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exo-nido- versus *closo*-Lanthanacarboranes. Synthesis and Structure of *exo-nido*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Ln(DME)_3$, [*exo-nido*-$\{(C_6H_5CH_2)_2C_2B_9H_9\}Ln(THF)_3]_2$ (Ln = Sm, Yb), and *closo-exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Sm_2Na_3$

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Treatment of LnI_2 with 1 equiv of $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ in THF at room temperature gave, after recrystallization from DME, the monomeric *exo-nido*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Ln(DME)_3$ (Ln = Sm (**1**), Yb (**2**)). They can react with another equivalent of $Na_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ to afford *closo-exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Ln_2Na_4(THF)_2$ (Ln = Sm (**4**), Yb (**5**)). Reaction of $YbCl_3$ with 2 equiv of $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ in THF/DME yielded **2**, while treatment of $SmCl_3$ with 2 equiv of $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ in THF generated a novel cluster *closo-exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Sm_2Na_3$ (**3**). LnI_2 reacted with 2 equiv of $Na_2[(C_6H_5CH_2)_2C_2B_9H_9]$ in THF to produce the dimeric [*exo-nido*-$\{(C_6H_5CH_2)_2C_2B_9H_9\}Ln(THF)_3]_2$ (Ln = Sm (**6**), Yb (**7**)). These new compounds were fully characterized by spectroscopy and elemental analyses. The solid-state structures of **1**−**3**, **6**, and **7** have been further confirmed by single-crystal X-ray analyses. This study indicates that steric factors dominate the formation of *exo-nido*-lanthanacarboranes. In case the substituents are benzyl groups, *closo*- and *exo-nido*-lanthanacarboranes of C_2B_{10} systems are exchangeable by changing the ratio of metal to carborane.

Introduction

Lanthanacarboranes are much less studied in comparison with the cyclopentadienyl-based organolanthanide compounds and metallacarboranes of d- and p-block metals.[1] Since the first compound of this class was reported in 1988,[2a] C_2B_9,[2] C_2B_{10},[3] and C_2B_4[4] ligand systems have been successively introduced to the lanthanide chemistry, resulting in a new class of organolanthanide compounds. The bondings between lanthanide metals and carborane anions are π-bond and/or 2e−3c B−H−Ln σ-bonds. Exclusive B−H−Ln bondings give *exo-nido*-lanthanacarboranes, while exclusive π-bondings usually afford monomeric *closo*-lanthanacarboranes. Multinuclear *closo*-lanthanacarboranes often contain both π-bonds and 2e−3c B−H−Ln σ-bonds. These bonding interactions may be affected by the substituents on the bonding face of the carborane anion. For instance, benzyl-substituted dicarbollide anion, $(C_6H_5CH_2)_2C_2B_9H_9{}^{2-}$, favors 2e−3c bonding, resulting in the isolation of an *exo-nido*-lanthanacarborane.[2c] We are interested in the effects of the substituents, the metal ions, and solvents on the carborane anion metal interactions. Such information would also help us to better understand the differences and similarities within various carborane ligand systems and between them and cyclic organic ligands in all aspects. We report here the syntheses and structures of several new *closo*- and *exo-nido*-lanthanacarboranes. The factors affecting the bonding interactions between lanthanide ions and carborane anions are discussed.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except MeCN) were freshly distilled from sodium benzophenone ketyl immediately prior to use. MeCN was freshly distilled from CaH_2. Anhydrous $LnCl_3$ (Ln = Yb, Sm) was prepared from the hydrates by standard procedures.[5] $LnI_2(THF)_x$ (Ln = Yb, Sm),[6] $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$,[2c] and $(C_6H_5CH_2)_2C_2B_{10}H_{10}$[2c] 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 Nicolet Magna 550 Fourier transform spectrometer. MS spectrum was recorded on a Bruker APEX FTMS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spec-

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trometer at 160.46 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 *exo-nido*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]Sm(DME)$_3$ (1). To a solution of $(C_6H_5CH_2)_2C_2B_{10}H_{10}$ (0.30 g, 0.92 mmol) in 15 mL of THF was added K metal (0.50 g, 12.79 mmol), and the mixture was stirred at room temperature for 24 h. After removal of excess K metal, the resulting clear yellow solution ($K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$) was slowly added to a THF solution of SmI_2 (17.4 mL of 0.053 M, 0.92 mmol) at room temperature, and the reaction mixture was stirred overnight. The color of the solution was turned to dark red from dark blue during the course of reaction. The white precipitate was filtered off, and the filtrate was concentrated to give a dark red solid. Recrystallization from DME (1,2-dimethoxyethane) yielded **1** as dark red crystals (0.54 g, 78%). ^1H NMR (pyridine-d_5): δ 7.25 (m, 10H, $C_6H_5CH_2$), 3.50 (br s, 4H, $C_6H_5CH_2$), 3.30 (br s, 12H, DME), 3.10 (s, 18H, DME). ^{13}C NMR (pyridine-d_5): δ 131.0, 128.1, 124.9, 123.5, 71.6, 58.3; the carbon atoms of the cage and methylene of benzyl groups were not observed. The ^{11}B NMR spectra consisted of extremely broad, unresolved resonances. IR (KBr, cm^{-1}): ν_{BH} 2509 (s), 2486 (s), 2408 (m). Anal. Calcd for $C_{24}H_{44}B_{10}O_4Sm$ (**1**−DME): C, 44.00; H, 6.77; Sm, 22.96. Found: C, 44.21; H, 6.55; Sm, 22.87.

Recrystallization of **1** from CH_3CN at room temperature resulted in the isolation of a small amount of colorless crystals identified as trimethyl-*s*-triazine.[7] ^1H NMR (acetone-d_6): δ 2.29 (s). MS (EI): *m/z* 123 (100%). Anal. Calcd for $C_6H_9N_3$: C, 58.54; H, 7.32; N, 34.15. Found: C, 58.44; H, 7.31; N, 34.16.

