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Synthesis and Structural Characterization of *closo*- and *exo-nido*-Lanthanacarboranes

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Treatment of anhydrous $LaCl_3$ with 1 equiv of Na_2[7,8-R_2-*nido*-7,8-$R_2C_2B_9H_9$] in THF afforded sandwich complexes *closo*-{$(THF)_2Na$}{$(R_2C_2B_9H_9)_2La(THF)_2$} (R = H (**1**), R = $C_6H_5CH_2$ (**2**)) in good yield. Reaction of SmI_2 with an equimolar amount of Na_2[7,8-*nido*-7,8-$(C_6H_5CH_2)_2C_2B_9H_9$] in THF, followed by the addition of 1,2-dimethoxyethane (DME), generated the dimeric *exo-nido*-$[((C_6H_5CH_2)_2C_2B_9H_9)Sm(DME)_2]_2$·DME (**3**) in 70% yield. All complexes were characterized by ^{1}H, ^{13}C, and ^{11}B NMR and IR spectroscopy as well as complexometric metal analyses. The molecular structures of complexes **1** and **3** were further confirmed by X-ray analyses. The coordination geometry of complex **1** is best described as distorted tetrahedral with two η^5-bonded $C_2B_9H_{11}$ ligands and two coordinated THF molecules. In the centrosymmetric dimer **3**, each of the two dibenzyldicarbollide ligands serves as a bridging ligand for two Sm atoms while bonding to one via upper belt B−H bonds (containing two carbon atoms) and the other through lower belt B−H bonds.

Introduction

Lanthanacarboranes are a new class of organometallic compounds and much less studied in comparison with the cyclopentadienyl-based organolanthanide compounds or metallacarboranes of d- and p-block metals.[1] The first compound of this class was reported by Hawthorne and co-workers in 1988.[2] Since then, they have published a series of papers describing the syntheses and structures of the sandwich and half-sandwich complexes of divalent and trivalent lanthanide metals (Sm, Yb, and Eu) with $C_2B_9H_{11}^{2-}$ and $C_2B_{10}H_{12}^{2-}$ ligands.[2−5] For example, reactions of $Na_2[C_2B_9H_{11}]$ with LnI_2 (Ln = Sm, Yb) in THF gave half-sandwich complexes of the type $Ln(C_2B_9H_{11})(THF)_4$, followed by oxidation with $[Tl(C_2B_9H_{11})]^-$ to generate sandwich complexes of the general formula $[Ln(C_2B_9H_{11})_2]^-$.[2,3] The reactions of LnI_2 (Ln = Sm, Eu, Yb) with the larger $C_2B_{10}H_{12}^{2-}$ were more complicated. Both polymeric and monomeric structures were obtained depending on both the nature of the lanthanide metals and the metal-to-ligand molar ratios employed in the reactions.[4,5] The smaller $[(Me_3Si)_2C_2B_4H_4]^{2-}$ anion was introduced to organolanthanide chemistry by Hosmane and co-workers.[6−12] This anion reacted with mid- to late-lanthanide trichlorides to produce various types of lanthanacarboranes depending on both the solvents and the metal-to-carborane molar ratios used in the reactions. For instance, the sandwich species of the general formula [1-Cl-1-(μ-Cl)-2,2′,3,3′-$(Me_3Si)_4$-5,6-[(μ-H)$_2$Li-(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]-1,1′-*commo*-Ln(2,3-$C_2B_4H_4)_2]^-$ were isolated in good yield from 1:2 (Ln to carborane) molar reaction stoichiometries in a TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)/benzene solvent system.[9] On the other hand, the results were quite different when THF was involved in the reactions, from which trinuclear lanthanacarborane clusters of the type {[η^5-1-Ln-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4]_3$[(μ_2-1-Li-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4)_3(\mu_3$-OMe)][(μ_2-Li(C_4H_8O))$_3(\mu_2$-O)} were isolated.[8]

