Articles

Samarium Hydride, Methyl, and Vinyl Complexes Supported by Calix-tetrapyrrole Ring Macrocycle. Thermal Decomposition to Samarium(II)

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Received September 27, 1999

Trivalent methyl and vinyl samarium derivatives supported by the calix-tetrapyrrole ligand system (Et_8-calix-pyrrole)(R)Sm(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$] [R = Me (**2a**), CH=CH_2 (**2b**)] were prepared via reaction of (Et_8-calix-pyrrole)(Cl)Sm[Li_2(THF)$_3$] (**1**) with the corresponding organolithium reagent. Complex **2a** reacts readily with H_2 at room temperature and atmospheric pressure to afford the corresponding samarium hydride (Et_8-calix-pyrrole)(THF)-Sm[Li(THF)]$_2$(μ^3-H) (**3**). Complexes **2a** and **3** are thermally robust. Conversely, the vinyl derivative **2b** rapidly and spontaneously decomposes at room temperature to afford the Sm^{II} derivative (Et_8-calix-pyrrole)(THF)Sm[Li(THF)]$_2$[Li(THF)$_2$](μ^3-Cl) (**4a**).

Introduction

The very high reactivity of hydride complexes of the lanthanides is responsible for a number of attractive transformations,[1] and as a result of the growing interest in the reactivity of these species, synthetic efforts have multiplied. Today, examples of dinuclear hydride-bridged complexes,[2] hydroaluminates,[3] and borohydrides[4] are abundant in the literature. Only lanthanide complexes containing terminally bonded hydrides remain rare[5] probably due to a particularly enhanced reactivity which can be expected for these species.

The employment of the calix-tetrapyrrole ligand system in lanthanide chemistry[6,7] provides an interesting alternative to the traditional cyclopentadienyl derivatives. For example, this family of macrocylic polyanions has allowed for both reversible fixation[8] and reduction[6,7] of dinitrogen and has provided a unique case in lanthanide chemistry of ethylene reversible fixation.[9]

Given the rarity of samarium hydrides,[2b,e,f,j,10] which to the best of our knowledge have been isolated exclusively with Cp-based ligands, we have now probed the possibility of taking advantage of the unique features of the calix-tetrapyrrole ligand system to stabilize novel

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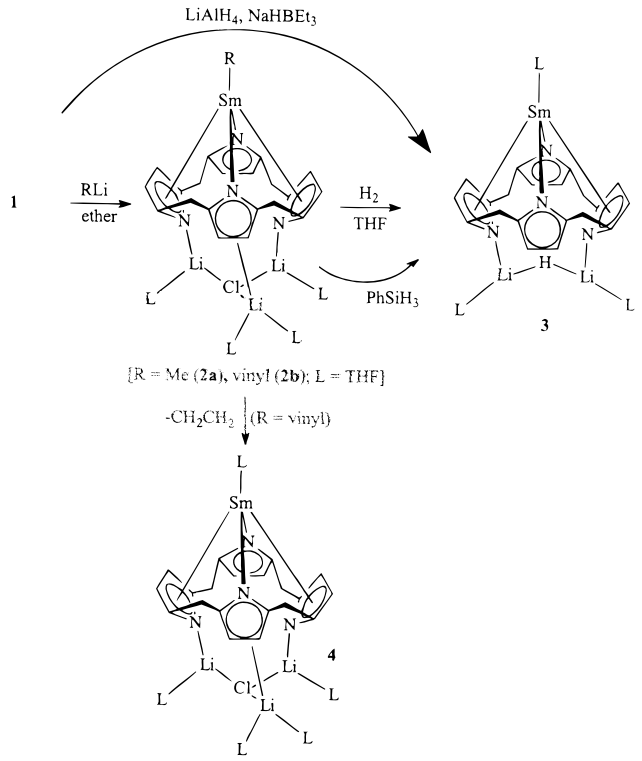
10.1021/om9907573 CCC: $19.00
Publication on Web 12/17/1999

Scheme 1



Sm hydride and alkyl derivatives. In this first paper, we wish to describe the preparation and characterization of novel calix-tetrapyrrole samarium hydride, methyl, and vinyl complexes and the spontaneous decomposition of the vinyl derivative to a Sm(II) complex.