Preparation of *exo-nido*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]Yb(DME)$_3$ (2). A THF solution of $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ (15 mL, 0.56 mmol) was added dropwise to a THF solution of YbI_2 (10.0 mL of 0.055 M, 0.55 mmol) at room temperature, and the reaction mixture was stirred overnight. The white precipitate was filtered off, and the clear orange filtrate was concentrated to give a red viscous solid. Recrystallization from DME yielded **2** as greenish yellow crystals (0.27 g, 64%). ^1H NMR (pyridine-d_5): δ 7.35−7.18 (m, 10H, $C_6H_5CH_2$), 3.60 (br s, 4H, $C_6H_5CH_2$), 3.17 (s, 12H, DME), 2.96 (s, 18H, DME). ^{13}C NMR (pyridine-d_5): δ 131.3, 129.3, 126.2, 125.8, 72.3, 58.8, 55.2, 46.8; the carbon atoms of the cage were not observed. ^{11}B NMR (THF/pyridine-d_5): δ 8.1 (1), −0.7 (1), −8.7 (1), −13.4 (2), −21.3 (2), −28.6 (3). IR (KBr, cm^{-1}): ν_{BH} 2507 (s), 2481 (s), 2381 (m). Anal. Calcd for $C_{24}H_{44}B_{10}O_4Yb$ (**2**−DME): C, 42.53; H, 6.54; Yb, 25.53. Found: C, 42.21; H, 6.35; Yb, 25.29.

Treatment of $YbCl_3$ with 2 equiv of $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ in THF at room temperature, followed by procedures similar to those used above, gave greenish yellow crystals in 50% yield identified as **2** by both spectroscopic and X-ray analyses.

Preparation of *closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$_4Sm_2Na_3$ (3). The mixture of $(C_6H_5CH_2)_2C_2B_{10}H_{10}$ (0.22 g, 0.68 mmol) and sodium (0.30 g, 13.0 mmol) in THF (15 mL) was stirred at room temperature for 24 h. The resulting clear pale yellow solution ($Na_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$) was slowly added to a suspension of $SmCl_3$ (0.088 g, 0.34 mmol) in THF (10 mL) at room temperature. The mixture was then stirred for 2 days. The color of the solution was turned to deep blue from yellow. After removal of the precipitates and addition of toluene (15 mL), the solution was concentrated to about one-third of its original volume. Dark blue crystals were obtained upon standing this solution at room temperature for days (0.13 g, 46% based on $SmCl_3$). ^1H NMR (pyridine-d_5): δ 10.40 (br s, 1H, para H), 8.25 (br s, 2H, meta H), 7.30 (br s, 2H, ortho H), 1.42 (br s, 2H, $C_6H_5CH_2$). ^{13}C NMR (pyridine-d_5): δ 153.2, 131.5, 128.6, 125.1, 45.8; the carbon atoms of the cage were not observed. ^{11}B NMR (THF/pyridine-d_5): δ 16.1 (1), 7.6 (1), −0.7 (1), −5.3 (2), −8.5 (1), −13.1 (2), −20.4 (2). IR (KBr, cm^{-1}): ν_{BH} 2517 (s), 2424 (s), 2318 (m). Anal. Calcd for $C_{64}H_{96}B_{40}Na_3Sm_2$: C, 46.09; H, 5.80; Sm, 18.04. Found: C, 45.75; H, 5.67; Sm, 18.09.

Recrystallization of **3** from THF/toluene solution at room temperature gave **3**·THF as dark blue crystals suitable for X-ray analysis.

Preparation of *closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$_4Sm_2Na_4(THF)_2$ (4). The mixture of $(C_6H_5CH_2)_2C_2B_{10}H_{10}$ (0.213 g, 0.66 mmol) and Na metal (0.23 g, 10.0 mmol) in 15 mL of THF was stirred at room temperature for 1 day. The resulting clear pale yellow solution ($Na_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$) was slowly added to a THF solution of SmI_2 (6.0 mL of 0.054 M, 0.32 mmol) at room temperature. The mixture was then stirred for 2 days, followed by procedures similar to those used in the synthesis of **3**, affording **4** as dark red crystals (0.12 g, 0.41%). ^1H NMR (pyridine-d_5): δ 6.83 (br, 20H, $C_6H_5CH_2$), 4.07 (br, 8H, $C_6H_5CH_2$), 3.45 (m, 4H, THF), 1.42 (m, 4H, THF). ^{13}C NMR (pyridine-d_5): δ 130.2, 128.3, 124.9, 122.0, 67.3, 25.2. The ^{11}B NMR spectra consisted of extremely broad, unresolved resonances. IR (KBr, cm^{-1}): ν_{BH} 2510 (s), 2466 (s), 2380 (m). Anal. Calcd for $C_{72}H_{112}B_{40}Na_4O_2Sm_2$: C, 47.13; H, 6.15; Sm, 16.39. Found: C, 46.85; H, 6.00; Sm, 16.25.

Recrystallization of **4** from CH_3CN at room temperature resulted in the isolation of a small amount of colorless crystals identified as trimethyl-*s*-triazine by ^1H and MS spectroscopy.[7]

Preparation of *closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$_4Yb_2Na_4(THF)_2$ (5). A THF solution of $Na_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ (16.0 mL, 0.64 mmol) was added dropwise to a THF solution of YbI_2 (4.0 mL of 0.078 M, 0.31 mmol) at room temperature. The reaction mixture was then stirred for 2 days, followed by procedures similar to those used in the synthesis of **3**, affording **5** as red crystals (0.15 g, 0.52%). ^1H NMR (pyridine-d_5): δ 7.38 (m, 20H, $C_6H_5CH_2$), 3.63 (s, 8H, $C_6H_5CH_2$), 3.65 (m, 4H, THF), 1.48 (m, 4H, THF). ^{13}C NMR (pyridine-d_5): δ 133.5, 131.4, 128.7, 122.9, 67.4, 56.1, 25.5. ^{11}B NMR (THF/pyridine-d_5): δ 20.1 (1), 10.2 (1), 2.6 (1), −1.7 (1), −4.5 (2), −9.6 (2), −17.3 (2). IR (KBr, cm^{-1}): ν_{BH} 2500 (s), 2434 (s), 2368 (m). Anal. Calcd for $C_{72}H_{112}B_{40}Na_4O_2Yb_2$: C, 46.00; H, 6.01; Yb, 18.40. Found: C, 46.36; H, 6.19; Yb, 18.25.

