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Synthesis, Structural Characterization, and Reactivity of Lanthanacarboranes Incorporating "Carbons-Adjacent" *nido*- and *arachno*-Carborane Anions of the C_2B_{10} System

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Group 1 salts of "carbons-adjacent" carborane anions of the C_2B_{10} system are useful synthons for the production of other metallacarboranes. Treatment of [{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}$_2Na_4(THF)_6$]$_n$ (**2**) with 2 equiv of $LnCl_3$ gave the novel half-sandwich lanthanacarboranes [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}Yb$(NC_5H_5)_3${Na$(NC_5H_5)_2$}$_{0.5}$]$_2$(μ-Cl) (**4**) and [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]LnCl$(THF)_3$ (Ln = Nd (**5**), Er (**6**), Y (**7**)), which represent the first lanthanacarboranes containing a terminal Ln−Cl bond in the C_2B_{10} systems. The chloro group in these complexes can be substituted by other moieties, leading to the isolation of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]Nd[(μ-H)$_3$BH]$(THF)_3$ (**8**) and [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]Y(η^5-C_5H_5)(THF) (**9**), respectively. Reduction of **6** or **7** with excess Li metal afforded the full-sandwich lanthanacarboranes {η^6-[μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$]$_2$Ln}{$Li_5(THF)_{10}$} (Ln = Er (**11**), Y (**12**)). Treatment of **6** with excess Na metal generated the full-sandwich lanthanacarborane cluster [{η^6-[μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$]$_2$Er}{$Na_5(THF)_6$}]$_4$ (**13**). These full-sandwich complexes were also prepared from the reaction of [{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}$Li_4(THF)_6$]$_2$ (**3**) with $LnCl_3$. Their Gd analogue {η^6-[μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$]$_2$Gd}{$Li_5(THF)_9$} (**10**) was prepared via a "one-pot" interaction between μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$ (**1**), excess Li metal, and $GdCl_3$. All complexes were fully characterized by various spectroscopic data and elemental analyses. Complexes **4**, **6**, **8**, **10**, **11**, and **13** were subjected to single-crystal X-ray analyses.

Introduction

It has been well-documented that *o*-$R_2C_2B_{10}H_{10}$ (R = H, alkyl, aryl) can be readily reduced by alkali metals to give the "carbons-apart" dianionic species [*nido*-$R_2C_2B_{10}H_{10}$]$^{2-}$, which are very useful versatile synthons for the production of numerous metallacarboranes of s, p, d, and f elements.[1] This reduction process leads to the complete cleavage of the cage C−C bond. In the presence of transition-metal halides, *o*-carborane can undergo four-electron reduction with excess alkali metals to form a *arachno*-$R_2C_2B_{10}H_{10}{}^{4-}$ tetraanion in which the two cage carbon atoms are further separated by at least two cage boron atoms.[2−5]

Metallacarboranes bearing "carbons-adjacent" carborane anions of the C_2B_{10} systems are very rare. Only two examples are known. One is (η^6-$MeC_2B_{10}H_{11}$)Co_2-$(PEt_3)_3$, prepared from the reaction of 1-Me-1,2-$C_2B_{10}H_{11}$ with 2 equiv of $Co(PEt_3)_4$, in which the cage C−C connectivity is believed to be maintained. However, the nonmethylated cage carbon atom is not definitely identified because of the disorder problem.[6] The other is [(η^5-C_5H_5)(η^6-(NC)$C_2B_{10}H_{11}$)]Co, prepared by treatment of [*arachno*-(NC)$C_2B_{10}H_{14}$]K with $CoCl_2$ followed by air oxidation.[7]

We have recently developed a method to prepare a new class of "carbons-adjacent" *nido*- and *arachno*-carborane anions by introducing a short bridge between the two cage carbon atoms, shown in Chart 1.[8] The group 1 salts of these anions allow us to make a novel class of "carbons-adjacent" metallacarboranes. We report herein the synthesis, structural characterization, and reactivity of "carbons-adjacent" lanthanacarboranes of the C_2B_{10} system.

Experimental Section

General Procedures. All experiments were preformed 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

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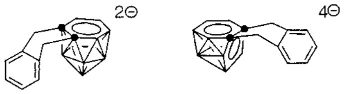
Chart 1. “Carbons-Adjacent” *nido*- and *arachno*-Carborane Anions



distilled from sodium benzophenone ketyl immediately prior to use. μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$ (**1**),[9] [{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}$_2$$Na_4(THF)_6$]$_n$ (**2**),[8] [{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}$Li_4(THF)_6$]$_2$ (**3**),[8] and $Nd(BH_4)_3(THF)_3$[10] were prepared according to literature methods. All chemicals were purchased from either Aldrich or Acros 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 300.13 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., Brunel University, Middlesex, U.K.

Preparation of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}-$Yb(NC_5H_5)_3${$Na(NC_5H_5)_2$}$_{0.5}$]$_2$(μ-Cl) (4). To a THF (10 mL) suspension of $YbCl_3$ (280 mg, 1.00 mmol) was added a THF solution (15 mL) of [{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}$_2$$Na_4(THF)_6$]$_n$ (**2**; 508 mg, 0.50 mmol) with stirring at room temperature, and the mixture was stirred overnight. During the course of reaction, the color changed from brown to dark red. The solvent was removed. The dark red solid was extracted with pyridine (10 mL × 3). The dark red pyridine solutions were combined and concentrated to about 10 mL, to which toluene (about 10 mL) was added. **4** was isolated as dark red crystals after this solution stood at room temperature for 2 weeks (245 mg, 32% based on **2**). ^1H NMR (pyridine-d_5): δ 8.71 (m, 8H, C_5H_5N-2-*H*), 7.55 (m, 4H, C_5H_5N-4-*H*), 7.20 (m, 8H, C_5H_5N-3-*H*), 7.27 (m, 4H, aryl *H*), 4.33 (br s, 4H, $C_6H_4(CH_2)_2$). ^{13}C NMR (pyridine-d_5): δ 149.2, 134.9, 122.9 (C_5H_5N), 138.8, 128.0, 125.9 ($C_6H_4(CH_2)_2$), 48.7, ($C_6H_4(CH_2)_2$); the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 8.69 (1B), 3.23 (2B), −2.82 (2B), −11.20 (2B), −18.34 (2B), −23.59 (1B). IR (KBr, cm^{-1}): ν 2954 (vs), 2505 (vs), 2443 (vs), 2314 (s), 1593 (s), 1440 (s), 1381 (w), 1259 (w), 1032 (vs), 803 (w), 750 (w). Anal. Calcd for $C_{60}H_{76}B_{20}ClN_8NaYb_2$: C, 47.10; H, 5.01; N, 7.33. Found: C, 47.03; H, 4.76; N, 7.53.