Results and Discussion

The trivalent (Et_8-calix-pyrrole)(Cl)Sm[$Li_2(THF)_3$] (**1**) was the precursor for the preparations described in this work. Its preparation was obtained via simple methathetic reaction of $SmCl_3(THF)_3$ with 1 equiv of the tetralithium derivative of the calixtetrapyrrole anion. The complex can be either easily isolated or more conveniently prepared and used in situ. This species displays fluxional behavior at room temperature and, different from the other compounds reported in this work, produced uninformative NMR spectra. Further reaction of **1** with equivalent amounts of RLi [R = Me, vinyl] (Scheme 1) afforded the corresponding terminally bonded derivatives (Et_8-calix-pyrrole)(R)Sm(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$] [R = Me (**2a**), vinyl (**2b**)], which have been isolated in crystalline form.

The X-ray crystal structures of both complexes showed two nearly isostructural species. In both structures, the samarium atom is placed in the center of the macrocyle and is bonded to the four pyrrole rings by adopting both the π- and σ-bonding modes. The two centroids of the two nearly parallel π-bonded rings define, together with the two nitrogen atoms of the two σ-bonded rings and the terminally bonded methyl (or vinyl) group, an almost regular trigonal bipyramidal coordination geometry (Figures 1 and 2). On the side of the molecule opposite that of the terminally bonded alkyl, three lithium atoms bridged by one chlorine are connected to the pyrrole rings of the macrocyle. Two are σ-bonded to the N atom, while the third is π-bonded to one of the four pyrrole rings. A total of four molecules of coordinated THF complete the coordination geometry around the three lithium atoms.

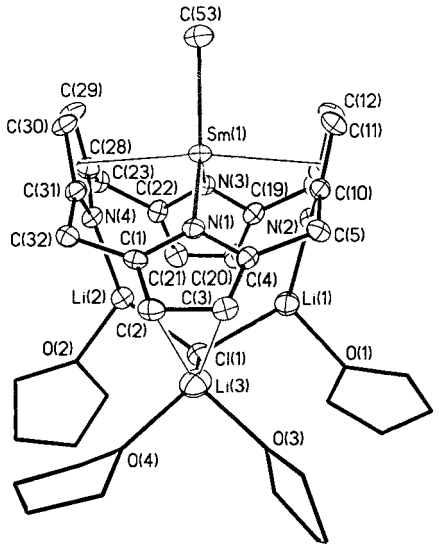


Figure 1. ORTEP drawing of **2a**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg). Ethyl groups attached to the ring have been omitted for clarity reasons.

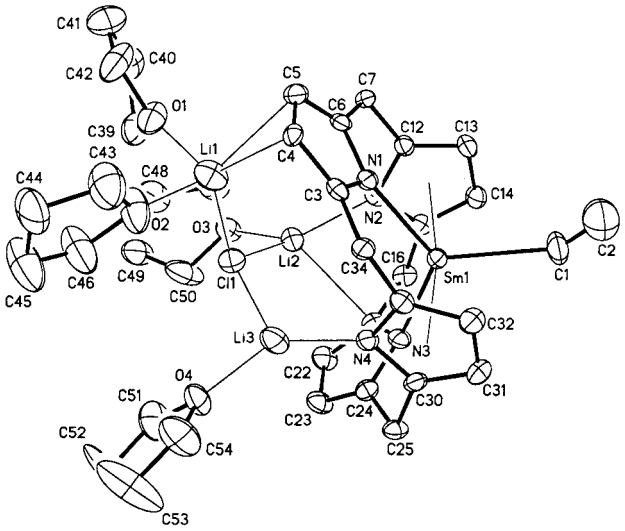


Figure 2. ORTEP drawing of **2b**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg). Ethyl groups attached to the ring have been omitted for clarity reasons.

Exposure of a THF solution of **2a** to hydrogen gas at room temperature and 1 atm gave a rapid reaction from which the new hydride derivative (Et_8-calix-pyrrole)(THF)Sm(μ-H)[Li(THF)]$_2$·3THF (**3**) was isolated in good yield and analytically pure form as pale yellow crystalline material. Complex **3** was also conveniently prepared via direct reaction of **1** with either $LiAlH_4$ or $NaHBEt_3$ or via reaction of **2** with $PhSiH_3$.

