

data set (4210 reflections), there should be no significant effect on the final results. The maximum discrepancy between two unaveraged measurements was 2σ , and most discrepancies were considerably less. We thank a very careful reviewer for drawing this point to our notice.

The structure was solved by using the Patterson heavy-atom method, which revealed the position of the Ru atom. Remaining atoms were located in successive difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined.

Acknowledgment. We are grateful to members of the 3M

Analytical and Properties Research Laboratory for spectroscopic and analytical data and to Robert Koshar for gifts of fluorocarbon acids.

Supplementary Material Available: Tables giving a summary of crystallographic procedures, calculated hydrogen atom positions (Table S1), bond distances and angles (Table S2), and general displacement parameters (Table S3) and figures showing atom-numbering schemes (14 pages); a listing of observed and calculated structure factors (Table S4) (43 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Biochemistry,
University of California, Los Angeles, California 90024-1569

Metallacarborane Complexes That Incorporate the Lanthanides. Synthesis, Molecular Structure, and Spectroscopic Characterization of Dicarbollide Complexes of Samarium and Ytterbium

Mark J. Manning, Carolyn B. Knobler, Rajesh Khattar, and M. Frederick Hawthorne*

Received May 8, 1990

The interaction of $\text{Na}_2[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]$ (1) with LnI_2 (Ln = Sm, Yb) in THF affords a complex with the composition $\text{Ln}(\text{C}_2\text{B}_9\text{H}_{11})(\text{THF})_4$ (Ln = Sm (2), Yb (3)). Both these complexes have been fully characterized by spectroscopic techniques, and the molecular structure of the DMF derivative of 3 has been established by a single-crystal X-ray diffraction study. The DMF derivative, $\text{Yb}(\text{C}_2\text{B}_9\text{H}_{11})(\text{DMF})_4$ (3b), crystallizes in the orthorhombic space group *Pbca* with $a = 10.208(1) \text{ \AA}$, $b = 17.005(3) \text{ \AA}$, $c = 31.627(5) \text{ \AA}$, $V = 5479 \text{ \AA}^3$, and $Z = 8$. Data were collected on a modified Picker FACS-1 diffractometer at 25°C using $\text{Mo K}\alpha$ radiation, to a maximum $2\theta = 50^\circ$, giving 4841 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was $R = 0.082$, $R_w = 0.084$ for 1424 independent reflections with $I > 2\sigma(I)$. The dicarbollide ligand is η^3 -bound to the Yb ion, and four DMF molecules are coordinated to Yb through the oxygen atoms. Complex 2 is fluxional in solution. The fluxionality of complex 2 in solution has been monitored by variable-temperature ^{11}B NMR spectroscopy, and a dynamic process involving the Sm^{2+} ion and the dicarbollide ligand has been proposed. The reaction of *closo*-1,1,1,1-(THF) $_4$ -1,2,3-Ln $\text{C}_2\text{B}_9\text{H}_{11}$ (Ln = Sm (2), Yb (3)) with $[\text{PPN}]^+[\text{closo-3,1,2-TiC}_2\text{B}_9\text{H}_{11}]^-$ in THF produces $[\text{3,3-(THF)}_2\text{-}i\text{cmm-3,3'}\text{-Ln(3,1,2-LnC}_2\text{B}_9\text{H}_{11})_2]^-[\text{PPN}]^+$ (Ln = Sm (4), Yb (5)), which has been characterized spectroscopically. The molecular structure of 4 has been established by an X-ray diffraction study. The complex 4 crystallizes in the triclinic space group $\bar{P}1$ with $a = 8.9374(3) \text{ \AA}$, $b = 17.8703(6) \text{ \AA}$, $c = 18.4989(7) \text{ \AA}$, $\alpha = 107.5402(9)^\circ$, $\beta = 91.085(1)^\circ$, $\gamma = 90.705(1)^\circ$, $V = 2816 \text{ \AA}^3$, and $Z = 2$. Data were collected at 25°C on a diffractometer equipped with a small Huber circle, using $\text{Mo K}\alpha$ radiation, to a maximum of $2\theta = 45^\circ$, giving 7358 unique reflections, and the structure was solved by a combination of conventional Patterson, Fourier, and full-matrix least-squares techniques. The final discrepancy index was $R = 0.053$, $R_w = 0.065$ for 5324 independent reflections with $I > 3\sigma(I)$. Both the dicarbollide ligands are η^2 -bound to the Sm ion in a nonparallel or bent fashion, and the coordination sphere about the Sm is completed by two THF molecules. The coordination geometry of 4 can be best described as a distorted tetrahedron. This is the first structurally authenticated example of a bis(dicarbollide)lanthanide complex. The structure of 4 is compared with related bis(cyclopentadienyl)lanthanides.

Introduction

Recognition of the isolobal analogy between the cyclopentadienyl anion, $[\text{C}_5\text{H}_5]^-$, and the dicarbollide dianion, $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ (1), laid the foundation for the field of metallacarborane chemistry.¹ Dicarbollide complexes have been synthesized with a wide range of metals (d-transition series,² main group,³ 5f block⁴), but there have been no previous reports of any complexes of the dicarbollide ligand with metals of the 4f block.⁵

Synthesis of the uranium complex $[\text{Li}(\text{THF})_4]_2[\text{3,3-(Cl)}_2\text{-}i\text{cmm-3,3'}\text{-U(3,1,2-UC}_2\text{B}_9\text{H}_{11})_2]^{4-}$ suggested that dicarbollide complexes of the lanthanides might be viable synthetic targets. Herein we report the synthesis of a new class of organolanthanide complexes, the *closo*-lanthanacarboranes. Both mono- and bis(di-

- (1) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.
- (2) Hawthorne, M. F. *J. Organomet. Chem.* **1975**, *100*, 97 and the references contained therein.
- (3) (a) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5369. (b) Bandman, M. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 2399.
- (4) Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769.

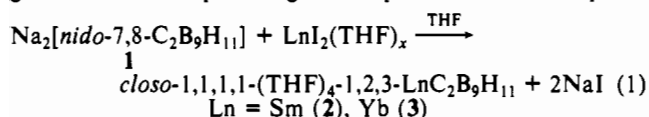
- (5) The synthesis of σ -bound C-carboranyl lanthanoids with La, Tm, and Yb has been communicated: Suleimanov, G. A.; Bregadze, V. I.; Koval'chuk, N. A.; Beletskaya, I. P. *J. Organomet. Chem.* **1982**, *235*, C17. A carboranyl complex with a Tm-B bond has also been reported: Bregadze, V. I.; Koval'chuk, N. A.; Godovikov, N. N.; Suleimanov, G. Z.; Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *241*, C13. A communication concerning the reactions of C-lithiocarboranes with LnI_2 (Ln = Sm, Eu, Yb) has also appeared: Suleimanov, G. Z.; Bregadze, V. I.; Koval'chuk, N. A.; Khalilov, Kh. S.; Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *255*, C5. The synthesis of $[\text{Gd}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ has been communicated: Lebedev, V. N.; Shemyakin, N. F.; Solodovnikov, S. P.; Zakharkin, L. I. *Metalloorg. Khim.* **1988**, *1*, 718; *Chem. Abstr.* **1988**, *111*, 134368v. The synthesis of sandwich compounds containing different ratios of Er or La, $\text{C}_2\text{B}_9\text{H}_{11}$, and THF are presented: Khimatov, M.; Volkov, V. V.; Mirsaidov, U.; Budnikova, V. I. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1988**, *27*; *Chem. Abstr.* **1988**, *111*, 57923t. No structural data appeared with any of these reports.

carbollide) complexes of samarium and ytterbium (*closo*-1,1,1,1-(THF)₄-1,2,3-LnC₂B₉H₁₁ and [3,3'-(THF)₂-*commo*-3,3'-Ln(3,1,2-LnC₂B₉H₁₁)₂]⁻[PPN]⁺; Ln = Sm, Yb) have been prepared, and these provide the subject of the spectroscopic and structural studies described in this paper. A preliminary account of this work has appeared elsewhere.⁶

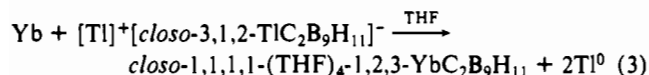
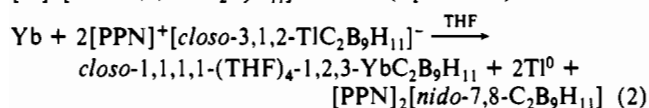
Results and Discussion

Synthesis and Characterization of Dicarbollide Complexes of Samarium and Ytterbium. Slow anaerobic addition of an equimolar THF⁷ solution of sodium dicarbollide (1) to a stirred solution of LnI₂ (Ln = Sm, Yb)⁸ in THF at room temperature resulted in the precipitation of an amorphous solid that was highly air- and moisture-sensitive. Commercial elemental analyses on these solids were not very reproducible (for the same sample) but were consistent with the formulation of one metal per dicarbollide cage. Further characterization data were supplied by the ¹H NMR spectra of the hydrolysis products of these complexes, which supported the ratio of four THF molecules per dicarbollide cage (integration showed 16 THF α -methylene protons relative to two carboranyl C-H protons). The solid-state IR spectra (Nujol mull, NaCl) displayed absorption attributable to coordinated THF. Complexometric metal analysis was consistent with a complex having four coordinated THF's, one metal, and one dicarbollide ligand, yielding the general formula (C₂B₉H₁₁)Ln(THF)₄ (Ln = Sm (2), Yb (3)). This formulation implies that these complexes still had the metal in the +2 oxidation state, and this was substantiated by solid-state room-temperature magnetic moment studies. A magnetic moment (μ_{eff}) of 3.8 μ_{B} was determined for dark red 2, agreeing with values found for other Sm(II) complexes (3.4–3.8 μ_{B}),⁹ while the bright yellow Yb complex 3 was found to be diamagnetic.

