Figure 1. Molecular structure of {Cp*Hf(Cl)[μ-CHĊHCH₂C-(Me)=C(Me)CH₂]}₂ (2). The only hydrogen atoms shown are from the former acetylene molecule. The molecule has a center of symmetry. Selected structural parameters (symmetry-related atoms are denoted by a prime): Hf-Cl = 2.393 (2) Å, Hf-C(11)′ = 2.134 (5) Å, Hf-C(11) = 2.246 (6) Å, C(11)-C(12) = 1.538 (6) Å, Hf-H(11)′ = 2.21 (11) Å, C(14)-C(16) = 1.336 (10) Å, ∠Hf-C-(11)-Hf′ = 94.4 (2)°, ∠C(11)-Hf-C(11)′ = 85.6 (2)°, ∠Hf′-C-(11)-H(11) = 87. (7)°.

single C-C bond (C(11)-C(12) = 1.538 (6) Å). The Hf₂C₂ unit shows several interesting features. The Hf₂C₂ ring is nearly rectangular (Hf-C(11)-Hf′ = 94.4 (2)°, C(11)-Hf-C(11)′ = 85.6 (2)°) with two different Hf-C distances, one of which (Hf-C(11) = 2.246 (6) Å) is quite normal for a Hf-C single bond[8] while the other (Hf-C(11)′ = 2.134 (5) Å) is significantly shorter, comparable to the Hf-C (ylide) bond in Cp₂Hf(Et)CH=PPh₃ (2.149 (6) Å) in which a considerable amount of Hf-C π-interaction is presumed.[9] The M-C bond sequence in the Hf₂C₂ ring is not unlike that of the Zr₂C₂ ring in the remarkable complex [(C₅H₄Me)₂Zr]₂(μ-C₂Ph)₂ described by Erker et al.[10] The sharp Hf′-C(11)-H(11) angle (87 (7)°) and the Hf′-H(11) distance (2.21 (11) Å, the same as the Zr-H distance in the "agostic" complex (C₅H₄Me)₂ZrCl(CH=CMe)Zr(C₅H₅)₂[11]) make a C-H-Hf interaction likely. The ¹³C NMR resonance[12] of the carbon atoms in the Hf₂C₂ ring is found at 190.9 ppm, i.e. at considerably lower field than in the dihafnacyclobutane (Cp₂Hf)₂(μ-CH₂)₂ (149.6 ppm).[13] The small ¹J_CH of 94 Hz indicates that the C(11)-H(11) bond has a considerable amount of C 2p character. C(11) shows a large distortion from tetrahedral geometry (Hf′-C-(11)-C(12) = 138.6 (5)°; Hf-C(11)-C(12) = 119.7 (4)°) with C(12) lying only 0.55 Å out of the Hf₂C₂ plane. The X-ray structure shows that the dimethylcyclopentenyl groups are forced into the diagonal plane between and parallel with the Cp* -rings. These steric requirements distort the ge-

ometry of C(12) (C(11)-C(12)-C(13) = 116.6 (5)°; C-(11)-C(12)-C(18) = 115.6 (5)°). This is reflected in a decrease of ¹J_CH in the ¹³C NMR spectrum for C(12) (δ 39.6 (d, 111 Hz)), and in this case it is unlikely that the metal atom exerts any influence (Hf···H(12) = 3.45 (5) Å).

The mechanism of product formation in this reaction is not clear as yet, but one possible reaction sequence is given in Scheme I. It consists of initial coordination of the acetylene to Hf and insertion of the acetylene molecule in the Hf-diene bond to give a 3,4-dimethylhafnacyclo-hepta-3,6-diene. This could be followed by a ring contraction (formally a type of 1,3-shift) to a carbene species, which can then dimerize to the final product 2. Attempts to trap a possible carbene intermediate in the reaction mixture with, e.g., ketones, olefins, or substituted acetylenes have failed so far, as these reagents either react themselves with 1 or prevent the acetylene from reacting (possibly by blocking a coordination site).

