Reactivity of Calix-Tetrapyrrole Sm^{II} and Sm^{III} Complexes with Acetylene: Isolation of an "N-Confused" Calix-Tetrapyrrole Ring

Tiffany Dubé, Jingwen Guan, Sandro Gambarotta,* and Glenn P. A. Yap[a]

Abstract: The nature of the substituents present on the calix-tetrapyrrole tetraanion ligand $\{[R_2C(C_4H_2N)]_4\}^{4-}$ ($R = \{-(CH_2)_5-\}_{0.5}$, Et) determines the type of reactivity of the corresponding Sm^{II} compounds with acetylene. With $R = \{-(CH_2)_5-\}_{0.5}$, dehydrogenation occurred to yield the nearly colorless dinuclear diacetylide complex $[\{\{[-(CH_2)_5-]_4$-calix-tetrapyrrole$\}Sm^{III}\}_2(\mu\text{-}C_2Li_4)]\cdot$THF as the only detectable reaction product. Conversely, with R = Et, acetylene coupling in addition to dehydrogenation resulted in the formation of a dimeric butatrienediyl enolate derivative $[\{(Et_8$-calix-tetrapyrrole$)Sm^{III}\{Li[Li(thf)]_2(\mu_3\text{-}OCH{=}CH_2)\}\}_2(\mu,\eta^2,\eta'^2\text{-}HC{=}C{=}C{=}CH)]$. Reaction of the trivalent hydride $[(Et_8$-calix-tetrapyrrole$)(thf)Sm^{III}\{(\mu\text{-}H)[Li(thf)]\}]_2$ or of the terminally bonded methyl derivative $[(Et_8$-calix-tetrapyrrole$)(CH_3)Sm^{III}\{[Li(thf)]_2[Li(thf)_2](\mu_3\text{-}Cl)\}]$ with acetylene resulted in a mixture of the carbide $[\{(Et_8$-calix-tetrapyrrole$)Sm^{III}\}_2(\mu\text{-}C_2Li_4)]\cdot Et_2O$ with the dimerization product $[\{(Et_8$-calix-tetrapyrrole$)Sm^{III}\{Li[Li(thf)]_2(\mu_3\text{-}OCH{=}CH_2)\}\}_2(\mu,\eta^2,\eta'^2\text{-}HC{=}C{=}C{=}CH)]$. The same reaction also yielded a third product, a trivalent complex $[\{(Et_8$-calix-tetrapyrrole*$)Sm^{III}[Li(thf)_2]\}_2]$, in which the macrocycle was isomerized by shifting the ring attachment of one of the four pyrrole rings.

Keywords: alkyne ligands · coordination chemistry · macrocycles · samarium

Introduction

The coordination chemistry of divalent samarium supported by Cp-based ligand systems is characterized by a series of remarkable reactions[1] in which the electrons necessary for these transformations are typically provided by the cooperative attack of two or more divalent samarium centers on the same substrate.[1] It is thus surprising that, given the uniqueness of this chemistry and the potential provided by these systems, information about the reactivity of divalent complexes based on ligand systems other than Cp derivatives remains so scarce.

As part of our efforts to develop the chemistry of divalent samarium with alternative ligand systems, we have been investigating the behavior of divalent samarium complexes with polypyrrole anions. The results have so far been encouraging. Four novel dinitrogen complexes have been isolated and characterized by using di- and tetrapyrrole ligands.[2, 3] The calix-tetrapyrrole ligand in particular has proven to be rather versatile, since it has allowed the encapsulation of dinitrogen into a Sm_2Li_4 octahedral cage.[4] In addition, the sole example in lanthanide chemistry of reversible fixation of ethylene[5] has also been obtained with this ligand system.

A few years ago, Evans et al. described the preparation and characterization of $[\{(C_5Me_5)_2Sm(thf)\}]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2)]$ obtained upon reaction of samarocene with acetylene. This species contains a C_2 unit bridging the two samarium centers in an end-on fashion.[6] We were particularly attracted by this strange reaction since the C_2 moiety is isoelectronic with N_2, and thus it may provide an interesting and convenient model for studying the remarkable complexity of factors which promote the fixation and reduction of dinitrogen. One of the objectives was an assessment of the role of the lithium cations, invariably retained within the calix-tetrapyrrole frame, which, similar to the case of dinitrogen reduction,[3, 4] could perhaps play an important role in acetylene activation.