The molecular connectivity of **3** was elucidated by a crystal structure. The complex is formed by a samarium atom surrounded by the macrocycle (Figure 3). Similar to complexes **2**, two of the four pyrrole rings are π-bonded to the metal, while the other two are coplanar with samarium and with which they form σ-bonds through the two nitrogen atoms. Each of the pyrrole

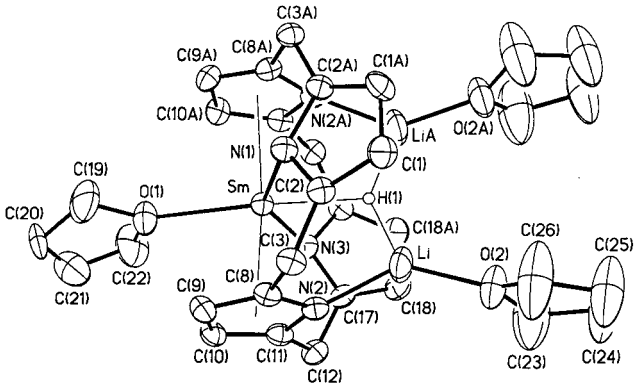


Figure 3. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg). Ethyl groups attached to the ring have been omitted for clarity reasons.

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 one molecule of THF. The two N−Li−O vectors are significantly bent, and as a result, the two lithium atoms are oriented toward each other. 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. One hydride, whose position was located and satisfactorily refined, was found in the middle of the $SmLi_2$ triangle and placed coaxial to the $Sm-O_{THF}$ vector. The Sm−H distance [2.25(7) Å] is rather long in comparison with that of the few cyclopentadienyl samarium hydride derivatives reported in the literature (2.05 Å)[2,f,j] and in the range of those observed for other dinuclear and hydrido-bridged lanthanide derivatives (1.98−2.48 Å).[2i]

The ^{1}H NMR spectra of **2a**, **2b**, and **3** are characterized by the same strong magnetic anisotropy previously observed in other samarium complexes of the same ligand system.[8,9] The ^{13}C NMR resonances of the methyl and vinyl α-carbon atoms attached to Sm could not be located in the HQMC spectra, probably because of their vicinity to the paramagnetic center. In the ^{1}H NMR spectra, the Me group of **2a** displays a broad resonance at 8.15 ppm, while the vinyl protons of **2b** show two sets of vinyl signals each featuring one pseudo-triplet and two doublets. The presence of two independent vinyl groups in the spectrum of **2b**, which was necessarily recorded at −30 °C because of the high thermal instability, is likely the result of the presence of two independent conformations. However, attempts to determine the coalescence temperature failed due to the thermal instability. Similar to the case of $(Cp^*_2SmH)_2$,[11] difficulties were also encountered in locating the resonance of the hydride in the ^{1}H NMR spectrum. The only difference between the ^{1}H NMR spectrum of **3** and that of the corresponding deuteride consists of the absence in the deuteride spectrum of a very broad resonance at 7.91 ppm. Since this resonance was uncoupled to either hydrogen or carbon resonances, we tentatively assign it to the hydride. Unfortunately, further efforts to substantiate this proposal have been hampered by the fact that complex **3** does not exchange with D_2 gas (room temperature, 1 atm). Furthermore, the IR of **3** was identical to that of the corresponding deuteride, prepared via either reaction of **1** with $LiAlD_4$ or reaction of **2a** with D_2, and regrettably, no resonance could be assigned to the Sm−H stretching. However, degradation experiments of **3** 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.

The hydride **3** reacts rapidly with ethylene gas at room temperature and 1 atm to form the vinyl derivative **2b** in significant yield through an unusual C−H σ-bond metathetic reaction, which is unprecedented in the chemistry of lanthanide hydrides. The identity of the compound was established by comparison of the spectroscopic and crystallographic parameters. The reaction is accompanied by evolution of H_2, which was collected and identified with a Toepler pump−GC combined experiment. The isolation of **2b** from this unusual reaction was possible only when **3** was prepared in situ via either hydrogenolysis of **2a** or reaction of **1** with $LiAlH_4$, thus in the presence of LiCl as a reaction byproduct. Conversely, exposure of a solution prepared by redissolving analytically pure **3** in THF to ethylene afforded a new compound. The ^{1}H NMR spectrum clearly showed the presence of the characteristic resonances of the vinyl group. This, together with the enhanced thermal instability of this new compound, is in line with the proposal that a compound closely related to **2b** but without LiCl retained in the molecular structure is perhaps formed.

