Dinuclear Complexes of Di-, Tri-, and Mixed-Valent Samarium Supported by the Calix-tetrapyrrole Ligand

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$SmCl_3(THF)_3$ reacts with $^1/_2$ equiv of (Et$_8$-calix-pyrrole)[Li(THF)]$_4$ to yield the dinuclear, trivalent complex (Et$_8$-calix-pyrrole)Sm$_2$\{(μ-Cl)$_2$[Li(THF)$_2$]\}$_2$ (**1**). This species undergoes alkylation in diethyl ether resulting in the formation of the nearly isostructural (Et$_8$-calix-pyrrole)Sm$_2$\{(μ-CH$_3$)$_2$[Li(THF)$_2$]\}$_2$ (**2**) Complex **1** is reduced by LiAlH$_4$ to produce either the mixed-valence (Et$_8$-calix-pyrrole)Sm$_2$(THF)$_2$(μ-Cl)$_2$[Li(THF)$_2$] (**3**) or the divalent (Et$_8$-calix-pyrrole)Sm$_2$(THF)$_4$ (**4**), depending on the reaction conditions employed. The alkyl compound **2** reacts with PhSiH$_3$ in THF, resulting in a complex mixture of products, from which a mixture of the trivalent, mononuclear hydride (Et$_8$-calix-pyrrole)(THF)Sm(μ-H)Li$_2$[LiOCH=CH$_2$]$_2$(THF)$_2$ (**5**) and (Et$_8$-calix-pyrrole)Sm(H)Li$_2$(THF)$_6$ (**6**) were isolated in modest yield. The structures of **1**−**5** were elucidated by X-ray crystallography.

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Introduction

The remarkable chemical transformations discovered in the chemistry of organolanthanides have significantly contributed to the steady growth of interest in the chemistry of the Ln−C functionality. For example, it has been documented that organolanthanide complexes are efficient catalysts for olefin hydrogenation,[1] dehalogenation,[2] hydrosilylation,[3] hydroboration,[4] oligomerization,[5] and reductive cyclization.[6] In this regard, complexes with the formula (C$_5$Me$_5$)$_2$LnX (X = alkyl,[7] hydride[8]) have been shown to be among the most versatile catalytically active species. Even low-valent complexes, such as in the case of divalent samarium compounds of cyclopentadienyl-based and constrained-geometry-type ligands, have displayed interesting activity as catalysts for both olefin polymerization[9] and metal-promoted organic synthesis.[10]

In terms of molecular activation, the most surprising and unpredictable reactivity is certainly displayed by divalent samarium. The ability of low-valent samarium to act as a strong reducing agent is, in principle, limited to only one-electron-reduction processes. Nevertheless, the cooperative interaction of more low-valent samarium centers on the same substrate, which appears to be a rather characteristic behavior of this metal, has allowed for multielectron reductions, which include four-electron dinitrogen reduction,[11] complex organic transformations,[12] CO oligomerization/deoxygenation,[13] etc. In the view of the importance of these transformations, the possibility of assembling polynuclear structures, containing two or more low-valent samarium atoms in the same molecular frame and at close proximity, becomes particularly attractive.

Today, metallocene derivatives remain the most extensively studied compounds in lanthanide chemistry, although there is steady growth of attention for the preparation and characterization of compounds of these elements stabilized by other ligands. While low-valent samarium alkoxides,[14] amides,[15] phosphides,[16] and pyrazolylborate[17] have been prepared and characterized and

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[1] (a) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266. (b) Jeske, G.; Jauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (c) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.

[2] (a) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295. (b) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770. (c) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707. (d) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716.

[3] (a) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Nagishi, E. J. *J. Am. Chem. Soc.* **1991**, *113*, 8564. (b) Fu, P. F.; Bard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (c) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347.

[4] (a) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal.* **1995**, *95*, 121. (b) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.

[5] (a) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. (b) Burger, B. J.; Thompson, M. E.; Bercaw, J. E.; Cotton, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 1566. (c) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

[6] (a) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415. (b) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123.

[7] (a) Marks, T. J., Fragala, I. L., Eds. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; D. Reidel: Dordrecht, The Netherlands, 1985. (b) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (c) Evans, W. J. *Polyhedron* **1987**, *6*, 803. (d) Evans, W. J. *J. Organomet. Chem.* **1983**, *250*, 217.

[8] Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193.

[9] (a) Jeske, G.; Lauke, H.; Mauermann, P. N.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (c) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

[10] See for example: (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283 and references therein. (c) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131 and references therein. (d) Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Chapter 50.

[11] (a) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem. Int. Ed.,* in press. (b) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.

[12] (a) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (b) Qian, C.; Ge, Y.; Deng, D.; Gu, Y.; Zhang, C. *J. Organomet. Chem.* **1988**, *344*, 175. (c) Qian, C.; Zhu, D.; Li, D. *J. Organomet. Chem.* **1992**, *430*, 175. (d) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406.

[13] Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728.

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display promising features, these species are invariably mononuclear. Aside from the triple-decker (C$_5$Me$_5$)(THF)$_x$-Sm(C$_8$H$_8$)Sm(THF)$_x$(C$_5$Me$_5$) ($x = 0$, 1),[18] examples of low-valent bimetallic lanthanide compounds remain limited to the only example of a dinuclear complex of the calix-tetrapyrrole ligand.[19] This compound is particularly unusual, on account of its very short intermetallic distance and corresponding unusually low paramagnetism as well as its potential for use as an alkali-metal-free starting material for further transformations.

Thus, in the view of the variety of reactivity displayed by both di- and trivalent samarium compounds and the potential provided by the tetrapyrrole ligand system as a binucleating agent, we have now extended the above-mentioned work on dinuclear disamarium calix-tetrapyrrole[19] to the preparation and characterization of a series of dinuclear Sm(II), Sm(III), and mixed-valence compounds.

Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen−vacuum line. Solvents were dried by passing through a column of Al$_2$O$_3$ under an inert atmosphere prior to use, degassed in vacuo, and transferred and stored under an inert atmosphere. SmCl$_3$(THF)$_3$,[20] SmI$_2$(THF)$_2$,[21] and (Et$_8$-calix-tetrapyrrole)[Li(THF)]$_4$ [22] were prepared according to literature procedures. PhSiH$_3$ was dried over molecular sieves prior to use. THF-d_8 was dried over Na/K alloy, vacuum-transferred into ampules, and stored under nitrogen prior to use. NMR spectra were recorded on Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum-sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FT-IR instrument from Nujol mulls prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods, and corrections for underlying diamagnetism were applied to the data.[23] Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

(Et$_8$-calix-tetrapyrrole)Sm$_2${(μ-Cl)$_2$[Li(THF)$_2$]}$_2$·2THF (1). A suspension of SmCl$_3$(THF)$_3$ (2.4 g, 5.2 mmol) in THF (100 mL) was treated with (Et$_8$-calix-tetrapyrrole)(LiTHF)$_4$ (2.2 g, 2.6 mmol). Within minutes the solid dissolved and the color changed to deep orange. After it was stirred at room temperature for 2 h, the solution was concentrated to 30 mL and subsequently allowed to stand at −30 °C for 2 days, yielding air-sensitive orange crystals of **1** (2.5 g, 1.8 mmol, 72%). IR (Nujol mull, cm^{-1}): ν 3109 (w), 3097 (w), 2729 (w), 1520 w), 1494 (s), 1458 (vs), 1379 (s), 1327 (w), 1277 (m), 1261 (m), 1240 (m), 1161 (m), 1134 (w), 1074 (m), 1039 (vs), 1024 (s), 980 (m), 914 (m), 893 (s), 827 (m), 791 (s), 771 (s), 721 (w), 677 (w). ^{1}H NMR (THF-d_8, 500 MHz, 23 °C): δ 7.18 (broad s, pyrrole, 8H), 6.26 (sext, CH$_2$ ethyl, 8H), 3.56 (m, free THF, 4H), 3.53 (broad s, coord. THF, 16H), 3.34 (sext, CH$_2$ ethyl, 8H), 1.79 (broad t, CH$_3$ ethyl, 24H), 1.72 (m, free THF, 4H), 1.68 (broad s, coord. THF, 16H). ^{13}C NMR (THF-d_8, 125.72 MHz, 23 °C): δ 149.02 (quaternary C pyrrole), 103.11 (C−H pyrrole), 68.22 (CH$_2$ free THF), 67.45 (CH$_2$ coord THF), 55.71 (quaternary C ring), 26.38 (coord THF), 25.62 (CH$_2$ ethyl), 25.48 (free THF), 9.77 (CH$_3$ ethyl). Anal. Calcd (found) for C$_{60}$H$_{96}$N$_4$O$_6$Sm$_2$Li$_2$Cl$_4$: C, 50.54 (49.99); H, 6.79 (6.83); N, 3.93 (4.09). $\mu_{\rm eff} = 2.84\ \mu_{\rm B}$.

(Et$_8$-calix-tetrapyrrole)Sm$_2${(μ-CH$_3$)$_2$[Li(THF)$_2$]}$_2$·2Et$_2$O (2). A solution of **1** (2.0 g, 1.5 mmol) in diethyl ether (100 mL) was treated at room temperature with a solution of MeLi in ether (4.2 mL, 1.4 M, 5.9 mmol). The color of the solution lightened slightly during the following minutes of stirring. After 30 min, the solution was filtered to remove LiCl and the resulting solution was concentrated to 75 mL. Standing at −30 °C for 2 days produced yellow prisms of **2** (1.5 g, 1.3 mmol, 85%). IR (Nujol mull, cm^{-1}): ν 3093 (w), 2773 (w), 2727 (w), 1620 (w), 1464 (vs), 1379 (s), 1325 (m), 1275 (s), 1242 (s), 1159 (s), 1134 (m), 1117 (w), 1051 (vs), 1022 (s), 978 (s), 918 (s), 891 (s), 827 (s), 791 (s), 764 (vs), 712 (w), 679 (w), 586 (s). ^{1}H NMR (THF-d_8, 500 MHz, 23 °C): δ 7.48 (s, 8H, pyrrole), 3.72 (m, 8H, CH$_2$ ethyl), 3.65, 3.58 (free and coord THF), 2.11 (s, 12H, Me), 1.77, 1.72 (free and coord THF), 1.27 (m, 8H, CH$_2$ethyl), 0.20 (m, 24H, CH$_3$ ethyl). ^{13}C NMR (THF-d_8, 125.72 MHz, 23 °C): δ 103 (broad resonance CH pyrrolyl), 144.72 (quaternary pyrrolyl ring), 90.63 (Me groups), 67.40 (THF), 50.58 (quaternary ring), 25.46 (THF), 24.41 (CH$_2$ ethyl), 8.08 (Me, ethyl). Anal. Calcd (found) for C$_{64}$H$_{112}$N$_4$Sm$_2$O$_6$Li$_2$: C, 57.18 (56.77); H, 8.10 (7.95); N, 4.17 (4.12). $\mu_{\rm eff} = 2.90\ \mu_{\rm B}$.

(Et$_8$-calix-tetrapyrrole)Sm$_2$(THF)$_2$(μ-Cl)$_2$[Li(THF)$_2$] (3). Solid LiAlH$_4$ (0.032 g, 0.8 mmol) was added to an orange solution of **1** (2.0 g, 1.5 mmol) in THF (100 mL), resulting in a vigorous reaction with effervescence and an immediate color change to deep red. Stirring was continued for an additional 3 h. The solution was concentrated to 75 mL and was allowed to stand overnight at room temperature, during which time dark red crystals of **3** separated (1.5 g, 1.2 mmol, 84%). IR (Nujol mull, cm^{-1}): ν 3089 (w), 2723 (w), 1506 (w), 1487 (s), 1458 (vs), 1377 (s), 1342 (w), 1325 (m), 1275 (s), 1246 (s), 1159 (m), 1134 (w), 1043 (vs), 978 (s), 920 (s), 891 (vs), 829 (m), 793 (w), 769 (vs), 754 (s), 735 (w), 683 (w), 667 (w), 588 (m). Anal. Calcd (found) for C$_{52}$H$_{80}$N$_4$O$_4$Sm$_2$LiCl$_2$: C, 51.88 (51.60); H, 6.70 (6.79); N, 4.65 (4.55). $\mu_{\rm eff} = 3.46\ \mu_{\rm B}$.