Preparation of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]-$NdCl(THF)_3$ (5). To a THF (10 mL) suspension of $NdCl_3$ (250 mg, 1.00 mmol) was added a THF (15 mL) solution of **2** (508 mg, 0.50 mmol) with stirring at room temperature, and the mixture was stirred overnight. After removal of the precipitate, the clear blue solution was concentrated to about 5 mL, to which toluene (about 10 mL) was added. **5** was isolated as blue microcrystals after this solution stood at room temperature for 2 days (411 mg, 64%). ^1H NMR (pyridine-d_5): δ 7.64−7.21 (m, 4H), 6.90 (s, 1H), 6.43 (s, 1H), 3.64 (m, 12H, THF), 1.77 (s, 1H), 1.66 (m, 12H, THF), −1.78 (s, 1H). ^{13}C NMR (pyridine-d_5): δ 138.4, 129.2, 128.5 ($C_6H_4(CH_2)_2$), 49.1 ($C_6H_4(CH_2)_2$), 67.6, 25.6 (THF); the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 6.17 (2B), 0.06 (2B), −8.61 (2B), −15.82 (2B), −19.04 (1B), −21.00 (1B). IR (KBr, cm^{-1}): ν 2963 (vs), 2879 (vs), 2516 (vs), 1606 (w), 1453 (s), 1039 (vs), 859 (s). Anal. Calcd for $C_{20}H_{38}B_{10}ClNdO_{2.5}$ (**5**−0.5THF): C, 39.62; H, 6.32. Found: C, 39.84; H, 6.42.

Preparation of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]-$ErCl(THF)_3\cdot C_7H_8\cdot 0.5THF$ (6·C_7H_8·0.5THF). This compound was prepared as pink crystals from the reaction of $ErCl_3$ (270 mg, 1.00 mmol) and **2** (508 mg, 0.50 mmol) in THF (25 mL) using procedures similar to those used in the synthesis of **5**: yield 548 mg (69%). ^1H NMR (pyridine-d_5): δ 7.23−7.11 (m, 9H, aryl *H* and $C_6H_5CH_3$), 4.28 (m, 2H, $C_6H_4(CH_2)_2$), 3.61 (m, 14H, THF), 3.28 (m, 2H, $C_6H_4(CH_2)_2$), 2.17 (s, 3H, $C_6H_5CH_3$), 1.54 (m, 14H, THF). ^{13}C NMR (pyridine-d_5): δ 137.5, 128.9, 128.1 ($C_6H_4(CH_2)_2$), 125.9, 125.5, 125.2, 20.8 ($C_6H_5CH_3$), 48.8, ($C_6H_4(CH_2)_2$), 67.3, 25.2 (THF); the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 10.14 (2B), 3.98 (2B), −4.63 (2B), −11.76 (2B), −15.07 (1B), −17.02 (1B). IR (KBr, cm^{-1}): ν 2945 (vs), 2520 (vs), 1604 (s), 1458 (s), 1264 (s), 1027 (vs), 820 (s). Anal. Calcd for $C_{29}H_{50}B_{10}ClErO_3$ (**6**−C_7H_8): C, 45.98; H, 6.65. Found: C, 45.90; H, 6.87.

Preparation of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]-$YCl(THF)_3$ (7). This compound was prepared as light yellow microcrystals from the reaction of YCl_3 (195 mg, 1.00 mmol) and **2** (508 mg, 0.50 mmol) in THF (25 mL) using procedures similar to those used in the synthesis of **5**: yield 329 mg (56%). ^1H NMR (pyridine-d_5): δ 7.11 (m, 2H, aryl *H*), 7.03 (m, 2H, aryl *H*), 4.07 (d, J = 15.6 Hz, 2H, $C_6H_4(CH_2)_2$), 3.94 (d, J = 15.6 Hz, 2H, $C_6H_4(CH_2)_2$), 3.64 (m, 12H, THF), 1.60 (m, 12H, THF). ^{13}C NMR (pyridine-d_5): δ 140.2, 126.0, 125.0 ($C_6H_4(CH_2)_2$), 48.3 ($C_6H_4(CH_2)_2$), 67.5, 25.5 (THF); the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 5.71 (3B), −3.61 (3B), −15.77 (1B), −18.42 (2B), −22.30 (1B). IR (KBr, cm^{-1}): ν 2960 (vs), 2877 (s), 2511 (vs), 1620 (w), 1453 (m), 1258 (s), 1041 (vs), 898 (m), 801 (s). Anal. Calcd for $C_{14}H_{26}B_{10}ClOY$ (**7**−2THF): C, 37.97; H, 5.92. Found: C, 38.25; H, 6.12.