Compounds **2a** and **3** are thermally robust, and we found no signs of degradation upon allowing their THF solutions to stand for a few weeks at room temperature or for a few hours at 60 °C. Conversely, the vinyl-Sm derivative (Et_8-calix-pyrrole)(CH=CH_2)Sm (μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$] (**2b**) (Scheme 1) decomposes rapidly at room temperature to yield a deep green divalent samarium compound, [Et_8-calix-pyrrole)(THF)Sm(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$] (**4a**), which was isolated as a dark green crystalline solid. The formation of **4a** is accompanied by the evolution of a substantial amount of ethylene that could be identified in NMR tube experiments despite the broad features arising from the paramagnetism of **4a**. Crystals of suitable quality could be grown only for the cyclohexyl homologue {[−$(CH_2)_5$−]$_4$-calix-pyrrole}(THF)Sm(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$] (**4b**), which was more conveniently prepared via reduction of the corresponding trivalent chloride derivative with Li under Ar. The structure of **4b** is very similar to **2**, the only difference arising from the replacement of the vinyl group with one molecule of THF (Figure 4). Consistent with the lower oxidation state of samarium, the bond distances are, on average, slightly longer than those observed in complexes **2**.

The transformation of **2b** to **4** with simultaneous formation of ethylene implies homolytic cleavage of the $Sm-C_{vinyl}$ bond. At first glance, the fact that complexes **4** did not give fixation of either ethylene or dinitrogen (both available to **4** during its formation) seems to be in contradiction with the reactivity of previously reported Sm(II) calix-tetrapyrrole complexes.[6,8] However, it should be reiterated that the extent of fixation of these substrates by these complexes (dinitrogen reduction[6]

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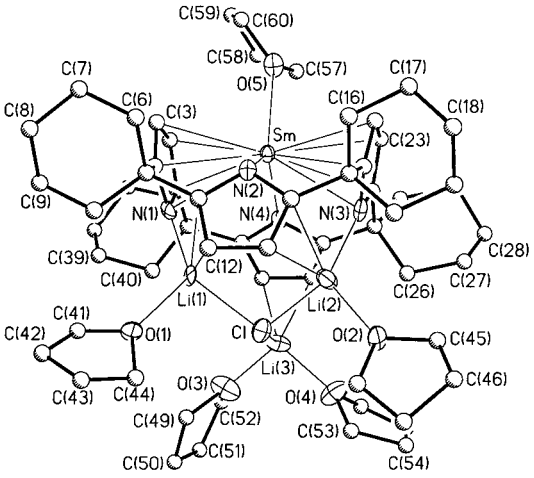

Figure 4. ORTEP drawing of **4b**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms (Å) and angles in degrees (deg).

versus dinitrogen reversible fixation[8]) is determined by the nature of the anion attached to the three lithium atoms (enolate versus chloride).[8,9] In addition, the substituents attached to the macrocyclic rings are also capable of determining the extent of ethylene and dinitrogen fixation.[8,9] Finally, the solvent (ether versus THF) also plays a critical role with this respect. This enhanced sensitivity of the reactivity of the metal center to minor ligand modifications and to the nature of groups not directly attached to the Sm center is surprising. This behavior provides insight into rationalizing and fine-tuning the reactivity of divalent samarium (notoriously uncontrollable) and remains the target of our continuing studies.

Experimental Part

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schenk-type glassware in combination with a nitrogen-vacuum line. $SmCl_3(THF)_3$,[12] Et_8-calix-tetrapyrrole, and Cy_4-calix-tetrapyrrole were prepared according to literature procedures.[6−9] C_6D_6 and THF-d_8 were dried over Na/K alloy, vacuum-transferred into ampules, and stored under nitrogen prior to use. NMR spectra were recorded on a 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 FTIR instrument from Nujol mulls or KBr pellets 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,[13] and corrections for underlying diamagnetism were applied to the data.[14] Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer.