The reaction scheme for the preparation of these divalent organolanthanide complexes is given in eq 1. The neutral complexes



formed in these metathetical reactions do not melt or sublime up to 200 °C and can be obtained in reasonable yields (2 (60%); 3 (52%)). The complex 3 can be obtained by the direct oxidation of Yb metal with either [PPN]⁺[*closo*-3,1,2-TiC₂B₉H₁₁]⁻ or [Ti]⁺[*closo*-3,1,2-TiC₂B₉H₁₁]⁻ in THF (eqs 2 and 3). All of these



compounds are exceedingly air- and moisture-sensitive but are stable for extended periods of time when stored in a N₂-filled drybox. Traces of oxygen in the drybox will immediately convert the intensely colored divalent complexes to white solids.

The divalent dicarbollide complexes 2 and 3 are only sparingly soluble in THF. Addition of THF to these solids results in no apparent dissolution of the organolanthanide; however, enough does dissolve to allow a conventional FTNMR spectrum to be taken. The ytterbium complex 3 is soluble in other coordinating solvents (e.g. CH₃CN, DMF),⁷ allowing the THF ligands to be displaced by the solvent (C₂B₉H₁₁)YbL₄ (L = CH₃CN (3a), DMF (3b)). Integration of the ¹H NMR spectra, of 3 in CH₃CN-*d*₃ (the spectrum of 3a) and 3 in DMF-*d*₇ (the spectrum of 3b) lends further support for the formulation of four THF ligands to one

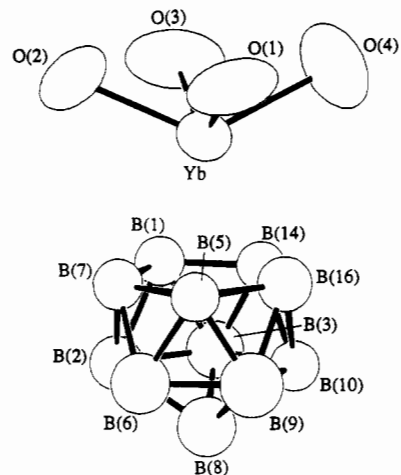


Figure 1. Molecular structure of 3b, showing the atom-labeling scheme. Only the oxygen atoms of the coordinated DMF ligands are shown. Due to disorder problems, the carbon and boron atoms in the upper belt of the carborane fragment could not be distinguished.

dicarbollide cage. Yellow-orange microcrystals of 3a can be isolated; the solid-state IR spectrum (taken as a Nujol mull) shows no coordinated THF but does have an absorption attributable to coordinated CH₃CN. The samarium complex 2 is also soluble in other coordinating solvents but rapidly decomposes to give [*nido*-7,8-C₂B₉H₁₂]⁻ (verified by ¹¹B NMR) in a yellow solution, which is indicative of a Sm³⁺ species. The fact that 2 is reactive with solvents in which it is soluble, whereas 3 undergoes ligand displacement reactions with these same solvents, is consistent with the higher reactivity of Sm(II) versus Yb(II).⁹ The ionic radius of seven-coordinate Sm(II) is 0.14 Å larger than the corresponding radius for Yb(II);¹⁰ consequently, divalent Sm complexes are less coordinatively saturated and usually more reactive than their ytterbium analogues.

With the characterization data available (*vide supra*) it was not possible to ascertain the nature of the bonding interaction between the metal and the dicarbollide ligand in these new organolanthanide complexes. A possible solid-state structure is one in which the divalent lanthanide metal ion "caps" the [*nido*-7,8-C₂B₉H₁₁]²⁻ ligand, giving a polyhedron with an overall *closo* geometry;¹¹ the remainder of the metal's coordination sphere could be taken up by the four coordinated THF ligands. In such a structure the metal is formally seven-coordinate (three coordination sites for the η^5 -dicarbollide ligand and one for each of the four THF's), which is entirely reasonable for a divalent organolanthanide complex.⁹ The limited solubility of 2 and 3 in THF could be due to some type of polymeric "chainlike" structure existing in the solid state. Such a polymeric structure has recently been established for the strontium carborane complex [*closo*-1,1,1-(MeCN)₃-1,2,4-SrC₂B₁₀H₁₂]_n.¹² With no other lanthanacarborane complexes available for comparison, it was necessary to perform a single-crystal X-ray analysis in order to elucidate the metal-ligand bonding in these complexes.

The solubility of 3 in a variety of coordinating solvents facilitated the growth of single crystals. The DMF adduct of 3 was prepared by dissolving the ytterbacarborane in dry, oxygen-free DMF, yielding a dark red solution of 3b. Single crystals suitable for an X-ray diffraction study were grown by layering diethyl ether over a DMF solution of 3b and allowing the solvents to diffuse together at room temperature for 1 week. A dark red crystal of 3b was mounted in a sealed glass capillary, and data were collected at room temperature; the resulting structure is presented in Figure 1.

Molecular Structure of 3b. The dicarbollide ligand of 3b is bound to the Yb ion in an η^5 -fashion, and four coordinated DMF

(6) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458.

(7) THF = tetrahydrofuran; DMF = *N,N*-dimethylformamide; CH₃CN = acetonitrile; PPN⁺ = bis(triphenylphosphoranylidene)ammonium cation.

(8) Namy, J. L.; Girard, P.; Kagan, H. B.; Caro, P. E. *Nouv. J. Chim.* **1981**, *5*, 479.

(9) Evans, W. J. *Polyhedron* **1987**, *6*, 803.

(10) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(11) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(12) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 2191.

molecules comprise the remainder of the coordination sphere about the ytterbous ion (only the oxygen atoms of the DMF ligands are shown in Figure 1). The ytterbium ion is symmetrically bound to the pentagonal face of the dicarbollide ligand with ytterbium-boron (top belt) distances ranging from 2.73 (4) to 2.77 (4) Å with an average value of 2.74 Å. The four oxygen atoms lie approximately in the same plane with the mean O–Yb–O angle close to 90°. The plane defined by the four oxygen atoms is nearly parallel to the plane containing the upper belt of the dicarbollide cage; the dihedral angle is 7°. The bonding in organolanthanide complexes is thought to be predominantly ionic;¹³ consistent with this is the configuration of ligands about the Yb ion in **3b** in a manner that minimizes interligand contacts.

The structure of **3b** would not satisfactorily refine due to a disorder, and it was not possible to distinguish between carbon and boron on the upper belt (these atoms are capped by the lanthanide) of the dicarbollide ligand. The disorder was especially pronounced for the methyl carbons of the coordinated DMF; attempts at collection of a low-temperature data set were unsuccessful as were efforts to obtain diffraction-quality crystals of **3** with more rigid coordinating ligands. The possibility of polyhedral carbon atom rearrangement¹⁴ was ruled out by the ¹¹B NMR spectrum of the hydrolysis product, which showed the boron-containing hydrolysate to be [*nido*-7,8-C₂B₉H₁₂]⁻, the monoanion which would be derived from an unrearranged dicarbollide ligand. The symmetrical bonding of the Yb ion with relation to the pentagonal face of the dicarbollide ligand discounts the presence of a "slip" distortion¹⁵ in the solid state; no such distortion was observed in the structure of the 5f-metallacarborane [Li(THF)₄]₂[3,3-(Cl)₂-*commo*-3,3'-U(3,1,2-UC₂B₉H₁₁)₂].⁴

The ytterbium to upper belt distances in **3b** compare rather well with the metal to ligand distances reported for other structurally characterized divalent organolanthanide complexes; reported values for Yb–C(C₅Me₅) distances in ytterbium(II) η⁵-pentamethylcyclopentadienyl complexes range from 2.66 to 2.77 Å.⁹ The only other structurally characterized seven-coordinate Yb(II) complex with a ligand bound in an η⁵-fashion is (C₅Me₅)₂Yb(THF),¹⁶ with a Yb–ring carbon bond length of 2.66 Å. The average Yb–O bond length for **3b** is 2.37 Å, slightly less than the Yb–O(THF) distance (2.41 Å) in the complex (C₅Me₅)₂Yb(THF).¹⁶

These divalent metallacarborane complexes represent a new structural class of organolanthanides. The ytterbacarborane **3b** represents, to the best of our knowledge, the first structurally characterized organolanthanide complex with a single η⁵-bound ligand and the remainder of the metal's coordination sphere composed only of solvent molecule. The only other structurally characterized organolanthanide complex with a single ligand bound to the metal in a multihapto fashion and the rest of the coordination sphere taken up by solvent ligands is (η⁸-C₈H₈)Yb(C₅H₅N)₃^{1/2}(C₅H₅N).^{17a} The minus two charge associated with both the cyclooctatetraene and dicarbollide ligands permits the formation of neutral complexes between these ligands and divalent lanthanide metals. The solubility properties of the dicarbollide complexes **2** and **3** are similar to that reported for the tris(pyridine) adduct, (η⁸-C₈H₈)Yb(C₅H₅N)₃^{1/2}(C₅H₅N), which is only slightly soluble in pyridine. Base-free cyclooctatetraene complexes of Sm, Eu, and Yb^{17,18} have been reported, but their insolubility in solvents with which they do not react has precluded any structural characterization. Substituted cyclopentadienyl complexes of the alkali metals lithium and potassium have recently been synthesized¹⁹ and shown to be structurally similar to **3b**; i.e. a single