In view of lanthanacarborane chemistry, we are more interested in the C_2B_9 system since there are no definitive reports on analogous species incorporating other lanthanide metals or dicarbollide derivatives except samarium and ytterbium complexes of the dicarbollide dianion ($C_2B_9H_{11}^{2-}$).[13] Furthermore, the fluxionality of complex $(C_2B_9H_{11})Sm^{II}(THF)_4$ in THF was observed by variable-temperature ^{11}B NMR spectroscopy; however, no *exo-nido* tautomer has yet been isolated.[3] It is rational to propose that the bulky substituents on the open pentagonal face (C_2B_3) may change the bonding interactions between the dicarbollide and Ln^{2+} ions and stabilize the *exo-nido* complex. As part of our attempt to further understand the chemical bonding of lanthanacarboranes and to exploit

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the similarities and the differences among C_2B_{10}, C_2B_9, and C_2B_4 systems, a program to explore the utility of dicarbollide ion and its derivatives in lanthanide chemistry has been initiated in our laboratory. We report herein the syntheses and structures of *closo*- and *exo-nido*-lanthanacarboranes, $\{(THF)_2Na\}\{(R_2C_2B_9H_9)_2La(THF)_2\}$ (R = H, $C_6H_5CH_2$) and $[\{(C_6H_5CH_2)_2C_2B_9H_9\}Sm(DME)_2]_2\cdot DME$.

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 CH_3OH) were freshly distilled from sodium benzophenone ketyl immediately prior to use. CH_3OH was distilled and stored over activated molecular sieves (4 Å). Anhydrous $LaCl_3$ was prepared from the hydrates by standard procedures.[14] SmI_2[15] and $[Me_3NH][C_2B_9H_{12}]$[16] were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Company and used as received unless otherwise noted. Infrared spectra were obtained from a KBr pellet prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. The electron impact mass spectrum was recorded on a HP5989A spectrometer. ^1H and ^{13}C NMR spectra were recorded either on a Bruker ARX-500 spectrometer at 500.12 and 125.77 MHz, respectively, or on a Bruker WM-250 spectrometer at 250.13 and 62.89 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units, with reference to internal or external TMS (0.00 ppm) for proton and carbon chemical shifts and to external $BF_3\cdot OEt_2$ (0.00 ppm) for boron chemical shifts. Complexometric metal analyses were conducted by titration with EDTA.

Preparation of $\{(THF)_2Na\}\{(C_2B_9H_{11})_2La(THF)_2\}$ (1). To a suspension of NaH (75.0 mg, 3.12 mmol) in 15 mL of THF was added the THF solution (10 mL) of $[Me_3NH][C_2B_9H_{12}]$ (200.0 mg, 1.04 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 solution was then added dropwise at room temperature through a cannula to a stirred suspension of $LaCl_3$ (255.0 mg, 1.04 mmol) in 10 mL of THF. The reaction mixture was stirred at room temperature for 2 days and then allowed to settle. The white precipitate was filtered off. After removal of three-quarters of the solvent and vapor diffusion of *n*-hexane, a colorless microcrystalline solid was formed. The product was then washed with *n*-hexane (2 × 3 mL) and dried under vacuum to give 241.0 mg of **1** (65% yield based on $C_2B_9H_{12}^-$). X-ray quality crystals were grown by slow evaporation of a THF solution of **1** over months. Complexometric anal. Calcd for $C_{20}H_{54}B_{18}LaNaO_4$: La, 19.42. Found: La, 19.20. ^1H NMR (pyridine-d_5): δ 3.62 (m, 16H), 2.42 (br s, 4H), 1.58 (m, 16H). ^{13}C NMR (pyridine-d_5): δ 67.8, 25.8, carboranyl $C-H$ was not observed. $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −7.9 (2), −13.7 (2), −14.7 (1), −19.2 (2), −30.1 (1), −34.6 (1). $^{11}B\{^1H\}$ NMR (THF): δ −8.8 (2), −14.7 (2), −15.5 (1), −20.2 (2), −31.1 (1), −35.8 (1). IR (cm^{-1}): ν_{BH} 2532 (vs), 2450 (vs), ν_{THF} 1048 (s), 840 (s).

$Na_2[C_2B_9H_{11}]$ reacted with $LaCl_3$ in a molar ratio of 2:1 under the same reaction conditions to give **1** in 70% yield.