We describe in this paper the reactivity of both Sm^{II} and Sm^{III} calix-tetrapyrrole complexes with acetylene as well as a rare example of ring isomerization closely reminiscent of the so-called N-confused systems reported in a few cases in porphyrin chemistry.

Experimental Section

All reactions 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 them through a column of Al_2O_3 under an inert atmosphere prior to use, degassed in vacuo,

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and transferred and stored under inert atmosphere. [(Et$_8$-calix-tetrapyrrole)(CH$_3$)Sm^{III}{[Li(thf)]$_2$[Li(thf)$_2$](μ_3-Cl)}],[7] [(Et$_8$-calix-tetrapyrrole)(thf)-Sm^{III}{(μ-H)[Li(thf)]$_2$}]·3THF,[7] [{(Et$_8$-calix-tetrapyrrole)(Et$_2$O)}Sm^{II}{[Li-(thf)$_2$][Li(thf)]$_2$(μ_3-OCH=CH$_2$)}] (**1b**),[5] and [{[−(CH$_2$)$_5$−]$_4$-calix-tetrapyrrole}[Li(thf)]$_4$][3, 8] were prepared according to literature procedures. High-purity acetylene (Matheson) was used as received. [D$_8$]THF was dried over Na/K alloy, vacuum-transferred into ampoules, 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 prepared inside the drybox. Magnetic susceptibility measurements were carried out at room temperature with a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods[9a] and corrections for underlying diamagnetism were applied to the data.[9b] Elemental analyses were carried out using a Perkin–Elmer Series II CHN/O 2400 analyzer.

[{[−(CH$_2$)$_5$−]$_4$-Calix-tetrapyrrole}(thf)Sm^{II}{Li$_2$[(Li(thf)](μ_3-OCH=CH$_2$)}] (1a): A suspension of [SmCl$_3$(thf)$_3$] (10.3 g, 21.8 mmol) in THF (150 mL) at −78 °C and under Ar was treated with equivalent amount of [{[−(CH$_2$)$_5$−]$_4$-calix-tetrapyrrole}[Li(thf)]$_4$] (19.5 g, 21.8 mmol). The mixture was warmed to room temperature and stirred overnight. A slight excess of finely subdivided Li foil (0.2 g, 22 mmol) was added to the resulting clear solution and stirring was continued under Ar for 36 h. The resulting dark green suspension was evaporated to dryness. The solid residue was gently heated in vacuo for one hour. The dark green residue was washed with two portions of ether and then re-dissolved in toluene (100 mL). The solution was filtered to eliminate small amount of insoluble light colored residue, concentrated to small volume and allowed to stand at room temperature for 2 d. Dark red crystals of **1a** (8.5 g, 9.5 mmol, 43 %) were obtained. Elemental analysis calcd (%) for C$_{50}$H$_{67}$Li$_3$N$_4$O$_3$Sm (943.25): C 63.66, H 7.16, N 5.94; found: C 63.22, H 7.96, N 5.92; IR (Nujol) $\tilde{\nu}$ = 1446(vs), 1365(vs), 1343(s), 1286(s), 1272(s), 1260(s), 1235(m, br), 1186(s), 1134(s), 1106(s, sh), 1042(vs, br), 990(m, br), 969(w), 931(w), 917(w), 902(vs, br), 877(vs, sh), 832(s, sh), 796(s, sh), 769(vs), 755(vs), 737(vs), 670(w), 584 cm^{-1} (w); μ_{eff} = 3.57 μ_B.