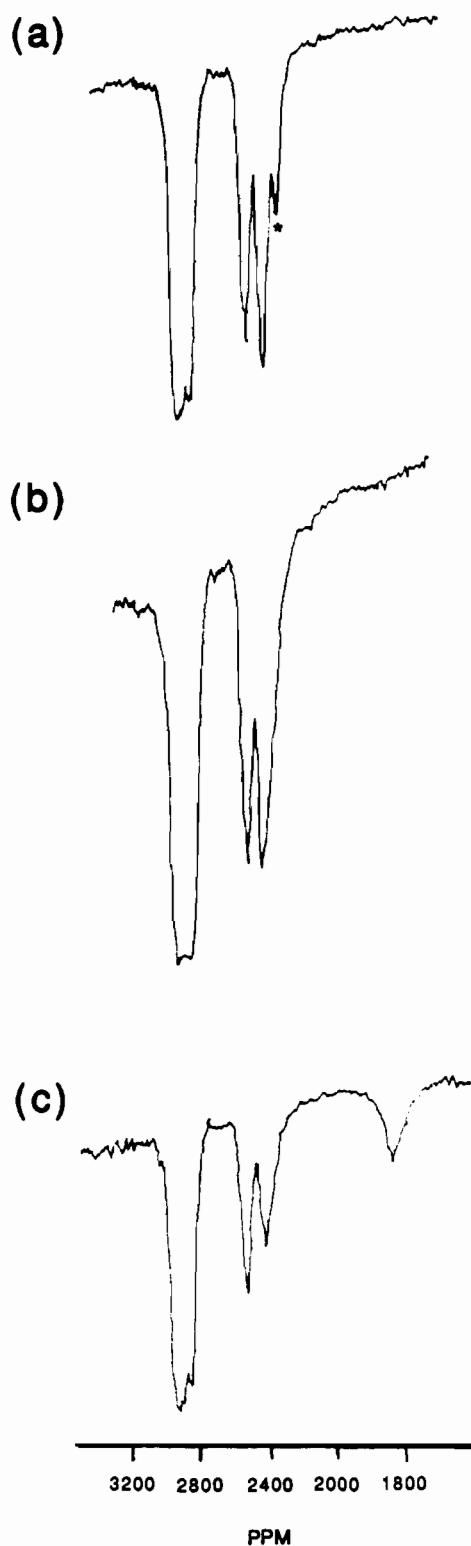


Figure 2. Solid-state IR spectra of (a) **2**, (b) **3**, and (c) **3c**. The starred peak in (a) at 2358 cm⁻¹ could be due to Sm–H–B stretching or, possibly, to an impurity. We cannot assign this peak with certainty without confirmation of a crystal structure determination.

η⁵-bound ligand is bonded to the metal and the remainder of the coordination sphere is comprised only of solvent ligands. These alkali-metal complexes, [(Me₃Si)₃C₅H₂Li·THF]^{19a} and [(CH₂-C₆H₅)₅C₅]K·3THF,^{19b} serve only to illustrate analogous structures and are not meant for comparison in a bonding sense.

- (13) Raymond, K. N.; Eigenbrot, C. W. *Acc. Chem. Res.* **1980**, *13*, 276.
 (14) Doi, J. A.; Mizusawa, E. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1984**, *23*, 1482 and the references contained therein.
 (15) (a) Wing, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 5599. (b) Wing, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4828. (c) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.
 (16) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999.
 (17) (a) Wayda, A. L.; Mukerji, I.; Dye, J. L.; Rogers, R. D. *Organometallics* **1987**, *6*, 1328. (b) Wayda, A. L.; Cheng, S.; Mukerji, I. *J. Organomet. Chem.* **1987**, *330*, C17.
 (18) Hayes, R. G.; Thomas, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 6876.

- (19) (a) Jutzi, P.; Leffers, W.; Pohl, S.; Saak, W. *Chem. Ber.* **1989**, *122*, 1449. (b) Lorberth, J.; Shin, S.; Wocadlo, S.; Massa, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 735.

IR Spectral Studies on the Dicarborollide Complexes of Samarium and Ytterbium. The solid-state IR spectra (Nujol mull, NaCl) of both **2** and **3**, in addition to having absorptions due to coordinated THF (1025 and 876 cm^{-1} for **2**, 1024 and 877 cm^{-1} for **3**) display unique fine structure in the region of their terminal B–H stretch. The spectra each show two distinct absorptions separated by about 100 cm^{-1} , as shown in Figure 2a,b. This fine structure is definitely attributable to an interaction with the metal; exposing the mull to air immediately gives a white solid with an IR spectrum that displays a “normal” absorption due to terminal B–H stretch (the ^{11}B NMR spectrum of this material shows it to be $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$). This particular kind of fine structure had not been seen before in the IR spectra of other metallacarborane complexes. The possibility of the lower energy absorption being due to a M–H–B stretch is rather remote; these stretches are generally much weaker than the corresponding terminal B–H absorptions and are also lower in energy (e.g. the M–H–B stretch reported for $\text{Ag}(\text{CB}_{11}\text{H}_{12})$,²⁰ 2380 cm^{-1} , is at the high-energy extreme of reported values²¹). Here the two absorptions are of nearly equal intensity with a low energy “extreme” of 2439 cm^{-1} in the case of **2**. The ytterbium–acetonitrile adduct, **3a**, also shows this splitting in addition to displaying absorptions due to coordinated CH_3CN at 2303 and 2271 cm^{-1} . A solution IR spectrum (in DMF) of **3b** possesses a strong, broad absorption centered at 2510 cm^{-1} ($\nu(\text{BH})$) that shows no unusual fine structure. The absence of any discernible fine structure in the solution spectrum could be attributed to the structural differences of these complexes in solution and the solid state (vide infra).

In an attempt to interpret the unique IR band “splitting” in the B–H stretching mode, selectively deuterated dicarborollide ligand was prepared and used in the synthesis of the corresponding deuterated lanthanacarboranes, *closo*-1,1,1,1-(THF)₄-1,2,3-LnC₂B₉H₉D₂ (Ln = Sm (**2a**), Yb (**3c**)).²² In these deuterated complexes the two nonadjacent borons (B(4) and B(6)) on the upper belt of the dicarborollide ligand are bound to deuterium and will exhibit a lower IR stretching frequency absorption due to deuterium substitution.²³ The IR spectrum (Nujol mull, NaCl) of **3c** is displayed in Figure 2c, and it contains an absorption at 1841 cm^{-1} that was absent in the spectrum of the isotopically normal compound and can be assigned to terminal B–D stretch. Along with this new absorption there is a concomitant decrease in the intensity of the low-frequency terminal B–H signal. The IR spectrum of **2a** exhibits similar behavior with a terminal B–D stretch at 1837 cm^{-1} . The ratio of $\nu(\text{BH})$ to $\nu(\text{BD})$ (using the low-frequency B–H absorption) is 1.32 for each of the two deuterated species. A ratio of 1.33 can be calculated for the monoanion precursor $\text{K}^+[\text{nido-7,8-C}_2\text{B}_9\text{H}_9\text{D}_2]^-$; the same ratio has also been reported for the perdeuterated analogue of the metallacarborane $[\text{Cu}^+]_2[\text{B}_{10}\text{H}_{10}]^{2-}$.²⁴ When the ratio is calculated by using the high-frequency B–H absorption, a value of 1.38 is obtained for both **2a** and **3c**. Given the consistency of $\nu(\text{BH})/\nu(\text{BD})$ ratios obtained by using the low-frequency absorption along with the observed decrease in intensity of this stretching band in the deuterated compound, it seems reasonable to assign the B–H absorptions near 2450 cm^{-1} to the upper belt terminal hydrogens. With no other lanthanacarborane complexes available for comparison, it is difficult to elucidate the origin of this unique split

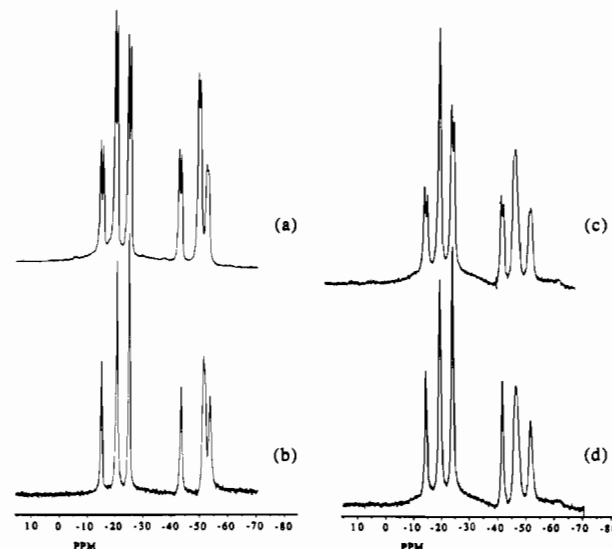


Figure 3. ^{11}B NMR spectra of **2** ((a) ^1H coupled and (b) ^1H decoupled) and of **2a** ((c) ^1H coupled and (d) ^1H decoupled) in THF measured at 25 $^\circ\text{C}$.

pattern in the IR spectra. One possible explanation stems from the configuration of the terminal hydrogens of the dicarborollide ligand; these hydrogens are bent “up” (in the direction of the capping lanthanide atom) out of the C_2B_3 plane by about 28° , and in a similar fashion the terminal hydrogens on the lower belt are bent “down” out of the B_3 plane by the same amount. It is not unreasonable to assume that the three terminal hydrogens on the upper belt, by virtue of being much closer to the capping metal, have a B–H stretching force constant different from that for the lower belt and apical borons. It may be possible that the ionic interactions between the cationic lanthanide ion and anionic dicarborollide ligand are indirectly altering the energy of the B–H stretch of the upper belt of the dicarborollide ligand.²⁵ On the basis of these IR correlation studies, it is reasonable to conclude that strong ionic interactions exist between the cationic lanthanide center and the anionic dicarborollide ligand; however, with the data in hand it is impossible to ascertain the relative degree of covalent bonding present. The observation of a split pattern in the B–H stretching mode of the IR spectrum may prove to be a diagnostic test for the presence of ionic bonding in metallacarborane complexes.