(Et$_8$-calix-tetrapyrrole)Sm$_2$(THF)$_4$·3THF (4). Method A. Treatment of a solution of SmI$_2$(THF)$_2$ (2.5 g, 4.6 mmol) in THF (80 mL) with solid (Et$_8$-calix-tetrapyrrole)[Li(THF)]$_4$ (1.9 g, 2.3 mmol) resulted in a brown solution which deposited

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(14) (a) Sen, A.; Chebolu, V.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 1821. (b) Evans, W. J.; Anwander, R.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5. (c) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2691. (d) Biagini, P.; Lugli, G.; Abis, L.; Millini, R. *J. Organomet. Chem.* **1994**, *474*, C16.

(15) (a) Chebolu, V.; Whittle, R. R.; Sen, A. *Inorg. Chem.* **1985**, *24*, 3082. (b) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575. (c) Evans, W. J.: Rabe, G. W.; Ziller, J. W. *Inorg. Chem.* **1994**, *33*, 3072. (d) White, J. P., III; Deng, H.; Boyd, E. P.; Gallucci, J.; Shore, S. G. *Inorg. Chem.* **1994**, *33*, 1685. (e) Evans, W. J.; Rabe, G. W.; Ziller, J. W. *Organometallics* **1994**, *13*, 1641. (f) Minhas, R.; Song, J.; Ma, Y.; Gambarotta, S. *Inorg. Chem.* **1996**, *35*, 1866. (g) Evans, J. W.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1996**, *35*, 5435. (h) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968. (i) Edelmann, F. T. *Coord. Chem. Rev.* **1995**, *95*, 403. (j) Schumann, H.; Rosenthal, E. C. E.; Winterfield, J.; Kociok-Kohn, G. *J. Organomet. Chem.* **1995**, *495*, C12.

(16) (a) Nief, F.; Ricard, L. *J. Organomet. Chem.* **1994**, *464*, 149. (b) Rabe, G.; Riede, J.; Schier, A. *Inorg. Chem.* **1996**, *35*, 2680. (c) Gosink, H. J.; Nief, F.; Ricard, L.; Mathey, F. *Inorg. Chem.* **1995**, *34*, 1306. (d) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1992**, *11*, 2967.

(17) (a) Takats, J. *J. Alloys Compd.* **1997**, *249*, 52. (b) Hasinoff, L.; Takats, J.; Zhang, X. W.; Bond, A. H.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 8833. (c) Ferrence, G. M.; McDonald, R.; Takats, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2233.

(18) Evans, W. J.; Clark, R. D.; Ansari, M. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 9555.

(19) Song, J.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2141.

(20) Anhydrous SmCl$_3$ was prepared and was transformed into the corresponding tetrahydrofuranate by following a standard procedure: (a) Freeman, J. H.; Smith, M. L. *J. Inorg. Nucl. Chem.* **1958**, *7*, 224. (b) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

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

(22) Gale, P. A.; Sessler, J. L.; Král, V.; Lynch, V. *J. Am. Chem. Soc.* **1996**, *118*, 5140.

(23) (a) Mabbs, M. B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973. (b) Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Selectionnes, Diamagnetisme, Paramagnetisme Relaxation Paramagnetique*; Masson: Paris, 1957.

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orange microcrystalline solid within minutes. The reaction mixture was stirred for an additional 2 h, during which time more solid accumulated. The suspension was heated gently until everything went into solution. Subsequent standing at −30 °C for 2 days produced dark brown crystals of **4** (1.8 g, 1.60 mmol, 70%). IR (Nujol mull, cm^{-1}): ν 3091 (w), 3076 (w), 2721 (w), 1591 (w), 1458 (s), 1375 (s), 1358 (m), 1323 (w), 1269 (m), 1248 (m), 1211 (w), 1157 (w), 1103 (m, br), 1039 (vs), 1018 (m), 974 (w), 922 (w), 889 (s), 829 (w), 800 (w), 754 (vs), 667 (w). Anal. Calcd (found) for $C_{64}H_{104}N_4O_7Sm_2$: C, 57.27 (57.36); H, 7.81 (7.71); N, 4.17 (4.03). $\mu_{eff} = 1.98\ \mu_B$.

Method B. A solution of **1** (2.0 g, 1.5 mmol) in THF (100 mL) was treated with excess $LiAlH_4$ (0.12 g, 3.2 mmol). The resulting deep red suspension was refluxed for 2 h until the solution turned brown. Concentration to 75 mL and standing at −30 °C for 2 days yielded crystals of **4** (65%).

Method C. Excess metallic lithium (0.025 g, 3.6 mmol) was added to a solution of **1** (1.5 g, 1.1 mmol) in THF (100 mL) under Ar. Stirring at room temperature for 16 h resulted in a dark brown solution, which was filtered to remove unreacted lithium. Concentration to 50 mL and standing at −30 °C yielded crystalline **4** (60%).

Reaction of 2 with $PhSiH_3$. Isolation of (Et_8-calix-pyrrole)(THF)Sm(μ-H)[μ-OCH=CH_2]$_2$$Li_4(THF)_2$ (5) and (Et_8-calix-pyrrole)Sm(H)(Li_2(THF)$_6$ (6). Method A. Dropwise addition of $PhSiH_3$ (3.2 mmol) to a stirred yellow solution of **2** (2.0 g, 1.6 mmol) in THF (100 mL) resulted in a color change to light yellow and then gradually to pale orange-yellow during the course of 1 h. The solvent was removed under reduced pressure, and the yellow residue was extracted with diethyl ether (50 mL). Concentration of the extracts to 15 mL and standing at −30 °C overnight resulted in the formation of a mixture of pale and bright yellow crystals of very distinctive shape (total gravimetric yield 0.8 g). The bright yellow crystals were the minor component and were identified to be (Et_8-calix-pyrrole)(THF)Sm(μ-H)[μ-OCH=CH_2]$_2$$Li_4(THF)_2$ (**5**), while the second was identified as (Et_8-calix-pyrrole)Sm(H)Li_2(THF)$_6$ (**6**). An attempt to separate the two components by fractional crystallization from ether/THF mixtures afforded exclusively analytically pure **6**. Anal. Calcd (found) for $SmLi_2C_{60}H_{97}N_4O_6$: C, 63.51 (63.10); H, 8.62 (8.82); N, 4.94 (4.82). IR (Nujol mull, cm^{-1}): ν 3068 (m), 2721 (w), 1657 (w), 1571 (w), 1461 (s), 1375 (s), 1323 (w), 1262 (m), 1240 (m), 1208 (w), 1154 (w), 1130 (w), 1047 (s), 973 (m), 886 (s), 841 (m), 780 (s), 735 (s), 693 (w), 665 (m). ^1H NMR (THF-d_8, 500 MHz, 23 °C): δ 6.12 (s, pyrrole, 4H), 5.72 (s, pyrrole, 4H), 4.08 (m, CH_2 ethyl, 4H), 3.61 (m, free THF, 12H), 3.58 (broad s, THF attached to Li, 8H), 2.12 (m, CH_2 ethyl, 4H), 2.11 (m, CH_2 ethyl, 4H), 1.84 (pseudo t, THF attached to Sm, 4H), 1.79 (m, free THF, 12H), 1.75 (broad s, THF attached to Li, 8H), 1.43 (t, CH_3 ethyl, 12H), 1.11 (m, CH_2 Et, 4H), 0.59 (pseudo t, THF attached to Sm, 4H), 0.29 (t, CH_3 ethyl, 12H). ^{13}C NMR (THF-d_8, 125.72 MHz, 23 °C): δ 162.79 (quaternary C pyrrole), 140.00 (quaternary C pyrrole), 97.87 (CH pyrrole), 95.73 (CH pyrrole), 68.13 (CH_2 coord THF), 67.75 (CH_2 coord THF), 50.94 (quaternary C ring), 31.32 (CH_2 ethyl), 26.37 (CH_2 ethyl), 25.19 (CH_2 coord. THF), 24.70 (CH_2 coord THF), 9.88 (CH_3 ethyl), 8.07 (CH_3 ethyl). $\mu_{eff} = 1.32\ \mu_B$.