[{{[−(CH$_2$)$_5$−]$_4$-Calix-tetrapyrrole}Sm^{III}}$_2$(μ-C$_2$Li$_4$)]·Et$_2$O (2a): Dark red crystals of **1a** (4.3 g, 4.6 mmol) were dissolved in hexane (100 mL) and the resulting dark green solution was exposed to acetylene (1 atm, RT). The color immediately turned purple then gradually light yellow over a 20 min period. Pale yellow **2a** separated as a fine, microcrystalline solid upon standing for 3 h at room temperature (1.5 g, 0.9 mmol, 39 %). Crystals suitable for X-ray were grown at room temperature by layering a concentrated solution of **2a** in THF with a small amount of diethyl ether and hexane. IR (Nujol): $\tilde{\nu}$ = 3088(w), 2731(w), 2664(w), 1658(w), 1564(w), 1344(s), 1309(m), 1290(s), 1267(s), 1235(s), 1136(m), 1070(s), 1050(s), 983(w), 932(w), 898(s), 876(s), 831(m), 777(s), 735(s), 688(m), 582 cm^{-1} (m); elemental analysis calcd (%) for C$_{86}$H$_{106}$Li$_4$N$_8$OSm$_2$ (1595.25): C 64.70, H 6.69, N 7.03; found: C 64.02, H 6.36, N 6.91; μ_{eff} = 2.37 μ_B. A similar experiment was carried out in a closed flask connected to the Toepler pump. A solution of **1a** (0.900 g, 0.96 mmol) in toluene (25 mL) was frozen with liquid N$_2$. Two equivalents of acetylene were condensed into the flask which was sealed and allowed to reach room temperature. When the reaction was completed, the solution was frozen. The non-condensable gas was passed through two traps cooled with liquid N$_2$ and compressed with a Toepler pump into a calibrated container. Hydrogen gas was recovered in 94 % of the expected amount and identified by GC using an instrument equipped with a thermal conductivity detector and a column of molecular sieves.

Reaction of [(Et$_8$-calix-tetrapyrrole)(thf)Sm^{III}(μ-H)[Li(thf)]$_2$] with acetylene: Isolation of [{(Et$_8$-calix-tetrapyrrole)Sm^{III}}$_2$(μ-C$_2$Li$_4$)]·Et$_2$O (2b) and [{(Et$_8$-calix-tetrapyrrole)Sm^{III}{Li[Li(thf)]$_2$(μ_3-OCH=CH$_2$)}}$_2$(μ,η^2,η'^2-HC=C=C=CH)] (3b): A stirred solution of [(Et$_8$-calix-tetrapyrrole)(thf)-Sm^{III}{(μ-H)[Li(thf)]$_2$}] (2.5 g, 2.2 mmol) in THF (50 mL) was saturated with acetylene (1 atm, RT). After 30 min, the resulting purple-red solution was evaporated to dryness and the residue was extracted with diethyl ether (100 mL). After standing for 24 h at room temperature red crystals of **3b** (0.6 g, 0.35 mmol, 32 %) separated (see below for characterization). The mother liquor was concentrated, filtered and allowed to stand at −30 °C, upon which colorless crystals of [{(Et$_8$-calix-tetrapyrrole)Sm}$_2$(μ-C$_2$Li$_4$)]·Et$_2$O (**2b**) (1.0 g, 0.6 mmol, 54 %) were obtained. Elemental analysis calcd (%) for C$_{78}$H$_{106}$Li$_4$N$_8$OSm$_2$ (1500.32): C 62.44, H 7.12, N 7.47; found: 62.42, H 7.37, N 7.16; IR (Nujol): $\tilde{\nu}$ = 3083(w), 2736(w), 2610(w), 1660(w), 1578(w), 1360(s), 1323(m), 1281(s), 1270(s), 1155(m), 1075(s), 1030(s), 965(w), 933(w), 895(m), 855(s), 830(m), 760(m), 730(s), 680 cm^{-1} (m); ^{1}H NMR (500 MHz, [D$_8$]THF, 23 °C, TMS): δ = 6.20 (br d, 8 H, pyrrole ring), 5.96 (br d, 8 H, pyrrole ring), 4.56 (br m, 4 H, CH$_2$), 3.58 (m, 8 H, CH$_2$), 3.25 (q, 4 H, CH$_2$ ether), 3.17 (br q, 4 H, CH$_2$), 2.17 (br s, 12 H, CH$_3$), 2.02 (br q, 8 H, CH$_2$), 1.95 (br q, 8 H, CH$_2$), 1.75 (br s, 24 H, CH$_3$), 1.10 (t, 6 H, -O-CH$_3$), 0.65 (pseudo t, 12 H, CH$_3$); ^{13}C NMR (125.72 MHz, [D$_8$]THF, 23 °C): δ = 105.45, 92.05 (CH pyrrole), 10.63, 8.81, 27.73 (-O-CH$_3$ groups), 34.24, 28.63, 26.01 (-O-CH$_2$- groups), 28.13, 8.41 (CH$_2$, CH$_3$, ether), 189.98, 135.08 (ring quaternary C atoms); μ_{eff} = 2.45 μ_B.

