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Synthesis, Structure, and Reactivity of Organolanthanide Carboranyl Compounds and Lanthanacarboranes Derived from a Versatile Ligand, $Me_2C(C_5H_5)(C_2B_{10}H_{11})$

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The compound $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (**I**) could be conveniently converted into the monoanion $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]^-$ (**I-1**) and the dianion $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ (**I-2**) by treatment with excess NaH and 2 equiv of *n*-BuLi, respectively. The monoanion **I-1** could be further converted into the trianion $[Me_2C(C_5H_4)(\textit{nido}\text{-}C_2B_{10}H_{11})]^{3-}$ (**I-3**) by reaction with 2 equiv of Na metal in THF and into the pentaanion $[Me_2C(C_5H_4)(\textit{arachno}\text{-}C_2B_{10}H_{11})]^{5-}$ in the presence of $LnCl_3$ and excess Na metal in THF. Reactions of $LnCl_3$ with the monoanion **I-1** in molar ratios of 1:1, 1:2, and 1:3 generated the mono-, bis-, and tris-ligated organolanthanide compounds $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]LnCl_2(S)_n$ ($(S)_n$ = $(THF)_3$, Ln = Er (**1**), Sm (**2**); $(S)_n$ = $(DME)_2$, Ln = Nd (**3**)), $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_2SmCl(THF)_2$ (**4**), and $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_3Sm\cdot 0.5C_7H_8$ (**5**), respectively. Reaction of $LnCl_3$ with 1 or 2 equiv of the dianion **I-2** gave the same compound, $[\{\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}_2Ln][Li(DME)_3]$ (Ln = Sm (**6**), Yb (**7**)). **6** could also be prepared by treatment of **2** with 1 equiv of the dianion **I-2**. Reaction of YbI_2 with 1 equiv of **I-2**, followed by treatment with 1 equiv of **I-1**, also gave compound **7**. However, YbI_2 reacted with 2 equiv of **I-1** to afford the organoytterbium(II) compound $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_2Yb(THF)_2$ (**8**). Interaction of SmI_2 with 2 equiv of **I-1** yielded two compounds, the redox product $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Sm(THF)_2$ (**9**) and the tris-ligated compound **5**. The compound $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$ (**10**), an analogue of **9**, was prepared by treatment of **1** with 2 equiv of Na metal or by reaction of $ErCl_3$ with 1 equiv of **I-3**. Treatment of **10** with excess Na metal gave the first organolanthanide compound containing a η^7-carboranyl ligand, $[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$ (**11**). Its Dy analogue, $[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Dy\}_2\{Na_4(THF)_9\}]_n$ (**12**), could also be prepared by a "one-pot" reaction of $DyCl_3$, **I-1**, and excess Na metal. Treatment of **11** with 2 equiv of $ErCl_3$ in THF gave the novel tetranuclear cluster $[\{\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})\}Er_2(\mu\text{-}Cl)(THF)_3]_2$ (**13**), in which the Er^{3+} ions replace all Na^+ ions in **11**. All of these compounds were fully characterized by various spectroscopic data and elemental analyses. The solid-state structures of compounds **4**−**11** and **13** have been confirmed by single-crystal X-ray analyses.

Introduction

By taking advantage of unique carborane molecules[1] and traditional cyclic π-ligands such as cyclopentadienyl and indenyl as well as bridging ligands,[2] we have designed two types of silicon-bridged versatile ligands, $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$[3] and $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$,[4] which have led to the isolation and structural characterization of a new class of organolanthanide compounds. Since the Me_2Si linkage is susceptible to nucleophilic attack,[4] the carbon-bridged ligand $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ was then recently developed in our laboratory.[5] The results show that both the cyclic organic group and the bridging atom have a large influence on the acidity of the CH proton of the carborane cage in these ligand systems, which in turn affects the reactivity of the resulting organolanthanide compounds.[3−5] They also indicate that the C−C(carborane) bond can be broken under traditional deboronation conditions such as KOH/MeOH[6] presumably due to the

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electron-withdrawing ability of the indenyl group, leading to the formation of *nido*-$C_2B_9H_{12}^-$.

To prepare a bridged trianion ligand bearing both a cyclopentadienyl ring and a dicarbollide group which may offer organometallic compounds with "self-correcting" behavior in the catalytic reactions,[7] we have paid attention to the $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ ligand[8] in the hope that the less electron-withdrawing power of the cyclopentadienyl group may enhance the stability of the C−C(carborane) bond toward nucleophilic attack, leading to the possible formation of $[Me_2C(C_5H_4)($*nido*-$C_2B_9H_{10})]^{3-}$ under deboronation conditions. On the other hand, it would allow us to make comparisons between the Me_2Si- and Me_2C-linked versatile ligands. Although all attempts to prepare a trianion of the type $[Me_2C(C_5H_4)($*nido*-$C_2B_9H_{10})]^{3-}$ suffered from the cleavage of the C−C(carborane) bond, our efforts have led to the isolation and structural characterization of the first example of a lanthanacarborane bearing a η^7-carboranyl ligand.

It has been well-documented that the alkali metals can reduce the neutral carborane $C_2B_{10}H_{10}R_2$ to the carborane dianion $[$*nido*-$C_2B_{10}H_{10}R_2]^{2-}$, which is able to form the 13-vertex *closo*-metallacarboranes with the metal ions in a η^6 fashion.[1,9] Such a metallacarborane can be further reduced by Na metal to form a 14-vertex *closo*-metallacarborane. For example, reaction of $(\eta^6\text{-}C_2B_{10}H_{12})Co(\eta^5\text{-}C_5H_5)$ with Na/naphthalene, followed by treatment with C_5H_5Na and $CoCl_2$, gave the 14-vertex *closo*-metallacarborane $[(\eta^6{:}\eta^6\text{-}C_2B_{10}H_{12})\{Co(\eta^5\text{-}C_5H_5)\}_2]$ with the proposed geometry of a bicapped hexagonal antiprism.[10] Although an X-ray confirmation of this species has not been reported, successful structural characterization of another 14-vertex *closo*-metallacarborane, $[\{\eta^6{:}\eta^6\text{-}(CH_3)_4C_4B_8H_8\}\{Fe(\eta^5\text{-}C_5H_5)\}_2]$, has indicated that the bicapped-hexagonal-antiprism species is indeed the thermodynamically favored form.[11] Nevertheless, the highest hapticity of carboranyl ligands in all of the known metallacarboranes described in the literature is 6, until our recent report on the unprecedented mixed-sandwich compound $[\{(\eta^7\text{-}C_2B_{10}H_{12})(\eta^6\text{-}C_2B_{10}H_{12})U\}\{K_2(THF)_5\}]_2$, in which the U atom is η^7-bound to one of the $C_2B_{10}H_{12}$ ligands.[12] We have found new members of this novel class of metallacarboranes[13] and report herein a detailed study on the syntheses, structural characterization, and reactivity of organolanthanide chlorides and carboranyl compounds as well as lanthanacarboranes containing a η^6- or η^7-carboranyl ligand. The mechanisms for the formation of these *closo*-lanthanacarboranes are also proposed. A portion of this work has been previously communicated.[13]

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen, with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous $LnCl_3$,[14] $LnI_2(THF)_x$ (Ln = Sm, Yb),[15] 6,6-dimethylfulvene,[16] and $Li_2C_2B_{10}H_{10}$[17] were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 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 reference to internal or external TMS (0.00 ppm) or with respect to the residual protons of the deuterated solvent 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 $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (I). This compound was prepared by using a modified literature method.[8] To a solution of *o*-$C_2B_{10}H_{12}$ (1.00 g, 6.90 mmol) in a dry toluene/diethyl ether (2:1) mixture at 0 °C was added a 1.60 M solution of *n*-BuLi in *n*-hexane (8.7 mL, 13.90 mmol) dropwise with stirring. The mixture was warmed to room temperature and stirred for 2 h. The solution was then cooled to 0 °C, and a solution of 6,6-dimethylfulvene (0.95 g, 9.00 mmol) in a toluene/diethyl ether (2:1) mixture was slowly added. The reaction mixture was stirred at 90 °C overnight and then quenched with 20 mL of a saturated NH_4Cl aqueous solution at 0 °C, transferred to the separatory funnel, and diluted with 30 mL of diethyl ether. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3×15 mL). The combined ether solutions were dried over anhydrous $MgSO_4$ and concentrated to give a crude white solid, which was recrystallized from a EtOH solution to give a white crystalline solid (1.48 g, 85%). ^1H NMR ($CDCl_3$): δ 6.52 (m, 1H, Cp), 6.47 (m, 1H, Cp), 6.21 (m, 1H, Cp), 3.33 (s, 1H, CH of carboranyl), 3.00 (m, 2H, methylene of Cp), 1.52 (s, 6H, C*Me*$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −4.7 (1B), −5.2 (1B), −9.8 (2B), −12.3 (2B), −14.6 (4B).[8]

Preparation of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (I-1). To a suspension of NaH (0.18 g, 7.5 mmol) in 20 mL of THF was slowly added a THF solution (20 mL) of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (**I**; 1.40 g, 5.6 mmol), and the mixture was stirred at room temperature overnight. The excess NaH was filtered off, and the clear colorless solution was then concentrated under vacuum to about 8 mL. After addition of *n*-hexane (20 mL), the white precipitate was collected, washed with *n*-hexane (10 mL × 2), and dried under vacuum, giving **I-1** as a white solid (1.85 g, 96%). ^1H NMR (pyridine-d_5): δ 6.40 (m, 2H, Cp), 6.30 (m, 2H, Cp), 3.65 (m, 4H, THF), 3.31 (s, 1H, CH of carboranyl), 1.70 (s, 6H, C*Me*$_2$), 1.62 (m, 4H, THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 103.4, 102.4 (C_5H_4), 92.1, 67.3 ($C_2B_{10}H_{11}$), 67.2, 25.1 (OC_4H_8), 41.5, 31.7 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −3.0 (2B), −5.0 (2B), −9.5 (3B), −13.9 (3B). IR (KBr, cm^{-1}): ν 3062 (m), 2985 (m), 2941 (m), 2879 (w), 2594 (vs), 1634 (w), 1456 (m), 1362 (m), 1261 (w), 1160 (w), 1075

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(m), 1017 (s), 894 (m), 801 (m), 733 (m), 666 (m), 629 (w). Anal. Calcd for $C_{10}H_{21}B_{10}Na$ (**I-1**−THF): C, 44.10; H, 7.77. Found: C, 44.45; H, 7.83.