Method B. A solution of **2** (2.0 g, 1.6 mmol) in THF (100 mL) was exposed to H_2 at room temperature and atmospheric pressure. The yellow color of the solution rapidly faded, affording a pale beige yellowish solution. Workup similar to that above yielded analytically pure, pale yellow crystals of **6** (0.8 g, 0.7 mmol).

X-ray Diffraction Studies. Suitable crystals were selected, mounted on thin glass fibers using viscous oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1K CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[25]

No symmetry higher than triclinic was evident from the diffraction data of **3**. Systematic absences in the diffraction data and unit-cell parameters were consistent for space groups $C2/c$ (No. 15) and Cc (No. 9) for **1** and **5** and, uniquely, $Pbcn$ (No. 60) for **2**. A close inspection of the diffraction data for **4** suggested merohedral twinning of Laue class $4/m$ simulating Laue class $4/mmm$. The systematic absences in the data for **4**, in Laue class $4/m$, were uniquely consistent for space group $I4_1/a$ (No. 88). In cases of ambiguous space group assignment, solution in the centric options yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. The compound molecules for **1** and **5** are located on 2-fold axes. The compound molecule of **2** is located at an inversion center. The compound molecule of **4** is located at a 4-fold rotoinversion axis. A coordinated THF molecule, a half-occupied cocrystallized THF molecule, and a quarter-occupied cocrystallized THF molecule were each located disordered over two positions in a roughly 50/50 site distribution for **4**. Identification of the oxygen atom positions for the cocrystallized THF molecules in **4** was not possible because of the severe disorder, and the ring positions were refined with carbon atom identities each approximating a [($^1/_5$O)/($^4/_5$$CH_2$)] fragment, but the correct empirical formula was used in intrinsic property calculations. A solvent molecule was each located cocrystallized in the asymmetric units of **1** (THF) and **2** (diethyl ether). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions, except the hydride ligand in **5**, which was located from the difference map and refined with a riding model. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library (Sheldrick, G. M. Bruker AXS, Madison, WI, 1997). Crystal data and structure analysis results for **1**−**5** are given in Table 1, and selected bond distances and angles for these complexes are given in Table 2.

Complex 1. The molecular structure of **1**, as determined by X-ray diffraction, consists of two samarium atoms held together by the calix-tetrapyrrole ligand. The ligand is centered on the Sm−Sm vector (Sm···Sm = 3.390 Å) and adopts a nearly symmetric conformation in which each pair of pyrrole rings at opposite positions of the macrocycle coordinates each of the two Sm atoms in an η^5 fashion. Thus, the two samarium atoms adopt a bent, samarocene-like coordination geometry. The two N atoms of each pair of pyrrole rings π-bonded to one samarium are also σ-bonded to the second one. As a result, each samarium is overall connected to the four pyrrole rings by adopting a η^1:η^5-bonding fashion. Two chlorine atoms bridge each samarium to a lithium atom, which is in turn coordinated to two molecules of THF. The coordination geometry about each Sm may be viewed as severely distorted octahedral, the two σ-bonded nitrogens and the bridging chlorides defining the equatorial plane, while the two centroids of the two η^5-bonded rings occupy the axial positions.

Complex 2. This species consists of a symmetry-generated dimer with structural parameters similar to those of **1**. The calix-tetrapyrrole ligand bridges two samarium atoms which are placed at rather close proximity (Sm···Sm = 3.485 Å). This distance is significantly longer than in the isostructural **1**. This is probably the result of the fact that the CH_3−Sm distances of **2** are significantly shorter than the corresponding Sm−Cl distances of **1**. The resulting closer proximity of the methyl groups to the macrocycle and consequent increase of steric hindrance is likely to pull the two samarium atoms farther

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(24) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics,* in press.

(25) Blessing, R. *Acta Crystallogr.* **1995**, A51, 33−38.

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Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**	**4**	**5**
formula	$C_{60}H_{96}Li_2N_4O_6Sm_2Cl_2$	$C_{64}H_{112}N_4Sm_2Li_2O_6$	$C_{52}H_{80}N_4O_4Sm_2LiCl_2$	$C_{64}H_{104}N_4Sm_2O_7$	$C_{52}H_{79}Li_4N_4O_5Sm$
fw	1425.94	1344.27	1203.74	1342.21	1018.39
space group	*C*2/*c*	*Pbcn*	$P\bar{1}$	$I4_1/a$	*C*2/*c*
a (Å)	22.2398(5)	14.2174(7)	11.661(1)	14.564(2)	14.686(3)
b (Å)	14.9113(3)	21.748(2)	11.770(1)	14.564(2)	19.930(3)
c (Å)	20.5018(4)	22.209(2)	22.869(3)	31.130(7)	18.326(3)
α (deg)			76.997(2)		
β (deg)	101.968(1)		88.379(2)		97.805(3)
γ (deg)			61.691(2)		
V ($Å^3$)	6651.1(2)	6866.7(9)	2681.2(5)	6603(2)	5325(2)
Z	4	8	2	4	4
Kα radiation (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T (°C)	−100	−100	−60	−60	−60
D_{calcd} (g cm^{-3})	1.420	1.304	1.491	1.350	1.273
μ_{calcd} (cm^{-1})	1.957	1.741	2.313	1.812	1.149
R1, wR2, GOF[a]	0.0234, 0.0591, 1.020	0.0423, 0.0977, 1.073	0.0378, 0.0852, 1.002	0.0320, 0.0807, 1.137	0.0575, 0.1367, 1.041

