2**; 556 mg, 1.0 mmol) from MeCN/toluene (3:1, 20 mL) at room temperature gave **3** as colorless crystals (398 mg, 79%). ^1H NMR (pyridine-d_5): δ 2.61 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.24 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.10 (s, 6H, $CH_2CH_2N(CH_3)_2$), 1.86 (s, 12H, CH_3CN). ^{13}C NMR (pyridine-d_5): δ 116.9 (CH_3CN), 77.6 (cage *C*), 60.7 ($CH_2CH_2N(CH_3)_2$), 47.0 ($CH_2CH_2N(CH_3)_2$), 45.0 ($CH_2CH_2N(CH_3)_2$), 0.3 (CH_3CN). ^{11}B NMR (pyridine-d_5): δ 15.9 (1B), 10.2 (1B), 1.0 (1B), −8.2 (2B), −12.9 (2B), −19.8 (2B), −30.1 (1B). IR (KBr, cm^{-1}): ν 2524 (vs) (BH), 2278 (m) (CN). Anal. Calcd for $C_{11}H_{28.5}B_{10}ClN_{3.5}Y$ (**3**−0.5MeCN): C, 29.84; H, 6.44; N, 11.08. Found: C, 29.60; H, 6.77; N, 11.13.

Preparation of [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]YCp″($\mu$-Cl)Li(THF)$_2$ (4). To a THF (25 mL) solution of [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]YCl(THF)$_3$ (**2**; 556 mg, 1.0 mmol) was slowly added a THF (10 mL) solution of Cp″Li (216 mg, 1.0 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 2 days. The precipitate was filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated to give a white solid. Recrystallization from toluene (10 mL) gave **4** as colorless crystals (441 mg, 63%). ^1H NMR (benzene-d_6): δ 7.03 (m, 1H, Cp″), 6.84 (m, 1H, Cp″), 6.14 (m, 1H, Cp″), 3.54 (m, 8H, THF), 2.84 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.42 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.30 (s, 6H, $CH_2CH_2N(CH_3)_2$), 1.39 (m, 8H, THF), 0.46 (s, 9H, $Si(CH_3)_3$), 0.32 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (benzene-d_6): δ 133.4, 126.0, 124.4 (Cp″), 68.2 (THF), 64.5 ($CH_2CH_2N(CH_3)_2$), 42.2 ($CH_2CH_2N(CH_3)_2$), 31.9 ($CH_2CH_2N(CH_3)_2$), 25.5 (THF), 1.1 ($Si(CH_3)_3$), 0.9 ($Si(CH_3)_3$), the cage carbon atoms were not observed. ^{11}B NMR (benzene-d_6): δ 14.5 (1B), −1.5 (1B), −0.8 (2B), −5.6 (3B), −10.3 (2B), −23.7 (1B). IR (KBr, cm^{-1}): ν 2527 (vs), 2486 (vs) (BH). Anal. Calcd for $C_{23}H_{54}B_{10}ClLiNO_{1.5}Si_2Y$ (**4**−0.5THF): C, 41.59; H, 8.19; N, 2.11. Found: C, 42.04; H, 8.10; N, 2.40.

Reaction of 2 with $AgBPh_4$. To a THF (25 mL) solution of [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]YCl(THF)$_3$ (**2**; 556 mg, 1.0 mmol) was added a THF solution of $AgBPh_4$ (427 mg, 1.0 mmol) at room temperature, and the reaction mixture was stirred overnight. After removal of the black precipitate (Ag), the clear solution was concentrated to dryness, to which was added *n*-hexane (10 mL). The mixture was stirred for 0.5 h. The white solid was collected by filtration and recrystallized from THF/*n*-hexane (2:1, 20 mL) to give a white solid (160 mg). ^{11}B NMR (THF): δ −6.9. The *n*-hexane solution was concentrated to give a white solid (100 mg, 46%), which was identified as **1** by the ^1H and ^{11}B NMR spectra.

Reaction of 2 with Potassium Phthalimide. To a THF (25 mL) solution of [η^1:η^6-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]YCl(THF)$_3$ (**2**; 556 mg, 1.0 mmol) was added a THF solution of potassium phthalimide (185 mg, 1.0 mmol) at room temperature, and the reaction mixture was stirred overnight. After removal of the solvent, the solid was extracted with *n*-hexane (10 mL × 2). The residue was dried under vacuum (388 mg) and did not contain any boron atoms as indicated by the ^{11}B NMR spectrum. The *n*-hexane solution was concentrated to give a white solid (155 mg, 72%), which was identified as **1** by the ^1H and ^{11}B NMR spectra.

Preparation of [η^1:η^5-$(Me_2NCH_2CH_2)C_2B_9H_{10}$]Sm[N(SiHMe$_2$)$_2$](THF)$_2$ (6). To a toluene (10 mL) solution of 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (**5**; 206 mg, 1.0 mmol) was slowly added a toluene (10 mL) solution of $Sm[N(SiHMe_2)_2]_3(THF)_2$ (691 mg, 1.0 mmol) with stirring at room temperature. The resulting solution was refluxed overnight to give a pale yellow solution with a yellow precipitate. The precipitate was collected by filtration and washed with toluene (5 mL × 2) to give a yellow solid. Recrystallization from THF (10 mL) gave **6** as yellow crystals (391 mg, 62%). ^1H NMR (pyridine-d_5): δ 3.63 (br s, THF), 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 2526 (vs) (BH), 2034 (s) (SiH). Anal. Calcd for $C_{18}H_{50}B_9N_2O_2Si_2Sm$: C, 34.29; H, 7.99; N, 4.44. Found: C, 34.32; H, 7.60; N, 3.99.

Preparation of [η^1:η^5-$(Me_2NCH_2CH_2)C_2B_9H_{10}$]Er[N(SiHMe$_2$)$_2$](THF)$_2$ (7). This complex was prepared as pink crystals from 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (**5**; 206 mg, 1.0 mmol) and $Er[N(SiHMe_2)_2]_3(THF)_2$ (710 mg, 1.0 mmol) in toluene using the same procedures as those used in the

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synthesis of **6**: yield 304 mg (47%). ^{1}H NMR (pyridine-d_5): δ 3.53 (br s, THF), 1.44 (br s, THF), and other broad, unresolved peaks. ^{11}B NMR spectra (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2539 (vs) (BH), 2058 (s) (SiH). Anal. Calcd for $\mathrm{C_{16}H_{46}B_9ErN_2O_{1.5}Si_2}$ (**7**−0.5THF): C, 31.41; H, 7.52; N, 4.58. Found: C, 31.17; H, 7.86; N, 4.82.