Preparation of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (I-2). To a solution of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (**I**; 0.50 g, 2.0 mmol) in a dry diethyl ether/*n*-hexane (2:1, 15 mL) mixture was slowly added a 1.60 M solution of *n*-BuLi in *n*-hexane (2.5 mL, 4.0 mmol) at 0 °C with stirring, and the mixture was warmed to room temperature and stirred overnight. The precipitate was filtered off, washed with *n*-hexane (10 mL × 3), and then dried under vacuum to yield a white powder (0.73 g, 89%). ^1H NMR (pyridine-d_5): δ 6.46 (m, 2H, Cp), 6.30 (m, 2H, Cp), 3.46 (q, $J = 6.9$ Hz, 8H, Et_2O), 2.14 (s, 6H, C*Me*$_2$), 1.28 (t, $J = 6.9$ Hz, 12H, Et_2O). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 104.7, 103.0, 102.8 (C_5H_4), 66.2, 15.9 ($(CH_3CH_2)_2O$), 42.4, 34.0 ($(CH_3)_2C$); the carbon atoms of the cage were not observed. $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −5.2 (5B), −9.4 (5B). IR (KBr, cm^{-1}): ν 3061 (w), 2986 (m), 2882 (w), 2596 (vs), 1606 (w), 1495 (w), 1457 (m), 1361 (m), 1261 (w), 1158 (w), 1076 (s), 1022 (s), 897 (w), 802 (m), 735 (m), 668 (w), 626 (w), 493 (m). Anal. Calcd for $C_{10}H_{20}B_{10}Li_2$ (**I-2**−2OEt$_2$): C, 45.62; H, 8.04. Found: C, 45.80; H, 8.30.

Preparation of $[Me_2C(C_5H_4)($*nido*$\text{-}C_2B_{10}H_{11})]Na_3(THF)_3$ (I-3). To a THF solution (15 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.18 g, 0.56 mmol) was added sodium metal (0.026 g, 1.13 mmol), and the mixture was stirred at room temperature until all the metal disappeared to give a colorless solution. This solution was concentrated to about 2 mL; *n*-hexane vapor diffusion gave a white solid (0.21 g, 70%). ^1H NMR (pyridine-d_5): δ 6.88 (m, 2H, Cp), 6.40 (m, 2H, Cp), 3.64 (m, 12H, THF), 2.69 (s, 1H, CH of carboranyl), 2.27 (s, 6H, C*Me*$_2$), 1.60 (m, 12H, THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 102.4, 100.3 (C_5H_4), 67.2, 25.1 (OC_4H_8), 46.9 ($C_2B_{10}H_{11}$), 44.0, 32.6 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −2.3 (1B), −6.6 (2B), −11.0 (3B), −15.9 (2B), −24.8 (1B), −34.7 (1B). IR (KBr, cm^{-1}): ν 3060 (w), 2960 (vs), 2874 (s), 2463 (vs), 1455 (m), 1365 (w), 1258 (w), 1100 (w), 1040 (vs), 901 (m), 802 (m), 726 (s), 503 (w). Anal. Calcd for $C_{14}H_{29}B_{10}Na_3O$ (**I-3**−2THF): C, 43.06; H, 7.49. Found: C, 43.32; H, 7.66.

Attempted Preparation of $[Me_3NH][Me_2C(C_5H_5)($*nido*$\text{-}C_2B_9H_{11})]$. To a mixture of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (**I**; 0.10 g, 0.40 mmol) and KOH (0.078 g, 1.4 mmol) was added distilled CH_3OH (10 mL) with stirring at 0 °C. The reaction mixture was warmed to room temparature and then refluxed overnight. After removal of the solvent, water (3 mL) was added. The aqueous solution was neutralized with diluted HCl. Addition of aqueous Me_3NHCl solution gave a white precipitate. The product was filtered off, washed with water, and dried under vacuum to give $[Me_3NH][$*nido*$\text{-}C_2B_9H_{12}]$ as a white solid (0.071 g, 91%). ^1H NMR (acetone-d_6): δ 3.09 (s, *Me*$_3$NH). $^{11}B\{^1H\}$ NMR (acetone-d_6): δ −7.3 (2B), −13.2 (3B), −18.0 (2B), −29.4 (1B), −34.1 (1B).[6c]

Other deboronation reagents such as *n*-Bu_4NF/THF,[18] KF/Al_2O_3/CH_3CN,[19] and pyrrolidine[20] were also examined. ^{11}B NMR was used to follow these reactions, and the results showed that only *nido*-$C_2B_9H_{12}^-$ was obtained and the C−C(carborane) bond was completely broken.

Preparation of $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]ErCl_2(THF)_3$ (1). A THF solution (20 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.27 g, 0.79 mmol) was slowly added to a suspension of $ErCl_3$ (0.22 g, 0.80 mmol) in 10 mL of THF at room temperature. The mixture was then stirred overnight. The precipitate was filtered off, and the clear pink solution was concentrated under vacuum to about 15 mL; *n*-hexane vapor diffusion resulted in a pink crystalline solid (0.29 g, 52%). ^1H NMR (pyridine-d_5): δ 17.4 (br s, 2H, Cp), 3.7 (s, 12H, THF), 1.6 (s, 12H, THF), 1.5 (s, 6H, C*Me*$_2$), −2.4 (br s, 2H, Cp). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 67.3, 25.3 (OC_4H_8); other carbon atoms were not observed. $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −11.1 (2B), −13.3 (4B), −17.6 (4B). IR (KBr, cm^{-1}): ν 3060 (w), 2959 (s), 2879 (m), 2575 (vs), 1627 (w), 1460 (w), 1380 (w), 1261 (w), 1144 (w), 1024 (s), 913 (w), 794 (m), 499 (m). Anal. Calcd for $C_{18}H_{37}B_{10}Cl_2ErO_2$ (**1**−THF): C, 34.22; H, 5.90. Found: C, 34.68; H, 5.55.

Preparation of $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]SmCl_2(THF)_3$ (2). To a suspension of $SmCl_3$ (0.21 g, 0.82 mmol) in THF (20 mL) was slowly added a THF solution of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.27 g, 0.79 mmol) at room temperature, followed by procedures similar to those used in the synthesis of **1**, affording **2** as a yellow crystalline solid (0.34 g, 62%). ^1H NMR (pyridine-d_5): δ 10.5 (s, 2H, Cp), 7.65 (s, 2H, Cp), 3.74 (s, 1H, CH of carboranyl), 3.65 (m, 12H, THF), 1.61 (m, 12H, THF), 1.07(s, 6H, C*Me*$_2$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 125.2, 112.1, 106.8 (C_5H_4), 86.2, 64.4 ($C_2B_{10}H_{11}$), 67.1, 25.1 (OC_4H_8), 42.8, 27.8 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −6.1 (3B), −11.0 (3B), −13.0 (2B), −15.2 (2B). IR (KBr, cm^{-1}): ν 3061 (w), 2982 (m), 2957 (m), 2886 (w), 2575 (vs), 1631 (w), 1459 (w), 1373 (w), 1262 (w), 1143 (m), 1077 (s), 1043 (s), 1018 (s), 857 (m), 789 (s), 735 (w), 702 (w). Anal. Calcd for $C_{14}H_{29}B_{10}Cl_2OSm$ (**2**−2THF): C, 30.98; H, 5.39. Found: C, 31.03; H, 5.74.

Preparation of $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]NdCl_2(DME)_2$ (3). A solution of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.27 g, 0.79 mmol) in THF (20 mL) was slowly added to a suspension of $NdCl_3$ (0.20 g, 0.80 mmol) in 20 mL of THF. The mixture was then stirred at room temperature overnight. After removal of the solvent, the residue was extracted with DME (10 mL × 2). The clear blue solution was concentrated to about 13 mL; *n*-hexane vapor diffusion resulted in a pale blue crystalline solid (0.19 g, 43%). ^1H NMR (pyridine-d_5): δ 5.48 (br s, 2H, Cp), 3.56 (s, 8H, DME), 3.33 (s, 12H, DME), −1.92 (s, 6H, C*Me*$_2$), −6.06 (br s, 2H, Cp). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 202.5, 187.9, 169.3 (C_5H_4), 81.5 ($C_2B_{10}H_{11}$), 71.8, 58.4 ($O_2C_4H_{10}$), 41.2, 29.9 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −3.0 (2B), −8.2 (3B), −9.1 (2B), −11.1 (1B), −12.5 (2B). IR (KBr, cm^{-1}): ν 3057 (w), 2992 (w), 2947 (m), 2890 (w), 2564 (vs), 1613 (w), 1454 (m), 1379 (m), 1261 (w), 1144 (w), 1080 (s), 1039 (vs), 847 (s), 780 (s), 736 (w), 705 (w). Anal. Calcd for $C_{14}H_{31}B_{10}Cl_2NdO_2$ (**3**−DME): C, 30.32; H, 5.63. Found: C, 29.86; H, 5.70.

Preparation of $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_2SmCl(THF)_2$ (4). To a suspension of $SmCl_3$ (0.064 g, 0.25 mmol) in THF (10 mL) was slowly added a THF solution (15 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.17 g, 0.49 mmol), and the mixture was stirred at room temperature overnight. The precipitate was filtered off, and the clear yellow solution was concentrated under vacuum to about 15 mL. **4** was isolated as yellow crystals after this solution stood at room temperature for days (0.087 g, 43%). ^1H NMR (pyridine-d_5): δ 8.24 (s, 4H, Cp), 7.65 (s, 4H, Cp), 3.64 (m, 8H, THF), 3.55 (s, 2H, CH of carboranyl), 2.02 (s, 12H, C*Me*$_2$), 1.59 (m, 8H, THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 123.6, 110.9, 99.2 (C_5H_4), 82.5, 63.4 ($C_2B_{10}H_{11}$), 67.1, 25.1 (OC_4H_8), 44.3, 29.5 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −4.5 (6B), −9.8 (6B), −11.8 (4B), −14.0 (4B). IR (KBr, cm^{-1}): ν 3055 (m), 2983 (m), 2950 (m), 2883 (m), 2563 (vs), 1632 (w), 1461 (w), 1371 (m), 1265 (w), 1141 (m), 1072 (s), 1023 (s), 869 (s), 847 (s), 760 (s), 699 (m). Anal. Calcd for $C_{24}H_{50}B_{20}ClOSm$ (**4**−THF): C, 38.09; H, 6.66. Found: C, 38.56; H, 6.66.