^1H NMR Spectral Studies on the Dicarborollide Complexes of Samarium and Ytterbium. Both the Sm and Yb monoxo complexes (**2** and **3**, respectively) are soluble enough in THF- d_6 to allow their ^1H NMR spectra to be obtained. Since the spectra are taken in THF, it is not possible to extract any information regarding the coordinated THF. The resonances attributable to the carboranyl C–H protons do, however, yield supporting data for the formulation of these compounds. The carboranyl C–H resonances for paramagnetic **2** appear as a broad, weak signal centered at 3.03 ppm; addition of a slight excess of H_2O to the sample causes the disappearance of this signal and the appearance of a new signal at 1.73 ppm. This upfield resonance is assigned to the carboranyl C–H protons of $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$,²⁶ the

(20) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

(21) Grimes, R. N. In *Metals Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 7.

(22) The selectively deuterated monoanion $\text{K}^+[9,11-(\text{D})_2\text{-nido-7,8-C}_2\text{B}_9\text{H}_9\text{D}_2]^-$, with deuterium replacing the bridge hydrogen (verified by ^{11}B FTNMR), can be prepared by stirring previously dried $\text{K}^+[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$ in 6 N $\text{DCl}/\text{D}_2\text{O}$ for 6 h.²³ Metathesis with $[\text{HN}(\text{CH}_3)_3]^+\text{Cl}^-$ and subsequent deprotonation with excess NaH in THF yields the selectively deuterated dicarborollide dianion $[9,11-(\text{D})_2\text{-nido-7,8-C}_2\text{B}_9\text{H}_9\text{D}_2]^{2-}$, which was used as before to synthesize the selectively deuterated complexes *closo*-1,1,1,1-(THF)₄-1,2,3-SmC₂B₉H₉D₂ (**2a**) and *closo*-1,1,1,1-(THF)₄-1,2,3-YbC₂B₉H₉D₂ (**3c**).

(23) Howe, D. V.; Jones, C. J.; Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 2516.

(24) Paxson, T. E.; Hawthorne, M. F.; Brown, L. D.; Lipscomb, W. N. *Inorg. Chem.* **1974**, *13*, 2772.

(25) Due to the ionic interaction of a cationic lanthanide ion and an anionic dicarborollide ligand, an ion-pair dipole is produced that is directed toward the anionic dicarborollide ligand on the z axis (–z) whereas the $\text{B}^{\delta+}\text{--H}^{\delta-}$ dipoles in the upper belt are directed toward the hydrogen atoms with a component along the z axis (+z). Thus, the z-axis components of the ion-pair dipole and the $\text{B}^{\delta+}\text{--H}^{\delta-}$ dipole interact in a complementary fashion, which reduces the B–H stretching force constant, and, as a result, the B–H vertices in the upper belt exhibit IR stretching absorptions at lower frequency than the remaining B–H vertices.

(26) The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (in THF) of $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$ exhibits six resonances: –11 (2), –17 (2), –18 (1), –22 (2), –32 (1), and –37 (1) (in ppm, relative intensities in parentheses). ^1H NMR (THF- d_6): δ 1.73 ($\mu\text{-H}$). The molecular structure of the monoanion has recently been published (Buchanan, J.; Hamilton, E. J. H.; Reed, D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 677).

hydrolysis product for both **2** and **3**. The broad shape of the carboranyl C–H signal at 3.03 ppm in **2** is consistent with the interaction of the dicarbollide ligand with a paramagnetic metal,²⁷ Sm(II) complexes have a $4f^6$ configuration with magnetic moments (μ_{eff}) in the range of 3.4–3.8 μ_{B} (3.8 μ_{B} for **2**) but have been shown to be NMR-accessible.²⁸ The ^1H NMR spectrum for the Yb complex **3** displays a broad singlet at 1.25 ppm, which is attributable to the carboranyl C–H protons; this resonance is not as broad as the corresponding signal for **2**, consistent with the diamagnetism of the ytterbium complex. Addition of a slight molar excess of H_2O to the NMR sample of **3** yields a spectrum which is identical with that of $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$.²⁶

^{11}B NMR Spectral Studies on the Dicarbollide Complexes of Samarium and Ytterbium. The ^1H -coupled and -decoupled ^{11}B NMR spectra²⁹ of **2** measured at room temperature are presented in Figure 3. The proton-decoupled spectrum exhibits a pattern accounting for nine borons of a dicarbollide complex: six resonances having relative areas 1:2:2:1:2:1 (proceeding from low field to high field). There were no additional resonances detected upfield or downfield from the displayed spectrum. The two upfield resonances at –46.7 and –51.8 ppm are significantly broader than the others (width at half-height ca. 260 Hz), and the coupled spectrum shows diminished proton coupling relative to the other signals. It would not be unreasonable to assign these resonances to the three borons on the upper belt, the ones presumably closest to the paramagnetic metal. A detailed study²⁷ on paramagnetic metallocarboranes of the transition metals showed that the borons directly bonded to the metal exhibit the most pronounced effects (isotropic shift, signal broadening) in their ^{11}B resonances. The fact that these resonances do not show large shifts away from the “normal” diamagnetic region (+15 to –40 ppm) is consistent with the absence of any significant covalent bonding in organo-lanthanide complexes.³⁰

The ^{11}B NMR spectra of the diamagnetic Yb complex, **3**, display a pattern of resonances similar to that found in the spectrum of $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$.²⁶ The chemical shifts differ slightly from those for the nido monoanion; the proton-coupled ^{11}B NMR spectrum of the hydrolysis product of **3** gives the authentic spectrum for $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$ complete with the “filled-in” doublet at –32 ppm due to additional coupling with the bridged proton. The appearance of a “monoanion-like” spectrum for **3** is entirely reasonable given the diamagnetism of the ytterbous ion along with the presumed ionic bonding in these complexes. A solution structure that places the Yb ion closer to the unique boron than to one of the two symmetrical borons on the upper belt would impose the correct symmetry for a spectrum similar to that displayed by $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$; such a structure could also account for the absence of a spectrum similar to that of the free dicarbollide ligand (^{11}B NMR spectrum of $\text{Na}_2[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]$ in THF shows four resonances with relative areas 6:1:1:1).

Fluxional Behavior of the Dicarbollide Complexes of Samarium and Ytterbium in Solution. Synthesis of the monocationic complexes using a selectively deuterated dicarbollide ligand (vide supra) yields additional information about the structures of these complexes in solution. The room-temperature ^1H -decoupled ^{11}B NMR spectrum of **2a** in THF can be seen in Figure 3. Comparison of the decoupled spectrum of **2a** with the analogous spectrum of the undeuterated complex **2** shows them to be nearly identical. Examination of the two proton-coupled spectra reveals that the only difference between the two involves the resonance of area two centered at –19 ppm. This resonance shows no proton coupling

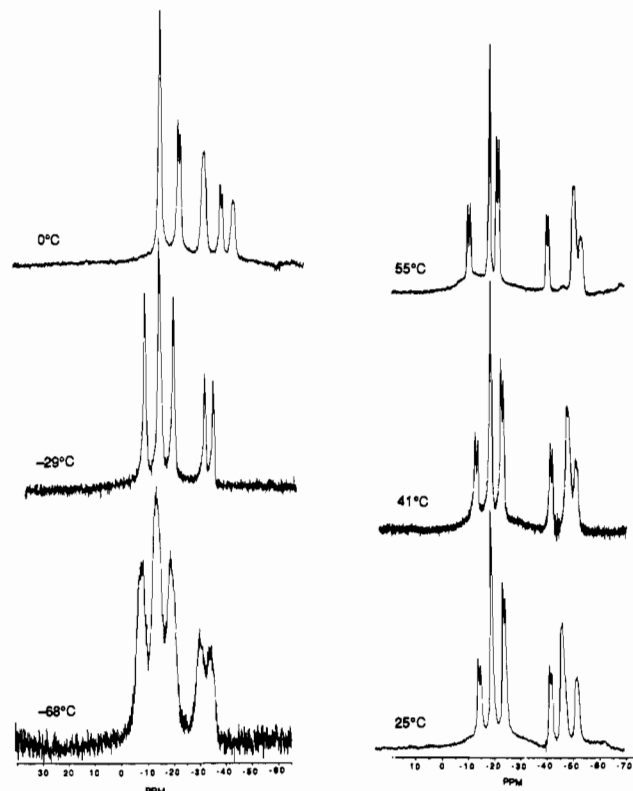


Figure 4. Variable-temperature ^{11}B NMR spectra (^1H coupled) of **2a** in THF.

in the spectrum of the selectively deuterated compound and is therefore due to the two borons that have been deuterated, the symmetry-equivalent pair on the upper belt. This assignment is in contradiction with the explanation offered previously for the spectrum of the undeuterated analogue: the broadened upfield resonance of area two had been assigned to the symmetrical borons on the upper belt. To ensure against the possibility of any deuterium rearrangement on the dicarbollide ligand, a ^{11}B NMR spectrum was taken of the hydrolysate of **2a** and it was shown to be identical with that for an authentic sample of $[\text{9,11-(D)}_2\text{-nido-7,8-C}_2\text{B}_9\text{H}_{10}\text{D}_2]^-$. One possible explanation is that the spectra are the result of an averaged solution structure that has the paramagnetic Sm ion interacting in some fashion with three borons (upfield resonances of area 2 and 1) of the dicarbollide ligand while having little or no interaction with the symmetrically placed borons on the upper belt. Since the coordination sphere of the metal is made up only of solvent and a single anionic ligand, a dynamic process in a coordinating solvent is not at all unreasonable.