Preparation of $[\eta^1{:}\eta^5\text{-}(\mathrm{Me_2NCH_2CH_2})\mathrm{C_2B_9H_{10}}]\mathrm{YCl(THF)_2}$ (8). To a suspension of $\mathrm{YCl_3(THF)_{3.5}}$ (448 mg, 1.0 mmol) in *n*-hexane (10 mL) was slowly added $\mathrm{LiN(SiHMe_2)_2}$ (278 mg, 2.0 mmol) with stirring at room temperature, and the mixture was stirred at room temperature for 12 h. After removal of the precipitate, the hexane solution was concentrated to give a white solid, presumably $\mathrm{ClY[N(SiHMe_2)_2]_2(THF)}_x$. This white solid was dissolved in 10 mL of toluene and then slowly added to a toluene (10 mL) solution of 7-$\mathrm{Me_2NHCH_2CH_2}$-7,8-$\mathrm{C_2B_9H_{11}}$ (**5**; 206 mg, 1.0 mmol). The mixture was refluxed overnight. The precipitate was collected by filtration and washed with toluene (5 mL × 2) to give a white solid (245 mg, 52%). Recrystallization from THF/toluene (2:1, 20 mL) gave **8** as colorless crystals. ^{1}H NMR (pyridine-d_5): δ 3.61 (m, 8H, THF), 2.39 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 2.20 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.12 (s, 6H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 1.58 (m, 8H, THF). ^{13}C NMR (pyridine-d_5): δ 66.9 (THF), 64.9 (cage *C*), 61.0 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 46.8 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 35.6 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 24.9 (THF). ^{11}B NMR (pyridine-d_5): δ −2.2 (1B), −4.5 (1B), −8.7 (1B), −10.0 (1B), −13.0 (1B), −17.2 (1B), −28.0 (1B), −32.7 (1B), −36.3 (1B). IR (KBr, cm^{-1}): ν 2529 (vs) (BH). Anal. Calcd for $\mathrm{C_{14}H_{36}B_9ClNO_2Y}$: C, 35.62; H, 7.69; N, 2.97. Found: C, 35.73; H, 7.50; N, 2.79.

Alternative Preparation of 8. To a suspension of KH (88 mg, 2.2 mmol) in THF (10 mL) was added a THF solution (10 mL) of 7-$\mathrm{Me_2NHCH_2CH_2}$-7,8-$\mathrm{C_2B_9H_{11}}$ (**5**; 206 mg, 1.0 mmol), and the mixture was stirred overnight at room temperature. The resulting solution (presumably $\mathrm{K_2[Me_2NCH_2CH_2C_2B_9H_{10}]}$) was then added dropwise at room temperature through a cannula to a suspension of $\mathrm{YCl_3}$ (195 mg, 1.0 mmol) in THF (15 mL). The reaction mixture was stirred at room temperature for 2 days and then allowed to settle. The precipitate was filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated under vacuum to about 10 mL. Complex **8** was isolated as colorless crystals after this solution stood at room temperature for two weeks (175 mg, 37%).

Preparation of $[\eta^1{:}\eta^1{:}\eta^5\text{-}(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_9H_9}]\mathrm{Y}(\mu\text{-}\mathrm{Cl})_2\mathrm{K(THF)_2}$ (10). To a suspension of KH (88 mg, 2.2 mmol) in THF (15 mL) was added a THF solution (10 mL) of 7-$\mathrm{Me_2NHCH_2CH_2}$-8-$\mathrm{MeOCH_2CH_2}$-7,8-$\mathrm{C_2B_9H_{10}}$ (**9**; 264 mg, 1.0 mmol), and the mixture was stirred overnight at room temperature. The resulting solution ($\mathrm{K_2[(MeOCH_2CH_2)(Me_2NCH_2CH_2)C_2B_9H_9]}$) was then added dropwise at room temperature through a cannula to a suspension of $\mathrm{YCl_3}$ (195 mg, 1.0 mmol) in THF (15 mL). The reaction mixture was stirred at room temperature for 2 days and then allowed to settle. The precipitate was filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated under vacuum to about 10 mL. Complex **10** was isolated as colorless crystals after this solution stood at room temperature for two weeks (254 mg, 42%). ^{1}H NMR (pyridine-d_5): δ 3.90 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{OCH_3}$), 3.62 (m, 8H, THF), 3.34 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 3.25 (s, 3H, $\mathrm{CH_2CH_2OC}\mathit{H}_3$), 2.90 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OCH_3}$), 2.78 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.16 (s, 6H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 1.58 (m, 8H, THF). ^{13}C NMR (pyridine-d_5): δ 79.3, 73.8 (cage *C*), 67.1 (THF), 65.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2OCH_3}$), 62.5 ($\mathrm{CH_2CH_2O}\mathit{C}\mathrm{H_3}$), 60.9 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 46.9 ($\mathit{C}\mathrm{H_2CH_2OCH_3}$), 45.1 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 31.1 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 25.1 (THF). ^{11}B NMR (pyridine-d_5): δ −2.7 (1B), −9.3 (4B), −16.8 (1B), −27.4 (1B), −32.9 (1B), −35.9 (1B). IR (KBr, cm^{-1}): ν 2525 (vs) (BH). Anal. Calcd for $\mathrm{C_{17}H_{42}B_9Cl_2KNO_3Y}$: C, 33.77; H, 7.00; N, 2.32. Found: C, 34.06; H, 6.78; N, 2.74.

Preparation of $[\mathrm{YCl_2(THF)_5}][$*nido*-$(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_9H_{10}}]\cdot\mathrm{THF}$ (11·THF). This complex was initially isolated as colorless crystals after many times of recrystallization of **10** from a THF/toluene solution. It was then prepared by a controlled hydrolysis. A stock solution of toluene containing 0.5% water was prepared by adding 2.5 mL of water into 500 mL of dry toluene. Complex **10** (605 mg, 1.0 mmol) was dissolved in a mixed solvent of THF (10 mL) and toluene (4 mL) of the stock solution under stirring to give a clear colorless solution. Slow evaporation of the solvents over days afforded **11** as colorless crystals, which were suitable for X-ray analyses (376 mg, 48%). ^{1}H NMR (pyridine-d_5): δ 3.89 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{OCH_3}$), 3.62 (m, 24H, THF), 3.25 (s, 3H, $\mathrm{CH_2CH_2OC}\mathit{H}_3$), 2.96 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 2.65 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OCH_3}$), 2.48 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.23 (s, 6H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 1.58 (m, 24H, THF). ^{13}C NMR (pyridine-d_5): δ 73.8, 73.4 (cage *C*), 67.2 (THF), 65.1 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2OCH_3}$), 60.7 ($\mathrm{CH_2CH_2O}\mathit{C}\mathrm{H_3}$), 57.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 45.2 ($\mathit{C}\mathrm{H_2CH_2OCH_3}$), 44.9 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 34.4 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 25.1 (THF). ^{11}B NMR (pyridine-d_5): δ −9.3 (2B), −11.0 (1), −13.9 (1B), −16.7 (3B), −32.7 (1B), −35.7 (1B). IR (KBr, cm^{-1}): ν 2520 (vs) (BH). Anal. Calcd for $\mathrm{C_{23}H_{55}B_9Cl_2NO_{4.5}Y}$ (**11**−1.5THF): C, 40.94; H, 8.22; N, 2.08. Found: C, 40.83; H, 7.94; N, 2.08.