Preparation of $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_3Sm\cdot 0.5C_7H_8$ (5). A THF solution (10 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.13 g, 0.52 mmol) was slowly added to a suspension of $SmCl_3$ (0.044 g, 0.17 mmol) in THF (5 mL). The mixture was stirred at room temperature overnight. The precipitate was filtered off, and the clear yellow solution was then concentrated under vacuum to about 2 mL. After addition of

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toluene (15 mL), yellow crystals were obtained from this solution upon standing at room temperature for several days (0.091 g, 57%). ^{1}H NMR (pyridine-d_5): δ 12.65 (s, 6H, Cp), 11.96 (s, 6H, Cp), 7.24 (m, 2.5H, $C_6H_5CH_3$), 4.43 (s, 3H, CH of carboranyl), 1.42 (s, 1.5H, $C_6H_5CH_3$), 0.05 (s, 18H, C*Me*$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 129.0, 128.3, 125.4, 22.5 ($C_6H_5CH_3$), 107.9, 103.1 (C_5H_4), 77.7, 62.9 ($C_2B_{10}H_{11}$), 46.4, 28.5 (($CH_3)_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ −3.9 (6B), −9.3 (9B), −11.5 (6B), −13.6 (9B). IR (KBr, cm^{-1}): ν 3061 (m), 2970 (m), 2909 (w), 2580 (vs), 1607 (w), 1457 (m), 1382 (s), 1262 (w), 1139 (m), 1032 (s), 784 (s), 733 (w), 506 (m). Anal. Calcd for $C_{37}H_{71}B_{30}Sm$ (**5**+0.5(toluene)): C, 44.86; H, 7.22. Found: C, 44.73; H, 7.16.

Preparation of [{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}$_2$Sm][Li(DME)$_3$] (6). To a suspension of $SmCl_3$ (0.069 g, 0.27 mmol) in 10 mL of THF was slowly added a THF solution (10 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ (**I-2**; 0.22 g, 0.54 mmol) at room temperature. The reaction mixture was then stirred overnight. After removal of the solvent under vacuum, the residue was extracted with toluene (15 mL × 2) to give a clear yellow solution. After addition of a few drops of DME, the solution was concentrated until some small crystals appeared on the wall of the flask, which was then allowed to stand at room temperature for 1 day, giving yellow crystals (0.15 g, 60%). ^{1}H NMR (pyridine-d_5): δ 11.08 (s, 2H, Cp), 8.40 (s, 2H, Cp), 6.74 (s, 2H, Cp), 4.11 (s, 6H, C*Me*$_2$), 3.52 (s, 6H, C*Me*$_2$), 3.49 (s, 8H, DME), 3.26 (s, 12H, DME), −1.17 (s, 2H, Cp). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 151.3, 112.7, 108.2, 102.7, 101.4 (C_5H_4), 87.8 ($C_2B_{10}H_{10}$), 71.4, 57.9 ($O_2C_4H_{10}$), 51.0, 35.4 (($CH_3)_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ −3.3 (2B), −4.7 (2B), −5.7 (4B), −8.3 (8B), −13.6 (4B). IR (KBr, cm^{-1}): ν 3081 (w), 2981 (m), 2930 (s), 2830 (m), 2554 (vs), 1602 (w), 1456 (m), 1369 (m), 1247 (m), 1186 (m), 1123 (s), 1085 (vs), 1033 (s), 867 (m), 833 (w), 773 (s), 696 (w). Anal. Calcd for $C_{28}H_{60}B_{20}LiO_4Sm$ (**6**−DME): C, 40.30; H, 7.25. Found: C, 39.84; H, 7.33.

Reaction of $SmCl_3$ with $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ (**I-2**) in THF in a molar ratio of 1:1 also gave compound **6** in 51% yield.

Alternate Method. To a THF solution (15 mL) of [η^5-$Me_2C(C_5H_4)(C_2B_{10}H_{11})]SmCl_2(THF)_3$ (**2**; 0.27 g, 0.39 mmol) was added a THF solution (10 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ (**I-2**; 0.16 g, 0.40 mmol) dropwise. The mixture was stirred at room temperature overnight, followed by the procedures used above to give **6** as yellow crystals (0.098 g, 54% based on **I-2**).

Preparation of [{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}$_2$Yb][Li(DME)$_3$] (7). This compound was prepared as orange-yellow crystals from $YbCl_3$ (0.064 g, 0.23 mmol) and $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ (**I-2**; 0.19 g, 0.46 mmol) in 25 mL of THF using the procedures given above for **6**. Yield: 0.15 g (69%). ^{1}H NMR (pyridine-d_5): δ 133.1 (br s, 1H, Cp), 88.6 (br s, 1H, Cp), 52.3 (br s, 1H, Cp), 21.5 (br s, 1H, Cp), 17.6 (br s, 1H, Cp), 13.0 (br s, 1H, Cp), 3.5 (s, 8H, DME), 3.2 (s, 12H, DME), −4.3 (br s, 1H, Cp), −26.6 (s, 6H, C*Me*$_2$), −31.0 (s, 6H, C*Me*$_2$), −91.6 (br s, 1H, Cp). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 71.7, 58.2 ($O_2C_4H_{10}$); other carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 65.8 (2B), 34.6 (2B), 16.0 (4B), 12.1 (2B), 2.66 (2B), −4.09 (2B), −13.6 (2B), −23.3 (4B). IR (KBr, cm^{-1}): ν 3091 (w), 2980 (m), 2930 (s), 2826 (m), 2587 (vs), 1471 (m), 1451 (m), 1365 (m), 1244 (m), 1188 (m), 1124 (s), 1086 (vs), 1050 (s), 1025 (s), 868 (m), 836 (w), 786 (s), 739 (w), 703 (w). Anal. Calcd for $C_{32}H_{70}B_{20}LiO_6Yb$: C, 40.58; H, 7.45. Found: C, 40.23; H, 7.35.

Reaction of $YbCl_3$ with $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ (**I-2**) in THF in a molar ratio of 1:1 also gave compound **7** in 50% yield.

Alternate Method. To a THF solution of $YbI_2(THF)_x$ (8.6 mL, 0.41 mmol) was added a solution of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ (**I-2**; 0.17 g, 0.41 mmol) in THF (10 mL). The mixture was then stirred at room temperature overnight to give a dark red solution, which was filtered into a THF solution (10 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.14 g, 0.41 mmol). The mixture was then refluxed for 3 days. The color of the solution gradually changed to red. This clear solution was then concentrated to about 5 mL. After addition of toluene (15 mL) and a few drops of DME, the resulting solution was allowed to stand at room temperature overnight, giving **7** as orange-yellow crystals (0.13 g, 33%).

Preparation of [η^5-$Me_2C(C_5H_4)(C_2B_{10}H_{11})$]$_2$Yb(THF)$_2$ (8). To a THF solution of $YbI_2(THF)_x$ (7.0 mL, 0.40 mmol) was added dropwise a THF solution (20 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.28 g, 0.81 mmol) with stirring. The mixture was then stirred at room temperature overnight. After removal of the solvent under vacuum, the residue was extracted with hot toluene (10 mL × 3). Slow evaporation of the solvent at room temperature gave dark red crystals (0.15, 45%). ^{1}H NMR (pyridine-d_5): δ 6.06 (m, 4H, Cp), 5.96 (m, 4H, Cp), 3.73 (m, 8H, THF), 2.80 (s, 2H, CH of carboranyl), 1.64 (s, 12H, C*Me*$_2$), 1.61 (m, 8H, THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.8, 107.6, 105.9 (C_5H_4), 88.6, 65.7 ($C_2B_{10}H_{11}$), 67.1, 25.1 (OC_4H_8), 40.2, 30.9 (($CH_3)_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ −3.9 (4B), −9.1 (4B), −11.3 (4B), −13.5 (8B). IR (KBr, cm^{-1}): ν 3047 (w), 2967 (m), 2886 (w), 2573 (s), 1614 (w), 1454 (w), 1383 (s), 1261 (m), 1077 (s), 1031 (vs), 876 (w), 806 (s), 746 (m), 698 (w). Anal. Calcd for $C_{28}H_{56}B_{20}O_2Yb$: C, 41.21; H, 7.16. Found: C, 41.06; H, 7.09.

Preparation of [η^5:η^6-$Me_2C(C_5H_4)(C_2B_{10}H_{11})$]Sm(THF)$_2$ (9). To a THF solution of $SmI_2(THF)_x$ (3.0 mL, 0.30 mmol) was slowly added a THF solution (15 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.21 g, 0.61 mmol) at room temperature with stirring. The reaction mixture was then stirred overnight. After removal of the solvent under vacuum, the residue was extracted with hot toluene (10 mL × 3). The toluene solutions were combined and concentrated to about 10 mL; *n*-hexane vapor diffusion resulted in the production of golden yellow crystals (0.045 g, 28%). Concentration of the mother liquor and slow evaporation of the solvents gave some yellow crystals, identified as **5** by single-crystal X-ray analyses and spectroscopic data. Data for **9** are as follows. ^{1}H NMR (pyridine-d_5): δ 12.76 (s, 1H, Cp), 11.38 (s, 1H, Cp), 9.61 (s, 1H, Cp), 3.92 (s, 1H, Cp), 3.49 (m, 4H, THF), 2.97 (s, 3H, C*Me*$_2$), 1.72 (s, 3H, C*Me*$_2$), 1.41 (m, 4H, THF), −0.63 (br s, 1H, CH of carboranyl). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 116.7, 109.8, 101.8 (C_5H_4), 67.1, 25.1 (OC_4H_8), 54.8, 31.0, 28.5 (($CH_3)_2C$); the carbon atoms of the cage were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −3.2 (5B), −8.9 (5B). IR (KBr, cm^{-1}): ν 3069 (w), 2959 (m), 2897 (m), 2507 (s), 2420 (m), 1607 (w), 1449 (m), 1380 (m), 1259 (m), 1091 (s), 1014 (vs), 910 (w), 849 (m), 795 (s), 675 (w), 540 (w). Anal. Calcd for $C_{18}H_{37}B_{10}O_2Sm$: C, 39.75; H, 6.86. Found: C, 39.34; H, 7.07.