Preparation of [*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}Sm(THF)$_3$]$_2$ (6). To a suspension of NaH (0.20 g, 8.33 mmol) in 20 mL of THF was added a THF solution (15 mL) of $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$ (0.254 g, 0.68 mmol), and the mixture was refluxed overnight. The generated Me_3N was then removed along with approximately half of the solvent under vacuum. The suspension was allowed to settle. The resulting clear solution ($Na_2[(C_6H_5CH_2)_2C_2B_9H_9]$) was then added dropwise to a stirring THF solution of SmI_2 (5.2 mL of 0.065 M, 0.34 mmol) at room temperature, and the reaction mixture was stirred for 2 days. After removal of the precipitate and most of THF, toluene (15 mL) was added to give a dark blue solution. Slow evaporation of the solvents afforded dark blue crystals (0.16 g, 69%). ^1H NMR (pyridine-d_5): δ 8.71 (br, 2H, para H),

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

	1	2	3·THF	6	7
formula	$C_{28}H_{54}B_{10}O_6Sm$	$C_{28}H_{54}B_{10}O_6Yb$	$C_{68}H_{104}B_{40}Na_3OSm_2$	$C_{56}H_{94}B_{18}O_6Sm_2$	$C_{56}H_{94}B_{18}O_6Yb_2$
crystal size (mm)	0.22 × 0.16 × 0.12	0.60 × 0.40 × 0.20	0.30 × 0.27 × 0.26	0.16 × 0.14 × 0.12	0.65 × 0.35 × 0.20
fw	745.2	767.9	1739.6	1358.6	1404.0
crystal class	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$Pna2_1$	$C2/c$	$C2/c$
a, Å	10.166(2)	10.208(1)	31.711(1)	26.442(5)	26.641(1)
b, Å	13.491(3)	16.330(1)	21.452(1)	18.531(4)	18.313(1)
c, Å	13.933(3)	12.113(1)	15.907(1)	16.141(2)	16.118(1)
β, deg	97.80(3)	111.91(1)	90.00	122.73(1)	123.61(1)
V, Å^3	1893.2(7)	1873.4(3)	10821.0(7)	6654(2)	6549.0(6)
Z	2	2	4	4	4
D_{calcd}, Mg/m^3	1.307	1.361	1.068	1.356	1.424
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.0−51.0	4.0−55.0	3.0−51.0	3.0−51.2	3.0−53.4
μ, mm^{-1}	1.586	2.532	1.120	1.793	2.884
F(000)	764	780	3508	2768	2832
T, K	294	294	293	293	293
no. of indep reflns	3489	7362	12603	4948	6397
no. of obsd reflns ($I > 2\sigma(I)$)	3359	7214	12553	4899	6391
no. of params refnd	512	407	1031	383	437
goodness of fit	1.04	1.06	1.289	1.054	1.01
R_1	0.047	0.040	0.078	0.071	0.045
wR_2	0.114	0.107	0.1927	0.0178	0.120
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.63, −0.34	0.87, −1.01	0.98, −0.38	1.37, −0.55	0.77, −1.22

7.33 (br, 4H, meta H), 7.21 (br, 4H, ortho H), 3.75 (br, 4H, $C_6H_5CH_2$), 3.49 (m, 12H, THF), 1.45 (m, 12H, THF). ^{13}C NMR (pyridine-d_5): δ 148.5, 132.6, 127.9, 125.1, 67.3, 25.2. ^{11}B NMR (pyridine-d_5): δ −4.0 (2), −5.5 (1), −13.1 (4), −28.3 (1), −31.1 (1). IR (KBr, cm^{-1}): ν_{BH} 2523 (s), 2446 (s), 2385 (m). Anal. Calcd for $C_{56}H_{94}B_{18}O_6Sm_2$: C, 49.50; H, 6.97; Sm, 22.14. Found: C, 49.31; H, 7.38; Sm, 22.23.

Preparation of [*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}Yb(THF)$_3$]$_2$ (7). To a THF solution of YbI_2 (10.0 mL of 0.054 M, 0.54 mmol) was slowly added a clear THF solution of $Na_2[(C_6H_5CH_2)_2C_2B_9H_9]$ (20 mL, 1.09 mmol) at room temperature. The mixture was stirred at room temperature overnight, followed by procedures similar to those used in the synthesis of **6**, affording **7** as orange-yellow crystals (0.23 g, 61%). ^{1}H NMR (pyridine-d_5): δ 7.66 (m, 10H, $C_6H_5CH_2$), 3.55 (s, 4H, $C_6H_5CH_2$), 3.47 (m, 12H, THF), 1.41 (m, 12H, THF). ^{13}C NMR (pyridine-d_5): δ 145.2, 130.4, 127.0, 124.4, 67.3, 42.8, 25.2. ^{11}B NMR (pyridine-d_5): δ −18.0 (2), −21.5 (3), −24.5 (2), −46.5 (2). IR (KBr, cm^{-1}): ν_{BH} 2535 (s), 2424 (s), 2388 (m). Anal. Calcd for $C_{48}H_{78}B_{18}O_4Yb_2$ (**7**−2THF): C, 45.76; H, 6.24; Yb, 27.47. Found: C, 45.31; H, 6.38; Yb, 27.23.