Preparation of $[\eta^1{:}\eta^1{:}\eta^5\text{-}(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_9H_9}]\mathrm{YCp''}$ (12). To a suspension of KH (88 mg, 2.2 mmol) in THF (15 mL) was added a THF solution (10 mL) of 7-$\mathrm{Me_2NHCH_2CH_2}$-8-$\mathrm{MeOCH_2CH_2}$-7,8-$\mathrm{C_2B_9H_{10}}$ (**9**; 264 mg, 1.0 mmol), and the mixture was stirred overnight at room temperature. The resulting solution (presumably $\mathrm{K_2[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9]}$) was then added dropwise at room temperature through a cannula to a suspension of $\mathrm{Cp''_2YI(THF)}$ (707 mg, 1.0 mmol) in THF (15 mL). The reaction mixture was refluxed overnight. The precipitate was filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated under vacuum to about 10 mL. Complex **12** was isolated as colorless crystals after this solution stood at room temperature for a week (291 mg, 52%). ^{1}H NMR (pyridine-d_5): δ 7.17 (m, 1H, Cp″), 6.94 (m, 1H, Cp″), 6.87 (m, 1H, Cp″), 4.32 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{OCH_3}$), 4.09 (s, 3H, $\mathrm{CH_2CH_2OC}\mathit{H}_3$), 3.79 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 3.62 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OCH_3}$), 2.98 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.61 (s, 6H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 0.46 (s, 9H, $\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$), 0.34 (s, 9H, $\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$). ^{13}C NMR (pyridine-$d_5$): δ 128.0, 126.0, 125.0 (Cp″), 81.0, 73.8 (cage *C*), 67.6 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2OCH_3}$), 65.1 ($\mathrm{CH_2CH_2O}\mathit{C}\mathrm{H_3}$), 62.1 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 48.5 ($\mathit{C}\mathrm{H_2CH_2OCH_3}$), 46.2 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 34.0 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 0.6 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$), 0.4 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$). ^{11}B NMR (pyridine-$d_5$): δ −5.9 (2B), −8.4 (3B), −17.0 (1B), −27.2 (1B), −32.7 (1B), −35.8 (1B). IR (KBr, cm^{-1}): ν 2526 (vs) (BH). Anal. Calcd for $\mathrm{C_{20}H_{47}B_9NOSi_2Y}$: C, 42.90; H, 8.46; N, 2.50. Found: C, 43.39; H, 8.25; N, 2.10.

Alternative Preparation of 12. To a THF (25 mL) solution of $[\eta^1{:}\eta^1{:}\eta^5\text{-}(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_9H_9}]\mathrm{Y}(\mu\text{-}\mathrm{Cl})_2\mathrm{K(THF)_2}$ (**10**; 605 mg, 1.0 mmol) was slowly added a THF (10 mL) solution of Cp″Li (216 mg, 1.0 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 2 days. The precipitate was filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated under vacuum to about 10 mL. Complex **12** was isolated as colorless crystals after this solution stood at room temperature for a week (241 mg, 43%)

Preparation of $[\eta^1{:}\eta^1{:}\eta^5\text{-}(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_9H_9}]\mathrm{ErCp''}$ (13). This complex was prepared as pink crystals from KH (88 mg, 2.2 mmol), 7-$\mathrm{Me_2NHCH_2CH_2}$-8-$\mathrm{MeOCH_2CH_2}$-7,8-$\mathrm{C_2B_9H_{10}}$ (**9**; 264 mg, 1.0 mmol), and $\mathrm{Cp''_2ErI(THF)}$ (785 mg, 1.0 mmol) in THF using the same procedures as those used in the synthesis of **12**: yield 357 mg (56%). ^{1}H NMR (pyridine-d_5): many broad, unresolved resonances. ^{11}B NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2530 (vs) (BH). Anal. Calcd for $\mathrm{C_{20}H_{47}B_9ErNOSi_2}$: C, 37.63; H, 7.42; N, 2.19. Found: C, 37.90; H, 7.78; N, 2.58.

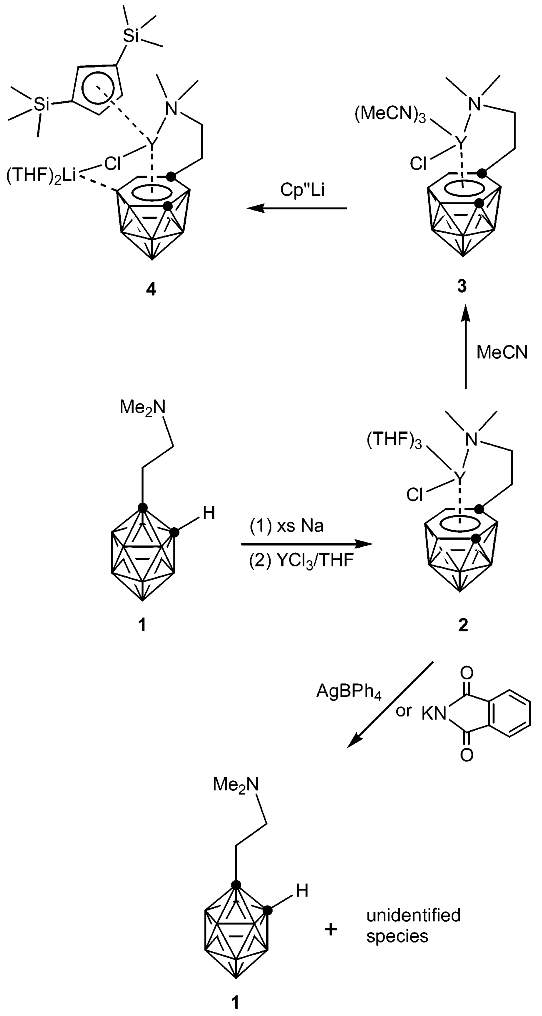
X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under $\mathrm{N_2}$ in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[15] 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.[16] 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 Tables 1 (for **3**, **4**, **6**, and **7**) and 2 (for **8**, **11**−**13**). Selected bond distances are compiled in Tables 3 (for **3** and **4**) and 4 (for **6**−**8**, **12**, and **13**). Further details are included in the Supporting Information.