Preparation of [η^5:η^6-$Me_2C(C_5H_4)(C_2B_{10}H_{11})$]Er(THF)$_2$ (10). A THF solution (20 mL) of [η^5-$Me_2C(C_5H_4)(C_2B_{10}H_{11})]ErCl_2(THF)_3$ (**1**; 0.56 g, 0.80 mmol) was added to a suspension of Na metal (0.037 g, 1.60 mmol) in THF (10 mL) at room temperature. The mixture was stirred until the Na disappeared from the solution (about 3 days). The precipitate was filtered off, and the clear orange solution was concentrated under vacuum to about 6 mL. After addition of toluene (10 mL) to the above solution, pink crystals were obtained when this solution was allowed to stand at room temperature for several days (0.22 g, 48%). ^{1}H NMR (pyridine-d_5): δ 25.6 (br s, 2H, Cp), 10.8 (br s, 2H, Cp), 4.8 (s, 8H, THF), 2.6 (s, 8H, THF), −17.1 (s, 3H, C*Me*$_2$), −18.0 (s, 3H, C*Me*$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 64.6, 22.5 (OC_4H_8); other carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −52.4 (2B), −110.3 (4B), −115.1 (2B), −151.4 (2B). IR (KBr, cm^{-1}): ν 3084 (w), 2967 (m), 2892 (m), 2512 (vs), 2450 (s), 1625 (w), 1460 (w), 1381 (m), 1258 (w), 1003 (s), 847 (s), 790 (m), 676 (w), 493 (w). Anal. Calcd for $C_{16}H_{33}B_{10}ErO_{1.5}$ (**10**−0.5THF): C, 36.61; H, 6.34. Found: C, 36.21; H, 6.79.

Alternate Method. To a suspension of $ErCl_3$ (0.060 g, 0.22 mmol) in THF (5 mL) was slowly added a THF solution (10 mL) of $[Me_2C(C_5H_4)(nido\text{-}C_2B_{10}H_{11})]Na_3(THF)_3$ (**I-3**; 0.12 g, 0.22 mmol) at room temperature. The reaction mixture was then stirred overnight, followed by procedures used above to afford **10** as pink crystals (0.075 g, 61%).

Preparation of $[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$ (11). A THF solution (20 mL) of $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$ (**10**; 0.50 g, 0.89 mmol) was added to a suspension of Na metal (0.10 g, 4.35 mmol) in THF (10 mL) at room temperature, and the mixture was stirred at room temperature for 4 days. The excess Na metal was filtered off, and the clear orange solution was then concentrated under vacuum to about 8 mL. After addition of toluene (15 mL) to the above solution, pink crystals were obtained when this solution was allowed to stand at room temperature for several days (0.53 g, 76%). ^1H NMR (pyridine-d_5): δ 3.6 (s, 36H, THF), 2.2 (s, 6H, C*Me*$_2$), 1.5 (s, 36H, THF), 0.1 (s, 6H, C*Me*$_2$), −12.7 (br s, 4H, Cp), −66.0 (br s, 4H, Cp). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 67.0, 25.0 (OC_4H_8); other carbon atoms were not observed. $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −8.5 (br). IR (KBr, cm^{-1}): ν 3081 (w), 2961 (m), 2872 (w), 2398 (br s), 1678 (w), 1613 (w), 1451 (w), 1383 (vs), 1260 (w), 1090 (s), 1045 (s), 900 (w), 803 (m), 518 (w). Anal. Calcd for $C_{42}H_{86}B_{20}Er_2Na_4O_{5.5}$ (**11**−3.5THF): C, 38.16; H, 6.56. Found: C, 38.29; H, 6.69.

This compound can also be prepared by reaction of **1** with excess sodium metal in THF at room temperature for 1 week in 54% yield.

Preparation of $[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Dy\}_2\{Na_4(THF)_9\}]_n$ (12). A THF solution (10 mL) of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**; 0.27 g, 0.78 mmol) was added dropwise to a suspension of $DyCl_3$ (0.21 g, 0.78 mmol) in 10 mL of THF, and the mixture was stirred overnight at room temperature. After removal of the white precipitate, sodium metal (0.094 g, 4.1 mmol) was added to the resulting clear pale yellow solution. The mixture was then stirred for 4 days at room temperature, followed by procedures similar to those used in the synthesis of **11** to give yellow microcrystals (0.24 g, 40%). ^1H NMR (pyridine-d_5): many broad, unresolved resonances. $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 67.5, 25.7 (OC_4H_8); other carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ 216 (2B), 12.6 (2B), −8.53 (10B), −20.6 (2B), −122 (2B), −237 (2B). IR (KBr, cm^{-1}): ν 3086 (w), 2964 (s), 2872 (s), 2410 (vs), 2354 (s), 1608 (m), 1455 (m), 1368 (w), 1256 (w), 1047 (vs), 902 (m), 809 (m), 746 (w), 512 (m). Anal. Calcd for $C_{44}H_{90}B_{20}Dy_2Na_4O_6$ (**12**−3THF): C, 39.19; H, 6.73. Found: C, 39.13; H, 7.09.

Preparation of $[\{\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})\}Er_2(\mu\text{-}Cl)(THF)_3]_2$ (13). To a suspension of $ErCl_3$ (0.11 g, 0.40 mmol) in THF (10 mL) was slowly added a solution of $[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$ (**11**; 0.32 g, 0.20 mmol) in THF (20 mL). The mixture was stirred at room temperature overnight. The precipitate was filtered off, and the clear orange solution was concentrated under vacuum to about 10 mL. After addition of toluene (15 mL) to the above solution, pink crystals were obtained when this solution was allowed to stand at room temperature for several days (0.20 g, 60%). ^1H NMR (pyridine-d_5): δ 78.1 (br s, 2H, Cp), 54.9 (br s, 2H, Cp), 3.6 (m, 12H, THF), 2.0 (s, 6H, C*Me*$_2$), 1.5 (m, 12H, THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 136.9, 128.2, 127.5 (C_5H_4), 66.7, 24.6 (OC_4H_8), 30.5, 20.1 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −16.7 (br). IR (KBr, cm^{-1}): ν 3080 (w), 2965 (s), 2884 (m), 2514 (s), 2451 (s), 2401 (m), 1621 (w), 1458 (w), 1382 (m), 1260 (w), 1188 (w), 1023 (vs), 863 (s), 799 (m), 729 (w), 476 (m). Anal. Calcd for $C_{34}H_{70}B_{20}Cl_2Er_4O_{3.5}$ (**13**−2.5THF): C, 27.38; H, 4.73. Found: C, 27.36; H, 4.93.

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 an MSC/Rigaku RAXIS-IIC imaging plate using Mo Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program.[21] 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 Siemens SHELXTL program package (PC version).[22a] Most of the carborane hydrogen atoms were located from different Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter x toward 0.[22b] Two methylene groups (C11 and C21) of the two THF molecules in **10** are disordered over two sets of positions with 0.44:0.56 and 0.6:0.4 occupancies, respectively. Six methylene groups (C48, C51, C54, C57, C66, and C74) of the five THF molecules in **11** are disordered over two sets of positions with 0.5:0.5, 0.75:0.25, 0.5:0.5, 0.6:0.4, 0.6:0.4, and 0.6:0.4 occupancies, respectively. Crystal data and details of data collection and structure refinement are given in Table 1. Selected bond distances and angles are listed in Table 2. Further details are included in the Supporting Information.

Results and Discussion

Ligand. Treatment of $Li_2C_2B_{10}H_{10}$ with 1.3 equiv of 6,6-dimethylfulvene in a mixed solvent of toluene and diethyl ether (2:1) at reflux temperature gave, after hydrolysis with a saturated NH_4Cl aqueous solution and then recrystallization from a EtOH solution, compound $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (**I**) as a white crystalline solid in 85% yield (Scheme 1). The ^1H NMR spectrum indicates that the CMe_2 group in **I** bonds only to the sp^2 carbon of the cyclopentadienyl ring. The ^{11}B NMR spectrum exhibits a 1:1:2:2:4 splitting pattern which is similar to that of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$[5] but differs from that of $Me_2Si(R)(C_2B_{10}H_{11})$ (R = ^tBu,[17] C_5H_5,[3] C_9H_7[4]).

Like the versatile ligands $Me_2C(C_9H_7)(C_2B_{10}H_{11})$,[5] $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$,[3] and $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$,[4] **I** could be conveniently converted into the monoanion $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]^-$ (**I-1**) and the dianion $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ (**I-2**) by treatment with excess NaH and 2 equiv of *n*-BuLi, respectively. The monoanion **I-1** could be further converted into the trianion $[Me_2C(C_5H_4)(nido\text{-}C_2B_{10}H_{11})]^{3-}$ (**I-3**) by reaction with 2 equiv of Na metal and into the pentaanion $[Me_2C(C_5H_4)(arachno\text{-}C_2B_{10}H_{11})]^{5-}$ in the presence of $LnCl_3$ and excess Na metal.

Unlike its Si analogues, treatment of **I** with 3 or more equiv of Na metal does not give the pure trianion **I-3** on the basis of the ^1H and ^{11}B NMR spectra, presumably due to the lower acidity of the proton on the sp^3 carbon of the cyclopentadiene. The acidity of the silyl-substituted cyclopentadiene in the Me_2Si linked ligands is high, so that the acidic proton reacts vigorously with Na metal. In an alkyl-substituted cyclopentadiene such as **I**, Na metal may react simultaneously with both the carborane cage and cyclopentadiene or even react with the cage first to generate $[Me_2C(C_5H_5)(nido\text{-}C_2B_{10}H_{11})]^{2-}$, which then undergoes a proton-transfer reaction, affording $[Me_2C(C_5H_4)(\mu\text{-}CH\text{-}nido\text{-}CB_{10}H_{11})]^{2-}$.[23] As a result, a mixture of products would be generated.

Although the Me_2C linkage is less susceptible to nucleophilic attack than the Me_2Si linkage, the C−C(car-

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[21] Higashi, T. ABSCOR-An Empirical Absorption Correction Based on Fourier Coefficient Fitting; Rigaku Corp., Tokyo, 1995.