[a] $R1 = \sum F_o - F_c/\sum F_o$; $wR_2 = [\sum(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

from the ligand, thus stretching the Sm···Sm distance. Two pairs of methyl groups bridge each samarium to one lithium atom, which is in turn coordinated to two molecules of THF. Thus, **2** may be regarded as the MeLi adduct of (Et_8-calix-pyrrole)[Sm(CH_3)]$_2$. The Sm−C bond distances are, within error limits, similar to those observed in terminally bonded Sm complexes of the same ligand system.[24]

Complex 3. The molecular structure of **3** is also dinuclear. Similar to **1** and **2**, each samarium shares the same calix-tetrapyrrole ligand with which it engages in both σ- and π-bonding interactions. Whereas the two samarium atoms in **1** and **2** are in a similar environment, complex **3** is asymmetric. Two chlorine atoms bridge one samarium atom and a lithium atom, which is in turn solvated by two molecules of THF, while the second samarium atom bears only two molecules of THF. The Sm−Sm distance (3.430 Å) is comparable to those observed for **1** and **2**.

Complex 4. The complex has a structure very similar to that of the previously reported (Et_8-calix-pyrrole)[Sm(Et_2O)]$_2$,[19] the only notable difference arising from the presence of two molecules of THF coordinated to each Sm instead of one molecule of diethyl ether. As a probable consequence of the increased steric bulk, the Sm−Sm distance in **4** (3.442(1) Å) is slightly longer than that observed in (Et_8-calix-pyrrole)[Sm-(Et_2O)]$_2$.[19]

Complex 5. The monomeric **5** is formed by a samarium atom surrounded by the macrocycle. Two of the four pyrrole rings are π-bonded to the metal, while the other two are coplanar with samarium, with which they form σ-bonds with the two nitrogen atoms. Each of the pyrrole rings σ-bonded to samarium is also π-bonded to one lithium atom. Each of the two lithium atoms is in turn σ-bonded to the nitrogen atom of a second ring and to the oxygen atom of one of the two Li-(enolate) moieties. The enolate lithium atoms are each coordinated to one molecule of THF. The four lithium atoms define a rather regular tetrahedron, which caps the cavity of the macrocycle opposite to the samarium atom and which contains the hydride. One molecule of THF is bonded to samarium and is placed on the axis perpendicular to the plane defined by the four nitrogen atoms of the macrocycle and on the side opposite to that occupied by the hydride moiety. The hydride is located in the center of the $SmLi_2$ triangle and is apparently responsible for the substantial bending of the N−Li−O vector (N(1)−Li(1)−O(2) = 160.6(10)°).

Results and Discussion

The room-temperature reaction of 2 equiv of $SmCl_3$-($THF)_3$ with (Et_8-calix-tetrapyrrole)[Li(THF)]$_4$ in THF formed an orange, air-sensitive solution from which

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

Compound **1**

Sm−Cl(1) = 2.7231(9)
Sm−Cl(2) = 2.7236(8)
Li−Cl(1) = 2.329(6)
Li−Cl(2) = 2.354(7)
Sm−N(1) = 2.716(3)
Sm−C(4) = 2.860(3)
Sm−C(5) = 2.969(3)
Sm−C(6) = 2.967(3)
Sm−C(7) = 2.856(3)
Sm−N(2) = 2.648(3)
Sm···Sm(a) = 3.391(3)

N(2)−Sm−Cl(1) = 169.10(6)
N(2)−Sm−Cl(2) = 88.64(6)
Cl(1)−Sm−Cl(2) = 80.65(3)
Sm−Cl(1)−Li = 91.1(2)

Compound **2**

Sm−C(20) = 2.582(4)
Sm−C(21) = 2.574(3)
Li−C(20) = 2.163(7)
Li−C(21) = 2.171(8)
Sm−N(1) = 2.769(3)
Sm−C(4) = 2.885(3)
Sm−C(5) = 2.966(4)
Sm−C(6) = 2.974(4)
Sm−C(7) = 2.896(3)
Sm−N(2) = 2.721(3)
Sm···Sm(a) = 3.485(4)

N(2)−Sm−C(20) = 173.01(10)
N(2)−Sm−C(21) = 86.29(10)
C(20)−Sm−C(21) = 86.74(12)

Compound **3**

Sm(1)−O(1) = 2.589(4)
Sm(1)−O(2) = 2.613(4)
Sm(1)−N(2) = 2.828(3)
Sm(1)−C(10) = 2.982(4)
Sm(1)−C(13) = 2.988(4)
Sm(1)−N(3) = 2.790(4)
Sm(2)−N(2) = 2.623(4)
Sm(2)−N(3) = 2.751(3)
Sm(2)−C(19) = 2.858(4)
Sm(2)−C(21) = 2.932(4)
Sm(1)−Sm(2) = 3.4300(4)
Sm(2)−C(22) = 2.845(4)
Sm(2)−Cl(1) = 2.8006(11)
Sm(2)−Cl(2) = 2.7638(12)
Li−Cl(1) = 2.370(10)

O(1)−Sm(1)−O(2) = 73.60(14)
O(1)−Sm(1)−N(1) = 92.01(12)
O(1)−Sm(1)−N(3) = 165.52(12)
N(2)−Sm(2)−Cl(2) = 166.78(7)
N(2)−Sm(2)−Cl(1) = 88.19(7)
Cl(1)−Sm(2)−Cl(2) = 78.63(3)

Compound **4**

Sm−O(1) = 2.634(4)
Sm−N(1) = 2.748(4)
Sm−C(1) = 3.022(4)
Sm−C(4) = 2.931(5)
Sm−N(1b) = 2.865(4)
Sm−Sm(a) = 3.442(1)

N(1a)−Sm−N(1b) = 107.47(17)
N(1a)−Sm−O(1) = 89.37(15)
N(1a)−Sm−O(1c) = 162.67(16)