Results and Discussion

Yttrium Complexes with η^6-*nido*-[$Me_2NCH_2CH_2C_2B_{10}H_{11}$]$^{2-}$ Ligand. Treatment of 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1**) with excess finely cut Na metal in THF gave presumably [$Me_2NCH_2CH_2C_2B_{10}H_{11}$]$Na_2(THF)_x$, which reacted with 1 equiv of YCl_3 in THF to afford [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_{10}H_{11}$]YCl$(THF)_3$ (**2**) in 67% yield. Recrystallization of **2** from a MeCN/toluene solution produced [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_{10}H_{11}$]YCl$(MeCN)_3$·MeCN (**3**·MeCN) in 79% yield. This result indicated that the coordinated THF molecules in **2** were labile and were able to be replaced by other Lewis bases. Complexes **2** and **3** can be viewed as analogues of Cp_2LnCl, in which the terminal Y−Cl bond offered an opportunity for further derivatization. Reaction of **2** with 1 equiv of Cp″Li in THF gave [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_{10}H_{11}$]YCp″(μ-Cl)Li$(THF)_2$ (**4**) in 63% isolated yield. Treatment of **2** with 1 equiv of potassium phthalimide or 1 equiv of $AgBPh_4$ generated the neutral ligand **1** plus other unidentified species. No salt metathesis products were generated. Obviously, redox reactions occurred, probably due to the strong reducing power of the *nido*-$Me_2NCH_2CH_2C_2B_{10}H_{11}{}^{2-}$ ligand.[2] Reaction of **2** with 1 equiv of RLi (R = Me, Me_3SiCH_2, $(Me_3Si)_2N$) or Me_3SiCH_2MgCl in THF resulted in the formation of a mixture of products as indicated by the ^{11}B NMR spectra. Many attempts to isolate the pure product failed. These results implied that the resultant ($Me_2NCH_2CH_2C_2B_{10}H_{11}$)YR$(THF)_x$ were unstable and decomposed during the reactions. The aforementioned reactions were outlined in Scheme 1.

The ^1H NMR spectra of **2**−**4** showed the presence of $Me_2NCH_2CH_2$ protons and supported a ratio of three THF molecules per carboranyl ligand in **2**, four MeCN molecules per carboranyl ligand in **3**, and two THF molecules per carboranyl ligand in **4**. The ^1H NMR spectrum of **4** also exhibited three multiplets at 7.08, 6.84, and 6.14 ppm and two singlets at 0.46 and 0.32 ppm attributable to the Cp″ protons. Their ^{13}C NMR spectra were consistent with the results derived from the ^1H NMR spectra. The ^{11}B NMR spectra exhibited a 1:1:1:2:2:2:1 splitting pattern for **2** and **3** and a 1:1:2:3:2:1 splitting pattern for **4**, respectively. The solid-state IR spectra of **2**−**4** displayed a characteristic B−H absorption at about 2525 cm^{-1}.

Scheme 1



Single-crystal X-ray analyses confirmed that **3** is a monomeric half-sandwich complex in which the Y atom is η^6-bound to a hexagonal C_2B_4 bonding face, σ-bound to a terminal chloro ligand, and coordinated to the nitrogen atom of the sidearm and three MeCN molecules in a highly distorted-octahedral geometry with N(2) and carboranyl occupying the axial positions (Figure 1). As shown in Table 3, the Y-cage atom distances range from 2.649(4) to 3.135(5) Å with an

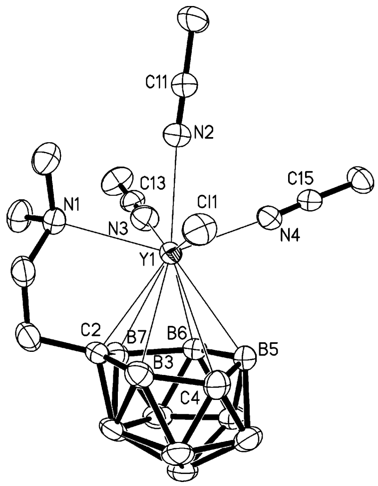


Figure 1. Molecular structure of [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_{10}H_{11}$]YCl$(MeCN)_3$ (**3**).

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[15] Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

[16] Sheldrick, G. M. *SHELXTL*, 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

Table 1. Crystal Data and Summary of Data Collection and Refinement Details for 3, 4, 6, and 7

	3·MeCN	**4**	**6**	**7**
formula	$C_{14}H_{33}B_{10}ClN_5Y$	$C_{25}H_{58}B_{10}ClLiNO_2Si_2Y$	$C_{18}H_{50}B_9N_2O_2Si_2Sm$	$C_{18}H_{50}B_9ErN_2O_2Si_2$
cryst size (mm)	0.40 × 0.40 × 0.30	1.10 × 0.50 × 0.50	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.10
fw	503.9	700.3	630.4	647.3
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	*P*(−1)	*P*2$_1$/*n*	*P*1	*P*2$_1$/*n*
a, Å	10.207(1)	10.545(1)	10.349(2)	24.005(5)
b, Å	10.930(1)	17.897(1)	17.459(4)	10.377(2)
c, Å	12.218(1)	21.296(1)	18.070(4)	26.378(5)
α, deg	89.49(1)	90.00	99.41(3)	90.00
β, deg	88.04(1)	98.91(1)	99.45(3)	102.38(3)
γ, deg	82.10(1)	90.00	91.37(3)	90.00
V, Å^3	1349.2(2)	3970.4(3)	3173.2(11)	6418(2)
Z	2	4	4	8
D_{calcd}, Mg/m^3	1.240	1.172	1.320	1.340
radiation (*λ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	3.3 to 56.2	3.0 to 56.0	3.0 to 51.0	2.6 to 50.0
μ, mm^{-1}	2.272	1.619	1.944	2.708
F(000)	516	1472	1292	2632
no. of obsd reflns	6432	9581	9983	7253
no. of params refnd	324	424	613	614
goodness of fit	0.835	0.864	1.096	1.075
R1	0.056	0.059	0.052	0.074
wR2	0.115	0.138	0.136	0.237

Table 2. Crystal Data and Summary of Data Collection and Refinement Details for 8 and 11−13

	8	**11**·THF	**12**	**13**
formula	$C_{14}H_{36}B_9ClNO_2Y$	$C_{33}H_{75}B_9Cl_2NO_7Y$	$C_{20}H_{47}B_9NOSi_2Y$	$C_{20}H_{47}B_9ErNOSi_2$
cryst size (mm)	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.60 × 0.20 × 0.10	0.80 × 0.50 × 0.20
fw	472.1	855.0	560.0	638.3
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*2$_1$/*n*	*P*2$_1$/*c*	*Cc*	*Cc*
a, Å	11.269(2)	12.018(1)	16.311(1)	16.275(4)
b, Å	13.902(3)	30.909(2)	18.546(1)	18.463(4)
c, Å	15.197(3)	13.683(1)	10.267(1)	10.243(2)
β, deg	104.42(3)	102.89(1)	100.01(1)	100.05(1)
V, Å^3	2305.8(8)	4954.7(6)	3058.4(4)	3030.8(12)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.360	1.146	1.216	1.399
radiation (*λ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	4.0 to 50.0	2.6 to 50.0	3.4 to 56.0	3.4 to 56.0
μ, mm^{-1}	2.655	1.323	2.000	2.863
F(000)	976	1816	1176	1292
no. of obsd reflns	3735	6472	5745	5568
no. of params refnd	253	478	307	307
goodness of fit	1.066	0.926	0.974	1.027
R1	0.052	0.068	0.039	0.028
wR2	0.128	0.192	0.086	0.073