Preparation of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]-Nd[(μ-H)$_3$BH]$(THF)_3\cdot 0.5THF$ (8·0.5THF). To a THF (10 mL) solution of $Nd(BH_4)_3(THF)_3$ (405 mg, 1.00 mmol) was added a THF (15 mL) solution of **2** (508 mg, 0.50 mmol) with stirring at room temperature, and the mixture was stirred overnight. After removal of the precipitate, the clear blue solution was concentrated to about 5 mL, to which toluene (about 15 mL) was added. **8**·0.5THF was isolated as blue crystals after this solution stood at room temperature for 2 weeks (421 mg, 64%). ^1H NMR (pyridine-d_5): δ 7.64−7.20 (m, 4H, aryl *H*), 6.90 (s, 1H), 6.43 (s, 1H), 3.69 (m, 14H, THF), 1.79 (s, 1H), 1.67 (m, 14H, THF), −1.77 (s, 1H). ^{13}C NMR (pyridine-d_5): δ 144.4, 129.4, 128.7 ($C_6H_4(CH_2)_2$), 44.1, ($C_6H_4(CH_2)_2$), 67.9, 25.8 (THF); the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 56.94 (2B), 47.28 (3B), 14.04 (2B), −3.04 (1B), −6.72 (1B), −20.32 (1B), −22.51 (1B). IR (KBr, cm^{-1}): ν 2961 (vs), 2893 (s), 2516 (vs), 2420 (s), 2288 (s), 2222 (s), 1640 (w), 1452 (s), 1258 (s), 1109 (vs), 1041 (vs), 1017 (vs), 869 (s). Anal. Calcd for $C_{20}H_{42}B_{11}NdO_{2.5}$ (**8**−0.5THF): C, 41.01; H, 7.23. Found: C, 40.77; H, 7.01.

Alternate Method. To a THF (15 mL) solution of **5** (321 mg, 0.50 mmol) was added $NaBH_4$ powder (38 mg, 1.00 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 days, followed by the procedures used above to give **8** as blue microcrystals (164 mg, 53%).

Preparation of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]Y-(η^5-C_5H_5)(THF) (9). To a THF (15 mL) solution of **7** (587 mg, 1.00 mmol) was added a THF (15 mL) solution of C_5H_5Na (88 mg, 1.00 mmol) dropwise with stirring at room temperature, and the mixture was refluxed overnight. After removal of the precipitate, the clear colorless solution was concentrated to about 5 mL, to which toluene (about 10 mL) was added. **9** was isolated as colorless microcrystals after this solution stood at room temperature for 2 days (250 mg, 53%). ^1H NMR (pyridine-d_5): δ 7.25 (m, 2H, aryl *H*), 7.14 (m, 2H, aryl *H*), 6.59 (s, 1H, C_5H_5), 6.34 (s, 2H, C_5H_5), 6.26 (s, 1H, C_5H_5), 6.10 (s, 1H, C_5H_5), 4.24 (d, J = 15.6 Hz, 2H, $C_6H_4(CH_2)_2$), 4.16 (d, J = 15.6 Hz, 2H, $C_6H_4(CH_2)_2$), 3.66 (m, 4H, THF), 1.60 (m, 4H, THF). ^{13}C NMR (pyridine-d_5): δ 138.9, 126.7, 126.4 ($C_6H_4(CH_2)_2$), 113.8, 113.0, 111.5, 111.1 (C_5H_5), 49.6 ($C_6H_4(CH_2)_2$), 68.2, 26.2 (THF);

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the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 3.40 (2B), −2.77 (3B), −11.43 (2B), −18.61 (1B), −21.86 (1B), −23.82 (1B). IR (KBr, cm^{-1}): ν 2960 (s), 2899 (m), 2512 (vs), 1450 (m), 1258 (m), 1010 (vs), 853 (s), 797 (vs). Anal. Calcd for $C_{19}H_{31}B_{10}OY$: C, 48.30; H, 6.61. Found: C, 48.15; H, 6.72.

Preparation of $\{\eta^6\text{-}[\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}]_2\text{-}Gd\}\{Li_5(THF)_9\}$ (10). To a THF (25 mL) solution of μ-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$ (**1**; 246 mg, 1.00 mmol) was added finely cut Li metal (110 mg, 15.9 mmol), and the mixture was stirred at room temperature overnight. To the resulting solution was added $GdCl_3$ powder (260 mg, 1.00 mmol); the reaction mixture was then stirred at room temperature for 1 week. The precipitate and excess Li metal were filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated under vacuum to about 10 mL, from which **10** was isolated as brick red crystals after this solution stood at room temperature for 2 weeks (493 mg, 74%). ^1H NMR (pyridine-d_5): δ 3.64 (br s), 1.61 (br s) (THF), and other broad, unresolved resonances. ^{13}C NMR (pyridine-d_5): δ 69.8, 27.8 (THF); other carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 10.41 (2B), 8.34 (2B), −0.74 (2B), −11.47 (2B), −16.90 (2B). IR (KBr, cm^{-1}): ν 2959 (vs), 2887 (vs), 2507 (vs), 2424 (s), 2322 (s), 1626 (m), 1460 (m), 1261 (m), 1042 (vs), 801 (s). Anal. Calcd for $C_{48}H_{92}B_{20}GdLi_5O_7$ (**10**−2THF): C, 48.47; H, 7.80. Found: C, 48.54; H, 8.30.

Preparation of $\{\eta^6\text{-}[\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}]_2\text{-}Er\}\{Li_5(THF)_{10}\}$ (11). To a THF (10 mL) solution of **6** (665 mg, 1.00 mmol) was added finely cut Li metal (110 mg, 15.9 mmol), and the mixture was stirred at room temperature for 1 week. The precipitate and excess Li metal were filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated under vacuum to about 10 mL, from which **11** was isolated as orange-red crystals after this solution stood at room temperature for 2 weeks (481 mg, 68%). ^1H NMR (pyridine-d_5): δ 3.69 (br s), 1.71 (br s) (THF), and other broad, unresolved resonances. ^{13}C NMR (pyridine-d_5): δ 67.7, 25.8 (THF); other carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 10.66 (2B), 8.75 (2B), −0.30 (2B), −11.20 (2B), −16.46 (2B). IR (KBr, cm^{-1}): ν 2964 (s), 2877 (s), 2515 (vs), 2425 (s), 2348 (m), 1633 (vs), 1451 (m), 1258 (m), 1091 (s), 1042 (vs), 801 (s). Anal. Calcd for $C_{52}H_{100}B_{20}ErLi_5O_8$ (**11**−2THF): C, 49.12; H, 7.93. Found: C, 48.95; H, 8.36.