[22] (a) SHELXTL V 5.03 Program Package; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

Table 1. Crystal Data and Summary of Data Collection and Refinement for 4−11 and 13

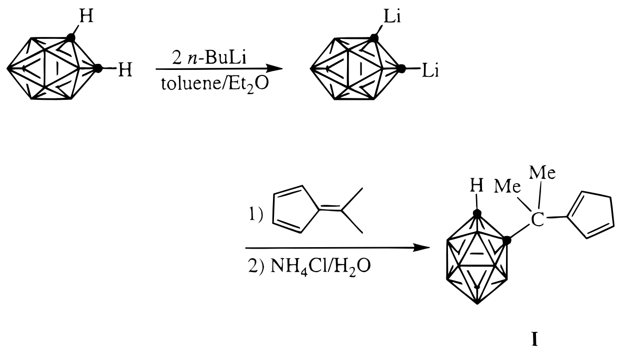
	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**13**
formula	$C_{28}H_{58}B_{20}Cl$-O_2Sm	$C_{67}H_{134}B_{60}$-Sm_2	$C_{32}H_{70}B_{20}$-LiO_6Sm	$C_{32}H_{70}B_{20}$-LiO_6Yb	$C_{28}H_{58}B_{20}$-O_2Yb	$C_{18}H_{37}B_{10}$-O_2Sm	$C_{18}H_{37}B_{10}$-ErO_2	$C_{56}H_{114}B_{20}$-$Er_2Na_4O_9$	$C_{44}H_{90}B_{20}$-$Cl_2Er_4O_6$
cryst size (mm)	0.41 × 0.22 × 0.20	0.38 × 0.28 × 0.22	0.21 × 0.28 × 0.40	0.40 × 0.26 × 0.22	0.38 × 0.20 × 0.18	0.16 × 0.15 × 0.13	0.34 × 0.26 × 0.25	0.20 × 0.20 × 0.10	0.30 × 0.25 × 0.17
fw	828.7	1889.0	924.4	947.1	816.0	543.9	560.8	1574.2	1671.3
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic	monoclinic	trigonal
space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$	$R\bar{3}$
a, Å	7.670(1)	22.254(5)	9.868(1)	9.910(2)	13.565(3)	9.870(1)	9.853(2)	13.076(1)	18.033(2)
b, Å	23.433(2)	20.737(4)	28.436(1)	28.006(6)	13.608(6)	14.331(2)	14.272(3)	26.212(2)	18.033(1)
c, Å	11.522(1)	24.968(5)	17.340(1)	17.547(4)	23.802(6)	17.309(2)	17.056(3)	23.061(1)	18.033(1)
α, deg	90.00	90.00	90.00	90.00	100.73(2)	90.00	90.00	90.00	84.36(1)
β, deg	91.74(1)	110.23(3)	92.19(1)	92.62(3)	99.06(1)	90.00	90.00	104.84(1)	84.36(1)
γ, deg	90.00	90.0	90.00	90.00	104.76(2)	90.00	90.00	90.00	84.36(1)
V, Å^3	2070(1)	10811(4)	4862(1)	4865(2)	4076(2)	2448(1)	2398(1)	7641(1)	5784(2)
Z	2	4	4	4	4	4	4	4	3
D_{calcd}, Mg/m^3	1.330	1.161	1.263	1.293	1.330	1.476	1.553	1.368	1.439
radiation (λ), Å	Mo Kα (0.710 73)								
2θ range, deg	5.0−51.1	2.6−50.0	2.8−51.1	2.9−51.1	3.18−50.0	3.7−51.0	3.9−51.0	3.3−51.0	3.1−51.1
μ, mm^{-1}	1.511	1.112	1.246	1.960	2.321	2.412	3.513	2.251	4.411
F(000)	842	3840	1900	1932	1648	1092	1116	3208	2424
no. of indep rflns	6494	14390	7654	4069	8500	3843	3551	8384	6246
no. of obsd rflns	6478	14390	7654	4069	8500	3843	3551	8384	6246
no. of params refnd	471	1163	542	542	920	282	252	796	344
goodness of fit	0.997	1.070	1.088	0.926	1.095	1.072	1.170	1.115	1.018
R1	0.053	0.076	0.045	0.039	0.084	0.061	0.079	0.077	0.063
wR2	0.152	0.210	0.121	0.103	0.234	0.147	0.224	0.182	0.152

Table 2. Average Bond Lengths (Å) and Angles (deg)[a,b]

	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**13**
Ln	Sm	Sm	Sm	Yb	Yb	Sm	Er	Er	Er
Ln−C(C_5 ring)	2.771(3)	2.744(4) [2.721(6)]	2.695(2)	2.596(5)	2.725(6) [2.722(6)]	2.670(5)	2.602(5)	2.671(8)	2.597(4)
Ln−C(σ)			2.522(2)	2.447(3)					
Ln−C(cage)						2.764(3)	2.770(4)	2.410(6)	2.386(5)
Ln−B(cage)						2.829(3)	2.680(3)	2.671(7)	2.655(7)
Ln···B								2.919(7)	2.787(4)
Ln−O	2.566(2)				2.462(4) [2.395(4)]	2.415(3)	2.301(3)		2.388(3)
C(C_5 ring)−C−C(cage)	109.1(3)	109.0(3) [107.4(4)]	112.3(1)	111.5(4)	109.9(5) [111.0(5)]	98.5(3)	100.0(3)	101.9(6)	112.0(3)
Cent−Ln−Cent	129.6	119.9 [119.8]	129.0	128.7	132.6 [133.2]	116.2	118.4	135.6	

[a] Cent = the centroid of the five- or six-membered ring of the cyclopentadienyl or carboranyl groups. [b] Distances and angles in brackets are those of a second molecule.

Scheme 1



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borane) bond is surprisingly broken under various deboronation conditions such as KOH/MeOH,[6] n-Bu$_4$NF/THF,[18] KF/Al_2O_3/CH_3CN,[19] and pyrrolidine,[20] leading to the formation of *nido*-$C_2B_9H_{12}^-$ in almost quantitative yield, as indicated by ^{11}B NMR. The reasons for the cleavage of the C−C(carborane) bond are not clear yet but must be related to the electron-withdrawing ability of the cyclopentadienyl ring. The above-mentioned transformations are summarized in Scheme 2.

Mono-, Bis-, and Tris-Ligated Organolanthanide Compounds. Treatment of anhydrous $LnCl_3$ with 1, 2, or 3 equiv of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**) in THF gave mono-, bis-, or tris-ligated organolanthanide compounds in good yield, respectively (Scheme 3). These compounds are soluble in polar organic solvents such as THF, DME, and pyridine and slightly soluble in toluene but insoluble in n-hexane. The mono- and bis-ligated compounds can lose the coordinated THF molecules under vacuum even at room temperature. All these compounds were characterized by various spectroscopic data and elemental analyses. The molecular structures of compounds **4** and **5** have been further confirmed by single-crystal X-ray analyses.

The solid-state structure of **4** is similar to that of [η^5-

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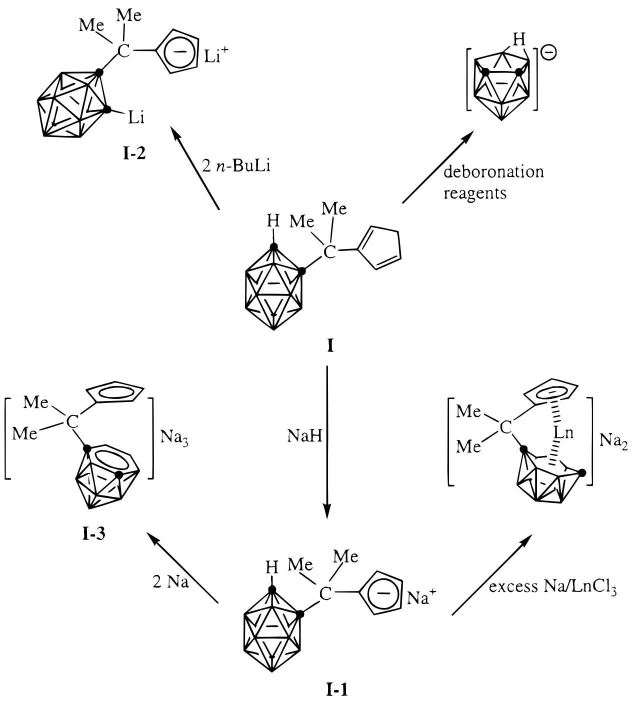
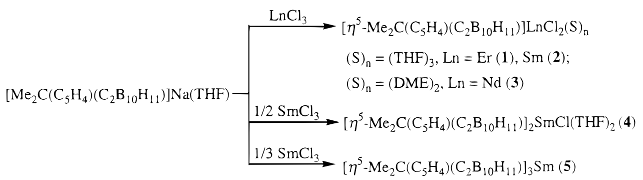
(23) For examples of protonation of $[nido\text{-}C_2B_{10}H_{12}]^{2-}$, see: (a) Tolpin, E. I.; Lipscomb, W. N. *J. Chem. Soc., Chem. Commun.* **1973**, 257. (b) Tolpin, E. I.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 2257. (c) Dunks, G. B.; Wiersema, R. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 899.

Scheme 2



Scheme 3



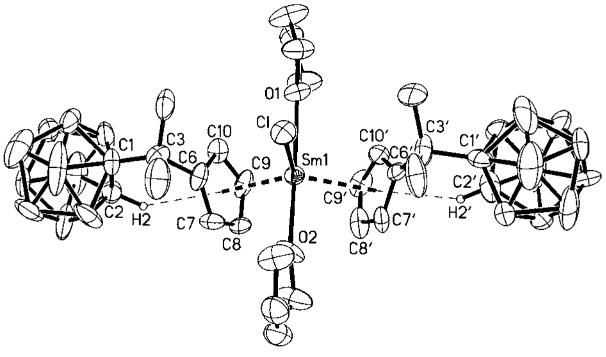


Figure 1. Molecular structure of [η^5-$Me_2C(C_5H_4)(C_2B_{10}H_{11})]_2$-$SmCl(THF)_2$ (**4**) (thermal ellipsoids drawn at the 35% probability level).

$Me_2Si(C_5H_4)(C_2B_{10}H_{11})]_2SmCl(THF)_2$.[3c] The Sm atom is η^5-bound to each of two cyclopentadienyl rings and σ-bound to one chlorine atom and two oxygen atoms from the coordinated THF molecules in a distorted-trigonal-bipyramidal geometry (Figure 1). The average Sm−C, Sm−O, and Sm−Cl distances and related bond angles are all close to those in [η^5-$Me_2Si(C_5H_4)$-$(C_2B_{10}H_{11})]_2SmCl(THF)_2$.