There is precedent for a dynamic process involving a transition metal (rhodium) and the dicarbollide ligand.³¹ The metal is involved in a *cis*o (metal above the open face of the cage)–*exo-nido* (metal bound to the side of the cage through Rh–H–B bridges) equilibrium, which has been seen in a number of phosphine-substituted rhodacarboranes.³¹ The solid-state structures³² of the *exo-nido* tautomers have shown these complexes to be formally composed of a $[(\text{PR}_3)_2\text{Rh}]^+$ moiety bound to the anionic carborane cage through two Rh–H–B interactions. Of course, one must be cautious when drawing comparisons between the transition-metal systems and the complexes of the f-block metals; however, the fact that there exists a precedent for a metal cation to undergo polytopal migration serves to illustrate the potential for the dicarbollide ligand to act like a “three-dimensional” cyclopentadienyl ligand and exhibit other modes of bonding inter-

(27) Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 761.

(28) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507.

(29) The low solubility of these complexes in THF made it necessary to use a 10-mm quartz NMR tube in order to eliminate the interference caused by the broad signal from the borosilicate glass in a conventional Pyrex tube. Using the quartz tube, it was possible to obtain spectra with excellent signal to noise in a reasonable number of scans (ca. 2000).

(30) ^{11}B NMR spectra of paramagnetic d-block metallocarboranes have displayed isotropically shifted resonances over approximately an 800 ppm range; see ref 27.

(31) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979.

(32) Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990.

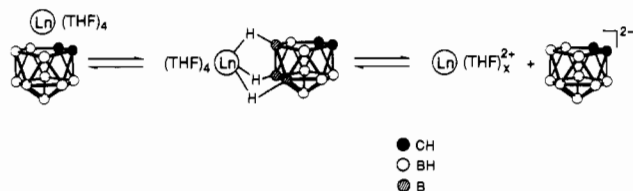


Figure 5. Proposed dynamic process involving Ln^{2+} ion and the dicarbollide ligand.

actions in addition to the conventional one offered by the pentagonal face.

A variable-temperature ^{11}B NMR study was performed on these monocage complexes in order to learn more about their behavior in solution with regard to any possible fluxional processes involving the metal and the dicarbollide ligand. Variable-temperature ^{11}B NMR spectra (in THF) for *closo*-1,1,1,1-(THF)₄-1,2,3-SmC₂B₉H₉D₂ (**2a**) are displayed in Figure 4. As the temperature is lowered to -68°C , there is a change from the six-line pattern seen at room temperature to a low-temperature spectrum with five resonances having relative areas 2:3:2:1:1 (low field to high field). This low-temperature spectrum is very similar to the pattern of resonances exhibited by [*nido*-7,8-C₂B₉H₁₂]⁻ (vide supra). The low-temperature spectrum also has the chemical shifts of its resonances concentrated in the normal diamagnetic region, like the *nido* monoanion, with no signals exhibited upfield. The spectrum obtained at $+55^\circ\text{C}$ shows no change from the room-temperature spectrum in the four most downfield signals, while the two broadened upfield resonances have shifted closer together (at -50 ppm) and both show evidence for proton coupling. If these upfield signals are due to the borons having the greatest interaction with the paramagnetic metal, it would seem logical that they would also exhibit the largest temperature dependence. In contrast, the variable-temperature ^{11}B NMR spectra of the deuterated ytterbium complex, **3c**, show no temperature dependence whatsoever.

A possible explanation for the variable-temperature spectra of these complexes is shown in Figure 5. A dynamic process that involves an interconversion between three tautomers is consistent with the NMR data if the spectra result from an averaged solution structure. This proposed process involves an equilibrium between two extreme tautomers: one in which the metal and the dicarbollide ligand exist as a discrete ion pair, [$\text{Sm}(\text{THF})_n$]²⁺·[*nido*-7,8-C₂B₉H₁₁]²⁻, and another with the metal capping the open face of the dicarbollide ligand. Interconversion between these two tautomers would proceed through an intermediate third tautomer in which the lanthanide ion simultaneously interacts with the B-H vertices of the top and lower belt via Ln-H-B interactions, similar to those observed in the complex [*closo*-1,1,1,1-(MeCN)₅-1,2,4-SrC₂B₁₀H₁₂]_n.¹² The proposed fluxional process is structurally similar to the *closo*-*exo-nido* tautomerism observed earlier in the rhodacarborane.³¹

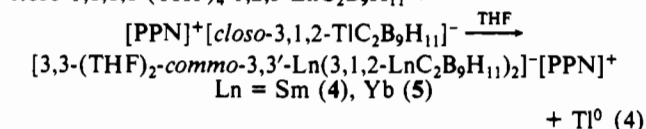
The tautomers shown in Figure 5 represent the two extremes covering the range of proposed metal-dicarbollide interactions in these monocage complexes. It is reasonable to assume that at lower temperature the *exo-nido* tautomer would predominate because, as the temperature is lowered, it would be less likely for the metal to lose additional coordinated THF and revert back to the *closo* tautomer. The well-established oxophilicity of the lanthanides³³ and the low-temperature ^{11}B NMR spectra are consistent with this premise. As the temperature is raised (0°C or above), the fluxional process becomes more rapid. This behavior is exemplified by the ^{11}B NMR spectrum of the Sm complex, **2a**, in which the two upfield resonances become sharper and seem to be merging. If the interconversion between these tautomers is rapid (on the NMR time scale), then the spectra at higher temperatures represent a "time average" of the species in solution rather than a single discrete tautomer.

The suggested equilibrium presented here is a speculative one based on the variable-temperature ^{11}B NMR spectra for these

complexes. Possible comparisons with the *closo*-*exo-nido* rhodacarboranes have been in a structural sense only; ^{11}B NMR spectra for the rhodium complexes were broad and unresolved, so spectral comparisons were not possible. This particular type of dynamic behavior (metal moving on and off the η^5 -ligand) has not been previously reported with lanthanide complexes; however, these are the first organolanthanide complexes with a single η^5 -ligand and the remainder of the metal's coordination sphere composed only of solvent. With this arrangement of ligands about the metal, the possibility for fluxional behavior in a coordinating solvent certainly exists. The proposed dynamic process is reliant on the existence of both the *closo* (metal over the bonding face of the dicarbollide ligand) and the *exo-nido* (metal ion completely solvated) tautomers; to date, there have been no reports of divalent lanthanide ions that are completely solvated. We have recently performed a single-crystal X-ray structure determination on [$\text{Yb}(\text{THF})_6$]²⁺·[*nido*-7,8-C₂B₉H₁₁]²⁻, which was obtained as an unexpected byproduct in a reaction involving **3**.³⁴ The existence in the solid state of such a species, along with the aforementioned structure determination of *closo*-1,1,1,1-(DMF)₄-1,2,3-YbC₂B₉H₁₁, does support the possible existence in solution of the two tautomers.

Synthesis and Characterization of Bis(dicarbollide) Complexes of Samarium and Ytterbium. Bis(dicarbollide) complexes that contain a transition metal¹ or a main-group metal² are known, and the associated structural studies showed that the two dicarbollide ligands were always configured in a nearly parallel fashion with respect to each other. None of these complexes contained other ligands in the metal's coordination sphere. Arguments have been advanced that cite the steric bulk of the [*nido*-7,8-C₂B₉H₁₁]²⁻ ligand as the reason for this preferred geometry as well as the increased stability of certain transition-metal dicarbollide complexes relative to their cyclopentadienyl analogues.³⁵ The synthesis and structural characterization of [Li(THF)₄]₂[3,3-(Cl)₂-*commo*-3,3'-U(3,1,2-UC₂B₉H₁₁)₂] proved that the use of a larger f-block metal permitted the two dicarbollide ligands to be configured in a bent fashion about the metal.⁴ This is the first metallacarborane complex that is structurally similar to the "bent" metallacenes.³⁶ The ionic radius¹⁰ of U⁴⁺ is similar to the radii for Sm and Yb (di- and trivalent oxidation states), and it seemed reasonable that the use of these 4f metals would allow the ligands to be configured in a similar geometry. One rational approach to the synthesis of a 4f metallacarborane sandwich complex of this type is the addition of a second dicarbollide ligand to the monocage complexes **2** and **3**.

The reaction of *closo*-1,1,1,1-(THF)₄-1,2,3-LnC₂B₉H₁₁ (Ln = Sm (**2**), Yb (**3**)) with [PPN]⁺[*closo*-3,1,2-TiC₂B₉H₁₁]⁻ in THF affords the desired bis(dicarbollide)lanthanide complex with the composition [Ln(C₂B₉H₁₁)₂(THF)₂]⁻[PPN]⁺ (Ln = Sm (**4**), Yb (**5**)) according to the reaction given in eq 4. Both the Sm and



Yb complexes can be synthesized as their PPN salts according

(34) The compound crystallized in the rhombohedral space group $R\bar{3}m$ with the following unit cell parameters. Hexagonal indices: $a = 11.423$ (1) Å, $c = 31.277$ (5) Å, $V = 3531$ Å³, and $Z = 3$. Rhombohedral indices: $a = 12.331$ (2) Å, $\gamma = 55.15$ (2)°, $V = 1177$ Å³, and $Z = 1$. Data were collected at 298 K on a diffractometer equipped with a small Huber circle, using Mo K α radiation, to a maximum $2\theta = 50^\circ$, giving 733 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was $R = 0.075$, $R_w = 0.078$ for 468 independent reflections with $I > 3\sigma(I)$. The six THF ligands are configured about the Yb²⁺ ion in an octahedral fashion with the positive charge of [$\text{Yb}(\text{THF})_6$]²⁺ being balanced by two disordered [*nido*-7,8-C₂B₉H₁₁]⁻ anions. The Yb-O(THF) distance is 2.298 Å. Full crystallographic details of this compound will be published elsewhere.

(35) Hanusa, T. P. *Polyhedron* **1982**, *1*, 663.