(8) Typical values for Hf-C σ-bonds in Hf-alkyl compounds lie in the region of 2.23-2.29 Å. For example see: Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. E.; Atwood, J. L. *Organometallics* 1983, *2*, 750. Bristow, G. S.; Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* 1984, 399 and ref 9.
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(12) ¹³C NMR of 2 (50.3 MHz, C₆D₆, 20 °C): 190.9 (d, 94 Hz, Hf₂CH), 131.3 (s, =C(Me)), 129.9 (s, =C(Me)), 120.4 (s, C₅Me₅), 51.9 (t, 133 Hz, CH₂), 51.4 (t, 129 Hz, CH₂), 39.6 (d, 111 Hz, CH), 13.8 (q, 125 Hz, =C-(CH₃)), 12.1 ppm (q, 127 Hz, C₅(CH₃)₅).
(13) Van De Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickel-haupt, F. *J. Organomet. Chem.* 1986, *308*, 1.

Scheme I

Synthesis and X-ray Structure of a Bis(carboranyl)aluminate Derived from *nido*-(2,7-C₂B₆H₈)²⁻

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Summary: Synthesis and characterization of Na[Al(η²-2,7-C₂B₆H₈)₂] (Na[**3**]) is described, and the results of a single-crystal X-ray structure determination for Na[**3**] are presented. The anion [**3**]⁻ exists as enantiomers in the solid state. Variable-temperature ¹H and ¹¹B NMR studies indicate that in solution at room temperature this anion exhibits fluxional behavior such that its two enantiomeric forms rapidly interconvert.

Our recent studies regarding aluminum-containing carborane compounds have focused attention on the variety of bonding modes exhibited by aluminum in these unusual species. For example, structurally characterized aluminacarborane compounds are now known which contain aluminum–carborane cage connectivities ranging from three-center Al–H–B interactions[1] to π-bonding interactions of tri-,[2] penta-,[1] and bis(penta)hapticity.[3] Recently, we have reported the synthesis and structural characterization of aluminacarboranes which feature aluminum–carbon σ-bonds as their sole aluminum–carborane cage connectivities. These include nido-μ-6,9-{AlEt(OEt$_2$)}-6,9-C$_2$B$_8$H$_{10}$ (1)[4] and nido-[Al(η^2-6,9-C$_2$B$_8$H$_{10}$)$_2$]$^-$ ([2]$^-$),[5] each of which exhibit aluminum metal centers bound to the open faces of formal nido-[6,9-C$_2$B$_8$H$_{10}$]$^{2-}$ cages via aluminum–carbon σ-bonds only. In this paper we describe the synthesis and structural characterization of a bis-(carboranyl)aluminate complex containing the nido-[2,7-C$_2$B$_6$H$_8$]$^{2-}$ ligand which is structurally related to complex [2]$^-$.

Closo ten-vertex transition-metal complexes derived from 1,3-C$_2$B$_7$H$_{13}$ have been reported previously.[6] Most of these complexes contain one of the isomeric dicarbazapide ([C$_2$B$_7$H$_9$]$^{2-}$) ligands. Recently, in an attempt to prepare an aluminum derivative of this cage system, the reaction of Na[1,3-C$_2$B$_7$H$_{12}$]·OEt$_2$ with diethylaluminum chloride in a 2:1 mole ratio, respectively, was carried out in refluxing toluene. This reaction resulted in the somewhat unexpected formation of the unusual bis(carboranyl)aluminum complex Na[Al(η^2-2,7-C$_2$B$_6$H$_8$)$_2$] (Na[3]).[7] Purification by repeated recrystallization led to the isolation of Na[3] as an air-sensitive, white, crystalline solid in 42% yield.[8]