Alternate Method. To a THF (10 mL) suspension of $ErCl_3$ (137 mg, 0.50 mmol) was added a THF solution (15 mL) of $\{[\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}]Li_4(THF)_6\}_2$ (**3**; 706 mg, 0.50 mmol) with stirring at room temperature, and the mixture was stirred overnight. Following workup procedures similar to those used above afforded orange-red crystals (510 mg, 72%) identified as **11** by both spectroscopic and X-ray analyses.

Preparation of $\{\eta^6\text{-}[\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}]_2Y\}\text{-}\{Li_5(THF)_{10}\}$ (12). This compound was prepared as orange-red crystals from the reaction of **7** (294 mg, 0.50 mmol) and Li metal (105 mg, 15.1 mmol) in THF (25 mL) using procedures similar to those used in the synthesis of **11**: yield 214 mg (64%). ^1H NMR (pyridine-d_5): δ 7.16 (m, 2H, aryl H), 7.10 (m, 2H, aryl H), 4.14 (d, J = 15.3 Hz, 1H, $C_6H_4(CH_2)_2$), 3.96 (d, J = 15.3 Hz, 1H, $C_6H_4(CH_2)_2$), 3.84 (d, J = 14.7 Hz, 1H, $C_6H_4(CH_2)_2$), 3.64 (m, 20H, THF), 2.74 (d, J = 14.7 Hz, 1H, $C_6H_4(CH_2)_2$), 1.63 (m, 20H, THF). ^{13}C NMR (pyridine-d_5): δ 144.7, 140.6, 129.7, 129.0, 126.8, 126.0 ($C_6H_4(CH_2)_2$), 49.4, 43.5 ($C_6H_4(CH_2)_2$), 68.2, 26.2 (THF); the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 10.58 (2B), 8.61 (1B), −0.45 (3B), −11.23 (1B), −16.61 (3B). IR (KBr, cm^{-1}): ν 2960 (vs), 2880 (s), 2400 (vs), 2349 (vs), 2317 (vs), 1631 (w), 1495 (m), 1259 (m), 1035 (vs), 803 (s). Anal. Calcd for $C_{34}H_{64}B_{20}Li_5O_{3.5}Y$ (**12**−6.5THF): C, 47.01; H, 7.43. Found: C, 47.14; H, 7.69.

Alternate Method. This compound was prepared as orange microcrystals from the reaction of YCl_3 (100 mg, 0.50 mmol) and **3** (706 mg, 0.50 mmol) in THF (25 mL) using procedures similar to those used above: yield 308 mg (46%).

Table 1. Crystal Data and Summary of Data Collection and Refinement Details for 4, 6·C_7H_8·0.5THF, and 8·0.5THF

	4	**6**·C_7H_8·0.5THF	**8**·0.5THF
formula	$C_{60}H_{76}B_{20}ClN_8NaYb_2$	$C_{31}H_{54}B_{10}ClErO_{3.5}$	$C_{24}H_{50}B_{11}NdO_{3.5}$
cryst size (mm)	0.56 × 0.44 × 0.42	0.42 × 0.34 × 0.31	0.51 × 0.50 × 0.48
fw	1530.0	793.6	657.8
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a, Å	18.262(2)	13.688(1)	11.025(1)
b, Å	11.260(1)	16.744(2)	12.674(1)
c, Å	21.324(2)	33.639(4)	14.215(1)
α, deg	90	90	94.77(1)
β, deg	111.45(1)	93.27(1)	99.65(1)
γ, deg	90	90	110.68(1)
V, Å^3	4081.0(6)	7697.2(14)	1810.1(2)
Z	2	8	2
D_{calcd}, Mg/m^3	1.245	1.370	1.207
radiation (λ), Å		Mo Kα (0.710 73)	
2θ range, deg	3.7−50.0	2.4−50.0	4.0−50.0
μ, mm^{-1}	2.353	2.281	1.458
F(000)	1520	3224	674
no. of obsd rflns	7145	4944	6340
no. of params refnd	499	399	376
goodness of fit	1.086	1.328	1.027
R1	0.047	0.094	0.072
wR2	0.128	0.193	0.182

Preparation of $[\{\eta^6\text{-}[\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}]_2\text{-}Er\}\{Na_5(THF)_6\}]_4$ (13). This compound was prepared as orange-red crystals from the reaction of **6** (333 mg, 0.50 mmol) and Na metal (110 mg, 4.78 mmol) in THF (25 mL) using procedures similar to those used in the synthesis of **11**: yield 229 mg (76%). ^1H NMR (pyridine-d_5): δ 3.68 (br s), 1.68 (br s) (THF), and other broad, unresolved resonances. ^{13}C NMR (pyridine-d_5): δ 67.6, 25.6 (THF); other carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 10.82 (2B), 8.94 (1B), −0.19 (3B), −10.90 (1B), −16.30 (3B). IR (KBr, cm^{-1}): ν 2960 (s), 2911 (w), 2401 (vs), 2347 (vs), 1625 (m), 1453 (m), 1260 (m), 1086 (vs), 1033 (vs), 804 (s). Anal. Calcd for $C_{128}H_{240}B_{80}Er_4Na_{20}O_{12}$ (**13**−12THF): C, 38.78; H, 6.10. Found: C, 39.07; H, 6.25.

X-ray Structure Determination. All single crystals were immersed in Paratone-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.[11] 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.[12] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For the noncentrosymmetric structures **10** and **11**, the Flack parameters are 0.858(11) and 0.000(7), respectively.[13] Crystal data and details of data collection and structure refinements are given in Tables 1 and 2. Key structural data are listed in Table 3. Further details are included in the Supporting Information.