Compound **5**

Sm−O(1) = 2.595(8)
Sm−N(1) = 2.691(6)
Sm−C(1) = 2.779(7)
Sm−C(2) = 2.924(8)
Sm−C(3) = 2.923(8)
Sm−C(4) = 2.789(7)
Sm−N(2) = 2.448(6)
Sm−H(1) = 2.417(9)
H(1)−Li(1) = 1.68(2)
H(1)..Li(2) = 2.54(2)
Li(1)−O(2) = 1.755(19)
O(2)−C(21) = 1.453(15)
C(21)−C(22) = 1.377(19)

O(1)−Sm−N(2) = 107.45(15)
N(2)−Sm−N(2a) = 145.1(3)
Sm−H(1)−Li(1) = 106.4(2)
N(1)−Li(1)−O(2) = 160.6(10)
O(2)−C(21)−C(22) = 109.8(13)

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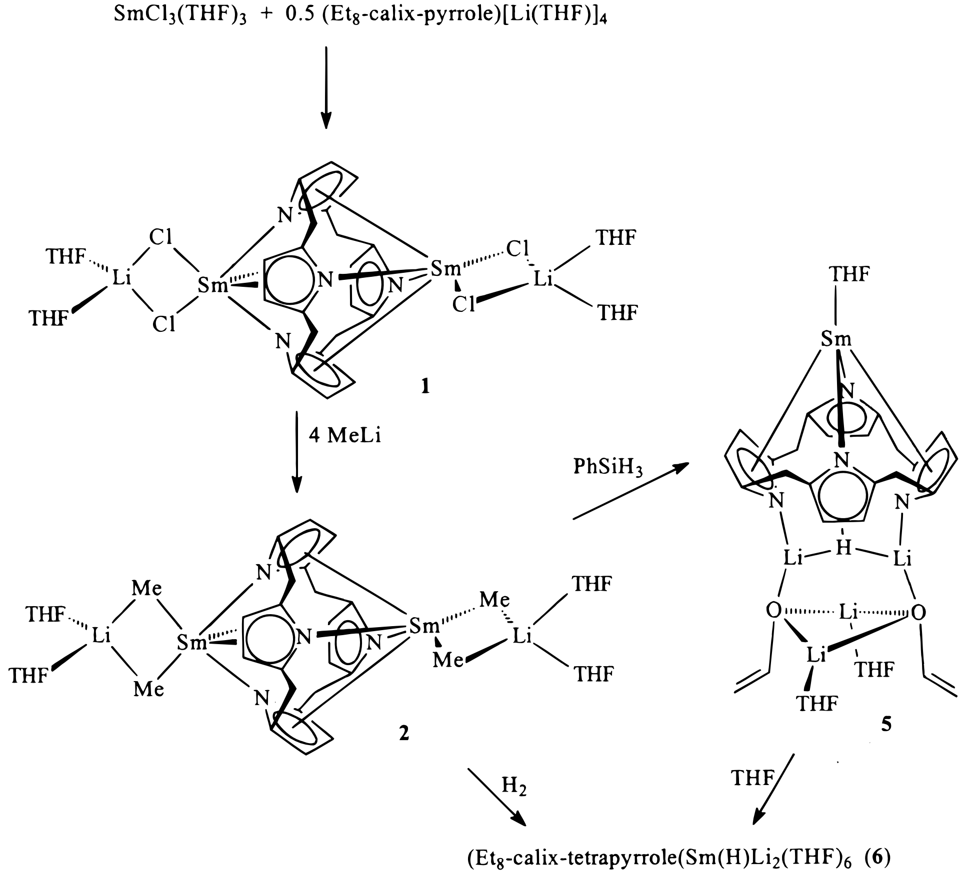
Scheme 1



orange blocks of the paramagnetic (Et$_8$-calix-tetrapyrrole)Sm$_2${(μ-Cl)$_2$[Li(THF)$_2$]}$_2$ (**1**) were isolated in good yield upon crystallization from THF (Scheme 1). Combustion analysis data were in agreement with the formulation, as elucidated by an X-ray crystal structure (Figure 1). Solution NMR spectra were well-resolved. Consistent with the high symmetry of the molecule, only one resonance was present in both the ^{1}H and ^{13}C NMR spectrum for the pyrrolyl CH groups. Conversely, the ethyl groups produced two well-separated resonances for the two geminal CH$_2$ hydrogens as two reasonably well-resolved pseudo-sextuplets centered at 6.26 and 3.34 ppm and coupled to the same resonance at 25.62 ppm of the ^{13}C NMR spectrum. The strong magnetic anisotropy of the two geminal CH$_2$ hydrogens is surprising, yet it is a rather common feature among trivalent samarium complexes of this particular ligand system.[26] The CH$_3$ parts of the ethyl groups gave only one poorly solved pseudo-triplet centered at 1.79 ppm.

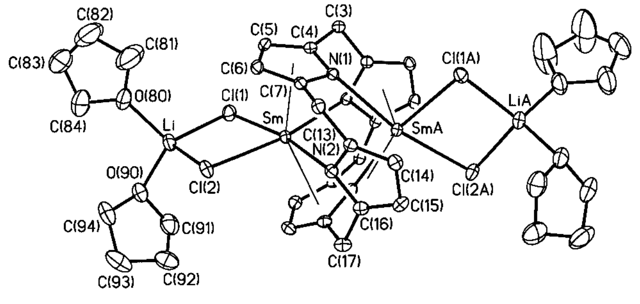


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg). Ethyl groups attached to the ring have been omitted for clarity reasons.

A simple metathetic reaction of **1** with MeLi in ether afforded yellow crystals of (Et$_8$-calix-tetrapyrrole)Sm$_2$-{(μ-CH$_3$)$_2$[Li(THF)$_2$]}$_2$ (**2**) in good yield (Scheme 1). The complex is basically isostructural with the starting **1**, with the crystal structure (Figure 2) showing the same solid-state features and arrangement of the ligand around the two metal centers. Also similar to **1**, the ^{1}H NMR spectrum showed only one signal for the pyrrole ring C−H groups and two well-separated resonances for the geminal hydrogens of the CH$_2$ groups. Only one resonance was observed for the methyl groups of the

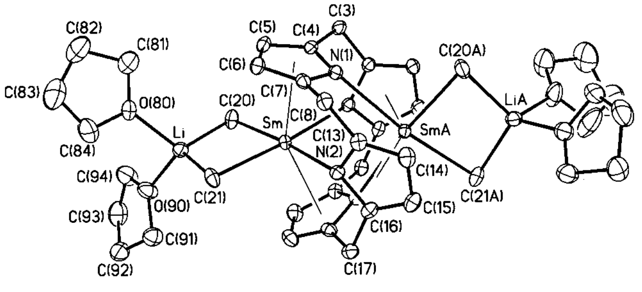


Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg). Ethyl groups attached to the ring have been omitted for clarity reasons.