Table 3. Selected Bond Lengths (Å) for 3 and 4

	3	**4**
Y−C(2)	2.649(4)	2.637(4)
Y−B(3)	2.958(5)	2.819(5)
Y−C(4)	3.135(5)	2.864(4)
Y−B(5)	2.785(5)	2.694(5)
Y−B(6)	2.740(5)	2.854(5)
Y−B(7)	2.801(5)	2.900(5)
Y−Cl(1)	2.561(1)	2.628(1)
Y−N(sidearm)	2.598(3)	2.585(3)
Y−N(MeCN)	2.466(4) 2.466(4) 2.539(4)	
Y−C(Cp″)		2.633(4) 2.645(4) 2.666(4) 2.670(4) 2.705(4)

average value of 2.845(5) Å, indicating a highly asymmetrical η^6-bonding. Such a slip distortion may result from the intramolecular interactions between Y and the nitrogen atom of the sidearm. This measured value can be compared to the average Er−cage atom distance of 2.765(18) Å found in [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]$ErCl(THF)_3$[3] if the differences in Shannon's ionic radii are taken into account.[17] The terminal Y−Cl distance of 2.561(1) Å is comparable to those normally observed in organoyttrium chloride complexes,[1a] for example, 2.572(2) Å in [$Me_2Si(C_5Me_4)(C_5H_3CH_2CH_2NMe_2)$]YCl[18] and 2.541(8) Å in [1,2-(Me_2Si)($Me_2SiOSiMe_2$)](4-$Me_3SiC_5H_2$)$_2$YCl(THF).[19] The Y−N(sidearm) distance of 2.598(3) Å compares to that of 2.502(5) Å found in [$Me_2Si(C_5Me_4)(C_5H_3CH_2CH_2NMe_2)$]YCl.[18] Complex **3** represents one of the very rare structurally characterized examples of half-sandwich lanthanacarboranes containing a terminal Ln−Cl bond.[2c]

The solid-state structure of **4** is shown in Figure 2. It is a mixed-sandwich complex, in which the Y atom is η^5-bound to a Cp″ ligand and η^6-bound to a hexagonal C_2B_4 bonding face of the carborane, σ-bound to a doubly bridging chloro ligand, and coordinated to a nitrogen atom of the sidearm in a distorted-tetrahedral geometry. The coordinated LiCl cannot be removed by recrystallization from hot toluene, indicating strong interactions between Y and Cl atoms. The Y atom is asymmetrically bonded to the carborane cage with an average Y−cage atom distance of 2.795(5) Å, which is shorter than the corresponding value of 2.845(5) Å observed in **3**. On the

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(18) Schumann, H.; Erbstein, F.; Weimann, R.; Demtschuk, J. *J. Organomet. Chem.* **1997**, *536*−*537*, 541.

(19) Ihara, E.; Yoshioka, S.; Furo, M.; Katsura, K.; Yasuda, H.; Mohri, S.; Kanehisa, N.; Kai, T. *Organometallics* **2001**, *20*, 1752.

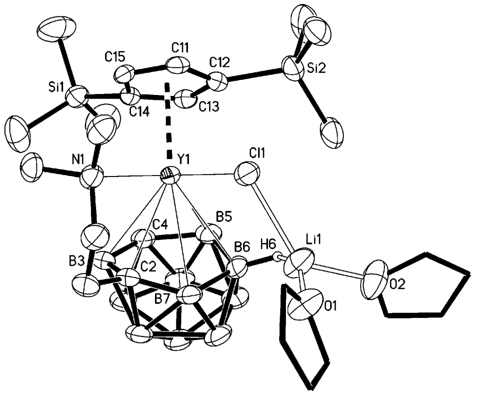
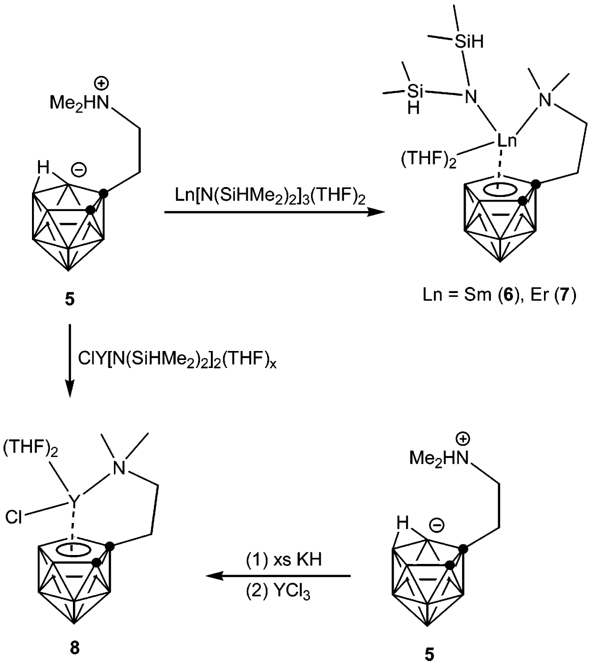


Figure 2. Molecular structure of $[\eta^1{:}\eta^6\text{-}(Me_2NCH_2CH_2)C_2B_{10}H_{11}]YCp''(\mu\text{-}Cl)Li(THF)_2$ (**4**).

other hand, the Y atom is symmetrically bonded to the Cp″ with an average Y−C(Cp″) distance of 2.664(4) Å. This measured value is close to the corresponding value of 2.654(4) Å in $Cp''_2YI(THF)$[14] and 2.667(3) Å in $Cp''_2Y(\mu\text{-}Cl)_2Li(THF)_2$.[20] The Y−N(sidearm) distance of 2.585(3) Å is close to that of 2.598(3) Å observed in **3**. As expected, the Y−Cl(*μ*) distance of 2.628(1) Å is longer than the terminal Y−Cl distance of 2.561(1) Å observed in **3**, but is very comparable to the corresponding values of 2.6307(9) and 2.6260(9) Å found in $Cp''_2Y(\mu\text{-}Cl)_2Li(THF)_2$.[20]