(36) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729 and references contained therein.

to this route in up to 50% yields (^{11}B NMR spectra of the reaction mixture demonstrate yields to be in excess of 80%). In this case the divalent lanthanide has been oxidized to the +3 state with the concomitant reduction of thallos ion to thallium metal. The metal in the trivalent oxidation state accommodates the high negative charge developed by two dicarbollide ligands. Like monocage divalent lanthanacarboranes, these biscage trivalent lanthanacarboranes **4** and **5** do not analyze well; however, magnetic studies, ^1H NMR spectra, and the complexometric metal analysis support the proposed formulation. Room-temperature magnetic measurements (in the solid state) showed these complexes to possess the metal in the +3 oxidation state. The Sm complex **4** has magnetic moment $1.6 \mu_{\text{B}}$, while the Yb complex **5** has magnetic moment $4.5 \mu_{\text{B}}$; both values are well within the reported range observed for other trivalent Sm and Yb complexes.³⁷ The solid-state IR spectra of **4** and **5** exhibit absorption due to coordinated THF ligands along with a broad, but strong, absorption centered at 2520 cm^{-1} due to the terminal B–H unit. It is interesting to note that the spectra do not display the unique split B–H stretch observed with the divalent monocage complexes. Both these new complexes are extremely moisture sensitive but are stable for indefinite periods of time when stored in an inert atmosphere. The ^1H NMR spectrum of **4** in CD_2Cl_2 displays two broad resonances at 2.74 and 1.34 ppm, which can be assigned to the methylene protons of coordinated THF. The addition of a slight excess of $\text{CH}_3\text{CN}-d_3$ causes these resonances to disappear with the simultaneous appearance of two signals attributable to free THF at 3.59 and 1.76 ppm. Obviously, both the Sm and Yb sandwich complexes undergo exchange of coordinated THF by acetonitrile. The carboranyl C–H protons appear as a broad singlet at 4.89 ppm in the ^1H NMR spectrum of **4** (in CD_2Cl_2). It was not possible to definitively assign the signals in the ^1H NMR spectrum of **5**; the large magnetic moment of Yb(III) leads to weak, broad signals that are displayed over an 80 ppm range, +30 to –50 ppm. The addition of a slight excess of D_2O to NMR samples of **4** and **5** (in CD_2Cl_2) results in colorless solutions that display spectra attributable to $[\text{nido-7,8-}\text{C}_2\text{B}_9\text{H}_{12}]^-$, the expected hydrolysis product.

The spectroscopic data observed for **4** and **5** support the existence of η^5 -interactions between the dicarbollide ligands and the trivalent metal; however, with no other bis(dicarbollide)lanthanide complexes available for comparison, it was not possible to elucidate the coordination geometry without a crystal structure determination. Single crystals of **4** suitable for an X-ray diffraction study were grown from a saturated THF solution; a greenish yellow crystal was mounted in a sealed glass capillary inside the glovebox, and data were collected at room temperature. The results are presented in Figure 6.

Molecular Structure of 4. The coordination geometry of **4** can be best described as a distorted tetrahedron with the two η^5 -bound dicarbollide ligands and the two coordinated THF molecules comprising the coordination sphere about Sm. The ring centroid–Sm–O(THF) angles range from 104.2 to 111.7°. The large deviations involved in the distortion are found for O(THF)–Sm–O(THF) and for ring centroid–Sm–ring centroid. There is no evidence for any "slipping"^{15,38} of the dicarbollide ligand relative to the metal, the kind of distortion seen in electron-rich d-block metallocarboranes. It was possible to locate the carbon atoms of the dicarbollide ligand in this structure, and they were seen to adopt a transoid configuration about the samarium ion. This configuration places the carbon atoms of the two ligands far apart from one another, as is the case in most other structurally characterized metallocarborane sandwich complexes.^{3,15,38} The PPN cation was completely ordered, and there were no unusually close interionic contacts between the cation and the anion.

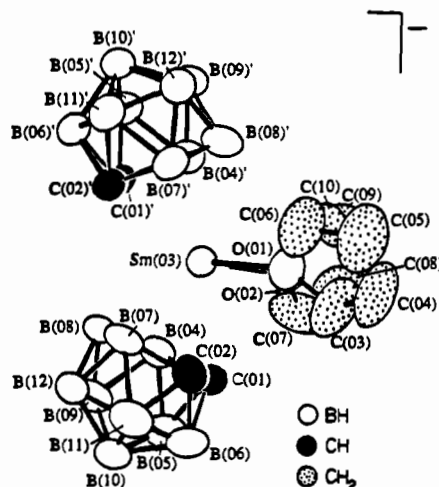


Figure 6. Molecular structure of $[3,3\text{-(THF)}_2\text{-commo-}3,3'\text{-Sm(3,1,2-SmC}_2\text{B}_9\text{H}_{11})_2\text{]}^-\text{[PPN]}^+$ (**4**), showing the atom-labeling scheme. Selected interatomic distances (Å): Sm(03)–C(01') = 2.732 (8), Sm(03)–C(02') = 2.731 (8), Sm(03)–B(04') = 2.712 (9), Sm(03)–B(07') = 2.695 (10), Sm(03)–B(08') = 2.734 (10), Sm(03)–C(01) = 2.722 (12), Sm(03)–B(08) = 2.776 (10), Sm(03)–centroid' = 2.318 (16), and Sm(03)–centroid = 2.356 (16). Selected angles (deg): centroid–Sm(03)–O(01) = 105.6 (4), centroid–Sm(03)–O(02) = 104.2 (4), centroid'–Sm(03)–O(01) = 111.5 (4), centroid'–Sm(03)–O(02) = 111.7 (4), and centroid–Sm(03)–centroid' = 131.9 (5).

The plane defined by Sm and the two oxygens is nearly normal (89.2°) to the plane containing Sm and the two ring centroids; this is very similar to the analogous dihedral angle (92.9°) in the divalent complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$.³⁹ The angle formed by the two oxygens and the Sm is nearly identical for these two organosamarium complexes, 79.5° for **4** and 82.6° for $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$.³⁹ The ring centroid–Sm–ring centroid angle for **4** is 131.9° , similar to that reported for the trivalent bis-(pentamethylcyclopentadienyl)lanthanide complexes containing other ligands in the metal's coordination sphere.³⁹ This value is expected to be smaller than the corresponding angle (137°) in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$,³⁹ mainly due to the larger ionic radius of Sm^{2+} (eight-coordinate, 1.27 Å) versus Sm^{3+} (eight-coordinate, 1.079 Å).¹⁰ Evans and co-workers have recently synthesized a cationic trivalent samarium complex $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]^+\text{[BPh}_4\text{]}^-$, and the subsequent structure determination showed the cation to have a ring centroid–Sm–ring centroid angle of 134.7° ,⁴⁰ intermediate between the values for the complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ and **4**. This series of nearly isostructural complexes provides a unique opportunity for a comparison of the bonding capabilities of the $[\text{nido-7,8-}\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ and $[\text{C}_5\text{Me}_5]^-$ ligands; here the centroid–Sm–centroid angles support the contention³⁵ that the two ligands have similar steric requirements.

The structure determination of **4** along with a comparison of its bond distances with those of other organolanthanide complexes supports a bonding description for this complex that is predominantly ionic. The Sm to dicarbollide ligand distances range from 2.693 (10) to 2.785 (9) Å with an average value of 2.735 Å. This value compares favorably well to Sm–C(C_5Me_5) distances found in other eight-coordinate trivalent Sm complexes: 2.72 and 2.73 Å for $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{I})(\text{THF})$,⁴¹ 2.72 Å for $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{Cl})(\text{THF})$,⁴¹ 2.73 (1) and 2.745 (9) Å for $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}_6\text{H}_5)(\text{THF})$,⁴¹ and 2.71 (4) Å for $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]^+$.⁴⁰ The close agreement of metal to η^5 -ligand distances in this series of structurally similar Sm^{3+} complexes strongly suggests that the $[\text{nido-7,8-}\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ and $[\text{C}_5\text{Me}_5]^-$ ligands are participating in

(37) (a) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 856. (b) Boncella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710.

(38) (a) Zalkin, A.; Templeton, D. H.; Hopkins, T. E. *J. Am. Chem. Soc.* **1965**, *87*, 3988. (b) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1966**, *5*, 1189. (c) Zalkin, A.; Hopkins, T. B.; Templeton, D. H. *Inorg. Chem.* **1967**, *6*, 1911.

(39) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941 and references contained therein.

(40) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *J. Am. Chem. Soc.*, submitted for publication.

(41) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112 and references contained therein.

the same type of bonding interaction with the metal, namely ionic. This contention is further supported by an application of Raymond's structural paradigm¹³ to the metal-dicarbollide distances in **4**. When the samarium to upper belt average distance of 2.735 Å is used, the effective ionic radius for the dicarbollide ligand is calculated to be 1.656 Å (ionic radius for the eight-coordinate Sm³⁺ is 1.079 Å). This value is essentially identical with that already determined for the dicarbollide ligand in the complex **3b** (1.66 Å) and is rather close to the value suggested for the cyclopentadienyl ligand, 1.64 ± 0.04 Å.¹³ A cone packing model has been applied to trivalent organolanthanide complexes, and these studies⁴² show that the [nido-7,8-C₂B₉H₁₁]²⁻ and [C₅Me₅]⁻ ligands are very similar in the steric saturation they offer to lanthanide complexes and would be expected to form complexes with structures that closely parallel one another, as has been shown with **4** and (C₅Me₅)₂Sm(THF)₂.

Conclusions

The complexes described in this paper represent the first well-characterized examples of organometallic complexes containing the dicarbollide ligand and the 4f metals. Use of the dicarbollide ligand with its minus two charge has allowed the synthesis of neutral divalent lanthanacarboranes that, to the best of our knowledge, are the first organolanthanides having a single η⁵-ligand bound to the metal with the remainder of the coordination sphere composed only of solvent. Spectroscopic evidence supports the possibility of fluxional behavior in solution for these compounds as a consequence of this unique configuration of ligands about the lanthanide ion. Structural studies performed on both the mono- and bis cage complexes suggests that the bonding in these lanthanacarboranes is largely ionic and does not differ greatly from the bonding observed in the analogous cyclopentadienyl compounds. We are currently investigating the synthesis of metallacarboranes incorporating other 4f-block metals, the lanthanide congeners Sc, Y, and La, and the alkaline-earth metals^{12,43} in an attempt to expand this exciting new area of organometallic chemistry.