Results and Discussion

Synthesis and Reactivity. Interaction of $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$ (**2**) with 2

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

(12) Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.

(13) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

Table 2. Crystal Data and Summary of Data Collection and Refinement Details for 10, 11, and 13

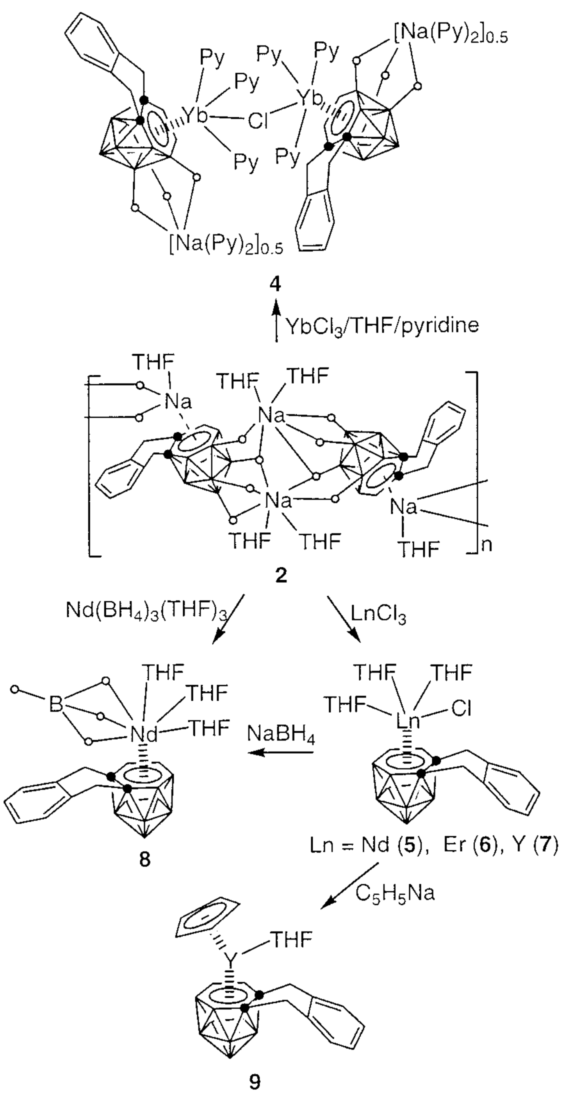
	10	**11**	**13**
formula	$C_{56}H_{108}B_{20}$-$GdLi_5O_9$	$C_{60}H_{116}B_{20}$-$ErLi_5O_{10}$	$C_{176}H_{336}B_{80}$-$Er_4Na_{20}O_{24}$
cryst size (mm)	0.50 × 0.34 × 0.30	0.50 × 0.15 × 0.15	0.54 × 0.52 × 0.50
fw	1333.6	1415.7	4830.1
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1$	$P2_1$	$P\bar{1}$
a, Å	11.775(1)	11.744(2)	19.154(2)
b, Å	24.968(2)	24.878(4)	20.997(2)
c, Å	13.371(1)	13.357(2)	21.110(2)
α, deg	90	90	113.22(1)
β, deg	102.54(1)	102.39	106.03(1)
γ, deg	90	90	93.34(1)
V, Å^3	3837.2(5)	3811.5(10)	7363.3(7)
Z	2	2	1
D_{calcd}, Mg/m^3	1.154	1.234	1.089
radiation (λ), Å		Mo Kα (0.710 73)	
2θ range, deg	3.1−50.0	3.3−50.0	2.2−50.0
μ, mm^{-1}	0.909	1.151	1.204
$F(000)$	1390	1478	2476
no. of obsd rflns	9152	10314	19215
no. of params refnd	821	593	1474
goodness of fit	0.955	0.882	0.998
R1	0.096	0.074	0.079
wR2	0.223	0.149	0.238

Table 3. Selected Structural Data for *o*-Carboranes and Their Metal Complexes

	C_{cage}−C_{cage} (Å)	av M−C_{cage} (Å)	av M−B_{cage} (Å)	av M−C_2B_4 (Å)	av M···B_3 (Å)	av C_{cage}−C−C_{aryl} (deg)
1[a]	1.646(3)					115.6(2)
2 (M = Na)[b]	1.444(4)	2.876(4)	2.844(4)	2.854(4)	3.026(4)	114.8(3)
3 (M = Li)[b]	1.562(6)	2.297(8)	2.325(9)	2.315(9)	2.654(10)	111.0(4)
4 (M = Yb)	1.439(3)	2.917(2)	2.883(4)	2.894(4)		114.0(2)
6 (M = Er)	1.45(2)	2.85(2)	2.72(2)	2.77(2)		111.6(14)
8 (M = Nd)	1.423(8)	2.967(7)	2.825(10)	2.872(10)		111.5(6)
10 (M = Gd)	1.535(9)	2.587(6)	2.738(6)	2.688(6)		113.2(6)
11 (M = Er)	1.486(6)	2.471(4)	2.680(4)	2.610(4)		112.1(5)
13 (M = Er)	1.558(6)	2.559(4)	2.654(4)	2.622(4)		110.4(4)

[a] See ref 9b. [b] See ref 8a.