Rare Earth Complexes with η^5-*nido*-$[Me_2NCH_2CH_2C_2B_9H_{10}]^{2-}$ Ligand. The previous section shows that *nido*-$Me_2NCH_2CH_2C_2B_{10}H_{11}{}^{2-}$ is a strong reducing reagent, just like *nido*-$C_2B_{10}H_{12}{}^{2-}$, which may cause side reactions. In this regard, *nido*-$Me_2NCH_2CH_2C_2B_9H_{10}{}^{2-}$ should be a better ligand. Furthermore, its conjugate acid $Me_2NHCH_2CH_2C_2B_9H_{11}$ makes the amine/alkane elimination reaction possible.[6,21,22] Treatment of 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (**5**) with 1 equiv of $Ln[N(SiHMe_2)_2]_3(THF)_2$ in toluene gave, after recrystallization from THF/toluene, half-sandwich lanthanacarboranes of the general formula $[\eta^1{:}\eta^5\text{-}(Me_2NCH_2CH_2)C_2B_9H_{10}]LnN(SiHMe_2)_2(THF)_2$ (Ln = Sm (**6**), Er (**7**)) in moderate yields, respectively. $[\eta^1{:}\eta^5\text{-}(Me_2NCH_2CH_2)C_2B_9H_{10}]YCl(THF)_2$ (**8**) was synthesized in 52% yield from the reaction of **5** with $ClY[N(SiHMe_2)_2]_2(THF)_x$ prepared in situ from the reaction of $YCl_3(THF)_{3.5}$ with 2 equiv of $LiN(SiHMe_2)_2$ in *n*-hexane. Complex **8** was also prepared in 37% yield from an equimolar reaction of [*nido*-$(Me_2NCH_2CH_2)C_2B_9H_{10}]Na_2(THF)_x$ with YCl_3 in THF (Scheme 2). Successful isolation of complexes **6** and **7** prompted us to prepare the corresponding alkyl derivatives via alkane elimination reaction. Treatment of **5** with 1 equiv of $Ln(CH_2SiMe_3)_3(THF)_2$[23] (Ln = Y, Er) in toluene at room temperature gave a mixture of products as indicated by the ^{11}B and ^1H NMR spectra. No pure product was isolated, although many attempts were made. We then turned to a more sterically demanding reagent, $LiCH(SiMe_3)_2$.[24] Reaction of **8** with 1 equiv of $LiCH(SiMe_3)_2$ in THF afforded, again, a mixture of products according to the ^{11}B and ^1H NMR spectroscopic analyses. Only a sticky oil was obtained, and no pure product was isolated. These results showed that the resultant lanthanacarborane alkyl complexes were not stable. On the other hand, the corresponding half-sandwich lanthanacarborane amide complexes were stable even in refluxed toluene solution probably due to a much stronger Ln−N bond.

Scheme 2



Complexes **6**−**8** were extremely air- and moisture-sensitive, but remained stable for months at room temperature under an inert atmosphere. They were quite soluble in polar organic solvents such as THF and pyridine, sparely soluble in toluene, and insoluble in *n*-hexane.

The NMR spectra of **6** and **7** were not informative because of the strong paramagnetism of Sm^{3+} and Er^{3+}. However, **8** was found to provide interpretable NMR data. The ^1H NMR spectrum of **8** showed the presence of $Me_2NCH_2CH_2$ protons and supported the ratio of two THF molecules per carborane cage. Its ^{13}C NMR spectrum was in line with the ^1H NMR one. Its ^{11}B NMR spectrum exhibited a 2:2:3:1:1 splitting pattern. The solid-state IR spectra displayed a characteristic B−H absorption at about 2525 cm^{-1} for **6**−**8** and a characteristic Si−H absorption at about 2045 cm^{-1} for both **6** and **7**.

Single-crystal X-ray analyses revealed that complexes **6** and **7** are isostructural but not isomorphous. There are two independent molecules in the unit cell of both **6** and **7**. Figure 3 shows the representative structure of **6**. The Ln metal is η^5-bound to the pentagonal C_2B_3 bonding face of the carborane, *σ*-bound to a nitrogen atom of $N(SiHMe_2)_2$ ligand, and coordinated to the nitrogen atom of the sidearm and two THF molecules

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Table 4. Selected Bond Lengths (Å) for 6−8, 12, and 13

	6 (Ln = Sm)[a]	**7** (Ln = Er)[a]	**8** (Ln = Y)	**12** (Ln = Y)	**13** (Ln = Er)
Ln−C(1)	2.894(7) [2.911(7)]	2.885(12) [2.914(12)]	2.729(4)	2.759(4)	2.731(5)
Ln−C(2)	2.804(7) [2.786(7)]	2.779(13) [2.780(16)]	2.653(4)	2.728(3)	2.715(4)
Ln−B(3)	2.670(7) [2.624(8)]	2.601(14) [2.630(14)]	2.537(5)	2.611(5)	2.597(5)
Ln−B(4)	2.654(8) [2.677(9)]	2.633(15) [2.605(19)]	2.571(5)	2.616(4)	2.603(7)
Ln−B(5)	2.791(7) [2.825(8)]	2.736(14) [2.800(13)]	2.647(5)	2.638(5)	2.620(6)
Ln···Si(1)	3.744(6) [3.744(6)]	3.802(12) [3.735(12)]			
Ln···Si(2)	3.165(6) [3.186(6)]	3.210(12) [3.178(12)]			
Ln−N(sidearm)	2.626(6) [2.614(6)]	2.604(10) [2.602(10)]	2.502(4)	2.531(4)	2.510(4)
Ln−O(sidearm)				2.359(3)	2.348(3)
Ln−N(amido)	2.328(5) [2.330(5)]	2.315(9) [2.310(10)]			
Ln−O(THF)	2.488(5) [2.488(4)]	2.439(8) [2.421(8)]			
	2.521(4) [2.496(4)]	2.501(8) [2.508(8)]			
Ln−C(Cp″)				2.651(4)	2.641(6)
				2.670(4)	2.650(5)
				2.673(4)	2.665(5)
				2.687(4)	2.667(7)
				2.695(4)	2.668(4)

[a] Distances in brackets are those of a second molecule.

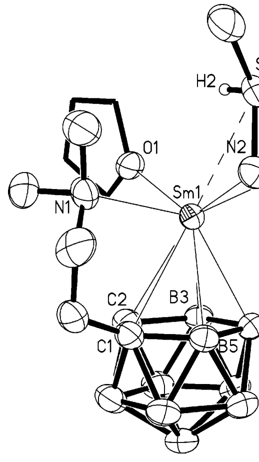

Figure 3. Molecular structure of [η^1:η^5-($Me_2NCH_2CH_2$)-$C_2B_9H_{10}$]Sm[N($SiHMe_2$)$_2$](THF)$_2$ (**6**) showing one of the two independent molecules in the unit cell.