Experimental Section

All manipulations were performed under atmospheres of dinitrogen and argon with the rigid exclusion of air and moisture. Chemicals were handled by using a combination of Schlenk, vacuum-line, and glovebox (Vacuum Atmospheres HE-43-2 Dri Lab) techniques.

Materials. The solvents THF and Et₂O were distilled over Na/benzophenone whereas MeCN was distilled over P₂O₅ prior to use. Traces of O₂ were removed by three freeze-pump-thaw cycles; the solvents were then taken into the glovebox and stored over activated molecular sieves (4 Å). [HN(CH₃)₃]⁺[nido-7,8-C₂B₉H₁₂]⁻⁴⁴ and [PPN]⁺[closo-3,1,2-TiC₂B₉H₁₁]⁻⁴⁵ were prepared according to the literature procedure. Solutions of SmI₂(THF)_x and YbI₂(THF)_x were prepared from excess Sm and Yb metal (Research Chemicals, Phoenix, AZ), respectively, and 1,2-C₂H₄I₂ (Aldrich) in THF solution.⁸ These solutions were dried over activated molecular sieves (4 Å) and then filtered through Celite; the solvent was removed in vacuo to yield SmI₂(THF)_x (dark purple) and YbI₂(THF)_x (yellow) as free-flowing powders.

Physical Measurements. ¹H and ¹¹B FTNMR measurements were performed on a Bruker AM-500 instrument at 500.13 and 160.463 MHz, respectively. Proton chemical shifts were referenced to residual solvent protons: CH₃CN-*d*₃, 1.93 ppm; THF-*d*₆, β-methylene protons at 1.72 ppm; DMF-*d*₇, methyl protons at 2.74 ppm. Boron chemical shifts were externally referenced to BF₃·OEt₂ in C₆D₆; peaks upfield of the reference are designated as negative. Samples for ¹¹B NMR spectroscopy were prepared in 10-mm quartz NMR tubes. IR spectra were obtained from a Nujol mull (NaCl); spectra were taken immediately after the mull was prepared in the glovebox) on a Beckman FT 1100 Fourier transform

spectrometer. Solid-state magnetic measurements (298 K) were made on a Johnson Matthey magnetic susceptibility balance. Complexometric metal analyses were conducted by titration with EDTA.⁴⁶

closo-1,1,1,1-(THF)₄-1,2,3-SmC₂B₉H₁₁ (2). [Me₃NH]⁺[nido-7,8-C₂B₉H₁₂]⁻ (0.75 g; 3.9 mmol) was dissolved in 50 mL of THF and then cannulated into a 250-mL Schlenk flask (with stir bar) that had already been charged with 0.28 g of NaH (11.7 mmol) in 75 mL of THF. The Schlenk pot was attached to a reflux condenser, and the system was refluxed under Ar for 4 h. After reflux, approximately half of the solvent was removed in vacuo (to help remove the (CH₃)₃N that had been produced). Once the solvent had been pulled off, an additional approximately 50-mL portion of THF was added to the reaction flask and the slurry was allowed to settle. The solution was then cannula filtered through a Schlenk frit (medium frit layered with Celite) to give approximately 90 mL of a clear, colorless solution of sodium dicarbollide, Na₂[nido-7,8-C₂B₉H₁₁]. The dicarbollide solution was added dropwise at room temperature to a stirred solution of SmI₂ (1.92 g in 125 mL of THF, 0.9 equiv; 3.5 mmol). Once addition was complete (ca. 2 h) the reaction was allowed to stir overnight. Stirring was stopped, the reaction mixture was allowed to settle, and the supernatant was cannulated away from the dark red solid that had precipitated during the course of the reaction. The solid was washed with THF (4 × 75 mL) and then dried in vacuo to give 1.2 g of **2** (60% yield). Complexometric anal. Calcd for SmC₁₈H₄₃O₄B₉: Sm, 26.35. Found: Sm, 25.5. The effective magnetic moment (25 °C) was 3.8 μ_B. IR (cm⁻¹): 2537 s, 2439 s, 2358 m, 1297 w, 1249 w, 1180 w, 1078 m, 1025 s, 974 w, 917 w, 876 s, 735 w, br. ¹H NMR (ppm, THF-*d*₆): 3.03 (s, carboranyl CH). Hydrolysis of **2** in CH₃CN-*d*₃ with a slight molar excess of H₂O and subsequent examination by NMR methods showed the presence of THF and [nido-7,8-C₂B₉H₁₂]⁻ in the ratio of 4:1. ¹¹B[¹H] NMR (ppm, THF, areas given in parentheses): -16.1 (1), -19.6 (2), -25.0 (2), -42.6 (1), -45.1 (2) (width at half-height, 258 Hz), -51.5 (1) (width at half-height, 241 Hz).

closo-1,1,1,1-(THF)₄-1,2,3-YbC₂B₉H₁₁ (3). [Me₃NH]⁺[nido-7,8-C₂B₉H₁₂]⁻ (0.50 g; 2.6 mmol) was deprotonated with excess NaH as previously described. A THF solution of the dicarbollide ligand (ca. 80 mL) was added dropwise at room temperature to a stirred solution of YbI₂ (1.31 g in 125 mL of THF, 0.88 equiv; 2.3 mmol). Once addition was complete (ca. 2 h) the reaction was allowed to stir overnight. Stirring was stopped, the reaction mixture was allowed to settle, and the supernatant was cannulated away from the bright yellow solid that had precipitated during the course of the reaction. The product was washed with THF (4 × 75 mL) and was dried in vacuo to give 0.71 g of **3** (52% yield).

Alternatively, complex **3** can be prepared by the direct oxidation of Yb metal with either [PPN]⁺[closo-3,1,2-TiC₂B₉H₁₁]⁻ or [Ti]⁺[closo-3,1,2-TiC₂B₉H₁₁]⁻. In a typical reaction, Yb metal (0.1 g, 0.57 mmol) was stirred with [PPN]⁺[closo-3,1,2-TiC₂B₉H₁₁]⁻ (1 g, 1.14 mmol) or [Ti]⁺[closo-3,1,2-TiC₂B₉H₁₁]⁻ (0.312 g, 0.57 mmol) in THF (25 mL) at room temperature for 60 h. Stirring was stopped, the reaction mixture was allowed to settle, and the supernatant was cannulated away from the light green solid that had precipitated during the course of the reaction. The light green product was washed with THF (3 × 15 mL) and was dried in vacuo. The product was dissolved in MeCN and filtered through Celite (to remove thallium metal) to afford an orange solution. Removal of solvent produces an orange residue. The orange residue was then stirred in 25 mL of THF. Removal of solvent gives 0.236 g of **3** (69% yield). Complexometric anal. Calcd for YbC₁₈H₄₃O₄B₉: Yb, 29.16. Found: Yb, 29.98. The effective magnetic moment (25 °C) was 0.0 μ_B. IR (cm⁻¹): 2540 s, 2452 s, 1295 w, br, 1251 w, br, 1174 w, 1083 w, 1024 s, 975 m, 949 w, 917 w, 877 s. ¹H NMR (ppm, DMF-*d*₇) for **3b**: 1.25 (s, carboranyl CH). Hydrolysis of **3** in CH₃CN-*d*₃ and DMF-*d*₇ with a slight molar excess of H₂O and subsequent examination by NMR methods showed the presence of both THF and [nido-7,8-C₂B₉H₁₂]⁻ in the ratio of 4:1. ¹¹B[¹H] NMR (ppm, THF, areas given in parentheses): -12.0 (2), -17.5 (2), -18.4 (1), -23.2 (2), -34.7 (1), -39.7 (1).

[3,3-(THF)₂-commo-3,3'-Sm(3,1,2-SmC₂B₉H₁₁)₂][PPN]⁺ (4). In the glovebox a 250-mL Schlenk flask was charged with 1.0 g (1.1 mmol) of [PPN]⁺[closo-3,1,2-TiC₂B₉H₁₁]⁻ and 100 mL of THF. To this solution was added 0.63 g (1.1 mmol) of **2** as a solid. The resultant slurry was stirred at room temperature for 12 h. The reaction mixture was then allowed to settle, and the greenish yellow supernatant was filtered through Celite to remove any traces of the thallium metal that had formed during the course of the reaction. The volume of the filtrate was concentrated to approximately 15 mL, and the solution was then allowed to stand undisturbed at room temperature, affording greenish yellow crystals. The crystals were isolated by filtration, washed with Et₂O (3 × 30 mL), and dried in vacuo to give 0.64 g of **4** (53% yield). Complexometric anal. Calcd for SmC₄₈H₆₈O₂B₁₈P₂N: Sm, 13.17. Found:

- (42) (a) Xing-Fu, L.; Fischer, R. D. *Inorg. Chim. Acta* **1984**, *94*, 50. (b) Xing-Fu, L.; Xi-Zhang, F.; Ying-Ting, X.; Hai-Tung, W.; Jie, S.; Li, L.; Peng-Nian, S. *Inorg. Chim. Acta* **1986**, *116*, 85. (c) Bagnall, K. W.; Xing-Fu, L. *J. Chem. Soc., Dalton Trans.* **1982**, 1365.
 (43) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.
 (44) Wiesbock, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.
 (45) [PPN]⁺[closo-3,1,2-TiC₂B₉H₁₁]⁻ is prepared via anhydrous metathesis of PPN⁺Cl⁻ with [Ti][closo-3,1,2-TiC₂B₉H₁₁] in CH₃CN. [Ti][closo-3,1,2-TiC₂B₉H₁₁] was prepared according to: Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

- (46) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115.