Figure 1. Structure of one enantiomer of Na[3], with hydrogen atoms omitted for clarity and thermal ellipsoids drawn at 50% probability level: Al–C(2a) = 2.018 (5) Å, Al–C(2b) = 2.018 (5) Å, Al–C(7a) = 2.017 (5) Å, Al–C(7b) = 2.020 (5) Å, Al–B(3a) = 2.282 (6) Å, Al–B(3b) = 2.276 (6) Å, Al–B(6a) = 2.517 (6) Å, Al–B(6b) = 2.517 (6) Å, Al–B(8a) = 2.517 (6) Å, Al–B(8b) = 2.511 (6) Å; C(2a)–Al–C(7a) = 82.40 (2)°, C(2b)–Al–C(7b) = 81.88 (2)°.

Since the structure of Na[3] could not be proven on the basis of spectroscopic data alone, a single-crystal X-ray diffraction study was undertaken.[9] Two crystallographically unrelated enantiomeric anions were present in the unit cell, designated as [3]$^-$ and [3]$'^-$, each of which was associated with a sodium cation. While these anions were not related crystallographically, they were found to be enantiomers within experimental error and, therefore, can be regarded as one chemically equivalent complex which displays stereoisomerism. An ORTEP representation of the structure of Na[3], together with selected interatomic distances and angles, is shown in Figure 1. The structure was well-ordered, and all atomic positions were located unambiguously including those for hydrogen. The aluminum center is surrounded by a distorted tetrahedral array of four carboranyl carbon atoms. The two metal–ligand C–Al–C angles are very similar and average 82.14°. The four Al–C bond lengths are also nearly equal and average 2.020 Å. The shortest Al–B distances are those between aluminum and the boron atoms in the 3-positions of each of the two formal nido-2,7-C$_2$B$_6$H$_8$ ligands, which average 2.280 Å. The roughly equal distances between aluminum and the four boron atoms in the 6- and 8-positions of each carborane cage are longer still, averaging

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(7) Preparation of Na[3]. All manipulations were carried out under dry N$_2$ by using standard Schlenk line and glovebox apparatus. In a typical experiment, 1.0 g of 1,3-C$_2$B$_7$H$_{13}$ (8.9 mmol) in 50 mL of Et$_2$O was added to a suspension of 0.5 g of NaH in 50 mL of Et$_2$O. The mixture was stirred at room temperature for 15 min and then filtered through a medium porosity frit. Solvent was removed in vacuo from the resulting filtrate to give solid Na[1,3-C$_2$B$_7$H$_{12}$] as a diethyl ether solvate. This etherate salt was warmed at 60 °C under hard vacuum for ca. 6 h. Examination by ^{1}H NMR spectroscopy of samples of carborane salt prepared in this manner indicated that they were roughly monoetherate solvates, and heating in vacuo for an additional 24 h did not substantially reduce the solvent content. To this salt was added 200 mL of dry freshly distilled toluene. A 1.0 M solution Et$_2$AlCl (4.5 mL) in hexane was added rapidly to the suspension. The flask was fitted with a condenser and the mixture refluxed under N$_2$ for 16 h. The mixture was filtered to remove precipitated NaCl and the filtrate volume reduced in vacuo to ca. 50 mL. Crude product was precipitated by addition of dry heptane. Purification of the product by three recrystallizations from toluene/heptane resulted in 0.46 g (42% yield) of Na[3].
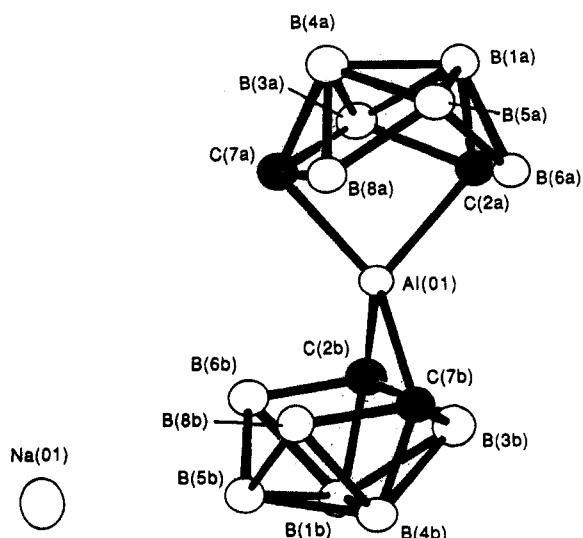
(8) Characterization data for Na[3]: 160.5-MHz ^{11}B NMR (CD$_2$Cl$_2$; referenced to external BF$_3$·OEt$_2$ at 0 ppm with chemical shifts upfield of 0 ppm reported as negative; ambient temperature) δ 21.6, 7.1, –15.0, –33.2 (br); 200.1-MHz ^{1}H NMR (toluene-d$_8$; referenced to residual benzyl protons in C$_7$D$_8$ at 2.09 ppm; ambient temperature) δ 2.96 (carborane C–H), ca. –0.5 to 5.1 ppm (br, B–H); characteristic IR (cm^{-1}, Nujol mull) 3040 (w, carborane C–H), 2525 (vs, B–H str), 1466 (m), 1392 (m), 1191 (w), 1125 (m), 1092 (m), 1060 (s), 1013 (s), 932 (m), 872 (s), 834 (m), 762 (m), 740 (m), 702 (m), 632 (m).