Figure 2 shows the solid-state structure of **5**. It is the first tris-ligated organolanthanide compound containing three carborane cages to be reported. There are two crystallographically independent molecules in the unit cell with one solvated toluene molecule. The Sm atom is η^5-bound to each of three cyclopentadienyl rings in a trigonal-planar geometry, a typical structure for $(C_5R_5)_3$-Ln types of compounds.[2] Two carborane cages are located on one side of this trigonal plane, and the other sits on the other side to minimize steric effects. The average Sm−C distance of 2.744(4) Å (or 2.721(6) Å) is comparable to that of 2.771(3) Å in **4**.

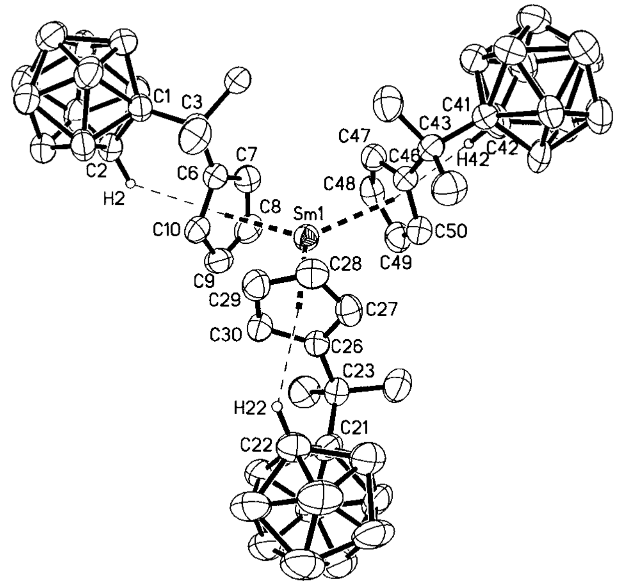


Figure 2. Molecular structure of [η^5-$Me_2C(C_5H_4)(C_2B_{10}H_{11})]_3$-Sm·0.5(toluene) (**5**) (the solvated toluene molecule is not shown; thermal ellipsoids drawn at the 35% probability level).

There are no direct interactions between the metal center and the B−H bonds of the carborane cages in both **4** and **5**. However, the acidic C−H proton of the cage forms nonclassical hydrogen bonds with the cyclopentadienyl rings at an average distance of 2.578 Å for **4** and 2.586 Å (or 2.527 Å) for **5**, respectively. These measured values fall in a range 2.184−2.765 Å normally observed for this type of bonding.[3,4,24]

[{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}$_2$Ln][Li(DME)$_3$]. Reaction of $LnCl_3$ with 1 or 2 equiv of [$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (**I-2**) in THF, after recrystallization from a toluene/DME solution, afforded the ionic compounds [{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}$_2$Ln][Li(DME)$_3$] (Ln = Sm (**6**), Yb(**7**)). No [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-$LnCl(DME)_x$ compound was isolated. Surprisingly, treatment of [η^5-$Me_2C(C_5H_4)(C_2B_{10}H_{11})]SmCl_2(THF)_3$ (**2**) with 1 equiv of **I-2** also gave compound **6**, presumably due to the ligand redistribution of the intermediate [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Sm[$\eta^5$-$Me_2C(C_5H_4)(C_2B_{10}H_{11})$]($\mu$-Cl)Li(THF)$_x$. It is noteworthy that [η^5:σ-$Me_2Si(C_9H_7)$-$(C_2B_{10}H_{10})$]Er[η^5-$Me_2Si(C_9H_7)(C_2B_{10}H_{11})$]($\mu$-Cl)-$Na(THF)_3$ is stable and structurally characterized.[4b] These results indicate that steric factors play a predominant role in stabilizing this type of compound. Scheme 4 summarizes the above transformations.

Both compounds **6** and **7** were fully characterized by various spectroscopic and elemental analyses. Although they are isostructural, their ^1H, ^{13}C, and ^{11}B NMR spectra are different from each other due to the paramagnetism of the central metal ions. Their IR spectra are quite similar.

The solid-state structures of compounds **6** and **7** as derived from single-crystal X-ray diffraction studies

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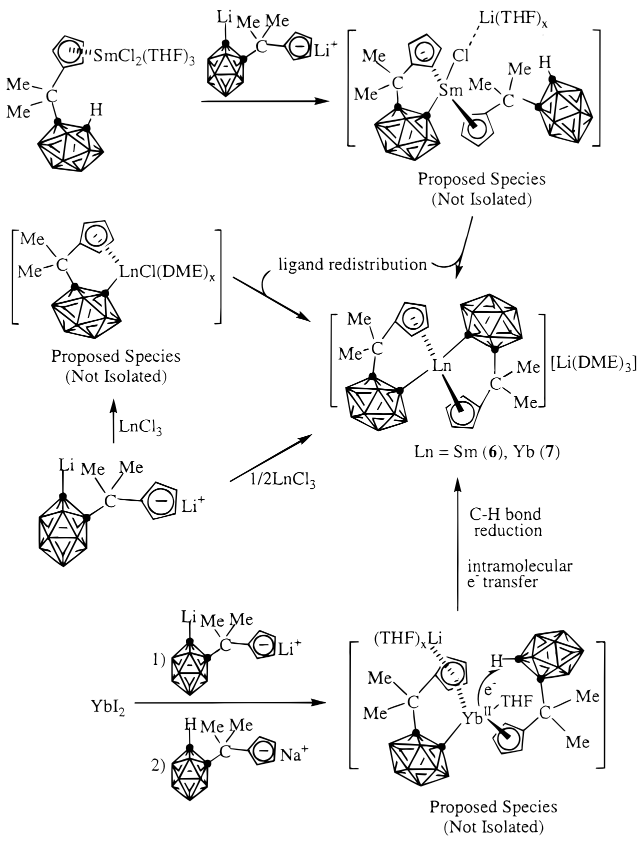
(24) Blanch, R. J.; Williams, M.; Fallon, G. D.; Gardiner, M. G.; Kaddour, R.; Raston, C. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 504.

Scheme 4



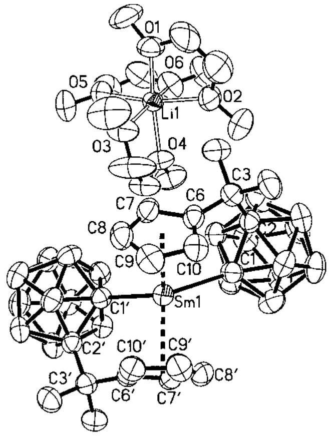
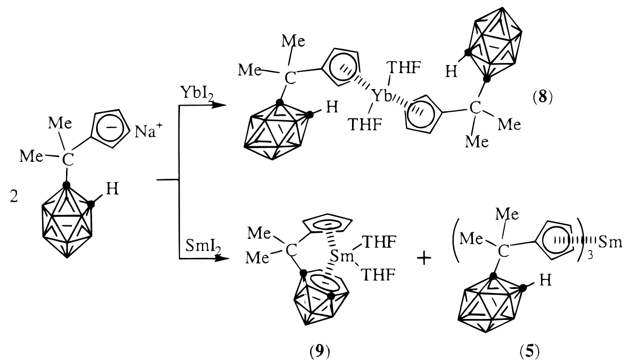


Figure 3. Molecular structure of $[\{\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}_2Sm][Li(DME)_3]$ (**6**) (thermal ellipsoids drawn at the 35% probability level).

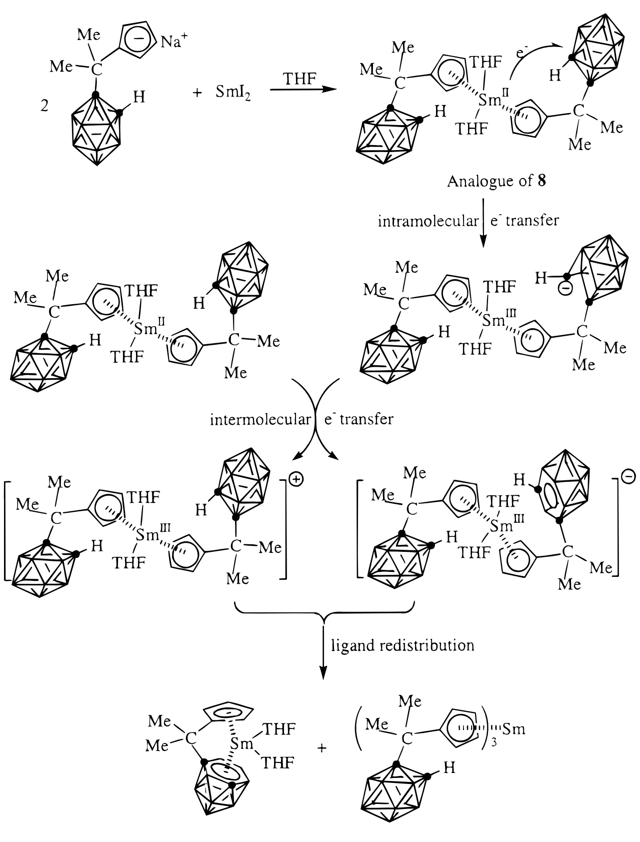
reveal that they are isostructural and isomorphous. Figure 3 shows their representative structure. Both of them consist of well-separated, alternating layers of the discrete tetrahedral anion $[\{\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}_2Ln]^-$ and octahedral cation $[Li(DME)_3]^+$. In each anion, the Ln ion is η^5-bound to each of two cyclopentadienyl rings and σ-bound to each of two carbon atoms from two carborane cages in a distorted-tetrahedral arrangement, similar to that of $[\{\eta^5:\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Ln]^-$.[3]

The average Ln−C(C5 ring) distance of 2.695(2) Å in **6** and 2.596(5) Å in **7** and the average Ln−C(σ) distance of 2.522(2) Å in **6** and 2.447(3) Å in **7** are all slightly shorter than the corresponding values found in $[\{\eta^5:\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Ln][Li(THF)_4]$,[3c] perhaps due to the shorter Me_2C linkage.