X-ray Structure Determination. All single crystals were immersed in Paraton-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.[8] 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, on F^2 using Siemens SHELXTL program package (PC version).[9] Most of the carborane hydrogen atoms was located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Three DME molecules in **1** are disordered over two sets of positions with 0.5:0.5 occupancies. Four out of six THF molecules in **7** are disordered over two sets of positions with 0.5:0.5 occupancies. Crystal data and details of data collection and structure refinements are given in Table 1. Selected interatomic distances are listed in Table 2. Further details are included in the Supporting Information.

Results and Discussion

***exo-nido*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]Ln(DME)$_3$.** It has been well-documented that $C_2B_{10}H_{12}$ can be reduced by alkali metals to [*nido*-$C_2B_{10}H_{12}$]$^{2-}$, which is capable of being η^6-bound to transition metals, affording a series of 13-vertex *closo*-metallacarboranes.[1] Similar to $C_2B_{10}H_{12}$, 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ can also be reduced to [*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$^{2-}$ by Na or K metal in THF at room temperature. Treatment of LnI_2 with 1 equiv of K_2[*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$] in THF at room temperature gave, after recrystallization from DME, the colored compounds *exo-nido*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]Ln(DME)$_3$ in good yield (eq 1).

$$K_2[\textit{nido}\text{-}(C_6H_5CH_2)_2C_2B_{10}H_{10}] + LnI_2 \xrightarrow{\text{THF/DME}} \textit{exo-nido}\text{-}[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Ln(DME)_3 + 2KI \quad (1)$$
$$Ln = Sm\ (\mathbf{1}),\ Yb\ (\mathbf{2})$$

These two compounds are extremely air- and moisture-sensitive but remain stable for months in the mother liquor under an inert atmosphere. However, the transparent crystals will gradually become powder by keeping them away from the mother liquor, indicating the loss of the coordinated DME molecules. Traces of air immediately convert the dark red **1** to a pale yellow powder, and the greenish yellow **2** to a white powder.

Their ^{1}H NMR spectra support the ratio of three DME molecules per carborane anion. The ^{11}B NMR spectrum of **2** shows a 1:1:1:2:2:3 splitting pattern, while that of **1** exhibits many broad, unresolved resonances. The solid-state IR spectra exhibit both a characteristic doublet B−H stretching mode centered around 2497 cm^{-1} and a medium band at about 2400 cm^{-1} attributable to a Ln−H−B stretching mode.[3,10] The monomeric nature of these two compounds has been confirmed by single-crystal X-ray analyses.

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Table 2. Selected Interatomic Distances (Å)

	Compound **1**		
Sm(1)−O(1)	2.685(3)	Sm(1)−O(6)	2.637(2)
Sm(1)−O(2)	2.668(3)	Sm(1)···B(5)	3.112(2)
Sm(1)−O(3)	2.650(2)	Sm(1)···B(9)	2.980(3)
Sm(1)−O(4)	2.638(3)	Sm(1)···B(10)	3.018(2)
Sm(1)−O(5)	2.646(2)		
	Compound **2**		
Yb(1)−O(1)	2.497(5)	Yb(1)−O(5)	2.541(5)
Yb(1)−O(2)	2.516(4)	Yb(1)−O(6)	2.495(6)
Yb(1)−O(3)	2.569(4)	Yb(1)···B(5)	2.832(7)
Yb(1)−O(4)	2.462(5)	Yb(1)···B(4)	2.956(6)
	Compound **3**		
Sm(1)−C(11)	3.033(4)	Sm(2)−C(1)	3.069(5)
Sm(1)−C(12)	2.794(4)	Sm(2)−C(2)	2.793(4)
Sm(1)−B(13)	2.988(5)	Sm(2)−B(3)	2.935(5)
Sm(1)−B(14)	3.061(5)	Sm(2)−B(4)	3.045(5)
Sm(1)−B(15)	3.080(5)	Sm(2)−B(5)	3.004(5)
Sm(1)−B(16)	2.864(5)	Sm(2)−B(6)	2.964(6)
Sm(1)···B(35)	2.996(5)	Sm(2)···B(25)	3.115(5)
Sm(1)···B(40)	3.039(5)	Sm(2)···B(29)	2.965(5)
Sm(1)···B(41)	3.005(5)	Sm(2)···B(30)	3.030(5)
Sm(1)···C(20)	2.939(5)	Sm(2)···C(4)	3.079(4)
Sm(1)···C(23)	3.061(5)	Sm(2)···C(5)	3.162(4)
Sm(1)···C(27)	2.950(5)	Sm(2)···C(9)	3.148(4)
Na(1)−C(31)	2.704(5)	Na(2)−C(21)	3.002(5)
Na(1)−C(32)	3.007(5)	Na(2)−C(22)	2.769(5)
Na(1)−B(33)	2.894(6)	Na(2)−B(23)	2.853(7)
Na(1)−B(34)	2.867(5)	Na(2)−B(24)	3.009(7)
Na(1)−B(35)	3.069(5)	Na(2)−B(25)	2.995(5)
Na(1)−B(36)	3.009(6)	Na(2)−B(26)	2.804(5)
Na(1)···B(5)	3.152(5)	Na(2)···B(15)	2.991(5)
Na(1)···B(9)	2.923(6)	Na(2)···B(19)	2.981(6)
Na(1)···B(10)	2.993(5)	Na(2)···B(20)	2.917(5)
Na(1)···C(60)	2.941(6)	Na(2)···C(38)	2.923(5)
Na(1)···C(59)	3.008(5)	Na(2)···C(39)	2.973(6)
Na(1)···C(57)	3.071(5)	Na(3)···B(25)	2.986(5)
Na(3)···B(5)	3.009(5)	Na(3)···B(26)	3.023(5)
Na(3)···B(6)	3.098(5)	Na(3)···B(34)	3.090(5)
Na(3)···B(15)	3.001(5)	Na(3)···B(35)	3.066(5)
Na(3)···B(16)	3.129(5)		
	Compound **6**		
Sm(1)−O(1)	2.531(4)	Sm(1)···B(4)	3.031(3)
Sm(1)−O(2)	2.549(3)	Sm(1)···B(4A)	3.178(5)
Sm(1)−O(3)	2.557(3)	Sm(1)···B(9A)	2.977(5)
Sm(1)···B(3)	2.946(4)	Sm(1)···B(8A)	3.196(5)
	Compound **7**		
Yb(1)−O(1)	2.444(5)	Yb(1)···B(4)	2.909(6)
Yb(1)−O(2)	2.547(12)	Yb(1)···B(8)	3.073(6)
Yb(1)−O(3)	2.316(9)	Yb(1)···B(4A)	3.014(6)
Yb(1)···B(3)	2.795(6)	Yb(1)···B(9A)	2.853(8)