Table I. Crystallographic Data for 3b and 4

	3b	4
chem formula	C ₁₄ H ₃₉ YbB ₉ O ₄ N ₄	C ₄₈ H ₆₈ SmB ₁₈ P ₂ NO ₂
space group	Pbca	P1̄
fw	597.82	1097.36
a/Å	10.208 (1)	8.9374 (3)
b/Å	17.005 (3)	17.8703 (6)
c/Å	31.627 (5)	18.4989 (7)
α/deg		107.5402 (9)
β/deg		91.085 (1)
γ/deg		90.705 (1)
V/Å ³	5479	2816
Z	8	2
ρ _{calcd} /g cm ⁻³	1.32	1.29
T/K	298	298
λ/Å	0.7107	0.7107
μ(Mo Kα)/cm ⁻¹	34.1	11.38
R (R _w)	0.082 (0.084)	0.053 (0.065)

Sm, 13.31. The effective magnetic moment (25 °C) was 1.6 μ_B. IR (cm⁻¹): 2524 s, br, 1588 w, 1462 s, 1315 s, br, 1184 m, 1115 s, 1011 s, 968 m, 919 w, 859 s, 744 m, 724 s, 692 s. ¹H NMR (ppm, CD₂Cl₂): Broad unresolved resonances appear from 10.5 to 9.7, 4.0 to 2.6, and -2.0 to -3.1 (terminal BH), 4.89 (s, br; carboranyl CH), 2.74 (s, br; coordinated THF), 1.34 (s, br; coordinated THF). ¹¹B{¹H} NMR (ppm, CH₂Cl₂): -14.1, -18.2, -20.6, -23.1, -36.6, -39.1.

[3,3-(THF)₂-*commo*-3,3'-Yb(3,1,2-YbC₂B₉H₁₁)₂][PPN]⁺ (5). In the glovebox a 250-mL Schlenk flask was charged with 0.6 g (0.66 mmol) of [PPN][*closo*-3,1,2-TiC₂B₉H₁₁]⁻ and 80 mL of THF. To the pale yellow solution was added 0.39 g (0.66 mmol) of 3 as a solid. The resultant slurry was stirred at room temperature for 12 h. The reaction mixture was then allowed to settle, and the red supernatant was filtered through Celite to remove any traces of the thallium metal that had formed during the reaction. The volume of the filtrate was concentrated to approximately 10 mL. Excess Et₂O was allowed to vapor diffuse into the THF solution at room temperature over a period of 4 days, yielding dark red crystals. The crystals were isolated, washed with Et₂O (2 × 30 mL), and dried in vacuo to give 0.36 g of 5 (49% yield). Complexometric anal. Calcd for YbC₄₈H₆₈O₂B₁₈P₂N: Yb, 15.46. Found: Yb, 15.8. The effective magnetic moment (25 °C) was 4.5 μ_B. IR (cm⁻¹): 2521 s, br, 1589 w, 1461 s, 1308 s, br, 1187 m, 1114 s, 1017 s, 970 m, 915 w, 862 s, 744 m, 726 s, 690 s. ¹H NMR (ppm, CD₂Cl₂): Broad unresolved resonances appear from +30 to -50 ppm. Hydrolysis of 5 in CD₂Cl₂ with a slight molar excess of H₂O and subsequent examination by NMR methods showed the presence of THF and [*nido*-7,8-C₂B₉H₁₂]⁻ in the ratio of 1:1. ¹¹B{¹H} NMR (ppm, CH₂Cl₂): -102, -108, -141, -250, -450 (very broad).

Collection and Reduction of X-ray Data for *closo*-1,1,1,1-(DMF)₄-1,2,3-YbC₂B₉H₁₁ (3b). A red parallelepiped-shaped crystal, obtained from a dimethylformamide solution, was sealed in a thin glass capillary on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for *0kl* reflections for which *k* ≠ 2*n*, for *hk0* reflections for which *h* ≠ 2*n*, and for *h0l* reflections for which *l* ≠ 2*n*. Unit cell parameters were determined from a least-squares fit of 24 accurately centered reflections (9.4 < 2θ < 20.4°). Data were collected at 25 °C in the θ-2θ scan mode. An attempt to collect data at 128 K failed because the crystal cracked. Three intense reflections (434, 434, 126) were monitored every 97 reflections to check stability. Intensities of these reflections decayed ca. 13% during the course of the experiment (50.4-h exposure). Of the 4841 unique reflections measured, 1424 were considered observed (*I* > 2σ(*I*)) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects but were not corrected for decay or extinction. Programs used in this work include locally modified versions of crystallographic programs listed in ref 47. No redundant data

were collected. A summary of crystallographic data is included in Table I.

Solution and Refinement of the Structure of *closo*-1,1,1,1-(DMF)₄-1,2,3-YbC₂B₉H₁₁ (3b). Atoms in *closo*-1,1,1,1-(DMF)₄-1,2,3-YbC₂B₉H₁₁ (3b) were located by the use of the heavy-atom method. All calculations for *closo*-1,1,1,1-(DMF)₄-1,2,3-YbC₂B₉H₁₁ (3b) were performed on the VAX 11/750 crystallographic computer. The scattering factors for hydrogen were obtained from Stewart and co-workers⁴⁸ and for other atoms from ref 49.

Anisotropic thermal parameters were refined for Yb and O atoms. All methyl hydrogen atoms were included in calculated positions, C-H = 1.0 Å, angles = 109.5°, U = 0.30 Å². Six H atoms of the icosahedron were located and included in structure factor calculations, U = 0.10 Å². Anomalous dispersion terms were applied to the scattering of Yb. The larger peaks on a final difference electron density map (2 e Å⁻³) were near Yb. No other peak was higher than 0.7 e Å⁻³.

Collection and Reduction of X-ray Data of [3,3-(THF)₂-*commo*-3,3'-Sm(3,1,2-SmC₂B₉H₁₁)₂][PPN]⁺ (4). A yellow crystal, obtained from THF as a parallelepiped with faces (011̄), (011), and (100), and normals to these of 0.23, 0.32, and 0.45 mm, was mounted in a glass capillary. Unit cell dimensions were determined from a least-squares fit of 71 accurately centered reflections (9.9 < 2θ < 20.1°). Data were collected on diffractometer equipped with a small Huber circle built by Professor C. E. Strouse of this laboratory. The θ-2θ scan mode was used to collect data to a limit in 2θ of 45°. Three reflections, 035̄, 050, and 212, were measured every 100 reflections to check stability. Intensities of these reflections decayed only slightly, less than 6% during the course of the experiment, 69.5 h of exposure. A total of 7358 unique reflections was measured. Of these 5324 were considered observed (*I* > 3σ(*I*)) and were used in subsequent structure analysis. Other conditions for collection and reduction were the same as those that were applied to *closo*-1,1,1,1-(DMF)₄-1,2,3-YbC₂B₉H₁₁ (3b). A summary of crystallographic data is included in Table I.

Solution and Refinement of the Structure of [3,3-(THF)₂-*commo*-3,3'-Sm(3,1,2-SmC₂B₉H₁₁)₂][PPN]⁺ (4). Atoms in [3,3-(THF)₂-*commo*-3,3'-Sm(3,1,2-SmC₂B₉H₁₁)₂][PPN]⁺ (4) were located by the use of the heavy-atom method. All calculations for [3,3-(THF)₂-*commo*-3,3'-Sm(3,1,2-SmC₂B₉H₁₁)₂][PPN]⁺ (4) were performed on the VAX 11/750 crystallographic computer. The scattering factors for hydrogen were obtained from Stewart and co-workers⁴⁸ and for other atoms from ref 49.

Most H atoms, including all H atoms of the C₂B₉ icosahedral fragment, were located and not refined but were included in structure factor calculations. H atoms of THF were included in calculated positions (H-C-H = 109.5°). All phenyl groups were included as rigid groups, C-C = 1.395 Å, C-H = 1.0 Å. A total of 397 parameters were refined, including rigid group parameters for C₆H₅ and positional and anisotropic thermal parameters for all other non-hydrogen atoms. Each hydrogen atom was assigned a thermal parameter, U = 0.08 Å². Anomalous dispersion terms were applied to scattering of Sm and P.

Acknowledgment. M.J.M. thanks the Office of Naval Research (Contract N00014-85-K-0702), and R.K. thanks the National Science Foundation (Grant CHE 88-06179) for the support of this work. We also thank Dr. A. Varadarajan for helpful discussions and Andrea Owyung for the illustrations.

Registry No. 2, 114907-29-8; 2a, 132259-30-4; 3, 114907-30-1; 3b, 114907-32-3; 3c, 132233-02-4; 4, 132259-27-9; 5, 132259-29-1; [Me₃NH]⁺[*nido*-7,8-C₂B₉H₁₂]⁻, 12543-22-5; Na₂[*nido*-7,8-C₂B₉H₁₁], 12541-50-3; SmI₂, 32248-43-4; YbI₂, 19357-86-9; Yb, 7440-64-4; [PPN]⁺[*closo*-3,1,2-TiC₂B₉H₁₁]⁻, 114885-51-7; [Ti]⁺[*closo*-3,1,2-TiC₂B₉H₁₁]⁻, 41721-58-8; K⁺[9,11-(D)₂-*nido*-7,8-C₂B₉H₉D₃]⁻, 124479-66-9; K⁺[*nido*-7,8-C₂B₉H₁₂]⁻, 12304-72-2.

Supplementary Material Available: For 3b and 4, tables of crystallographic data collection parameters, atom coordinates, bond distances and angles, and anisotropic thermal parameters (17 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

(47) Programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ABSORB (Coppens, Edwards, and Hamilton), absorption correction calculation; ORTEP (Johnson), figure plotting; SHELX76 (Sheldrick), structure analysis package.

(48) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(49) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.