[{(Et$_8$-calix-tetrapyrrole)Sm^{III}{Li[Li(thf)]$_2$(μ_3-OCH=CH$_2$)}}$_2$(μ_3,η^2,η'^2-HC=C=C=CH)] (3b): *Method A*: The exposure of a solution of [{(Et$_8$-calix-tetrapyrrole)(Et$_2$O)}Sm^{II}{[Li(thf)]$_2$[Li(thf)$_2$](μ_3-OCH=CH$_2$}] (**1b**) (1.3 g, 1.2 mmol) in diethyl ether (100 mL) to acetylene (1 atm, RT) instantly turned the color to purple-red. After standing at room temperature for 2 d cherry-red crystals of **3b** separated (0.8 g, 0.4 mmol, 66 %). IR (Nujol): $\tilde{\nu}$ = 3072(w), 2722(w), 1589(w), 1539(m), 1324(s), 1286(w), 1260(s), 1244(s), 1208(w), 1152(m), 1132(m), 1104(m), 1041(s), 971(m), 922(m), 889(s), 835(s), 781(s), 747(s), 672 cm^{-1} (w); elemental analysis calcd (%) for C$_{96}$H$_{136}$Li$_6$N$_8$O$_6$Sm$_2$ (1840.47): C 62.64, H 7.45, N 6.09; found: C 62.44, H 7.56, N 5.93; ^{1}H NMR (500 MHz, [D$_8$]THF, 23 °C, TMS): δ = 6.31 (s, 16 H, pyrrole), 4.55 (br s, 2 H, CH butatrienyl), 4.35 (br m, 8 H, CH$_2$), 3.35 (br s, 16 H, coordinated thf), 2.30 (br m, 8 H, CH$_2$), 2.25 (br m, 24 H, CH$_3$), 2.12 (br m, 8 H, CH$_2$), 1.35 (br s, 16 H, coordinated thf), 1.01 (br m, 8 H, CH$_2$), 0.10 (br m, 24 H, CH$_3$), −4.59 (br s, 4 H, enolate), −15.98 (br s, 2 H, enolate); ^{13}C NMR (125.72 MHz, [D$_8$]THF, 23 °C): δ = 96.19 (CH pyrrole), 25.31, 27.28 (CH$_2$ thf), 10.14, 30.19 (CH$_3$, CH$_2$ of four ethyl groups), 7.81, 28.19 (CH$_3$, CH$_2$ of four ethyl groups), 100.53 (CH butatrienedyil group), 169.23, 150.51, 98.79, 49.50 (quaternary C atoms), 2.5, −7.32 (enolate); μ_{eff} = 2.54 μ_B.

Method B: A solution of [(Et$_8$-calix-tetrapyrrole)(CH$_3$)Sm^{III}{[Li(thf)]$_2$-[Li(thf)](μ_3-Cl)}] (2.5 g, 2.4 mmol) in THF (100 mL) was exposed to acetylene (1 atm, RT) causing a color change to purple-red. After stirring the solution for 2 h at room temperature, the solvent was evaporated to dryness and the residue extracted with diethyl ether (100 mL). After filtration to remove a small amount of insoluble solid, the solution was allowed to stand at room temperature. After 24 h a mixture of **3b** as well as **2b** separated. After fractional separation from ether, the two products were identified on the basis of their analytical, spectroscopic and crystallographic properties.