Preparation of (Et_8-calix-pyrrole)(Cl)Sm[$Li_2(THF)_3$] (1). $SmCl_3(THF)_3$ (2.1 g, 4.4 mmol) and (Et_8-calixtetrapyrrole)-$Li_4(THF)_4$ (3.8 g, 4.4 mmol) were combined in 100 mL of freshly distilled anhydrous THF to give a suspension, which was heated gently for 10 min. The resulting golden yellow solution was stirred for 2 h. The solvent was removed in vacuo, and the pale yellow solid residue was resuspended and decanted with 30 mL of diethyl ether. After repeating the operation two more times, the solid was dried at room temperature and in vacuo to yield **1** as a pale yellow powder (4.0 g, 3.7 mmol, 84%). IR (Nujol mull, cm^{-1}) ν: 3012(w), 3080(w), 2732(w), 2704(w), 1610(w), 1456(s), 1370(s), 1322(m), 1256(m), 1210(w), 1160(w), 1110(s), 1045(s), 967(w), 933(w), 880(s), 760(s), 732(s). Anal. Calcd (Found) for $C_{48}H_{78}N_4O_3SmLi_2Cl$: C 60.12 (61.24), H 8.20 (8.06), N 5.84 (6.00). $\mu_{eff} = 1.61\ \mu_B$.

Preparation of (Et_8-calix-pyrrole)(Me)Sm(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$].[2a] A solution of MeLi (1.4 mL, 1.9 mmol) was added dropwise to a stirred suspension of **1** (2.0 g, 1.9 mmol) in diethyl ether (100 mL). The solution immediately became bright orange, and stirring was continued for 30 min. The solution was filtered to remove LiCl, concentrated to 50 mL, and allowed to stand overnight at −30 °C. Yellow-orange crystals of **2a** separated (1.5 g, 77%). Treatment of a toluene solution of **2a** (0.150 g) with 5 equiv of gaseous HCl afforded 85% of the equivalent amount of methane. Anal. Calcd (Found) for $C_{53}H_{83}N_4O_4SmLi_3Cl$: C 60.80 (60.43), H 7.99 (8.07), N 5.35 (4.99). IR (Nujol mull, cm^{-1}) ν: 3071(w), 2752(w), 2724(w), 1622(m), 1584(m), 1376(s), 1323(m), 1260(m), 1188(s), 1135(w), 1046(s), 970(m), 924(m), 889(s), 835(w), 871(s), 751(s), 687(w). ^{1}H NMR (benzene-d_6, 500 MHz, 23 °C) δ: 8.15 (m, 3H, Me), 6.33 (s, 2H, CH pyrr), 6.28 (s, 2H, CH pyrr), 5.86 (s, 2H, CH pyrr), 5.83 (s, 2H, CH pyrr), 4.20 (d, 1H, CH_2 ethyl), 3.96 (d, 1H, CH_2 ethyl), 3.65 (m, 16H, THF), 3.26 (q, 4H, CH_2, ether), 2.19 (q, 2H, CH_2 ethyl), 1.99 (m, 4H, CH_2 ethyl), 1.85 (m, 4H, CH_2 ethyl), 1.62 (s, 3H, CH_3 ethyl), 1.48 (m, 1H, CH_2 ethyl), 1.19 (m, 1H, CH_2 ethyl), 1.45 (m, 16H, THF), 1.11 (t, 3H, CH_3 ether), 0.99 (m, 2H, CH_2 ethyl), 0.92 (t, 3H, CH_3 ethyl), 0.53 (t, 3H, CH_3 ethyl), 0.51 (t, 12H, CH_3 ethyl) 0.41 (t, 3H, CH_3 ethyl). ^{13}C NMR (benzene-d_6, 125.72 MHz, 23 °C) δ: 107.00, 103.47, 99.73, 99.86 (CH pyrr), 87.19, 30.61, 30.48, 30.20, 25.51 (CH_2 ethyl), 105.99, 8.39, 8.31, 9.02, 8.73 (CH_3 ethyl), 65.84, 8.88 (ether), 68.17, 25.60 (THF), 9.81 (Me), 46.8 (quaternary C ring), 154.26, 153.78, 142.71, 141.63 (quaternary C pyrr). $\mu_{eff} = 1.67\ \mu_B$.