Scheme 1



equiv of $LnCl_3$ gave, after workup, the novel half-sandwich lanthanacarboranes $[\eta^6$-$\{\mu$-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}\}]LnCl(THF)_3$ (Ln = Nd (**5**), Er (**6**), Y (**7**)) in good yields. Under similar reaction conditions, treatment of $YbCl_3$ with **2** in a molar ratio of 2:1 in THF, however, resulted in the formation of the organoytterbium(II) complex $[\eta^6$-$\{\mu$-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}\}$-$Yb(NC_5H_5)_3\{Na(NC_5H_5)_2\}_{0.5}]_2(\mu$-Cl) (**4**), which suggested that **2** can reduce Yb^{3+} to Yb^{2+}.[14−16] Reaction of $[\{\mu$-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$ (**2**) with 2 equiv of $Nd(BH_4)_3(THF)_3$ in THF at room temperature gave, after workup, $[\eta^6$-$\{\mu$-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}\}]Nd[(\mu$-H$)_3BH](THF)_3$ (**8**) in 64% yield (Scheme 1). Complexes **5**−**7** represent the first examples of half-sandwich lanthanacarboranes containing a terminal Ln−Cl bond in the C_2B_{10} systems. The presence of a terminal Ln−Cl bond makes them very important starting materials. Reaction of **5** with 1 equiv of $NaBH_4$ in THF gave **8** in 53% isolated yield. Treatment of **7** with 1 equiv of C_5H_5Na in THF afforded the mixed-sandwich complex $[\eta^6$-$\{\mu$-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}\}]Y(\eta^5$-$C_5H_5)(THF)$ (**9**). Interaction of **6** or **7** with excess Li metal led to the isolation of the full-sandwich complexes $\{\eta^6$-[μ-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}]_2Ln\}$-$\{Li_5(THF)_{10}\}$ (Ln = Er (**11**), Y (**12**)). Treatment of **6** with excess Na metal yielded the full-sandwich cluster $[\{\eta^6$-[μ-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}]_2Er\}\{Na_5(THF)_6\}]_4$ (**13**). Complexes **11** and **12** were also prepared from an equimolar reaction of $[\{\mu$-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}\}Li_4(THF)_6]_2$ (**3**) with $LnCl_3$ in THF. Their Gd analogue $\{\eta^6$-[μ-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}]_2Gd\}$-$\{Li_5(THF)_9\}$ (**10**) was prepared by “one-pot” synthesis, mixing μ-1,2-[o-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$ (**1**), 1 equiv of $GdCl_3$, and excess Li metal in THF. It is noted that interactions between **7** and MeLi or $(Me_3Si)_2CHK$ did not lead to the isolation of a pure product, probably due to the deprotonation of the CH_2 groups, resulting in a mixture of complexes. The aforementioned transformations are outlined in Schemes 1 and 2, respectively.

These lanthanacarboranes are all soluble in polar organic solvents such as pyridine and THF, slightly soluble in toluene, and insoluble in n-hexane. They were characterized by various spectroscopic data and elemental analyses. The solid-state structures of complexes **4**,

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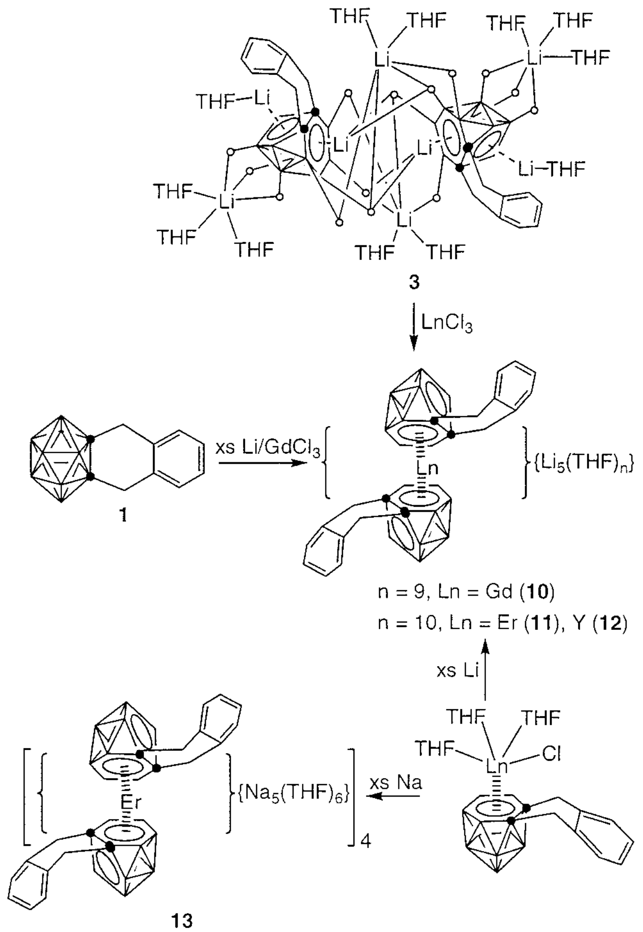
(14) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641.

(15) Xie, Z.; Liu, Z.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3603.

(16) Khattar, R.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 1970.

Scheme 2



6, **8**, **10**, **11**, and **13** were further confirmed by single-crystal X-ray analyses.

The NMR spectra of metallacarboranes of Gd and Er are not very informative, due to the strong paramagnetism of Gd^{3+} ($\mu_{eff} = 7.9\ \mu_B$) and Er^{3+} ($\mu_{eff} = 9.5\ \mu_B$).[17] The THF to carboranyl ligand ratios in these complexes are then determined from their hydrolysis products. The ^{1}H NMR spectra indicate that the two methylene protons of the *o*-xylenyl group in the complexes are nonequivalent and support the ratio of four pyridine, three THF, one THF, and five THF molecules per carboranyl ligand for **4**, **7**, **9**, and **12**, respectively. The ^{13}C NMR spectra are consistent with the results derived from their ^{1}H NMR spectra. The ^{11}B NMR spectra exhibit 1:2:2:2:2:1, 3:3:1:2:1, 2:3:2:1:1:1, and 2:1:3:1:3 splitting patterns for **4**, **7**, **9**, and **12**, respectively. The IR spectrum of **8** shows a typical strong and broad characteristic carborane B−H absorption at 2516 cm^{-1}, a characteristic doublet centered around 2420 cm^{-1}, and a shoulder at about 2240 cm^{-1} attributable to the tridentate BH_4^- anion with a M−H−B stretching mode.[18] The solid-state IR spectra of **5**−**7** and **9** show only a typical strong and broad characteristic B−H absorption at about 2520 cm^{-1}. Those of **4** and **10**−**13** display a characteristic doublet centered around 2450 cm^{-1} and a shoulder at about 2310 cm^{-1} attributable to a M−H−B stretching mode.[19,20]