Scheme 5



Scheme 6



$[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_2Yb(THF)_2$ and $[\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Ln(THF)_2$. We have previously reported an unprecedented redox reaction between SmI_2 and $[Me_2Si(C_5H_4)(C_2B_{10}H_{11})]^-$,[3b] which led to the isolation of the mixed lanthanacarborane $[\eta^5:\eta^6\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]Sm(THF)_2$. According to an earlier proposed reaction mechanism,[3c] other products should also be produced. We are very interested in this new reaction and have been trying hard to gain some insight into it. Treatment of $SmI_2(THF)_x$ with 2 equiv of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**) in THF resulted in the isolation of both the mixed-sandwich samaracarborane $[\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Sm(THF)_2$ (**9**) and the tris-ligated organosamarium compound $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_3Sm$ (**5**) (Scheme 5). The formation of these compounds can be rationalized by a reasonable mechanism, as shown in Scheme 6. Interaction of SmI_2 with **I-1** gives the first intermediate $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]_2Sm(THF)_2$, followed by intramolecular and then intermolecular electron transfer to generate the anion

$\{[\eta^5\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{11})][\eta^5\text{-Me}_2C(C_5H_4)(\textit{nido}\text{-}C_2B_{10}H_{11})]Sm^{III}(THF)_2\}^-$ and cation $\{[\eta^5\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{11})]_2Sm(THF)_2\}^+$; ligand redistribution affords the thermodynamically stable compounds **9** and **5**.

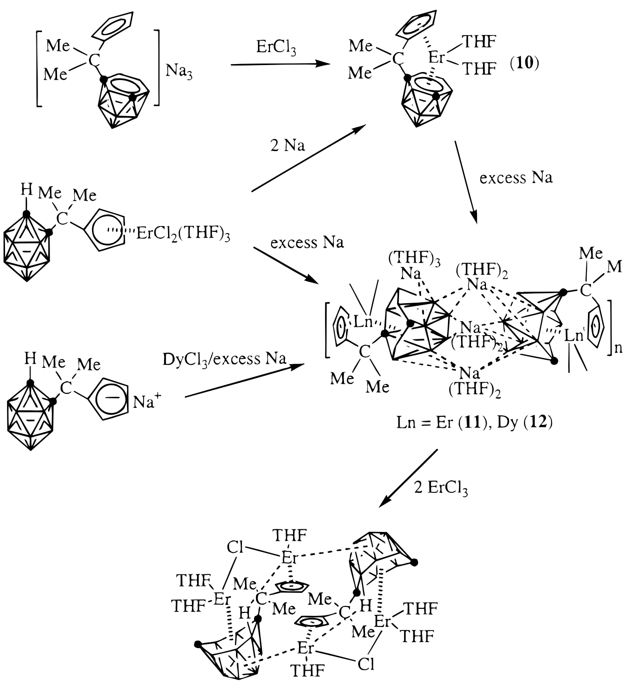
The less reactive $YbI_2(THF)_x$ reacted with 2 equiv of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**) in THF to give the organoytterbium(II) compound $[\eta^5\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{11})]_2Yb(THF)_2$ (**8**), which supports the formation of the first intermediate shown in Scheme 6. Treatment of $YbI_2(THF)_x$ with 1 equiv of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (**I-2**) followed by reaction with 1 equiv of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na(THF)$ (**I-1**) generated the unexpected cage C−H bond reduction product $[\{\eta^5:\sigma\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{10})\}_2Yb][Li(DME)_3]$ (**7**) (Scheme 4). This result differs significantly from that of the silicon analogue, in which only the organoytterbium(II) compound $[\eta^5:\sigma\text{-Me}_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb[\eta^5\text{-Me}_2Si(C_9H_6)(C_2B_{10}H_{11})]Na(THF)_3$[4a] was isolated and no redox reaction occurred. The above results indicate that the Me_2C linkage can enhance the reducing ability of Yb(II) to reduce the cage C−H bond, but not enough to reduce the carborane cage, which allows the isolation of **8**. This is one of a few examples showing that an organoytterbium(II) compound can reduce the C−H bond,[5,25] since Yb(II) is usually considered to be a less powerful reducing agent.[26]

An alternate method to prepare the mixed-sandwich compound containing both η^5-cyclopentadienyl and η^6-carboranyl ligands is through the reaction of $[Me_2C(C_5H_4)(\textit{nido}\text{-}C_2B_{10}H_{11})]Na_3(THF)_3$ (**I-3**) with $LnCl_3$ or the reduction of the compound $[\eta^5\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{11})]LnCl_2(THF)_3$ by 2 equiv of Na metal. For example, treatment of $[\eta^5\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{11})]ErCl_2(THF)_3$ (**1**) with 2 equiv of Na metal or reaction of $ErCl_3$ with 1 equiv of $[Me_2C(C_5H_4)(\textit{nido}\text{-}C_2B_{10}H_{11})]Na_3(THF)_3$ (**I-3**) in THF at room temperature gave $[\eta^5:\eta^6\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$ (**10**) in good yield (Scheme 7).

All compounds were fully characterized by various spectroscopic data and elemental analyses as well as X-ray diffraction studies. Their ^1H, ^{13}C, and ^{11}B NMR spectra are different from each other. The IR spectra of **9** and **10** are quite similar, showing a unique doublet centered at about 2510 cm^{-1}, typical of the ionic interaction between an anionic carborane ligand and a metal ion.[3,4,6,27,28] The IR spectra of **5** and **8** exhibit a strong B−H absorption of the neutral carborane cage at about 2575 cm^{-1}.

An X-ray analysis reveals that compound **8** crystallizes in space group $P\bar{1}$, and there are two crystallographically independent molecules in the unit cell. Figure 4 shows one of these two molecules. Each Yb^{2+} ion is η^5-bound to two cyclopentadienyl rings and coordinated to two THF molecules in a distorted-tetrahedral geometry, a typical structure for the $Cp_2Yb^{II}(L)_2$ compound.[2] Two carborane cages stay away from each other to minimize the steric interactions, and there are no direct interactions between the Yb^{2+} ion and any one of the B−H bonds from the carborane cages. Similar to compounds **4**, **5**, and $[\eta^5\text{-Me}_2Si(C_5H_4)(C_2B_{10}H_{11})]_2Yb(THF)_2$,[3b] the nonclassical hydrogen bonds between the H atom on the carbon atom of the carborane cage and the cyclopentadienyl ring are observed in compound **8** at an average distance of 2.547 Å (or 2.605 Å), which is comparable to those reported in the literature.[3,4,24] The average Yb−C distance of 2.725(6) Å (or 2.722(6) Å) is close to those normally observed in organoytterbium(II) compounds.[2]

Scheme 7



(**13**)

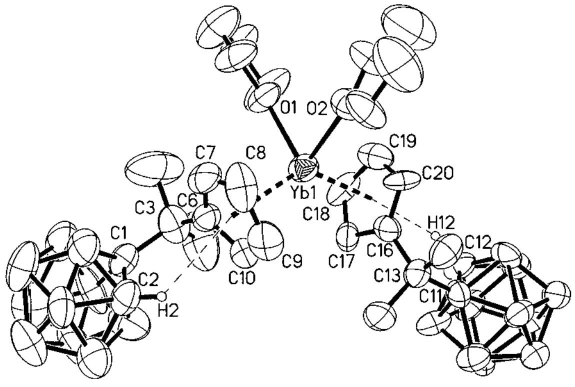


Figure 4. Molecular structure of $[\eta^5\text{-Me}_2C(C_5H_4)(C_2B_{10}H_{11})]_2Yb(THF)_2$ (**8**) (thermal ellipsoids drawn at the 35% probability level).

X-ray diffraction studies indicate that compounds **9** and **10** are isostructural and isomorphous although they were prepared from two different methods. Figure 5 shows their representative structure. The lanthanide ion is η^5-bound to the cyclopentadienyl ring, η^6-bound to the hexagonal C_2B_4 face of the carborane cage, and coordinated to two THF molecules in a distorted-tetrahedral arrangement. The average Sm−C(C_5 ring) distance of 2.670(5) Å, Sm−cage atom distance of 2.807(5) Å, and Sm−O distance of 2.415(3) Å in **9** are close

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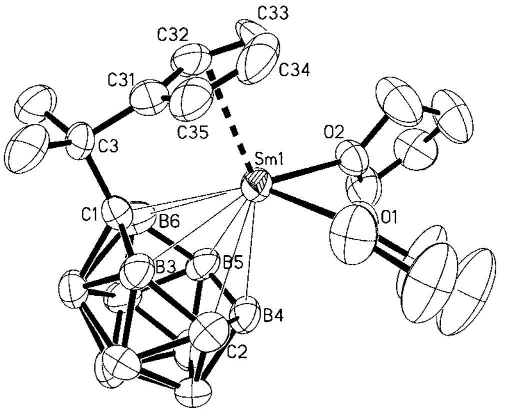

Figure 5. Molecular structure of $[\eta^5:\eta^6\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm(THF)}_2$ (**9**) (thermal ellipsoids drawn at the 35% probability level).

to the corresponding values in $[\eta^5:\eta^6\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm(THF)}_2$[3b] and are about 0.09 Å longer than those in **10**, which can be compared to the 0.075 Å difference between Shannon's ionic radii of eight-coordinate Sm^{3+} and Er^{3+}.[29]

$[\{[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Ln}\}_2\{\text{Na}_4(\text{THF})_9\}]_n$ and $[\{\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})\}\text{Er}_2(\mu\text{-Cl})(\text{THF})_3]_2$. Reaction of $[\eta^5\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{ErCl}_2(\text{THF})_3$ (**1**) or $[\eta^5:\eta^6\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er(THF)}_2$ (**10**) with excess Na metal in THF at room temperature generated, after workup, the novel 13-vertex metallacarborane $[\{[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}\}_2\{\text{Na}_4(\text{THF})_9\}]_n$ (**11**) in good yield. A "one pot" reaction of $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na(THF)}$ (**I-1**), DyCl_3, and excess Na metal in THF also afforded the same type of metallacarborane, $[\{[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Dy}\}_2\{\text{Na}_4(\text{THF})_9\}]_n$ (**12**) (Scheme 7).