(9) Crystallographic Data. Single crystals of Na[3] were grown from toluene/pentane. Na[3] (C$_4$H$_{16}$B$_{12}$AlNa) crystallizes in the monoclinic space group $P2_1$ with cell dimensions a = 10.035 (2) Å, b = 12.433 (3) Å, c = 11.690 (3) Å, β = 111.019 (7)°, V = 1367 Å^3, and Z = 4. The data were collected at 128 K on a modified Picker automated diffractometer (Mo Kα, λ = 0.7107 Å, max 2θ = 50°). The structure was solved by direct methods using MAGEX (Hull, S. E.; Viterbo, D.; Woolfson, M. M.; Zhang, Shao-hui *Acta Crystallogr., Sect. A; Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, 566) and was refined by full-matrix least-squares methods to an R value of 0.049 (R_w = 0.059, GOF = 2.08) using 2156 reflections for which $I > 3\sigma(I)$ (a total of 2507 unique reflections were measured). Comparable interatomic distances and angles within the two crystallographically unrelated anions are very similar.

2.508 Å. Each $[2,7\text{-}C_2B_6H_8]^{2-}$ ligand has local mirror symmetry, possessing a mirror plane which contains the aluminum center and passes through boron atoms 3 and 5. The average B–B bond length in the carborane ligand is 1.77 Å. The average B–C bond length is 1.62 Å.

Because of its asymmetry, complex $[3]^-$ would be expected to give rise to six lines in the $^{11}B\{^1H\}$ NMR spectrum. The room-temperature $^{11}B\{^1H\}$ NMR spectrum of Na[3] in toluene solution, however, exhibits only four relatively broad resonances at δ 22.1 (area 2), 7.6 (area 1), −13.8 (area 1), and −32.0 (area 2). These resonances were too broad to show distinct ^1H coupling in the undecoupled spectrum. The two area 2 resonances were assigned to the two pairs of boron atoms which lie off the local mirror plane of the $2,7\text{-}C_2B_6H_8$ cage (i.e. B(01), B(04) and B(06), B(08)). Upon warming the solution to 70 °C, the four resonances sharpened and the three highest field resonances exhibited clear ^1H coupling. The lowest field area 2 resonance remained broad. Upon cooling this solution, all the ^{11}B NMR resonances became extremely broad and then sharpened again below −80 °C. At −90 °C, the lowest temperature at which spectra could be obtained, the $^{11}B\text{-}\{^1H\}$ NMR spectrum exhibited five resonances, the highest field area 2 resonance having been replaced by two area 1 resonances at δ −26.9 and −28.8. The low-field area 2 resonance remained broad at all temperatures between −90 and 70 °C. The room-temperature ^1H NMR spectrum of Na[3] in toluene-d_8 solution exhibited a single carboranyl C–H resonance at δ 2.96 which sharpened somewhat upon warming to 70 °C. Upon cooling this solution, the carboranyl C–H proton resonance became very broad and moved to somewhat higher field. Below −80 °C this resonance sharpened and was replaced at −90 °C by two equal area resonances at δ 2.63 and 2.92.