[{(Et$_8$-calix-tetrapyrrole*)Sm^{III}[Li(thf)$_2$]}$_2$] (4b): The mother liquor of the above preparation (Method A) was allowed to stand at room temperature for 7 d resulting in the separation of large, bright yellow crystals of **4b** (0.15 g, 0.09 mmol, 15 %). Elemental analysis calcd (%) for C$_{88}$H$_{128}$Li$_2$-N$_8$O$_4$Sm$_2$ (1672.53): C 63.04, H 7.69, N 6.68; found: C 63.42, H 7.97, N 6.76; IR (Nujol): $\tilde{\nu}$ = 3080(w), 2730(w), 2600(w), 1640(w), 1568(w), 1340(s), 1300(m), 1295(s), 1260(s), 1125(m), 1075(s), 1030(s), 980(w), 930(w), 895(s), 875(s), 830(m), 770(s), 730(s), 688 cm^{-1} (m); ^{1}H NMR (500 MHz, [D$_8$]THF, 23 °C, TMS): δ = 6.95 (s, 2 H, CH pyrrole), 6.37 (s, 4 H, CH pyrrole), 5.95 (br s, 12 H, CH$_3$ ethyl), 5.81 (s, 2 H, CH pyrrole), 5.03 (s, 4 H, CH pyrrole), 4.67 (s, 2 H, CH pyrrole), 4.07 (s, 2 H, CH pyrrole), 3.59 (br s, 16 H, CH$_2$ thf), 3.40 (q, 2 H, CH$_2$ ethyl), 2.44 (br q, 2 H, CH$_2$ ethyl), 2.13 (q, 8 H, CH$_2$ ethyl), 1.73 (br s, 16 H, CH$_2$ thf), 1.50 (q, 2 H, CH$_2$ ethyl), 1.41 (t, 12 H, CH$_3$ ethyl), 1.06 (tt, 6 H, CH$_3$ ethyl), 0.78 (br q, 2 H, CH$_2$ ethyl), 0.62 (q, 8 H, CH$_2$ ethyl), 0.61 (q, 2 H, CH$_2$ ethyl), 0.60 (q, 4 H, CH$_2$ ethyl), 0.52 (br q, 2 H, CH$_2$ ethyl), 0.09 (t, 6 H, CH$_3$ ethyl), −1.53 (br s, 6 H, CH$_3$ ethyl), −4.56 (br s, 6 H, CH$_3$ ethyl); ^{13}C NMR (125.72 MHz, [D$_8$]THF, 23 °C): δ = 10.69, 9.75, 9.55, 9.21, 8.84, 8.30, 7.90, 7.04 (CH$_3$-CH$_2$-), 28.73, 30.99 (-CH$_2$-CH$_2$-), 105.44, 99.81 (CH pyrrole), 50.77 (quaternary C ring), 68.22, 26.38 (CH$_2$ thf). Quaternary carbon atoms of pyrrole could not be located. μ_{eff} = 2.57 μ_B.

X-ray diffraction studies: Suitable crystals were selected, mounted on thin, glass fibres using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1 k 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.[10]

Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structures were

Table 1. Crystal data and structure analysis results.[a]

	1a	**2a**	**3b**	**4b**
formula	$C_{50}H_{67}Li_3N_4O_3Sm$	$C_{86}H_{106}Li_4N_8OSm_2$	$C_{96}H_{136}Li_6N_8O_6Sm_2$	$C_{88}H_{128}Li_2N_8O_4Sm_2$
M_w	943.25	1596.25	1840.47	1672.53
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a [Å]	20.780(3)	12.645(3)	20.351(3)	14.070(4)
b [Å]	18.755(3)	30.089(7)	22.207(3)	14.752(4)
c [Å]	12.126(2)	20.604(5)	20.972(3)	21.220(6)
β [°]	99.509(2)	106.372(4)	97.927(3)	106.298(5)
V [Å^3]	4661(1)	7522(3)	9387(2)	4228(2)
Z	4	4	4	2
radiation Mo$_{K\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	203(2)	203	203	203
ρ_{calcd} [g cm^{-3}]	1.344	1.410	1.302	1.314
μ_{calcd} [cm^{-1}]	1.304	1.598	1.293	1.428
F_{000}	1960	3288	3832	1740
R[a]	0.0597	0.0451	0.0413	0.0544
$wR2$[b]	0.1434	0.1148	0.0981	0.887
G.o.F	1.040	1.004	1.048	1.007