Preparation of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$. To a solution of *o*-$C_2B_{10}H_{12}$ (500.0 mg, 3.47 mmol) in a dry toluene/Et_2O (2:1) mixture (15 mL) at 0 °C was added a 1.60 M solution of *n*-BuLi in hexane (6.0 mL, 9.60 mmol) dropwise with stirring. The mixture was allowed to warm up to room temperature and stirred for 30 min. The solution was then cooled to 0 °C, and freshly distilled $C_6H_5CH_2Br$ (1.78 g, 10.40 mmol) in toluene (3 mL) was added rapidly. The reaction mixture was refluxed overnight and then quenched with 10 mL of water. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic portions were dried over anhydrous $MgSO_4$. Removal of the solvents and addition of hexane gave pure white 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (809.8 mg, 72%): mp 147−148 °C. ^1H NMR (acetone-d_6): δ 7.38 (m, 10H), 3.89 (s, 4H). ^{13}C NMR (acetone-d_6): 137.0, 132.0, 129.7, 129.1, 81.9, 41.8. $^{11}B\{^1H\}$ NMR (acetone-d_6): −4.4 (2), −8.9 (2), −10.2 (6). MS (EI, 70eV): 324 (M^+, 50%). IR (cm^{-1}): ν_{BH} 2615 (vs), 2569 (vs), ν_{benzyl} 3028 (w), 1500 (m), 1454 (m).

Preparation of $[Me_3NH][7,8\text{-}(C_6H_5CH_2)_2\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_{10}]$. To a mixture of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (500.0 mg, 1.54 mmol) and KOH (285.0 mg, 5.09 mmol) was added distilled CH_3OH (15 mL) with stirring at 0 °C. The reaction mixture was allowed to warm up to room temperature within 30 min and then refluxed overnight. After removal of the solvent, water (10 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 (3 × 5 mL), and dried in vacuum to give $[Me_3NH][7,8\text{-}(C_6H_5CH_2)_2\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_{10}]$ as a white solid (552.0 mg, 96%). ^1H NMR (acetone-d_6): δ 7.21 (m, 10H), 3.66 (s, 4H), 3.09 (s, 9H), μ-H peak may be overlapped with those of acetone. ^{13}C NMR (acetone-d_6): δ 143.4, 130.2, 128.1, 125.8, 72.4, 46.1, 42.3. $^{11}B\{^1H\}$ NMR (acetone-d_6): δ −9.2 (2), −10.3 (1), −17.0 (2), −18.0 (2), −33.3 (1), −36.1 (1). IR (cm^{-1}): ν_{BH} 2513 (br vs).

Preparation of $\{(THF)_2Na\}\{[(C_6H_5CH_2)_2C_2B_9H_9]_2La(THF)_2\}$ (2). To a suspension of NaH (70.0 mg, 2.92 mmol) in 15 mL of THF was added the THF solution (8 mL) of $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$ (250.0 mg, 0.67 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 solution ($Na_2[(C_6H_5CH_2)_2C_2B_9H_9]$) was then added dropwise at room temperature through a cannula to a stirred suspension of $LaCl_3$ (164.0 mg, 0.67 mmol) in 15 mL of THF, followed by the same procedures as those for the preparation of **1**. Compound **2** was obtained as a white solid (198.0 mg, 55% yield based on the carborane anion). Complexometric anal. Calcd for $C_{48}H_{78}B_{18}LaNaO_4$: La, 12.92. Found: La, 12.90. ^1H NMR (pyridine-d_5): δ 7.26 (m, 20H), 3.58 (m, 8H), 3.63 (m, 16H), 1.59 (m, 16H). ^{13}C NMR (pyridine-d_5): δ 143.3, 130.3, 128.0, 125.6, 67.8, 42.5, 25.8, carboranyl $C-H$ was not observed. $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −10.5 (2), −11.9 (1), −18.4 (2), −19.6 (2), −34.8 (1), −37.4 (1). IR (cm^{-1}): ν_{BH} 2521 (br vs), ν_{THF} 1030 (s), 863 (s), ν_{benzyl} 1520 (w), 1425 (w).