The observation of four resonances in a 2:1:1:2 area ratio in the room-temperature $^{11}B\{^1H\}$ NMR spectrum of $[3]^-$ suggests the occurrence of a fluxional process in solution involving the interconversion of the two enantiomeric $[3]^-$ anions. At −90 °C this interconversion is apparently slow on the NMR time scale, resulting in the appearance of two resonances attributable to one of the boron atom pairs which lies off the local mirror plane of the ligand. The broadness of the resonances attributable to the other off-plane boron atom pair may obscure the expected symmetry nonequivalence of these atoms under slow-exchange conditions. The reason for the broadness of these boron resonances at all temperatures is not known. The variable-temperature behavior of carboranyl C–H proton resonances is also indicative of the occurrence of a fluxional process above −90 °C. The interconversion of the two $[3]^-$ enantiomers may occur by rotation of the two $nido\text{-}[2,7\text{-}C_2B_6H_8]^{2-}$ ligands about the aluminum center; however, fluxionality within the carborane cage ligand framework cannot be ruled out, and, indeed, both processes may occur simultaneously.

Bonding in $[3]^-$ is ostensibly similar to that in $[2]^{-5}$ in that each formal $nido\text{-}[2,7\text{-}C_2B_6H_8]^{2-}$ ligand can be viewed as donating four electrons to the metal center via two carbon-based orbitals directed toward roughly tetrahedral aluminum coordination sites. The relatively long aluminum–boron interatomic distances as well as the coordination geometry around aluminum indicates an absence of aluminum–boron bonding in this complex. Complex $[3]^-$, like complex $[2]^-$, can be thought of as a spiro aluminate complex. While complex $[2]^-$ possesses S_4 symmetry and therefore does not exhibit stereoisomerism, $[3]^-$ displays chirality characteristic of spiro compounds of lower symmetry.

Although the B–H functionality can act in some cases as an electron donor to metal centers, the structure of Na[3] appears to be that of a simple ionic salt with no significant B⋯H⋯Na interactions. No discrete coordination geometry of B–H moieties around the sodium cations could be discerned. For each stereoisomeric anion there is one relatively short and several intermediate Na⋯H interatomic distances. In the case of $[3]^{\prime-}$, the shortest such distance is 2.319 (7) Å for Na⋯H(5a)'. For $[3]^-$, the shortest cation–anion distance is 2.330 (7) Å for Na⋯H(6b).

The loss of a boron vertex from the C_2B_7 polyhedral cage fragment is not without precedent as the reaction of $Na_2[1\text{-}R\text{-}3\text{-}R\text{-}1,3\text{-}C_2B_7H_9]$ (R = H, Me) with $Mn(CO)_5Br$ or $Mn_2(CO)_{10}$ to yield $closo\text{-}[C_2B_6H_6R_2Mn(CO)_3]^-$ (R = H, $[4a]^-$; R = Me, $[4b]^-$) has been reported previously.[10] The mechanism whereby this vertex is lost is not known. In the present case, a formal loss of BH_3 and a proton from each $[1,3\text{-}C_2B_7H_{12}]^-$ anion is required for formation of the $[2,7\text{-}C_2B_6H_8]^{2-}$ ligand. Examination of crude reaction mixtures by ^1H and ^{11}B NMR spectroscopy, however, revealed complex mixtures of boron-containing byproducts, making a simple reaction mechanism for formation of $[3]^-$ difficult to support.