Preparation of (Et_8-calix-pyrrole)(vinyl)Sm(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$].[2b] A suspension of **1** (1.6 g, 1.54 mmol) in diethyl ether (100 mL) was treated with a freshly prepared solution of CH_2CHLi in diethyl ether (0.5 mL, 3.2 M, 1.55 mmol). The color immediately changed to bright yellow. After stirring for 10 min the solution was filtered to remove a small amount of LiCl and concentrated to 50 mL. Prolonged stirring at room temperature resulted in darkening of the solution to green with lower yields of **2b**. Upon standing at −30 °C for 2 days, the solution separated, forming light yellow crystals of **2b** (0.89 g, 0.840 mmol, 55%). Anal. (Calcd) for $C_{54}H_{83}Li_3N_4O_4SmCl$: C 61.33 (61.25), H 7.87 (7.90), N 5.05 (5.29). IR (Nujol mull, cm^{-1}) ν: 3081(w), 2725(w), 1650(w), 1575(w), 1457(s), 1377(s), 1324(m), 1259(m), 1025(w), 1043(s), 970(w), 924(m), 890(s), 855(m), 792(s), 784(s), 670(w). ^{1}H NMR (THF-d_8, 500 MHz, −20 °C) δ: This thermally unstable complex is fluxional at low temperature and shows two distinct series of resonances for the vinyl groups: 8.10, 7.90 (two pseudo t, 1H, CH_{vinyl}), 5.62, 5.52, 5.49, 5.47 (four broad s, 8H, CH_{pyrr}), 3.56 (partly overlapping broad s, 16H, THF), 3.32 (q, 4H, ether), 3.01, 2.15, 2.67, 1.99 (two doublets, 1H, CH_{2vinyl}), 2.61, 2.42, 1.81, 1.70 (four broad s, 16H, CH_{2Et}), 1.73 (broad s, 16H, THF), 1.06 (t, 6H, ether), 0.93, 0.22 (two broad s, 24H, CH_{3Et}). ^{13}C NMR (THF-d_8, 125.72 MHz, −20 °C) δ: 155.92, 154.74, 141.74 (ring and pyrr quaternary C), 123.71, 122.98 (CH_{2vinyl}), 101.20, 100.93, 99.05, 97.74 (CH_{pyrr}), 66.48, 15.81 (ether), 68.23, 26.37 (ether), 10.33, 10.15, 9.21, 9.14 (CH_{3ethyl}), 32.27, 32.03, 27.64, 27.60 (CH_{2ethyl}), $\mu_{eff} = 1.51\ \mu_B$.

Preparation of (Et_8-calix-pyrrole)(THF)Sm(μ-H)[Li(THF)]$_2$·3THF.[3] Method A. An orange solution of **2** (1.7 g, 1.9 mmol) in THF (75 mL) was stirred at room temperature

(12) Anhydrous $SmCl_3$ was prepared following a standard procedure: (a) Freeman, J. H.; Smith, M. L. *J. Inorg. Nucl. Chem.* **1958**, *7*, 224, and was transformed into the corresponding tetrahydrofuranate. (b) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(13) Mabbs, M. B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

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Table 1. Crystal Data and Structure Analysis Results

	2a	2b	3	4b
formula	$C_{53}H_{83}Li_3N_4O_4SmCl$	$C_{54}H_{83}Li_3N_4O_4SmCl$	$C_{60}H_{97}Li_2N_4O_6Sm$	$SmLi_3ClC_{60}H_{88}N_4O_5$
fw	1046.95	1058.86	1134.65	1151.96
space group	$P\bar{1}$	$P\bar{1}$	*Pnma*	$P2(1)/n$
a (Å)	12.771(8)	12.6505(12)	22.7546(9)	11.617(2)
b (Å)	21.395(9)	21.515(2)	13.8541(7)	26.453(3)
c (Å)	22.818(9)	22.788(2)	18.9224(9)	18.812(2)
α (deg)	112.85(4)	112.769(2)	90	90
β (deg)	100.51(5)	99.908(2)	90	95.390(3)
γ (deg)	91.85(5)	91.522(2)	90	90
V (Å^3)	5612(5)	5604.0(9)	5965.2(5)	5756(1)
Z	4	4	4	4
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073
T (°C)	−70	−70	−70	−70
D_{calcd} (g cm^{-3})	1.253	1.255	1.263	1.329
μ_{calcd} (cm^{-1})	1.140	1.141	1.035	1.117
R,[a] wR2, GoF	0.0503, 0.0981, 1.076	0.0510, 0.1471, 1.008	0.0533, 0.1408, 1.091	0.0641, 0.1340, 1.060

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. $R_w = [(\sum(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