in a four-legged piano stool geometry. As indicated in Table 4, both Sm and Er atoms are asymmetrically η^5-bonded to the cage with the average bond distances of 2.763(7) [2.765(8)] Å for **6** and 2.727(14) [2.746(15)] Å for **7**, respectively. Such a slip distortion may result from the sidearm effects. The average Sm−cage atom distance of 2.763(7) [2.765(8)] Å is comparable to the corresponding value of 2.721(9) Å found in [(η^5-$C_2B_9H_{11}$)$_2$-Sm(THF)$_2$]$^-$,[25] in which the Sm atom is bonded to the open C_2B_3 face in a symmetrical η^5-fashion. The average Er−cage atom distance of 2.727(14) [2.746(15)] Å compares to that of 2.641(13) Å found in [(η^5-$Me_2C_5H_5$)(η^5-(Me_3Si)$_2C_2B_4H_4$)Er]$_2$.[26] The Sm−N(2) distance of 2.328(5) [2.330(5)] Å and the Sm−N(1) distance of 2.626(6) [2.614(6)] Å are close to the average Sm−N distance of 2.320 Å found in Sm[N($SiHMe_2$)$_2$]$_3$(THF)$_2$[27] and the corresponding value of 2.648(11) Å found in [η^5:η^1:σ-Me_2-Si($C_9H_5CH_2CH_2NMe_2$)($C_2B_{10}H_{10}$)]Sm(μ-NHC$_6$H$_3$-2,6-Pr$^i_2$)-(μ-Cl)Li(THF).[8b] The Er−N(2) distance of 2.315(9) [2.310(10)] Å is longer than the average Er−N(amido) distance of 2.232(3) Å found in {[(Me_3Si)$_2$N]$_2$Er(THF)}$_2$(μ-η^2:η^2-N_2).[28]

Other interesting structural features observed in **6** and **7** are the asymmetric coordination mode of the silylamide moiety, as indicated by significantly smaller Ln−N(2)−Si(2) angles of 102.5(3)° [103.8(3)°] in **6** and 105.0(5)° [104.7(5)°] in **7** versus Ln−N(2)−Si(1) angles of 136.1(4)° [135.9(4)°] in **6** and 139.1(6)° [133.2(7)°] in **7** and shorter Ln···Si(2) distances of 3.165(6) [3.186(6)] Å in **6** and 3.210(12) [3.178(12)] Å in **7** versus the longer Ln···Si(1) distances of 3.744(6) [3.744(6)] Å in **6** and 3.802(12) [3.735(12)] Å in **7**. Such an asymmetrical β-Si agostic interaction is often observed in L_2Ln-N($SiMe_3$)$_2$ types of complexes (L_2 = *ansa* ligands)[29,30] but not in L_2Ln-N($SiHMe_2$)$_2$ systems, where symmetrical β-SiH agostic interactions are usually observed[21a] (except for [η^5:σ-^{i}Pr$_2$NB(C_9H_6)($C_2B_{10}H_{10}$)]NdN($SiHMe_2$)$_2$(THF)$_2$[22a] and (C_5Me_5)$_2$YN($SiHMe_2$)$_2$[21b]). Complexes **6** and **7** represent the first structurally characterized examples of half-sandwich lanthanacarborane amide complexes.

Figure 4 shows the molecular structure of **8**. The Y atom is asymmetrically η^5-bonded to a carboranyl ligand and σ-bound to a terminal chloro ligand, and coordinated to the nitrogen atom of the sidearm and two THF molecules in a four-legged piano stool geometry. It represents the first structurally characterized example of a half-sandwich lanthanacarborane chloride involving a C_2B_9 ligand system. The Y−cage atom distances range from 2.653(5) to 2.729(4) Å with an average value of 2.627(5) Å. This measured value is significantly shorter than the corresponding values observed in **3** and **4**, but is comparable to the corresponding value of 2.715(20) Å found in {[{η^5-(Me_3Si)$_2C_2B_4H_4$}$_2$YCl(THF)]Li(THF)}-{Li(THF)$_4$}.[5a] The terminal Y−Cl distance of 2.561(1) Å is the same as that of 2.561(1) Å found in **4**. The Y−N(sidearm) distance of 2.502(4) Å is shorter than that of 2.598(3) Å in **3** and 2.585(3) Å in **4**.

Rare Earth Complexes with η^5-*nido*-(Me_2NCH_2-CH_2)($MeOCH_2CH_2$)$C_2B_9H_9^{2-}$ Ligand. A monosubstituted carboranyl ligand can stabilize the half-sandwich lanthanide amide complexes, but cannot prevent the decomposition of lanthanide alkyl derivatives. A question subsequently arises as to whether bisfunctional carboranyl ligand could stabilize the half-sandwich lanthanide alkyl complexes. Treatment of 7-Me_2NHCH_2-CH_2-8-$MeOCH_2CH_2$-7,8-$C_2B_9H_{10}$ (**9**) with excess KH in

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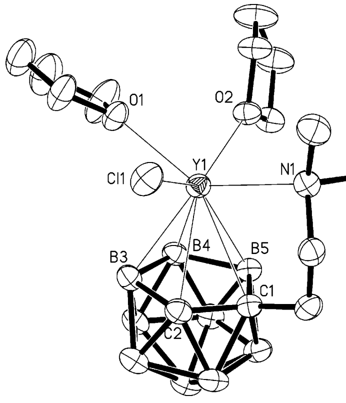


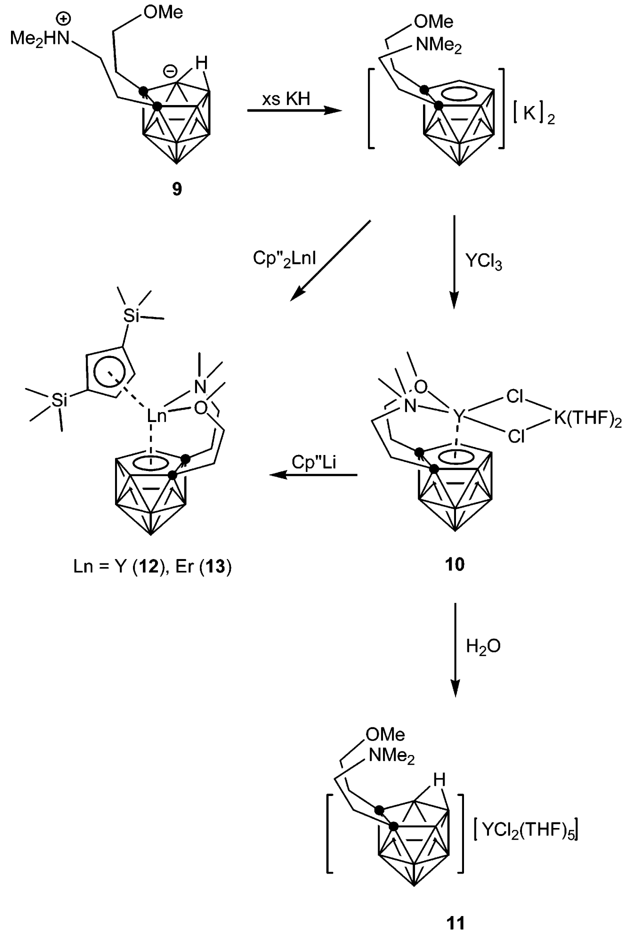
Figure 4. Molecular structure of $[\eta^1:\eta^5\text{-}(Me_2NCH_2CH_2)C_2B_9H_{10}]YCl(THF)_2$ (**8**).