The solid-state structures of **1** and **2** are shown in Figures 1 and 2, respectively. They are isomorphous but not isostructural. The common structural features are (1) the monomeric *exo-nido* structures formed by exclusive Ln−H−B bondings between the Ln ion and the carborane ligand and (2) the coordination sphere around the Ln metal being completed by three DME molecules. The coordination details between Ln and [*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}]^{2-}$ are, however, slightly different in the two compounds. The [*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}]^{2-}$ anion is bound to Sm^{2+} via three B−H bonds, one from the open hexagonal C_2B_4 face and the other two from the pentagonal belt (B_5), while this anion bonds to Yb^{2+} through two B−H bonds from the open hexagonal C_2B_4 face only. This difference should be due to the sizes of Ln ions.

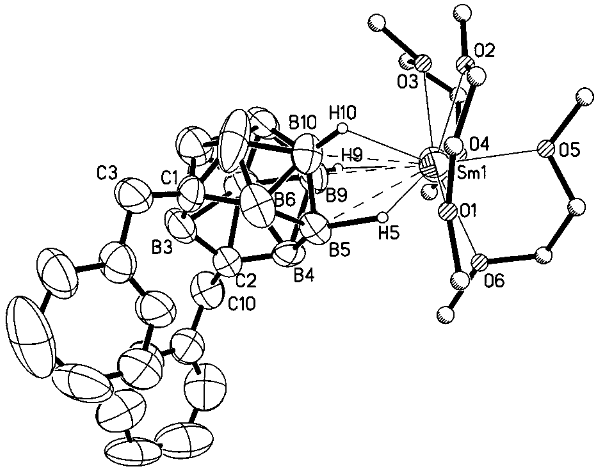

Figure 1. Molecular structure of **1**. All terminal hydrogen atoms are omitted for clarity.

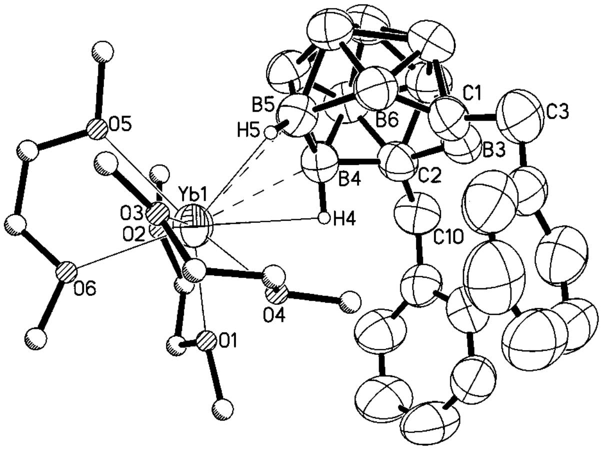

Figure 2. Molecular structure of **2**. All terminal hydrogen atoms are omitted for clarity.

The average Sm···B distance of 3.037(3) Å is very close to that of 3.042(8) Å in [*exo-nido*-$\{(C_6H_5CH_2)_2C_2B_9H_9\}Sm(DME)_2]_2$[2c] and to the average Eu···B distance of 3.04(1) Å in [*closo*-$(C_2B_{10}H_{12})Eu(MeCN)_3]_\infty$.[3b] The average Yb···B distance of 2.894(7) Å is similar to that of 2.94(2) Å in $(MeCN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}$[11] and is 0.143 Å shorter than that of Sm···B in **1**. This difference can be compared with the 0.18 Å difference between Shannon's ionic radii[12] of Sm^{2+} and Yb^{2+}. The average Sm−O distance of 2.635(3) Å falls in the range normally observed in samarium(II) DME compounds, 2.677 Å for [*exo-nido*-$\{(C_6H_5CH_2)_2C_2B_9H_9\}Sm(DME)_2]_2$,[2c] 2.618 Å for $SmI_2(DME)_2(THF)$,[13a] 2.641 Å for $SmI_2(DME)(THF)_3$,[13a] and 2.685 Å for $[\{(Me_3Si)_2N\}SmI(DME)(THF)]_2$.[13b] The average Yb−O distance of 2.513(6) Å falls in the range of 2.44−2.60 Å normally found in eight-coordinate Yb(II) DME and DIME (diethylene glycol dimethyl ether) compounds.[14]

Comparison of **1** and **2** with other lanthanacarboranes, for example, [*closo*-$(C_2B_{10}H_{12})Eu(MeCN)_3]_\infty$,[3b]