Preparation of $[\{(C_6H_5CH_2)_2C_2B_9H_9\}Sm(DME)_2]_2\cdot DME$ (3). To a suspension of NaH (100.0 mg, 4.16 mmol) in 25 mL of THF was added the THF solution (5 mL) of $[Me_3NH][(C_6H_5CH_2)_2C_2B_9H_{10}]$ (187.0 mg, 0.50 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 (9.0 mL of 0.054 M, 0.49 mmol) at room temperature, and the reaction mixture was stirred overnight. The color of the solution was changed from deep green to dark red during the course of reaction. After removal of the precipitate and most of the THF, 20 mL of 1,2-dimethoxyethane (DME) was added to give a dark red solution. Slow evaporation of the solvent yielded dark red crystals (236.0 mg, 70%). Some of them were suitable for X-ray analyses. Complexometric anal. Calcd for $C_{52}H_{96}B_{18}O_{10}Sm_2$: Sm, 21.84. Found: Sm, 22.04. ^1H NMR (pyridine-d_5): δ 7.39−7.18 (m,

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Scheme 1

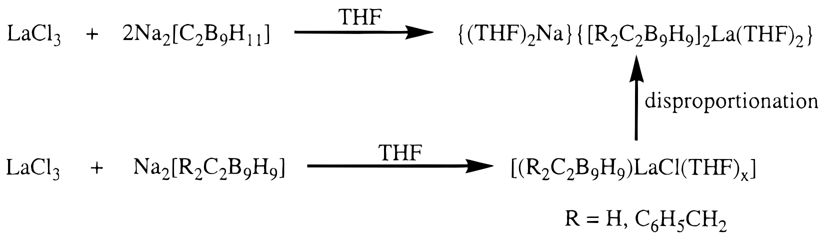

Table 1. Crystal Data and Summary of Data Collection and Refinement for 1 and 3

	1	3
formula	$C_{20}H_{54}B_{18}LaNaO_4$	$C_{52}H_{96}B_{18}O_{10}Sm_2$
cryst size (mm)	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.40
fw	715.1	1376.6
cryst class	monoclinic	orthorhombic
space group	*Cc*	*Pbcn*
a, Å	18.876(1)	16.351(1)
b, Å	9.508(1)	18.513(1)
c, Å	20.865(1)	22.174(1)
β, deg	90.05(1)	
V, Å^3	3740(2)	6712(3)
Z	4	4
D_{calcd}, Mg/m^3	1.263	1.360
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)
diffractometer	Rigaku RAXIS IIC	Rigaku RAXIS IIC
data collected	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$
2θ range, deg	3.0−55.0	3.0−55.0
μ, mm^{-1}	1.179	1.782
F(000)	1440	2800
T, K	294	294
no. of indep rflns	6865	6781
no. of obsd rflns ($\lvert F\rvert > 6\sigma\lvert F\rvert$)	5986	4511
no. of params refined	424	348
data-to-params ratio	14.1:1	13.0:1
goodness of fit	1.59	2.54
R_F	0.044	0.074
R_w	0.059	0.082
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.94, −0.69	0.80, −1.47

20H), 3.45 (m, 8H), 3.27 (s, 20H), 3.05 (s, 30H). ^{13}C NMR (pyridine-d_5): δ 143.6, 130.6, 128.3, 125.9, 72.5, 59.0, 42.8, carboranyl *C*−H was unable to be observed. ^{11}B{^{1}H} NMR (THF): δ −4.4 (2), −5.8 (1), −12.5 (2), −13.8 (2), −29.0 (1), −31.6 (1). IR (cm^{-1}): ν_{BH} 2517 (br vs), ν_{DME} 1062 (s), 855 (m).

X-ray Structure Determination of 1 and 3. All single crystals were sealed under N$_2$ and immersed in Paraton-N oil in a thin-walled glass capillary. Data were collected at 294 K on a 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.[17] Both 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* using the Siemens SHELXTL PLUS program package (PC version).[18] Most of the carborane hydrogen atoms, including four independent μ-H atoms in **3**, were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. The sodium atom in **1** is disordered over two sets of positions with 0.33:0.67 occupancies. Crystal data and details of data collection and structure refinement are given in Table 1. Further details are included in the Supporting Information.