The complexes $[4a,b]^-$ and $closo\text{-}C_2B_6H_8Co(C_5H_5)$ (5)[11] each contain $nido\text{-}[C_2B_6H_6R_2]^{2-}$ (R = H, Me) ligands and are closely related to $[3]^-$; however, in these $closo$ complexes the carborane ligands exhibit η^5 π-bonding to the transition metal. While multihapto π-bonding is exhibited by aluminum in some aluminacarboranes,[1-3] the σ-bonding mode present in $[3]^-$, as well as in 1 and $[2]^-$, appears to be emerging as a characteristic mode of an aluminum–carborane interaction. The present study shows that the $nido\text{-}[2,7\text{-}C_2B_6H_8]^{2-}$ ligand, like the $nido\text{-}[C_2B_8H_{10}]^{2-}$ ligand, can function as a 4e donor, as in $[3]^-$, or a 6e donor, as in $[4a,b]^-$ and 5, depending on the electronic requirements of the metal to which it is coordinated.

The existence of $[3]^-$ suggests the possibility of an isoelectronic carborane series of general formula $nido\text{-}2\text{-}R\text{-}7\text{-}R'\text{-}2,7\text{-}C_2B_6H_8$ (R = H, alkyl, etc.). While the compound $nido\text{-}C_2B_6H_{10}$ has been reported,[12] this compound appears to contain methine and bridging B–H–B groups. In a formal sense, $nido\text{-}[C_2B_6H_8]^{2-}$ can be considered to accept two protons in B–H–B bridging interactions to form $nido\text{-}C_2B_6H_{10}$. In an extension of this formalism, reaction of $nido\text{-}[C_2B_6H_8]^{2-}$ with two empty Al^{3+} sp^3-hybrid orbitals results in a species which contains Al–C two-center bonds, as found in $[3]^-$, rather than B–Al–B three-center interactions, and is derived from a hypothetical $nido\text{-}C_2B_6H_{10}$ isomer containing methylene groups. This is analogous to the pattern that has been observed recently for the interaction of $nido\text{-}[C_2B_8H_{10}]^{2-}$ with aluminum.[4,5]

We are currently attempting to isolate and identify the byproducts formed along with Na[3] as well as any possible reaction intermediates leading to this product.

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Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles (14 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Organolanthanide and Organoactinide Oxidative Additions Exhibiting Enhanced Reactivity. 4. Products, Stoichiometry, and Preliminary Kinetic Studies of the Reaction of (C₅Me₅)₂Smᴵᴵ·OEt₂ and (C₅Me₅)₂Euᴵᴵ·OEt₂ with Alkyl and Aryl Halides. Evidence for the Importance of Electron Transfer in Atom-Abstraction Oxidative Additions

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Summary: $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ exhibits oxidative addition reactions with alkyl and aryl halides faster than any f-block organometallic compound studied to date. The generalized stoichiometry displayed is $(a + b)(C_5Me_5)_2Sm^{II}\cdot OEt_2 + (a + c)RX \rightarrow (a - 2c)(C_5Me_5)_2Sm^{III}X + (b)(C_5Me_5)_2Sm^{III}R + (c)/z-[(C_5Me_5)_3Sm_2^{III}X_3]_z + (c)C_5Me_5R + (a + b)Et_2O + (a - b)R\cdot$ products. On the other hand, $(C_5Me_5)_2Eu^{II}\cdot OEt_2$ undergoes a *nonredox* reaction with alkyl and aryl halides, acting only as a "Euᴵᴵ–Grignard" reagent according to the stoichiometry: $1.0(C_5Me_5)_2Eu^{II}\cdot OEt_2 + 2.0RX \rightarrow 1.0EuX_2 + 2.0C_5Me_5R$. Comparisons of the relative rates of reaction between $(C_5Me_5)_2Sm^{II}\cdot OEt_2$, $(C_5Me_5)_2Eu^{II}\cdot OEt_2$, $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, and $(C_5Me_5)_2U^{III}(Cl)(THF)$ reveals the series Sm ≫ U > Yb ≫ Eu and supports the proposal that the transition state for these inner-sphere "atom-abstraction" oxidative addition reactions contains the anticipated contribution from electron transfer.