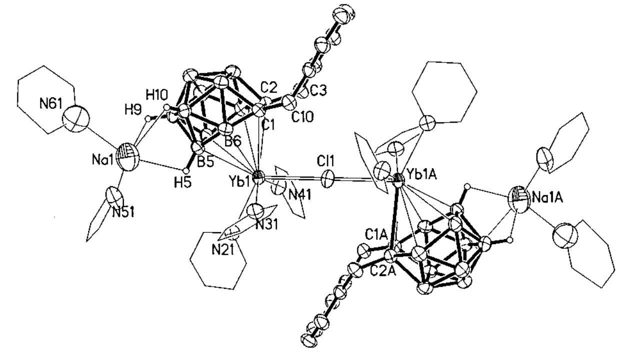


Figure 1. Molecular structure of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}Yb$(NC_5H_5)_3${Na$(NC_5H_5)_2$}$_{0.5}$]$_2$(μ-Cl) (**4**). Note that the Na atoms are positionally disordered over two sets of positions with 0.5:0.5 occupancies.

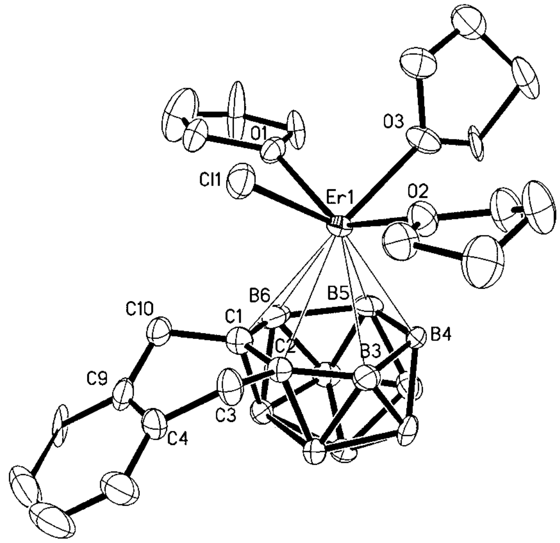


Figure 2. Molecular structure of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]ErCl(THF)$_3$ (**6**).

Molecular Structure. An X-ray analysis reveals that **4** is a centrosymmetric dimer with the Cl atom located at an inversion center, shown in Figure 1. Note that the Na atoms are positionally disordered over two sets of positions with 0.5:0.5 occupancies. The central Yb atom is η^6-bound to an open C_2B_4 bonding face, σ-bound to one doubly bridging Cl atom, and coordinated to three pyridine molecules in a highly distorted square-pyramidal geometry. The average Yb−cage atom distance of 2.894(4) Å compares to the 2.74 Å observed in (η^5-$C_2B_9H_{11}$)Yb(DMF)$_4$ (DMF = *N*,*N*-dimethylformamide).[21]

As shown in Figure 2, **6** is a monomeric half-sandwich molecule. The Er^{3+} ion is η^6-bound to a hexagonal bonding face of the "carbons-adjacent" carborane, σ-bound to a terminal chloro ligand, and coordinated to three

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[17] Cotton, S. *Lanthanides and Actinides*; Oxford University Press: New York, 1991; p 11.

[18] Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1983**, 206.

[19] (a) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Xue, F.; Mak, T. C. W. *Organometallics* **1998**, *17*, 489. (b) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907. (c) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641. (d) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 2420. (e) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 4478. (f) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 1578.

[20] (a) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 2191. (b) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.

[21] Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009.

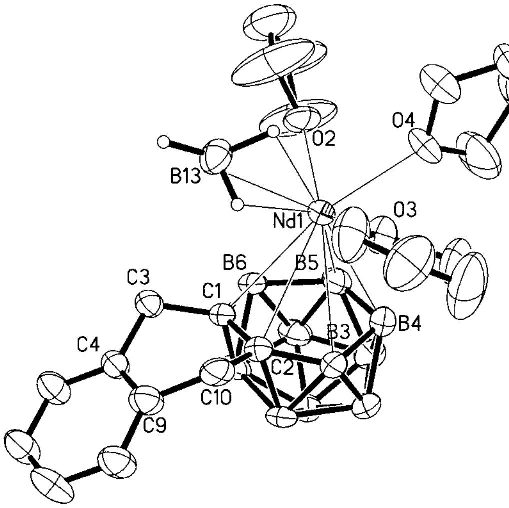

Figure 3. Molecular structure of [η^6-{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}]Nd[(μ-H)$_3$BH](THF)$_3$ (**8**).

THF molecules in a distorted-square-pyramidal geometry. The terminal Er−Cl distance of 2.542(4) Å is comparable to those normally observed in organoerbium chloride complexes.[22] The average Er−cage atom distance of 2.765(18) Å is comparable to the 2.705(7) Å found in [η^5:η^6-$Me_2C(C_5H_4)(C_2B_{10}H_{11})$]Er(THF)$_2$.[5c] To the best of our knowledge, **6** is the first structurally characterized example of a half-sandwich lanthanacarborane bearing a terminal Ln−Cl bond.