Results and Discussion

Synthesis and Characterization of *closo*-Lanthanacarboranes. Treatment of anhydrous LaCl$_3$ with 1 or 2 equiv of Na$_2$[7,8-*nido*-C$_2$B$_9$H$_{11}$] in THF at room temperature, removal of the precipitates and some of the solvent, and vapor diffusion of *n*-hexane into the resulting solution gave the same sandwich complex **1** as a colorless microcrystalline solid in 65−70% yield. Na$_2$[7,8-(C$_6$H$_5$CH$_2$)$_2$-*nido*-7,8-C$_2$B$_9$H$_9$] reacted with LaCl$_3$, in a molar ratio of 1:1, under the same reaction conditions, yielding the sandwich complex **2** in 55% yield. It is noteworthy that no desired half-sandwich mono(dicarbollide)lanthanum species such as (C$_2$B$_9$H$_{11}$)-LaCl(THF)$_x$ or [(C$_6$H$_5$CH$_2$)$_2$C$_2$B$_9$H$_9$]LaCl(THF)$_x$ was isolated in either case using a molar ratio of 1:1, indicating that benzyl substituents on the pentagonal face cannot prevent the disproportionation reaction, which differs significantly from the cyclopentadienyl systems.[19] All of these reactions are summarized in Scheme 1.

This disproportionation phenomenon has not been observed before in a C$_2$B$_9$ system, but it is well-known for unsubstituted cyclopentadienyl ligands with an early lanthanide chloride like (C$_5$H$_5$)$_2$LaCl.[1a,19] It has also been reported in a C$_2$B$_{10}$H$_{12}$$^{2-}$ system.[5] It is interesting to note that the reaction of HoCl$_3$ with 1 molar equiv of {(TMEDA)Li}$_2${(Me$_3$Si)$_2$C$_2$B$_4$H$_4$} did not give the expected half-sandwich complex [(Me$_3$Si)$_2$C$_2$B$_4$H$_4$]HoCl; instead, a dinuclear sandwich holmacarborane complex was isolated.[10] The above results indicate that the coordination of two identical or similar carborane ligands around a lanthanide ion is favored in all known carborane systems.

Complexes **1** and **2** were characterized by spectroscopic and complexometric metal analyses. The molecular structure of **1** was further confirmed by X-ray analyses. Commercial carbon and hydrogen analyses on these solids were not very reproducible, and the values found were generally less than the theoretical values, probably due to the loss of the labile THF molecules.[20] ^{1}H NMR spectra supported the ratio of two THF molecules per dicarbollide cage based on the integration showing 16 THF α-methylene protons relative to four carboranyl C−H protons or to eight methylene protons from benzyl groups. ^{11}B NMR spectra of **1** or **2** display a pattern of resonances similar to that found in spectra of [*nido*-7,8-C$_2$B$_9$H$_{12}$]$^-$ or [7,8-(C$_6$H$_5$-CH$_2$)$_2$-*nido*-7,8-C$_2$B$_9$H$_{10}$]$^-$, respectively. The appearance of such a “monoanion-like” spectrum in solution could be understood by placing the La ion closer to the unique boron than to one of the two symmetrical borons on the upper belt, which would impose the correct symmetry for a spectrum similar to that displayed by a monoanion rather than a dianion. The solid state IR spectra show a very strong and broad terminal B−H absorption at about 2500 cm^{-1}. This should be an extremely useful

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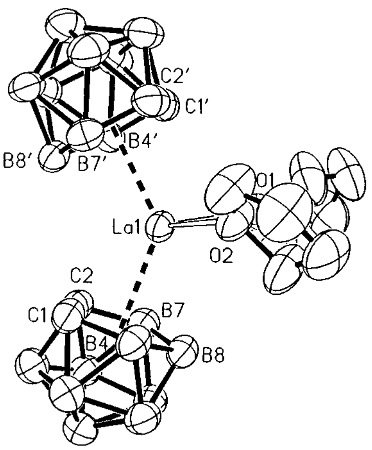

Figure 1. Molecular structure of the $[(C_2B_9H_{11})_2La(THF)_2]^-$ anion in **1** (thermal ellipsoids drawn at the 35% probability level).

technique to quickly identify the existence of the carborane ligands. On the basis of the above discussion, it could be suggested that complex **2** has a structure similar to that of complex **1** at least in solution.