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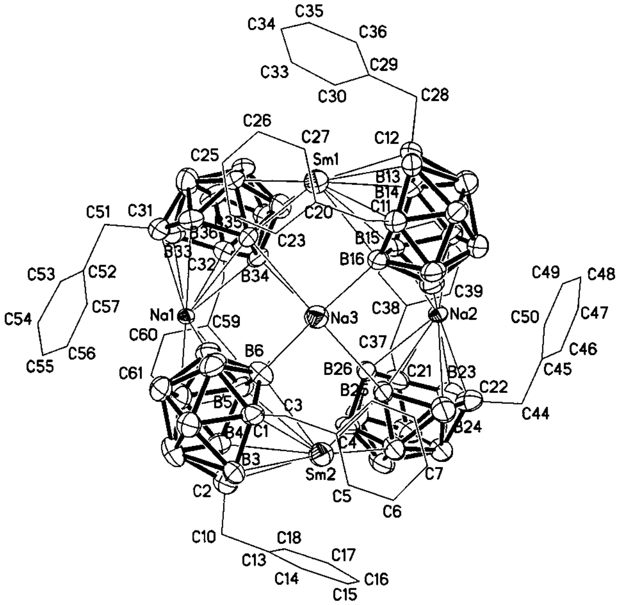

Figure 3. Molecular structure of **3**. All hydrogen atoms are omitted for clarity.

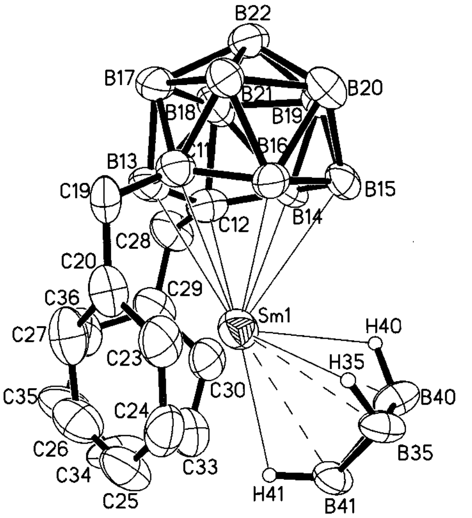

Figure 4. A typical coordination environment for Sm atom in **3**.

closo-[$Me_2Si(C_5H_4)(C_2B_{10}H_{11})$]Sm(THF)$_2$,[3d] and *closo*-[$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Sm(THF)$_2$,[15] suggests that steric factors play an important role in the formation of *exo-nido*-lanthanacarboranes and can also affect the coordination mode between lanthanide ions and carboranyl ligands at least with respect to **1** and **2**.

***closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$_4Sm_2Na_3$.** It has been reported that [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ is a strong reducing species that can reduce M(IV) to M(II) (M = Ti, Zr, Hf)[16] and Ln(III) to Ln(II) (Ln = Eu,[3b] Sm,[17] Yb[17]). Since $LnCl_3$ is a much less expensive starting material than LnI_2, alternate routes to **1** and **2** are then proposed. Reaction of $YbCl_3$ with 2 equiv of Na$_2$[*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$] in THF/DME gave **2** in 50% yield. However, treatment of $SmCl_3$ with 2 equiv of Na$_2$[*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$] in THF afforded, after workup, an unprecedented cluster *closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$_4Sm_2Na_3$ (**3**) as dark blue crystals in 46% yield (based on $SmCl_3$). The ^{1}H NMR spectrum shows the resonances attributable to the carboranyl ligand only. The ^{11}B NMR spectrum exhibits a 1:1:1:2:1:2:2 splitting pattern. Its IR spectrum displays both typical B−H and Ln−H−B stretching modes. Elemental analyses support the composition of **3**. This mixed-valence samaracarborane has been confirmed by single-crystal X-ray analysis.

An X-ray diffraction study reveals that **3** is a novel *closo-exo*-metallacarborane cluster with a central atom of sodium that bonds to four half-sandwich [η^6-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]M (M = Na, Sm) units in a distorted-tetrahedral arrangement via four sets of two B−H bonds from the open hexagonal C_2B_4 bonding face at an average Na···B distance of 3.050(5) Å (Figure 3). The four 13-vertex half-sandwich [η^6-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]M units are then connected to each other by four sets of three B−H−M bonds, one B−H bond from the open hexagonal C_2B_4 bonding face and the other two from the pentagonal belt. Figure 4 shows a typical coordination environment for the Sm atom.

The average Sm(1)−cage(1) distance of 2.970(5) Å is identical with the average Sm(2)−cage(2) distance of 2.968(5) Å. These measured values compare with the 2.823(4) Å in [η^5:η^6-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Sm^{III}(THF)$_2$,[15] 2.764(3) and 2.841(3) Å in [η^5:η^6-$Me_2Si(C_5H_4)(C_2B_{10}H_{11})$]Sm^{III}(THF)$_2$,[3d,17] 2.983(11) Å in [(η^6-$C_2B_{10}H_{12}$)Eu^{II}(MeCN)$_3$]$_\infty$,[3b] and 3.03(1) Å in [(η^6-$C_2B_{10}H_{12}$)$_2$Eu^{II}(THF)$_2$]$^{2-}$.[3b] The average Sm(1)···B (B_3 face) distance of 3.013(5) Å is very close to the average Sm(2)···B (B_3 face) distance of 3.037(5) Å, which can be compared with the 3.037(3) Å in **1**, 3.042(8) Å in [*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}Sm^{II}(DME)$_2$]$_2$,[2c] and 2.800(14) Å in {[(η^5-$(Me_3Si)_2C_2B_4H_4$)Sm^{III}]$_3$[(μ_2-$(Me_3Si)_2C_2B_4H_4Li$)$_3$(μ_3-OMe)][μ_2-Li(THF)$_3$]$_3$(μ_2-O)}.[4c] The closest approach of the benzyl substituents to Sm(1) and Sm(2) is through C(20) and C(4) at distances of 2.939(5) and 3.079(5) Å, respectively, and the smaller Sm(1)···C(20) distance corresponds to the smaller C(11)−C(19)−C(20) angle of 108.6(4)°. Comparison of these distances with those of 2.825(3) and 2.917(3) Å found in [$(C_5Me_5)_2Sm$][$B(C_6H_5)_4$][18] suggests that both Sm(1) and Sm(2) have certain interactions with the phenyl rings, which may be the reason no THF molecules coordinate to the metal ions in **3**.