THF gave presumably $[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9]K_2(THF)_x$, followed by reaction with 1 equiv of YCl_3 in THF to afford $[\eta^1:\eta^1:\eta^5\text{-}(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9]Y(\mu\text{-}Cl)_2K(THF)_2$ (**10**) in 42% yield. Partial hydrolysis product $[YCl_2(THF)_5]$[*nido*-$(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_{10}$]·THF (**11**·THF) was initially isolated by repeated recrystallization of **10** from a THF/toluene solution. Complex **11** was also prepared in 48% yield by a controlled hydrolysis of **10** in THF/toluene. Reaction of **10** with 1 equiv of $Cp''Li$ in THF afforded the mixed-sandwich complex $[\eta^1:\eta^1:\eta^5\text{-}(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9]YCp''$ (**12**) in 43% yield. Complex **12** and its Er analogue $[\eta^1:\eta^1:\eta^5\text{-}(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9]ErCp''$ (**13**) were also prepared from the reaction of $[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9]K_2(THF)_x$ with 1 equiv of $Cp''_2LnI(THF)$ in THF in moderate yields. It is noteworthy that both $I^-$and Cp''^- act as leaving groups in these reactions, indicating that the bonding interactions between Ln^{3+} and $[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_9]^{2-}$ are stronger than those between Ln^{3+} and Cp''^-. Treatment of **10** with 1 equiv of $(Me_3Si)_2CHLi$ or Me_3SiCH_2Li in THF gave a mixture of products as indicated by both ^{11}B and ^1H NMR spectra. An equimolar reaction of $Y(CH_2SiMe_3)_3(THF)_2$[23a] with **9** also afforded a mixture of products. Many attempts to isolate the pure products failed. These results suggested that the two functional sidearms on the carboranyl bonding face still cannot stabilize lanthanacarborane alkyl complexes. These transformations are summarized in Scheme 3.

The ^1H NMR spectra of **10**−**12** all showed the presence of the $MeOCH_2CH_2$ and $Me_2NCH_2CH_2$ groups and supported a ratio of two THF molecules per cage for **10** and six THF molecules per cage for **11**. The proton resonances corresponding to Cp″ were also observed in the ^1H NMR spectrum of **12**. Their ^{13}C NMR spectra were consistent with the results derived from the ^1H NMR data. The ^{11}B NMR spectra exhibited a 1:4:1:1:1:1 splitting pattern for **10**, a 2:1:1:3:1:1 splitting pattern for **11**, and a 2:3:1:1:1:1 splitting pattern for **12**, respectively. The solid-state IR spectra of **10**−**13** all displayed a characteristic B−H absorption at about 2530 cm^{-1}.

Single-crystal X-ray analyses revealed that **11** is an ionic structure consisting of well-separated, alternating layers of discrete cation $[YCl_2(THF)_5]^+$ and carboranyl monoanion [*nido*-$(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_{10}]^-$ and showed one THF of solvation. The cation adopts a pentagonal-bipyramidal geometry with two chloro ligands occupying the axial positions (Figure 5), which is the same as that in $[YCl_2(THF)_5]$[*nido*-$C_2B_9H_{10}$].[4] The full characterization of **11** supports the proposed structure of its parent complex **10**.

Scheme 3



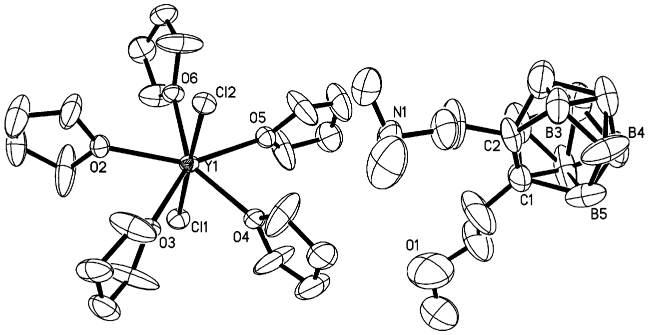


Figure 5. Molecular structure of $[YCl_2(THF)_5]$[*nido*-$(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_9H_{10}$] (**11**).

X-ray diffraction studies revealed that complexes **12** and **13** are isostructural and isomorphous. Figure 6 shows the representative structure of **12**. The Ln metal is η^5-bound to the *nido*-carborane and one Cp″ and coordinated to one oxygen atom and one nitrogen atom of the two pendant substituents in a distorted-tetrahedral geometry. The coordination of the second sidearm results in the formation of the neutral complexes, which can be compared to the 'ate' complex **4**.

The average Y−cage atom distance of 2.670(5) Å and the Y−N(1) distance of 2.531(4) Å in **12** are longer than the corresponding values of 2.627(5) and 2.502(4) Å

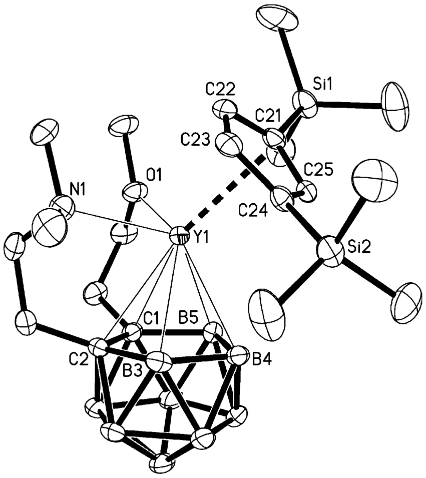


Figure 6. Molecular structure of [η^1:η^1:η^5-($Me_2NCH_2CH_2$)($MeOCH_2CH_2$)$C_2B_9H_9$]YCp″ (**12**).

observed in **8**. The average Er−cage atom distance of 2.653(5) Å and the Er−N(1) distance of 2.510(4) Å in **13** are much shorter than those of 2.727(14) [2.746(15)] and 2.604(10) [2.602(10)] Å in **7**. These data indicate that the substituents on the cage carbon atoms have some effects on the structural parameters and coordination environments of the central metal atoms. The average Y−C(Cp″) distance of 2.675(4) Å in **12** is close to that of 2.664(4) Å observed in **4** and the 2.654(4) Å found in Cp″$_2$YI(THF).[14] The average Er−C(Cp″) distance of 2.658(5) Å is close to that of 2.640(9) Å observed in Cp″$_2$ErI(THF).[14]

Conclusion

Several half-sandwich lanthancarboranes containing terminal chloro and amido groups were prepared and structurally characterized via salt metathesis and silylamine elimination methods. They represent the first structurally characterized examples of monomeric half-sandwich lanthanacarborane amide complexes. This work showed that sidearm effects are very important and can stabilize the half-sandwich lanthanacarborane chloride and amide complexes through the coordination of the heteroatoms to the lanthanide ion to fulfill the electronic and steric requirements. Unfortunately, all ligand systems examined, regardless of mono- or bisfunctional carboranes of the C_2B_9 or C_2B_{10} systems, cannot prevent the decomposition of half-sandwich lanthanacarborane alkyl complexes.

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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 **3**, **4**, **6**−**8**, and **11**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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