[a] $R = \Sigma F_0 - F_c/\Sigma F_0$. [b] $wR = [(\Sigma(F_0 - F_c)^2/\Sigma wF_0^2)]^{1/2}$.

solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. A molecule of cocrystallized diethyl ether solvent was located in **2a**. The compound molecule of **4b** and two symmetry-unique compound molecules of **3b** were located at inversion centers. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.03 program library (Sheldrick, 1997, WI). Crystal data are summarized in Table 1 while relevant bond lengths and angles are given in Table 2.

Compound 1a: The crystal structure consists of discrete monomeric units. The samarium atom is surrounded by a calix-tetrapyrrole ligand which adopted the characteristic basketlike conformation[5, 7] (Figure 1). Similar to the case of the previously reported **1b**,[5] the coordination geometry around the samarium atom is distorted pseudo trigonal bipyramidal with two nitrogen atoms of two σ-bonded pyrrole rings (Sm–N3 2.628(6), Sm–N4 2.861(6) Å) and the oxygen atom of a coordinated solvent molecule (Sm–O3 2.630(6) Å) defining the equatorial plane (O3-Sm-N3 143.83(19)°, O3-Sm-N4 120.67(19)°, N3-Sm-N4 73.28(18)°). Two centroids of the π-bonded pyrrole rings are on the axial positions. Three lithium atoms, bridged by the oxygen (Li1–O2 1.871(16), Li2–O2 1.826(16), Li3–O2 1.933(14) Å) of one enolate group (O2–C41 1.425(8), C41–C42 1.326(14) Å, O2-C41-C42 122.1(9)°), are placed on the opposite side of the ligand with respect to that occupied by the samarium atom. Two of the three lithium atoms are π-bonded to different portions of the same pyrrole ring (Li1–C23 2.410(19), Li1–C24 2.275(18), Li3–C21 2.666(16), Li3–C22 2.758(17) Å) and each σ-bonded to the N atom of another pyrrole ring

Table 2. Selected bond lengths [Å] and angles [°].