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[26] Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **1998**, *38*, 1432.

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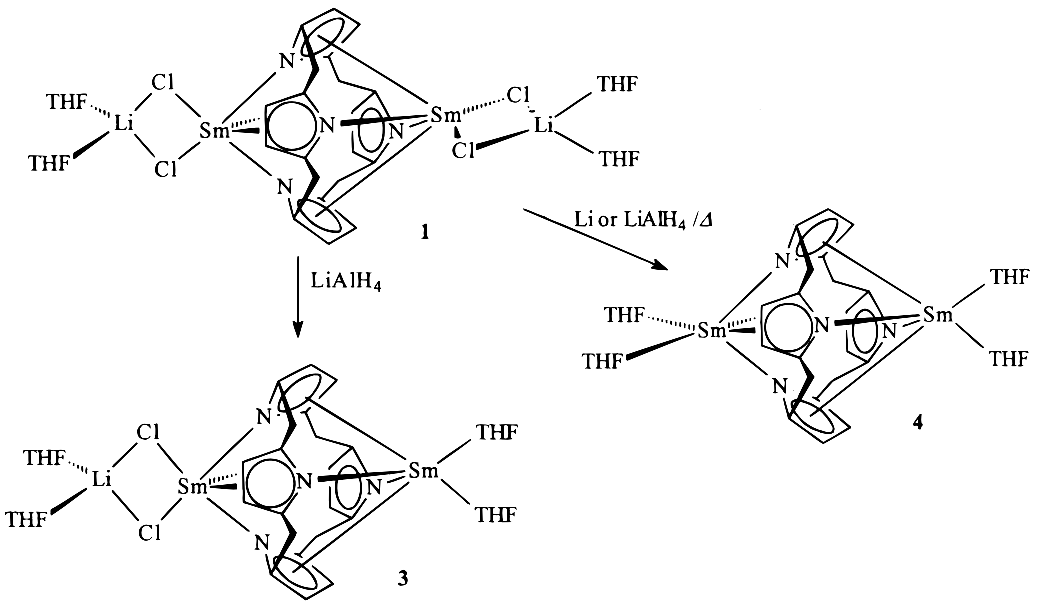
Scheme 2



ethyl substituents. The four methyl groups bridging the two samarium atoms to the two lithium atoms form a singlet at 2.11 ppm. Solutions of **2** were indefinitely stable in ether, while they slowly turned brown at room temperature in THF.

Attempts to form dinuclear samarium hydroaluminate compounds of similar structure were carried out by reacting complex **1** with LiAlH$_4$, affording instead two different compounds depending on the reaction conditions and with both arising from reduction of the metal center. Room-temperature reaction resulted in the formation of a deep red solution accompanied by significant effervescence. Deep red crystals of the mixed-valence (Et$_8$-calix-tetrapyrrole)Sm$_2$(THF)$_2$(μ-Cl)$_2$[Li-(THF)$_2$] (**3**) were obtained in good yield (Scheme 2). The molecular structure as elucidated by the X-ray crystal structure (Figure 3) revealed the same dinuclear arrangement as observed in **1** and **2** but with two non-equivalent samarium atoms. The first samarium is *formally* in its divalent state, since it is simply attached to two molecules of THF, while the second displays the same structural features of the starting **1**. Complex **3** is paramagnetic with the magnetic moment, as expected for the mixed-valence state, which is rarely observed in Sm chemistry.[27]

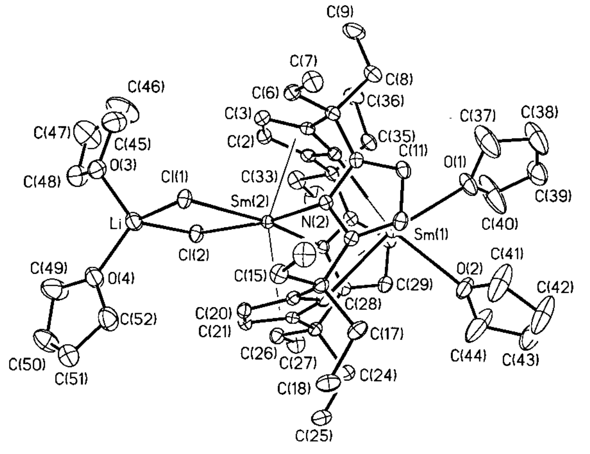


Figure 3. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg).

Conversely, reaction of excess LiAlH$_4$ with **1** in refluxing THF produced a brown solution from which the dinuclear and divalent (Et$_8$-calix-tetrapyrrole)Sm$_2$-(THF)$_4$·3THF (**4**) was obtained in acceptable yield and crystalline form (Scheme 2). The divalent oxidation state was clearly indicated by the solid-state crystal structure (Figure 4), which showed the same dinuclear structure of the complexes described above, except that each of the two samarium atoms is coordinated to two molecules of THF. The magnetic moment of **4** is surprisingly low and is even lower than in the mixed-valence **3**. This is probably a result of the remarkably short Sm−Sm distance (3.4417(9) Å), which perhaps is at the origin of some sort of intramolecular magnetic coupling. Solution NMR spectra displayed very broad signals and did not allow for reasonable spectral interpretation. Complex **4** was also conveniently prepared by direct reaction of SmI$_2$(THF)$_2$ with (Et$_8$-calix-tetrapyrrole)[Li(THF)]$_4$ or by reduction of **1** with metallic lithium under Ar.

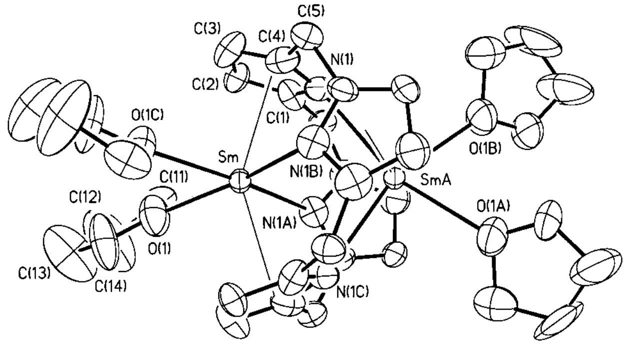


Figure 4. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg). Ethyl groups attached to the ring have been omitted for clarity reasons.