We report herein the results of product, stoichiometry, and preliminary kinetic and mechanistic investigations of the alkyl halide oxidative addition reactions of $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ and $(C_5Me_5)_2Eu^{II}\cdot OEt_2$. The only other *detailed* studies of organolanthanide and organoactinide oxidative additions are our recent report[1a–c] on

$(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and our earlier report[1d,e] on $(C_5Me_5)_2U^{III}(Cl)(THF)$.

Green/black crystalline $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ was prepared at Du Pont[2] from $SmBr_2$ and KC_5Me_5 by using methods analogous to the synthesis of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$.[3] The complex was pure as judged by ^1H NMR, elemental analysis, and IR.

Benzyl chloride emerged as a typical and convenient substrate for ^1H NMR product and stoichiometry studies following an examination of 15 alkyl and aryl halide oxidative additions to $(C_5Me_5)_2Sm^{II}\cdot OEt_2$. The product assignments provided below were made by comparison to authentic bibenzyl, $C_5Me_5CH_2Ph$,[4] $(C_5Me_5)_2Sm^{III}(Cl)$-(OEt_2),[5] and a product or products of net composition $[(C_5Me_5)_3Sm_2^{III}Cl_3]_z$.[6]

In a typical reaction, $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ (22 mg, 0.044 mmol), hexamethylbenzene (2 mg, 0.02 mmol) as an internal standard, benzene-d_6 (0.4 mL), and benzyl chloride were combined in an NMR tube. The $PhCH_2Cl$ was added (0.25 equiv at a time) via gas-tight syringe until it was no longer consumed and the excess was observable by ^1H NMR. During addition of the first 1.0 equiv of $PhCH_2Cl$, the ^1H NMR C_5Me_5 resonance of the green/black $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ solution shifts upfield from its initial δ 2.9 position to a broadened singlet at δ 0.9 (b s, 30 H, $lw_{1/2}$ = 30 Hz) characteristic of $(C_5Me_5)_2Sm^{III}Cl$.[5] Concomitantly, the solution becomes orange, confirming the formation of $(C_5Me_5)_2Sm^{III}(Cl)(OEt_2)$.[5] Further addition of 0.5 equiv of $PhCH_2Cl$ (0.25 equiv at a time, 1.5 equiv total)

(1) (a) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1986**, *5*, 598. (b) Finke, R. G.; Keenan, S. R.; Watson, P. L.; Schiraldi, D. A., manuscript in preparation. (c) Keenan, S. R. Ph.D. Dissertation, University of Oregon, Eugene, OR, 1986. It should be noted that a value of z = 1 (in (c)/z, eq 2, and in [(C₅Me₅)₃Sm₂Cl₃]ᵤ) is assumed therein; i.e., the possibility that z may be >1 is not treated in this thesis. (d) Finke, R. G.; Schiraldi, D. A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1875. (e) Schiraldi, D. A. Ph.D. Dissertation, University of Oregon, Eugene, OR, 1982.

(2) Green/black (C₅Me₅)₂Smᴵᴵ·OEt₂ shows λ_max = 680 nm and obeys Beer's law over the concentration range examined, (1.26–6.03) × 10⁻³ M (ε₆₈₀ 260 ± 8 M⁻¹ cm⁻¹). ¹H NMR (benzene-d₆): δ 2.85 (s, 30 H, lw₁/₂ = 14 Hz), -4.88 (b s, 4 H, lw₁/₂ = 16 Hz), 20.88 (b s, 6 H, lw₁/₂ = 16 Hz).

(3) (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (b) Watson, P. L.; Roe, D. C. *Ibid.* **1982**, *104*, 6471. (c) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (d) Watson, P. L. *J. Am.Chem. Soc.* **1983**, *105*, 6491. (e) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652.