Synthesis and Characterization of an *exo-nido*-Samaracarborane. Reaction of SmI_2 with an equimolar amount of $Na_2[7,8\text{-}(C_6H_5CH_2)_2\text{-}\mathit{nido}\text{-}7,8\text{-}C_2B_9H_9]$ in THF at room temperature, removal of most of THF, and addition of DME gave complex **3** as dark-red crystals in 70% yield according to eq 1. This complex is

$$SmI_2 + Na_2[(C_6H_5CH_2)_2C_2B_9H_9] \xrightarrow{\text{THF/DME}} 1/2[\{(C_6H_5CH_2)_2C_2B_9H_9\}Sm(DME)_2]_2(DME) + 2NaI \quad (1)$$

extremely air- and moisture-sensitive but remains stable for months at room temperature under an inert atmosphere. Traces of air immediately convert the intensely colored **3** to a pale yellow powder. Similar to other lanthanacarboranes of the C_2B_9 system, no satisfactory commercial carbon and hydrogen analyses were obtained.[20] It was, however, characterized by various spectroscopic studies, complexometric metal analyses, and X-ray diffraction studies. The ^1H NMR spectrum supported the ratio of 2.5 DME molecules per $[7,8\text{-}(C_6H_5CH_2)_2\text{-}\mathit{nido}\text{-}7,8\text{-}C_2B_9H_9]^{2-}$ anion based on the integration. ^{11}B NMR spectra display a pattern of resonances similar to that found in the spectra of monoanion $[7,8\text{-}(C_6H_5CH_2)_2\text{-}\mathit{nido}\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with downfield-shifted chemical shifts. The solid state IR spectrum shows a typical strong and broad B−H absorption at 2517 cm^{-1}.

With the characterization data available it was not possible to ascertain the nature of the bonding interaction between the metal and carborane anions in the above three new lanthanacarboranes. It was necessary to perform a single-crystal X-ray analysis in order to elucidate the metal−ligand bonding in these complexes.

Molecular Structure of 1. X-ray analyses confirm that complex **1** (Figure 1) is similar in structure to the Sm analogue, which was prepared from a different synthetic route *via* the reaction of $(C_2B_9H_{11})Sm^{II}(THF)_4$ with $[PPN][Tl(C_2B_9H_{11})]$ ($PPN = [(C_6H_5)_3P]_2N$) in THF.[3] The La ion is η^5-bound to the pentagonal C_2B_3 face of each of two dicarbollide cages and two coordinated THF molecules in a distorted tetrahedral geometry. The sodium cation is disordered over two sets of positions with 0.33:0.67 occupancies. Each of two coordinates to the oxygen atom of one THF molecule and three B−H bonds to form a highly distorted tetrahedron. Table 2 lists selected bond distances and angles. The La−cage atom distances range from 2.772(5) to 2.855(5) Å with an average value of 2.804(5) Å. This value compares well with the La−C distances for other eight-coordinate η^5-pentamethylcyclopentadienyl (Cp*) lanthanum complexes, 2.805 Å for $[Cp^*{}_2LaCH_2CN]_2$,[21b] 2.806 Å for $[Cp^*{}_2La]_2(C_{12}H_8N_2)$,[21a] and 2.85 Å for $Cp^*{}_2La(NHCH_3)(H_2NCH_3)$.[21c] It is also very close to the value of 2.816 Å which would be expected by adding the difference, 0.081 Å, between Shannon's ionic radii[22] of La^{3+} (1.160 Å) and Sm^{3+} (1.079 Å) to the average Sm−cage atom distance of an eight-coordinate samarium analogue, 2.735 Å in $[(C_2B_9H_{11})_2Sm(THF)_2]$.[3] This measured value, however, is significantly smaller than the value of 2.980 Å derived from the addition of the difference in ionic radii, 0.081 Å, to the average Sm−cage atom distance, 2.899 Å, in $\{[(Me_3Si)_2C_2B_4H_4]_2SmCl_2\}^{3-}$,[9] indicating that the interactions between Ln^{3+} and the C_2B_9 system may be stronger than those between Ln^{3+} and the C_2B_4 system. On the other hand, the La−face centroid distance in **1** (average 2.43 Å) is significantly shorter than those (2.52−2.60 Å) of pentamethylcyclopentadienyl organolanthanum complexes.[21] This dif-

Table 2. Selected Bond Distances (Å) and Angles (deg)[a]