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

2a	2b	3	4b
Sm−C(53) = 2.496(6)	Sm(1)−C(1) = 2.468(10)	Sm−N(1) = 2.436(5)	Sm−N(1) = 2.898(9)
Sm(1)−N(1) = 2.465(5)	C(1)−C(2) = 1.209(16)	Sm−N(2) = 2.682(4)	Sm−N(2) = 2.567(9)
Sm(1)−N(2) = 2.716(5)	Sm(1)−N(1) = 2.491(7)	Sm−C(8) = 2.785(5)	Sm−N(3) = 2.851(8)
Sm(1)−C(10) = 2.800(6)	Sm(1)−N(2) = 2.698(7)	Sm−C(9) = 2.934(5)	Sm−N(4) = 2.541(9)
Sm(1)−C(11) = 2.970(7)	Sm(1)−C(12) = 2.803(8)	Sm−C(10) = 2.926(5)	Sm(1)−C(1) = 2.886(11)
Sm(1)−C(12) = 2.966(7)	Sm(1)−C(13) = 2.935(9)	Sm−C(11) = 2.799(5)	Sm(1)−C(2) = 2.930(11)
Sm(1)−C(13) = 2.821(6)	Sm(1)−C(15) = 2.801(9)	Sm−O(1) = 2.559(6)	Sm(1)−C(3) = 2.936(10)
Li(1)−N(2) = 1.977(12)	Li(2)−N(2) = 2.020(16)	Sm−H(1) = 2.25(7)	Sm(1)−C(4) = 2.929(11)
Li(3)−N(1) = 3.136(14)	Li(3)−N(4) = 1.999(18)	Li−N(2) = 1.950(13)	Sm−O(5) = 2.612(8)
Li(3)−C(1) = 2.870(14)	Li(1)−C(4) = 2.381(14)	Li−H(1) = 1.68(3)	Cl−Li(1) = 2.306(19)
Li(3)−C(2) = 2.394(13)	Li(1)−C(5) = 2.375(18)	N(2)−Li−O(2) = 135.1(7)	Cl−Li(2) = 2.27(2)
Li(3)−C(3) = 2.379(14)	Li(1)−N(1) = 3.105(18)	Sm−H(1)−Li = 110.7(7)	Cl−Li(3) = 2.33(2)
Li(3)−C(4) = 2.851(14)	Li(1)−Cl(1) = 2.287(17)	Li−H(1)−Li(a) = 138.6(7)	N(2)−Sm−N(4) = 126.6(3)
Li(1)−O(1) = 1.989(12)	Li(2)−Cl(1) = 2.270(16)	O(1)−Sm−H(1) = 171.8(15)	N(2)−Sm−O(5) = 126.2(3)
Li(1)−Cl(1) = 2.228(12)	Li(3)−Cl(1) = 2.166(17)		N(4)−Sm−O(5) = 107.2(3)
Li(2)−Cl(1) = 2.270(10)	Sm(1)−C(1)−C(2) = 137.6(16)		

under 1 atm of H_2 for 1 h, during which time the color lightened to pale yellow. The clear solution was concentrated to 30 mL. After standing at −30 °C for 24 h large, pale yellow crystals of **3** separated (1.2 g, 1.0 mmol, 53%). 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). ^{1}H NMR (THF-d_8, 500 MHz, 23 °C) *δ*: 6.12 (s, pyrr, 4H), 5.72 (s, pyrr, 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 pyrr), 140.00 (quaternary C pyrr), 97.87 (C−H pyrr), 95.73 (C−H pyrr), 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 **1** (1.5 g, 1.4 mmol) in 75 mL of THF was treated with $LiAlH_4$ (0.05 g, 1.4 mmol). The color immediately changed from golden yellow to light greenish yellow. The mixture was stirred for 2 h at room temperature. After filtration, the solution was concentrated to 30 mL and was kept at −30 °C for 24 h for to yield pale yellow crystals of **3** (yield 66%).

Method C. A solution of $NaHB(C_2H_5)_3$ (1.4 mL, 1.0 M) in toluene was added to a solution of **1** (1.5 g, 1.4 mmol) in 75 mL of THF. The color immediately lightened. After stirring for 1 h the pale light yellow solution was concentrated to 25 mL. After standing for 24 h at −30 °C crystals of **3** separated (yield 49%).