The average Na(1)−cage(3) distance of 2.925(6) Å is close to the average Na(2)−cage(4) distance of 2.906(6) Å. These measured values are shorter than that of 3.084(11) Å in [η^5-$(Me_3Si)_2C_2B_4H_5$]Na(THF),[19] but are longer than the value of 2.76 Å that would be expected by subtracting the difference, 0.65 Å, between Shannon's ionic radii[12] of Cs$^+$ and Na$^+$ from the average Cs−cage distance of 3.41(5) Å in [*closo-exo*-{$(Me_3Si)_4C_4B_8H_8$}Cs$_2$(TMEDA)]$_\infty$ (TMEDA = tetramethylethylenediamine).[20]

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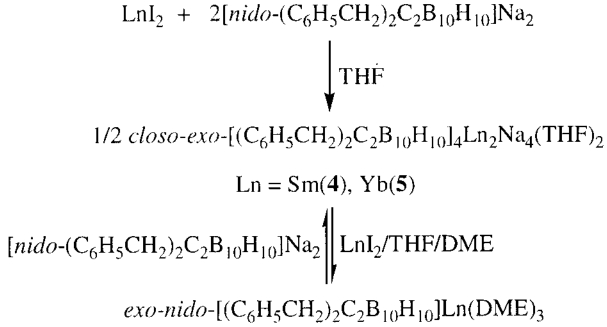
Scheme 1



The average Na(1)···B (B_3 face) distance of 3.023(6) Å is close to the average Na(2)···B (B_3 face) distance of 2.963(6) Å and the average Na(3)···B distance of 3.050(5) Å. These measured values are comparable to the value of 3.087(10) Å in [η^5-$(Me_3Si)_2C_2B_4H_5$]Na(THF)[19] and 2.99 Å derived from the subtraction of the difference in ionic radii, 0.65 Å, from the average Cs···B distance, 3.64(5) Å, in [*closo-exo*-{$(Me_3Si)_4C_4B_8H_8$}Cs_2(TMEDA)]$_\infty$.[20] The closest approach of the benzyl substituents to Na(1) and Na(2) is through C(60) and C(38) at distances of 2.941(6) and 2.923(6) Å, respectively, implying that both Na ions have certain interactions with the phenyl rings.[21]

These data show that the coordination environment for all four Na(1), Na(2), Sm(1), and Sm(2) atoms is almost identical and the two Sm ions are indistinguishable in terms of bond distances. The formal oxidation state for each Sm ion should then be +2.5. The formation of this mixed-valence samarium compound may be due to the incomplete reduction of Sm(III) by the [*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}]^{2-}$ anion.[22]

***closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Ln_2Na_4(THF)_2$.** It has been known that both [*nido*-$C_2B_{10}H_{12}]^{2-}$ and [*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}]^{2-}$ are capable of forming bis-ligated *closo*-lanthanacarboranes, *closo*-[$(C_2B_{10}H_{12})_2$Eu$(THF)_2]^{2-}$,[3a,b] and *closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Sm_2Na_3$. Reaction of **1** or **2** with 1 equiv of Na_2[*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$] or treatment of LnI_2 with 2 equiv of Na_2[*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}$] in THF gave the colored compounds that have been formulated as *closo-exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Ln_2Na_4(THF)_2$ (Ln = Sm (**4**), Yb (**5**)) in moderate yield. Treatment of them with 1 equiv of LnI_2 in THF afforded, after recrystallization from DME, compound **1** or **2**, respectively (Scheme 1).

The ^{1}H NMR spectra support the ratio of a half THF molecule per ligand. Their ^{13}C NMR spectra show the presence of the ligand and THF molecule. The ^{11}B NMR spectrum of **4** exhibits very broad, unresolved resonances, while that of **5** displays a 1:1:1:1:2:2:2 splitting pattern. The solid-state IR spectra exhibit both typical B−H and Ln−H−B stretching modes. Elemental analyses support the proposed molecular formulas for **4** and **5**. The data on IR spectra and the ratio of carborane/THF suggest that they are very unlikely to be monomers. They may have structures similar to **3**.

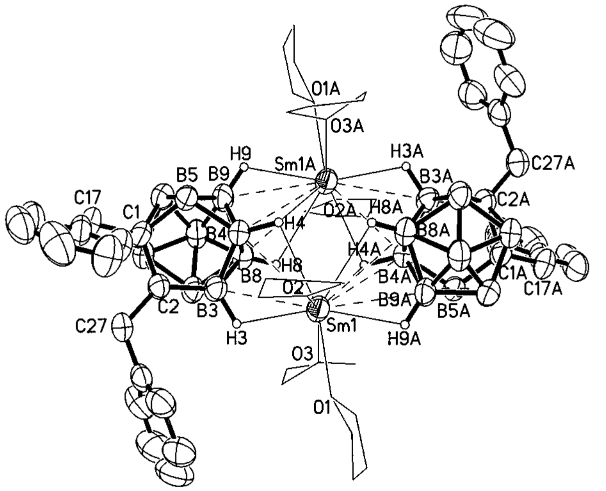


Figure 5. Molecular structure of **6**. All terminal hydrogen atoms are omitted for clarity.

Attempts to grow single crystals suitable for X-ray analysis from various solvents failed. It should be pointed out that CH_3CN should not be used as a crystallization solvent since it reacts with both **1** and **4,** affording a reduction product trimethyl-*s*-triazine.