The Na^+ ions in **11** can be completely replaced by other ions. For example, treatment of **11** with 2 equiv of ErCl_3 in THF at room temperature gave the novel tetranuclear metallacarborane cluster $[\{\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})\}\text{Er}_2(\mu\text{-Cl})(\text{THF})_3]_2$ (**13**) in 60% yield. It is noteworthy that the added Er^{3+} ions not only replace the Na^+ ions but also compete with the existing Er^{3+} ions for the coordination sites, resulting in the formation of a new structural motif, which offers an opportunity to prepare heteronuclear metallacarboranes.

Compounds **11**−**13** are extremely air- and moisture-sensitive but remain stable for months at room temperature under an inert atmosphere. They are soluble in polar organic solvents such as THF, DME, dioxane, and pyridine, sparingly soluble in toluene, and insoluble in *n*-hexane and decompose in CH_2Cl_2.

They were characterized by various spectroscopic data and elemental analyses. The molecular structures of **11** and **13** have been confirmed by single-crystal X-ray analyses. It is interesting to note that the B−H absorption frequencies in the IR spectra shift to lower field on going from $\text{C}_2\text{B}_{10}\text{H}_{11}\text{R}$ via $[nido\text{-C}_2\text{B}_{10}\text{H}_{11}\text{R}]^{2-}$ to $[arachno\text{-C}_2\text{B}_{10}\text{H}_{11}\text{R}]^{4-}$, for example, 2575 cm^{-1} for $[\eta^5\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{ErCl}_2(\text{THF})_3$ (**1**), 2512 cm^{-1} for $[\eta^5:\eta^6\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er(THF)}_2$ (**10**), and 2398 cm^{-1} for $[\{[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}\}_2\{\text{Na}_4(\text{THF})_9\}]_n$ (**11**). These results imply that the IR data on B−H absorption may serve as a quick reference for the formation of carborane anions in some cases.

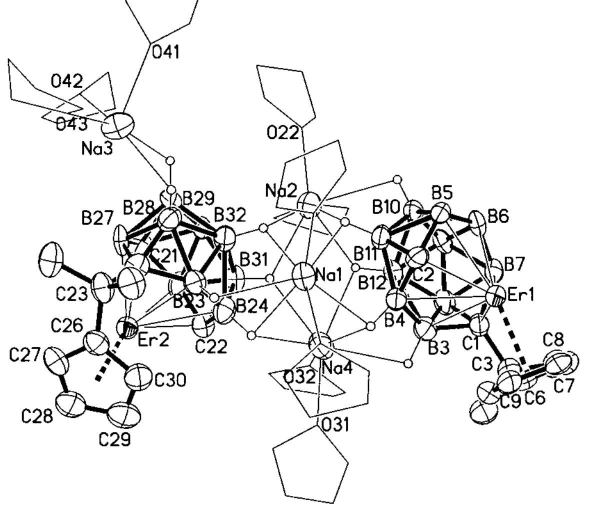

Figure 6. Molecular structure of $[\{[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}\}_2\{\text{Na}_4(\text{THF})_9\}]_n$ (**11**) (thermal ellipsoids drawn at the 35% probability level, showing one asymmetrical unit of the infinitive polymeric chain).

An X-ray diffraction study reveals that **11** is a coordination polymer. Each asymmetrical unit contains two $[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}^{2-}$ structural motifs that are connected by three Na atoms through several B−H−Na two-electron−three-center (2e−3c) bonds (Figure 6). The asymmetrical units are then linked to each other via B−H−Er bonds to form an infinite polymeric chain. Each Er^{3+} ion is η^7-bound to $[arachno\text{-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$, η^5-bound to cyclopentadienyl, and σ-bound to two B−H bonds from the neighboring $[arachno\text{-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$ unit in a distorted-tetrahedral arrangement. The novel 13-vertex *closo*-metallacarborane moiety in **11** is similar to that in $[\{(\eta^7\text{-C}_2\text{B}_{10}\text{H}_{12})(\eta^6\text{-C}_2\text{B}_{10}\text{H}_{12})\text{U}\}\{\text{K}_2(\text{THF})_5\}]_2$.[12]

The carborane ligand $[arachno\text{-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$ has a boatlike C_2B_5 bonding face in which the five B atoms are coplanar and the two C atoms are ca. 0.6 Å above this plane, resulting in an average Er−C(cage) distance being ca. 0.26 Å shorter than the average Er−B(cage) distance (Figure 7). In comparison with the Er−C σ bond distances of 2.528(2) Å in $[\{\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Er}][\text{Li(THF)}_4]$,[3d] 2.44(2) Å in $[(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-C}{\equiv}\text{CBu}^t)]_2$,[30] 2.458(19) Å in $(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-Me})_2\text{Li(tmed)}$,[31] and 2.526(6) Å in $[(\text{C}_5\text{H}_5)_2\text{Er}(\eta^2\text{-CHNBu}^t)]_2$,[32] it is suggested that the Er−C(cage) bonds (average 2.410(6) Å) should be best described as σ bonds. The average Er−C(C_5 ring) distance of 2.671(8) Å is longer than that of 2.602(5) Å in **10**. The average Er−B(cage) distance of 2.671(7) Å is very close to that of 2.680(3) Å in **10**. The average Er···B interatomic distance of 2.919(7) Å is significantly longer than that of 2.644(12) Å in $[\{(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4\}_2\text{Er}]_2[\text{Li(TMEDA)}_2]_2$,[33] presumably due to

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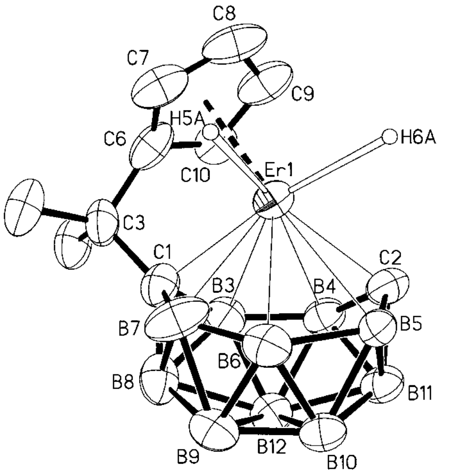

Figure 7. Closer view of the coordination environment for the Er atom in **11**.

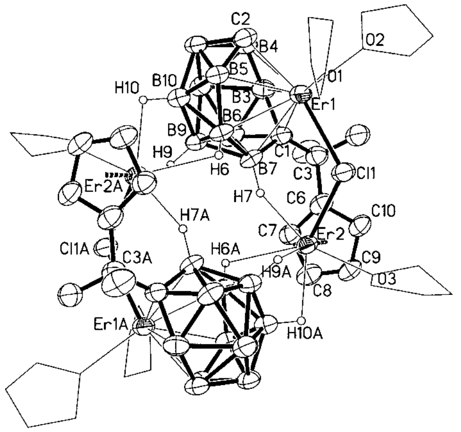

Figure 8. Molecular structure of $[\{\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})\}Er_2(\mu\text{-}Cl)(THF)_3]_2$ (**13**) (thermal ellipsoids drawn at the 35% probability level).

steric effects. The average Na(1)⋯B distance of 2.977(9) Å, Na(2)⋯B distance of 3.029(9) Å, and Na(4)⋯B distance of 3.015 Å are all comparable to those of 3.012(6) Å in $[(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Sm_2Na_3$[27] and 3.087(10) Å in $[\eta^5\text{-}(Me_3Si)_2C_2B_4H_5]Na(THF)$.[34] As far as we are aware, **11** is the first lanthanacarborane containing a η^7-carboranyl ligand to be reported.

The solid-state structure shows that **13** is a centrosymmetric tetranuclear metallacarborane cluster with two $\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er_2(\mu\text{-}Cl)(THF)_3\}$ units that are connected by two sets of three B−H−Er 2e−3c bonds (Figure 8). Each of the two Er(1) atoms is η^7-bound to $[\textit{arachno}\text{-}C_2B_{10}H_{11}]^{4-}$ and coordinated to two O atoms from THF molecules and one doubly bridging Cl atom in a distorted-tetrahedral geometry, a structure motif which differs from that of **11**. Each of the other two Er(2) atoms is η^5-bound to the cyclopentadienyl ring and coordinated to one O atom from the THF molecule, one B−H bond from $[\textit{arachno}\text{-}C_2B_{10}H_{11}]^{4-}$, one doubly bridging Cl atom, and three B−H bonds from the neighboring $[\textit{arachno}\text{-}C_2B_{10}H_{11}]^{4-}$ ligand in a distorted-pentagonal-bipyramidal geometry with the centroid of the cyclopentadienyl ring and H(9A) occupying the axial sites. The average Er(2)−C(C_5 ring) distance of 2.597(4) Å, Er(1)−B(cage) distance of 2.655(7) Å, and Er⋯B interatomic distance of 2.787(4) Å are all shorter than the corresponding values in **11**, perhaps due to steric reasons. It is noteworthy that the average Er(1)−C(cage) distance of 2.386(5) Å is shorter than that of 2.410(6) Å in **11**, and it is the shortest Er−C bond distance ever reported in the literature,[35] which again suggests that it is a σ bond.

Conclusion

The ligand $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ can be converted into the monoanion, the dianion, and the trianion by treatment with suitable reagents, which lead to the isolation and structural characterization of mono-, bis-, and tris-ligated organolanthanide compounds, organolanthanide carboranyl compounds, and mixed-sandwich lanthanacarboranes, a chemistry which is similar to that of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$.

The smaller Me_2C linkage does not largely affect the coordination geometry of the central metal ions or overall molecular structures of the resulting compounds, but it can enhance the reactivity of the organoytterbium(II) compound, resulting in a cage C−H bond reduction product, a reactivity pattern which is different from that of the silicon analogue. Although this linkage is more chemically inert than the Me_2Si linkage, it can still be attacked by OMe^-, F^-, and amine under deboronation conditions, affording $\textit{nido}\text{-}C_2B_9H_{12}^-$.

While the compound $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ cannot be directly converted into the pentaanion $[Me_2C(C_5H_4)(\textit{arachno}\text{-}C_2B_{10}H_{11})]^{5-}$, its monoanion $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]^-$ can accept four electrons from Na metal in the presence of $LnCl_3$ to form a novel class of 13-vertex lanthanacarboranes bearing a η^7-carboranyl ligand. Another type of 13-vertex lanthanacarborane, $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Ln(THF)_2$, is suggested to be the intermediate in the above reactions. The large and highly electropositive lanthanide or actinide metal ions may play an important role in the formation of such a novel class of 13-vertex metallacarboranes.

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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 compounds **4**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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