The solid-state structure of **8** is shown in Figure 3. Replacement of a chloride atom by a BH_4^- moiety does not alter the bonding interactions between the lanthanide ion and carborane anion. The tridentate bonding mode of the BH_4^- group is assigned by comparing the Nd(1)···B(13) distance of 2.660(9) Å with the reported values of 2.642(7) and 2.658(6) Å in [{$Ph_2C(\eta^5$-$C_{13}H_8)(\eta^5$-$C_5H_4)$}Nd{(μ-H)$_3$BH}$_2$][Li(THF)$_4$],[23] which is also supported by the IR spectroscopy.[18]

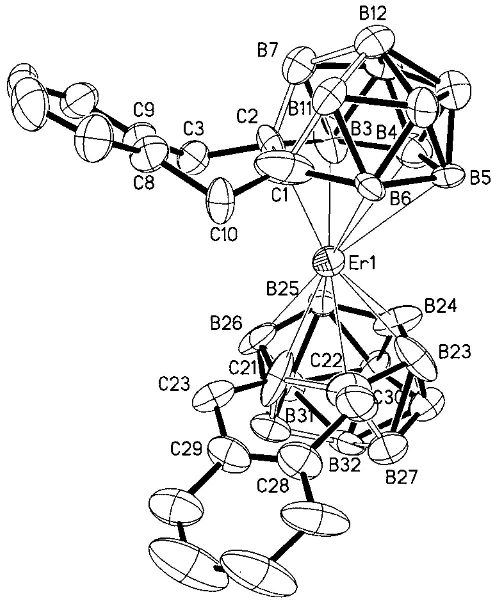

Figure 4. Molecular structure of the anion [{η^6-[μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$]$_2$Er}]$^{5-}$ in **11**.

The single-crystal X-ray analyses reveal that complexes **10** and **11** are isomorphous and isostructural, consisting of the full-sandwich lanthanacarborane moiety {η^6-[μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$]$_2$Ln}$^{5-}$ and five associated complex ions {Li(THF)$_x$}$^+$. Figure 4 shows their representative structure. It is noteworthy that the pentagonal C_2B_3 face (indicated by the open bonds) does not have any bonding interactions with the Li^+ ions, which differs significantly from the case for the parent lithium salt [{μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$}{$Li_4(THF)_6$}]$_2$ (**3**).[8a] The two hexagonal bonding faces are not parallel to each other, with dihedral angles of 20.5° in **10** and 14.1° in **11**, and the cent−Ln−cent angles are 152.1° in **10** and 156.2° in **11** (cent = the centroid of the C_2B_4 ring), respectively. It is interesting to note that these full-sandwich complexes have been observed to exist in a "cisoid" structure in which the cage carbon atoms of the opposing ligand cages reside on the same side of the molecule in a staggered configuration.

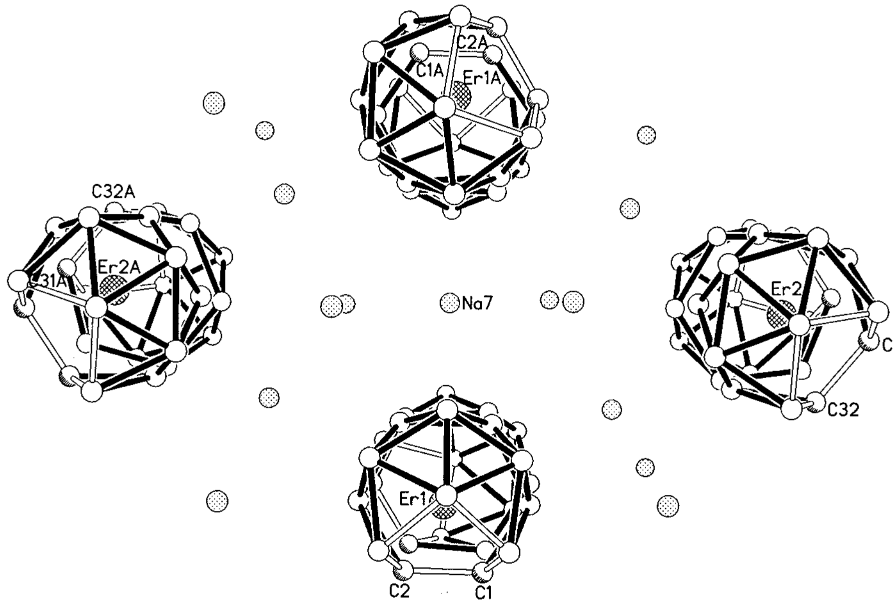

Figure 5. Molecular structure of [{η^6-[μ-1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$]$_2$Er}{$Na_5(THF)_6$}]$_4$ (**13**). All THF molecules, *o*-xylenyl groups, H atoms, terminal Na(THF)$_x^+$ complex ions, and bonds around Er and Na atoms are omitted for clarity.

An X-ray diffraction study shows that **13** is a novel centrosymmetric cluster with the Na(7) locating at an inversion center. The 4 full-sandwich structure motifs are connected to each other by 15 Na^+ ions via Na−H−B bonding interactions, shown in Figure 5. The charge is then compensated by complexation with five $Na(THF)_x{}^+$ complex ions, resulting in the formation of a large cluster. This result may indicate that the larger group 1 ions could facilitate the self-assembly of these full-sandwich metallacarboranes. The dihedral angles of the two hexagonal bonding faces are 12.7° in the Er(1) unit and 7.2° for the Er(2) moiety. The cent−Er−cent angles are 162.7 and 166.8° for Er(1) and Er(2) centers, respectively, which are much larger than the corresponding value in **11**. The average Er−cage atom distances of 2.616(5) and 2.628(5) Å are close to the value of 2.610(5) Å in **11** but significantly shorter than the 2.765(18) Å in **6**, suggesting that the Er^{3+} has much stronger interactions with *arachno*-carborane anions.

Conclusion

This work has demonstrated that the group 1 salts of "carbons-adjacent" *nido*- and *arachno*-carborane anions are very useful synthons for the production of other metallacarboranes, leading to the preparation and structural characterization of a new class of "carbons-adjacent" lanthanacarboranes.

Half-sandwich lanthanacarboranes containing a terminal Ln−Cl bond, analogues to Cp_2LnCl, have been structurally characterized for the first time. The results of this work show that they furnish important starting materials for the preparation of complexes bearing Ln−C and Ln−heteroatom bonds.

The full-sandwich lanthanacarborane complexes have two additional five-membered bonding faces readily available for bonding, which might result in the formation of multi-sandwich metallacarboranes.[1b]

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Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures giving atom-numbering schemes for complexes **4**, **6**, **8**, **10**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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