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(27) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292.

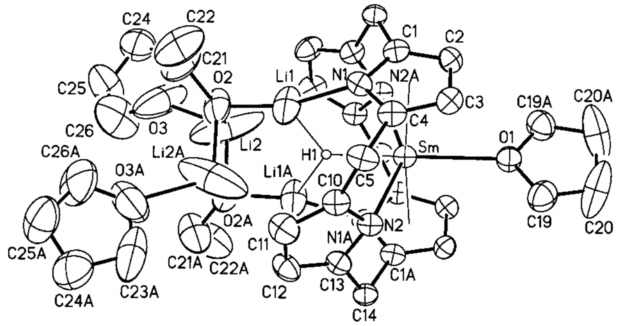

Figure 5. ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg). Ethyl groups attached to the ring have been omitted for clarity reasons.

The failure of this ligand system to support aluminohydride structures was rather surprising to us in the view that, in the chemistry of trivalent Sm supported by cyclopentadienyl ligands, aluminohydrides are readily prepared from reaction of $LiAlH_4$ with the corresponding halides to form dimeric[28] and polymetallic[29] complexes. The reaction of arylsilanes with transition-metal alkyls or their hydrogenolysis are both well-established methods for the preparation of hydride derivatives. Thus, further attempts to prepare hydride complexes were carried out by attempting reaction of **2** with either $PhSiH_3$ or H_2. Reaction of the dinuclear alkyl derivative **2** with $PhSiH_3$ was carried out at room temperature in THF and resulted in an immediate color change to pale yellow and then to pale orange-yellow over the course of 1 h. Subsequent workup resulted in the isolation of a crystalline mass composed by two different compounds. The minor component (less than 10%) was of sufficient quality to undertake a crystal structure determination. Formulation as the mononuclear hydride derivative $(Et_8\text{-calix-tetrapyrrole})(THF)Sm(\mu\text{-}H)[\mu\text{-}OCH{=}CH_2]_2Li_4(THF)_2$ (**5**) was provided by the X-ray crystal structure (Figure 5). Besides the presence of hydride encapsulated between the samarium and two lithium atoms, complex **5** possesses two $Li(OCH{=}CH_2)$ functions which are retained at the periphery of the molecule. Cleavage of THF is likely to be at the origin of their formation[30] and is perhaps the result of the attack on THF by two molecules of MeLi released by the samarium centers during the reaction. It should be reiterated, however, that the reaction requires a major molecular reorganization, since one samarium atom has been removed from the molecular frame, whose fate remains so far unclear. The second component was $(Et_8\text{-calix-tetrapyrrole})Sm(H)Li_2(THF)_6$ (**6**), clearly derived from **5** upon dissociation of two $Li(OCH{=}CH_2)$ units and probably possessing a very similar structure. Attempts to further spectroscopically characterize **5** were prevented by the ease of dissociation of the enolate groups in THF and poor solubility in hydrocarbon solvents. Upon dissolving a small amount of single crystals of **5** in THF followed by cooling at −30 °C, only complex **6** was obtained. Accordingly, attempts to record NMR spectra or **5** in THF-d_8 gave a small amount of insoluble material and spectra identical with those of **6**. Reaction of **2** at room temperature and under 1 atm of H_2 also led to the exclusive formation of the hydride derivative **6** and no sign for the presence of **5** or of enolate moieties. The formulation of **6** is based on degradation experiments, analytical and spectroscopic data. The complex reacts vigorously with protic solvents to liberate H_2 gas. Reaction of an analytically pure sample carried out with a Toepler pump and 4 equiv of anhydrous HCl afforded 76% of the expected amount of H_2, thus confirming the presence of the hydride function. Correlation experiments allowed a complete interpretation of the ^1H NMR spectrum. Difficulties were encountered only in locating the resonance of the hydride in the ^1H NMR spectrum.[31] The only difference between the ^1H NMR spectrum of **6** and that of the corresponding deuteride (prepared via deuteriolysis of **2**) consisted of the absence in the deuteride spectrum of a very broad resonance at 7.91 ppm. Since this resonance was coupled to none of the hydrogen or carbon resonances, it is tentatively assigned to the hydride. Unfortunately, further efforts to substantiate this proposal have been hampered by the fact that complex **6** does not exchange with D_2 gas (room temperature, 1 atm). We are currently attempting to improve the preparation of **6** from trivalent and mononuclear samarium complexes.

Conclusions

The calix-tetrapyrrole ligand is a versatile ligand system, effective in the stabilization of Sm(II), Sm alkyl, Sm chloride, and Sm(II)/Sm(III) dinuclear species. These dinuclear compounds may be synthesized cleanly, in good yield. Attempts to synthesize a Sm calix-pyrrole hydroaluminate complex were unsuccessfull, since **1** undergoes either complete or partial reduction in the presence of $LiAlH_4$ to produce a Sm(II) complex or a mixed-valence Sm(II)/Sm(III) complex, depending upon the reaction conditions. The ability of the dinuclear **1** to undergo either one- or two-electron reduction suggests that these compounds may perhaps have some potential in terms of catalytic applications. Reaction of the dinuclear methyl complex **2** with $PhSiH_3$ results in formation of a monomeric hydride, rather than a dinuclear species. Accompanying the rearrangement was generation of enolate fragments, presumably originating from THF cleavage.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC).

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] (a) Knjazhanski, S. Y.; Bulychev, B. M.; Belskii, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1987**, *327*, 173. (b) Gun'ko, Y. K.; Bulychev, B. M.; Sizov, A. I.; Bel'sky, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1990**, *390*, 153. (c) Belsky, V. K.; Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, *419*, 299.

[29] Belsky, V. K.; Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, *420*, 43.

[30] See for example: (a) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2641. (b) Aspinall, H. C.; Tillotson, M. R. *Inorg. Chem.* **1996**, *35*, 2163. (c) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291. (d) Jubb, J.; Gambarotta, S. *Inorg. Chem.* **1994**, *33*, 2503. (e) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1993**, *115*, 10410. (f) Dube, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3967.

[31] Similar difficulties have been encountered in the case of $(Cp^*_2SmH)_2$.[9a]

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