The formation of *closo-exo*-lanthanacarboranes of **3**−**5** may result from the intermolecular interactions that force the benzyl groups to adopt an orientation allowing the metal ions to bond to the carborane anion in a η^6-fashion.

[*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}$Ln(THF)_3]_2$. Previous results show that *exo-nido*- and *closo*-lanthanacarboranes of C_2B_{10} systems are exchangeable by changing the ratio of Ln/ligand. It is interesting to know if this is a common phenomenon for lanthanacarboranes or is only limited to C_2B_{10} systems. Treatment of LnI_2 with 2 equiv of Na_2[*nido*-$(C_6H_5CH_2)_2C_2B_9H_9]^{2c}$ in THF gave [*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}$Ln(THF)_3]_2$ (Ln = Sm (**6**), Yb (**7**)) in good yield (eq 2).

$$\begin{gathered}Na_2[\textit{nido}\text{-}(C_6H_5CH_2)_2C_2B_9H_9] + LnI_2 \xrightarrow{\text{THF}} \\ 1/2[\textit{exo-nido}\text{-}\{(C_6H_5CH_2)_2C_2B_9H_9\}Ln(THF)_3]_2 + \\ \text{Ln} = \text{Sm }(\mathbf{6}),\ \text{Yb }(\mathbf{7}) \\ 2NaI \quad (2)\end{gathered}$$

These two compounds do not react with excess Na_2[*nido*-$(C_6H_5CH_2)_2C_2B_9H_9$], which is significantly different from **1** and **2**, indicating that the same substituent has a different effect on C_2B_9 and C_2B_{10} systems. Both **1** and **2** have been fully characterized by spectroscopy, elemental analyses, and X-ray analyses.

The solid-state structures of **6** and **7** are shown in Figures 5 and 6, respectively. They are isomorphous. The main structural features are the presence of exclusive Ln−H−B bondings between Ln ions and carboranyl ligands and the coordination sphere around Ln being completed by three THF molecules, which are very similar to those of **1**, **2**, and [*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}$Sm(DME)_2]_2$.[2c] The coordination details between Ln and [*nido*-$(C_6H_5CH_2)_2C_2B_9H_9]^{2-}$ in **6** and **7** are only slightly different.

In the molecular structure of **6**, each of the two carboranyl moieties serves as a bridging ligand for two

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[21] (a) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1181. (b) Clark, D. L.; Hollis, R. V.; Scott, B. L.; Watkin, J. G. *Inorg. Chem.* **1996**, *35*, 667. (c) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 5903.

[22] The formation of mixed-valence organosamarium compounds by the incomplete redox reactions has been reported, see: (a) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292. (b) Evans, W. J.; Forrestal, K. J.; Ziller, W. J. *Polyhedron* **1998**, *17*, 4015.

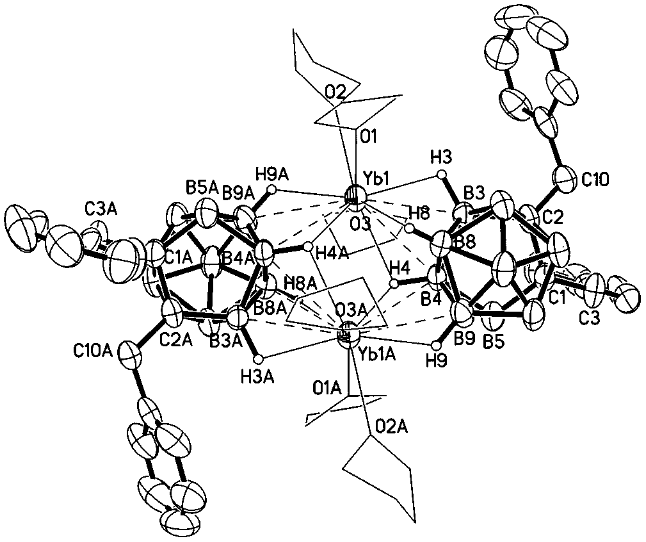

Figure 6. Molecular structure of **7**. All terminal hydrogen atoms are omitted for clarity.

Sm atoms while bonding to one via two B−H bonds from the open pentagonal C_2B_3 face and the other through three B−H bonds from the pentagonal belt (B_5) and the open pentagonal C_2B_3 face, respectively, to form a centrosymmetric dimer. The average Sm···B distance of 3.066(5) Å is close to that of 3.037(3) Å in **1**, 3.037(5) and 3.013(5) Å in **3**, and 3.042(8) Å in [*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}$Sm(DME)_2$]$_2$.[2c] In the dimeric structure of **7**, each of the two carboranyl moieties serves as a bridging ligand for two Yb atoms while bonding to one via two B−H bonds from the open pentagonal C_2B_3 face and the pentagonal belt (B_5) and the other through three B−H bonds from the pentagonal belt (B_5) and the open pentagonal C_2B_3 face, respectively. The average Yb···B distance of 2.929(8) Å is close to that of 2.894(7) Å in **2** and 2.94(2) Å in $(MeCN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}$.[11]

Comparison of **6** and **7** with their analogue [*exo-nido*-{$(C_6H_5CH_2)_2C_2B_9H_9$}$Sm(DME)_2$]$_2$[2c] suggests that both metal ions and solvents can affect the coordination details between metal ions and C_2B_9 ligand systems.

Conclusion

Steric factors play a key role in the formation of *exo-nido*-lanthanacarboranes or dominate the coordination mode between metal ions and carboranyl ligands. In the case where the substituents are benzyl groups, *closo*- and *exo-nido*-lanthanacarboranes of C_2B_{10} systems are exchangeable by changing the ratio of metal/carborane. The coordination details in *exo-nido*-lanthanacarboranes are also dependent upon the metal ions and coordinating solvents, which results in difficulty in accurately predicting the molecular structures of lanthanacarborane analogues.

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Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and figures giving atom-numbering schemes for **1**−**3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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