Preparation of [Et$_8$-calix-pyrrole)(THF)Sm(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$].[4a] A light yellow solution of **2b** (1.5 g, 1.4 mmol) in diethyl ether (150 mL) was stirred at room temperature for 2 days. The solvent of the resulting dark green solution was removed in vacuo and the solid residue redissolved in hexane (50 mL). A small amount of insoluble material was eliminated by filtration and the filtrate concentrated to small volume (25 mL). Dark green microcrystalline **4a** (0.5 g, 0.5 mmol, 35%) separated upon allowing the resulting solution to stand at −20 °C for 2 days. Anal. Calcd (Found) for $SmLi_3ClC_{56}H_{88}N_4O_5$: C 60.92 (60.73), H 8.03 (8.02), N 5.07 (5.05). IR (Nujol mull, cm^{-1}) *ν*: 3076(w), 2729(w), 1606(m), 1456(vs), 1377(vs), 1325(w), 1308(w), 1259(s), 1211(w), 1091(m), 1043(s), 1024(s), 976(m), 926(m), 889(m), 796(m), 752(s). $\mu_{eff} = 3.55\ \mu_B$.

Preparation of {[−(CH$_2$)$_5$−]$_4$-calix-pyrrole}(THF)Sm-(μ^3-Cl)[Li(THF)]$_2$[Li(THF)$_2$].[4b] A suspension of $SmCl_3(THF)_3$ (3.5 g, 7.4 mmol) in freshly distilled anhydrous THF (150 mL) under Ar was treated with colorless {[−(CH$_2$)$_5$−]$_4$-calix-pyrrole}-Li_4 (4.3 g, 7.4 mmol). The resulting golden yellow suspension was heated gently for 10 min until complete dissolution of the solid was reached and then was allowed to stir at room temperature for 2 h. Metallic lithium (0.07 g, 10 mmol) was added to the reaction mixture. The color deepened from yellow to dark green over 30 min. After stirring for 18 h the solvent was removed in vacuo, and the resulting deep green solid residue was extracted with a few portions of diethyl ether (total 75 mL). Deep green crystals of **4b** (7.7 g, 5.5 mmol, 75%) separated upon concentration and allowing the extracts to stand at room temperature for 24 h. IR (Nujol mull, cm^{-1}) *ν*: 3090(w), 2730(w), 2662(w), 1550(w), 1355(m), 1315(w), 1286(s),

1270(s), 1256(s), 1191(s), 1140(m), 1074(s), 970(m), 845(m), 780(s). Anal. Calcd (Found) for $SmLi_3ClC_{60}H_{88}N_4O_5$: C 62.55 (62.93), H 7.70 (7.22), N 4.86 (4.75). $\mu_{eff} = 3.70\ \mu_B$.

Reaction of 3 with Ethylene. A THF solution of **3**, prepared according to the experimental procedures described above either by exposing a solution of **2a** to H_2 gas or by reacting **1** with $LiAlH_4$, was exposed to 1 atm of ethylene. Within a few minutes the color darkened to orange-brown. The solvent was rapidly removed in vacuo and the residue redissolved in diethyl ether (25 mL). The resulting solution was promptly placed in a freezer and allowed to stand 2 days at −36 °C, upon which crystals of **2b** (38%) separated.

Structural Considerations. Suitable crystals were mounted with cooled viscous oil on thin glass fibers. 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[15] were applied. No symmetry higher than triclinic was observed for **2a** and **2b**. The reflection data for **3** were consistent for *Pnma* and $Pn2_1a$ ($Pna2_1$). However, solutions in the centric space group options, for **2a**, **2b**, and **3**, yielded chemically reasonable and computationally stable results of refinement. The data for **4b** were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with subsequent Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2.

(15) Blessing, R. *Acta Crystallogr. A* **1995**, *51*, 33−38.

Two symmetry-unique compound molecules were located in the asymmetric units of **2a** and **2b**. The compound molecule **3** was located on a mirror plane. A molecule of coordinated THF and three half-molecules of cocrystallized, noncoordinated THF molecules were also located, disordered by the mirror plane symmetry.

The carbon atoms of **4b** and the atoms of the cocrystallized solvent molecules of **3** were refined isotropically to conserve a reasonable data/parameter ratio. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned with idealized geometry and constrained with an isotropic, riding model. Crystallographic details are presented in Table 1. Selected bond distances and angles are given in Table 2. Additional information is given as Supporting Information. All scattering factors are contained in the SHELXTL 5.03 program library (Sheldrick, 1994, WI).

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

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **2a**, **2b**, **3**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9907573