	Complex **1**		
La(1)−C(1)	2.825(4)	La(1)−C(1′)	2.834(4)
La(1)−C(2)	2.803(4)	La(1)−C(2′)	2.830(5)
La(1)−B(4)	2.780(3)	La(1)−B(4′)	2.838(4)
La(1)−B(7)	2.777(5)	La(1)−B(7′)	2.772(5)
La(1)−B(8)	2.808(5)	La(1)−B(8′)	2.855(5)
La(1)−O(1)	2.537(3)	La(1)−O(2)	2.562(4)
La(1)−Cent(1)	2.446	La(1)−Cent(2)	2.411
O(1)−La(1)−O(2)	79.3(1)	Cent(1)−La(1)−Cent(2)	132.7
Cent(1)−La(1)−O(2)	104.9	Cent(2)−La(1)−O(1)	113.7
Cent(1)−La(1)−O(1)	103.4	Cent(2)−La(1)−O(2)	109.8
	Complex **2**		
Sm(1)−B(7)	3.025(8)	Sm(1)−O(1)	2.688(6)
Sm(1)−B(8)	3.041(9)	Sm(1)−O(2)	2.661(6)
Sm(1)−B(9A)	3.044(8)	Sm(1)−O(3)	2.707(7)
Sm(1)−B(12A)	3.058(8)	Sm(1)−O(4)	2.653(8)
Sm(1)−H(7)	2.480(9)	Sm(1)−H(8)	2.843(9)
Sm(1)−H(9A)	2.660(9)	Sm(1)−H(12A)	2.580(10)
B(7)−Sm(1)−B(8)	32.6(2)	O(3)−Sm(1)−O(4)	61.4(2)
B(7)−Sm(1)−O(1)	146.3(2)	B(7)−Sm(1)−B(9A)	135.0(2)
B(8)−Sm(1)−O(1)	142.7(2)	B(8)−Sm(1)−B(9A)	118.2(2)
B(7)−Sm(1)−O(2)	97.7(2)	O(1)−Sm(1)−B(9A)	78.7(2)
B(8)−Sm(1)−O(2)	82.0(2)	O(2)−Sm(1)−B(9A)	112.5(2)
O(1)−Sm(1)−O(2)	60.7(2)	O(3)−Sm(1)−B(9A)	79.2(2)
B(7)−Sm(1)−O(3)	82.6(2)	O(4)−Sm(1)−B(9A)	115.0(2)
B(8)−Sm(1)−O(3)	106.6(2)	B(7)−Sm(1)−B(12A)	123.3(2)
O(1)−Sm(1)−O(3)	109.3(2)	B(8)−Sm(1)−B(12A)	94.2(2)
O(2)−Sm(1)−O(3)	160.7(2)	O(1)−Sm(1)−B(12A)	83.7(2)
B(7)−Sm(1)−O(4)	90.7(2)	O(2)−Sm(1)−B(12A)	87.3(2)
B(8)−Sm(1)−O(4)	121.3(2)	O(3)−Sm(1)−B(12A)	108.8(2)
O(1)−Sm(1)−O(4)	69.8(2)	O(4)−Sm(1)−B(12A)	144.4(2)
O(2)−Sm(1)−O(4)	99.3(2)	B(9A)−Sm(1)−B(12A)	33.6(2)
B(7)−H(7)−Sm(1)	108.4(2)	B(8)−H(8)−Sm(1)	90.0(2)
B(9A)−H(9A)−Sm(1)	99.7(2)	B(12A)−H(12A)−Sm(1)	106.3(2)

[a] Cent(1) and Cent(2) are the centroids of the C1, C2, B4, B7, and B8 ring and the C1', C2', B4', B7', and B8' ring, respectively.

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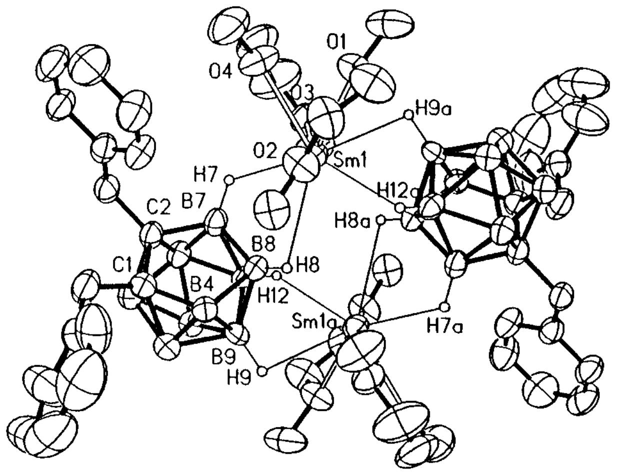

Figure 2. Molecular structure of dimeric $[\{(C_6H_5CH_2)_2C_2B_9H_9\}Sm(DME)_2]_2$ (thermal ellipsoids drawn at the 35% probability level). The solvated DME molecule is not shown.

ference may be derived from the larger size of the C_2B_3 relative to C_5 faces and also be attributable to the tighter bonding of the La^{3+} to the dicarbollide ligands than to the $C_5Me_5^-$ anions.