(4) C₅Me₅CH₂Ph was identified by its characteristic ¹H NMR spectrum (benzene-d₆):[1b,c] δ 2.65 (s, 2 H), 1.77 (s, 6 H), 1.57 (s, 6 H), 0.98 (s, 3 H), 7.03 (m, 5 H).

(5) Orange (C₅Me₅)₂Smᴵᴵᴵ(Cl)(OEt₂) was prepared independently by reaction of CHCl₃ with (C₅Me₅)₂Smᴵᴵ·OEt₂ in Et₂O. The composition of this well-established type of lanthanide complex,[3,8,10,11] while fixed with certainty by the reaction stoichiometries with good mass balance, was confirmed by elemental analysis on a crystalline sample prepared at Du Pont. Calcd for (C₅Me₅)₂SmᴵᴵᴵCl(OEt₂): C, 54.35; H, 7.60; Cl, 6.68; Sm, 28.35. Found: C, 54.25; H, 7.56; Cl, 6.49; Sm, 29.5% (repeat Sm analysis, 28.1%). The UV/visible spectrum displays a λ_max at 426 nm. The ¹H NMR spectrum is somewhat variable depending upon the amount of Et₂O (or other ligands), the amount of Smᴵᴵ, and the amount of Smᴵᴵᴵ species present, suggesting that aggregates form in solution.[7c] (C₅Me₅)₂Smᴵᴵᴵ(Cl)(OEt₂) alone shows (benzene-d₆): δ 0.88 (s, 30 H, lw₁/₂ = 10 Hz), 1.06 (b q, 4 H), 0.14 (b t, 6 H). The THF analogue exhibits its ¹H NMR C₅Me₅ resonance at δ 1.28 (s, 30 H). The resonances due to bound THF were not observable under the conditions used.

(6) The composition [(C₅Me₅)₃Sm₂Cl₃]ᵤ, *in solution following oxidative addition*, the conditions relevant to this work, is solidly based upon the 14 reaction stoichiometries in Table I (supplementary material), the application of mass balance, and NMR data showing the presence of three (different) types of C₅Me₅ groups. ¹H NMR (benzene-d₆): δ 1.15 (s, 15 H, lw₁/₂ = 6 Hz), 0.32 (s, 15 H, lw₁/₂ = 6 Hz), -0.99 (s, 15 H, lw₁/₂ = 6 Hz). However, the molecular weight and thus z value are not yet known. On the basis of the observation that ligands, L, such as pyridine or THF cleave the aggregate to yield (C₅Me₅)₂SmCl(L) (by ¹H NMR,[1c] one is led to think of z = 1 and a (C₅Me₅)₂SmCl·(C₅Me₅)SmCl₂ formulation.[1c] (However, the (C₅Me₅)SmCl₂ half of this aggregate is not detected (may not be detectable) by ¹H NMR in the L = py or THF cleavage experiments.) Note that z = 2 leads to possibilities such as [(C₅Me₅)₂SmCl]₃·SmCl₃ and that equilibria which are possible under the reaction conditions, such as (C₅Me₅)₂SmCl + SmCl₃ ⇌ 2(C₅Me₅)SmCl₂, and which we have demonstrated in the analogous Yb compounds (see p 169, ref 1c), have yet to be ruled out. The independent synthesis of [(C₅Me₅)₃Sm₂Cl₃]ᵤ (red, λ_max = 451 nm) from (C₅Me₅)₂SmᴵᴵᴵCl(OEt₂) plus 0.5 equiv of PhCH₂Cl does give the same ¹H NMR C₅Me₅ resonances listed above, but the high solubility of the product even in pentane has frustrated isolation attempts (see p 229, ref 1c). Recent isolation attempts at Du Pont produce an orange powder (possibly SmCl₃)[12] and red crystals; efforts at single-crystal X-ray diffraction structural analysis are in progress.

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