The Cent(1)−La(1)−Cent(2) angle of 132.7° is very close to the value of 131.9° found in the samarium analogue,[3] but is smaller than those (136.0−140.8°) reported for Cp*$_2$La complexes[21] and slightly greater than those (128.0 ± 0.6°) known in lanthanacarboranes with the C_2B_4 system.[9] The Cent−La(1)−O angles range from 103.4° to 113.7°, which are very similar to those found in the samarium analogue.[3]

Molecular Structure of 3. Figure 2 shows the molecular structure of **3**. The important bond distances and angles are listed in Table 2. The main feature of this structure is the presence of exclusive Sm−H−B bondings between Sm(II) and dibenzyldicarbollide anions. This is the first example of a structurally characterized *exo*-*nido*-lanthanacarborane of the C_2B_9 system to our knowledge. In this molecular structure, each of the two dicarbollide moieties serves as a bridging ligand for two Sm atoms while bonding to one *via* two B−H bonds from the upper belt (C_2B_3) and the other through two B−H bonds from the lower belt (B_5) to form a centrosymmetric dimer. The coordination sphere around each Sm atom is completed by two DME molecules. Thus, the formal coordination number of the Sm atom is 8. This result gives direct evidence for the fluxional mechanism proposed by Hawthorne.[3] Unlike metallacarboranes of d-transition elements,[23] this fluxional process does *not* involve any changes in the oxidation states of both Sm and the ligand.

The *exo*-polyhedral three-center, two-electron Sm−H−B bonds in complex **3** result in the much longer Sm−B distances ranging from 3.025(8) to 3.058(8) Å with an average value of 3.042(8) Å. This type of bonding is also known in other lanthanide boron complexes.[5,10,24] The direct Sm(II)−B(dicarbollide) distance is expected to be about 2.926 Å by addition of the difference, 0.191 Å, between Shannon's ionic radii[22] of Sm^{2+} (1.270 Å) and Sm^{3+} (1.079 Å) to the average Sm−cage atom distance of 2.735 Å in $[(C_2B_9H_{11})_2Sm(THF)_2]$.[3] The Sm−H−B bond is believed to be weaker in solution since it is not observed by ^{11}B NMR at room temperature. The Sm−O distances range from 2.653(8) to 2.707(7) Å with an average value of 2.677 Å. This value can be compared with those found in samarium(II) DME complexes, 2.618 Å for $SmI_2(DME)_2(THF)$,[25] 2.641 Å for $SmI_2(DME)(THF)_3$,[25] and 2.685 Å for $\{[(Me_3Si)_2N]SmI(DME)(THF)\}_2$.[26] The Sm−O(DME) distances are generally longer than those of Sm−O(THF).[25]

Conclusions

The isolation of an *exo*-*nido*-lanthanacarborane of the C_2B_9 system has been achieved for the first time by introducing two bulky benzyl substituents to the open pentagonal face C_2B_3 of the dicarbollide dianion. This implies that the substituents could change the coordination model between lanthanide ion and dicarbollide in some cases, which then in turn can affect the stability of the particular tautomer. The reaction of $LaCl_3$ with $[R_2C_2B_9H_9]^{2-}$ was also examined. The expected complex $[R_2C_2B_9H_9]LaCl(THF)_x$ does not result from 1:1 molar ratio reactions. Instead *closo*-$[(R_2C_2B_9H_9)_2La(THF)_2]^-$ was formed via a disproportionation reaction, which represents the first example of a structurally characterized early lanthanacarborane. In view of the C_2B_4, C_2B_9, and C_2B_{10} lanthanacarborane chemistry, it can be concluded that the coordination of two identical or similar carborane ligands around a lanthanide ion is favored.

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Supporting Information Available: Tables of crystallographic data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and atom-numbering schemes for both **1** and **3** (24 pages). Ordering information is given on any current masthead page.

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