1a	**2a**	**3b**	**4b**
Sm–N1 2.601(6)	Sm1–C81 2.559(8)	Sm1–C38 2.426(7)	Sm–N1 2.781(6)
Sm–N3 2.628(6)	C81–C82 1.224(10)	Sm1–C37 2.734(7)	Sm–C1 2.777(7)
Sm–O3 2.630(6)	Sm2–C82 2.578(8)	Sm1–C37A 3.076(7)	Sm–C2 2.854(6)
Sm–N4 2.861(6)	C81–Li1 2.530(15)	Sm1–N1 2.518(5)	Sm–C3 2.825(7)
Sm–C31 2.907(7)	C81–Li2 2.292(15)	Sm1–N2 2.765(5)	Sm–C4 2.796(7)
Sm–C32 2.954(7)	C81–Li3 2.521(16)	Sm1–C10 2.802(6)	Sm–N2 2.458(6)
Sm–C33 2.952(8)	C81–Li4 2.344(14)	Sm1–C11 2.850(6)	Sm–N4 2.455(6)
Sm–C34 2.912(7)	C82–Li1 2.353(15)	Sm1–C12 2.853(6)	Sm–N3 2.659(6)
Li1–N4 2.039(15)	C82–Li2 2.504(15)	Sm1–C13 2.820(6)	Sm–N1A 2.479(5)
Li1–C24 2.275(18)	C82–Li3 2.270(16)	C39–C40 1.436(10)	Li–N3 1.985(14)
Li1–C23 2.410(19)	C82–Li4 2.526(15)	O1–C39 1.406(8)	N1A-Sm-N2 99.49(19)
Li3–C22 2.758(17)	Sm1–N1 2.660(6)	C37–C38 1.295(9)	N1A-Sm-N4 129.8(2)
Li3–C21 2.666(16)	Sm1–N2 2.371(6)	C37–C37A 1.298(14)	N2-Sm-N4 130.66(19)
Li3–N2 2.080(15)	Sm1–C1 2.702(7)	C38-C37-C37A 155.0(10)	
Li2–N1 2.152(16)	Sm1–C2 2.774(7)	O1-C39-C40 117.2(7)	
Li2–C1 2.167(17)	Sm1-C3 2.778(7)	N1-Sm1-N3 119.22(17)	
Li2–C2 2.242(17)	Sm1–C4 2.707(7)		
Li2–C3 2.248(18)	Li1–N8 2.099(15)		
Li2–C4 2.177(17)	Li1–C32 2.385(15)		
Li1–O2 1.871(16)	Li1–C33 2.360(15)		
Li2–O2 1.826(16)	Sm1–C81-C82 179.3(7)		
Li3–O2 1.933(14)	Sm2-C82-C81 178.7(7)		
O2–C41 1.425(8)	C81-Li1-C82 28.7(3)		
C41–C42 1.326(14)	C81-Li2-C82 29.1(3)		
O2-C41-C42 122.1(9)	C81-Li3-C82 29.0(3)		
N1-Sm-N3 121.22(18)	C81-Li4-C82 28.8(3)		
N1-Sm-O3 94.94(19)	Li2-C81-Li4 169.0(6)		
N3-Sm-O3 143.83(19)	Li1-C81-Li4 87.2(5)		

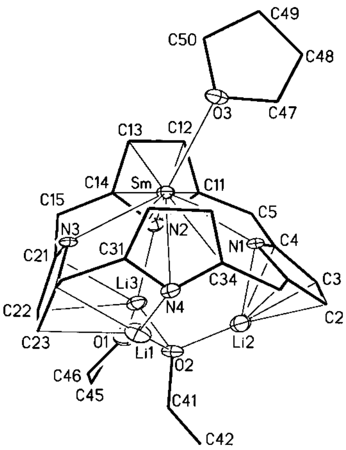


Figure 1. Partial thermal ellipsoid plot of **1a**. Thermal ellipsoids are drawn at the 30 % probability level.

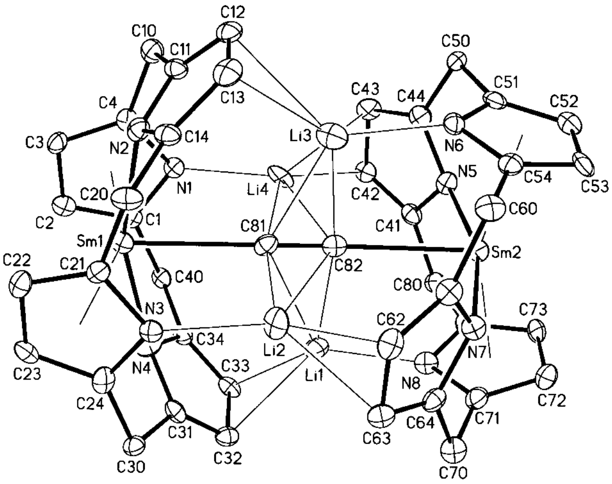


Figure 2. Thermal ellipsoid plot of **2a**. Thermal ellipsoids are drawn at the 30 % probability level. Cyclohexyl rings were omitted for clarity.

(Li1−N4 2.039(15), Li3−N2 2.080(15) Å). The third lithium is π-bonded in a rather symmetric manner to the fourth pyrrole ring (Li2−N1 2.152(16), Li2−C4 2.177(17), Li2−C3 2.248(18), Li2−C2 2.242(17), Li2−C1 2.167(17) Å). As mentioned above, the structure of this complex is very similar to that of **1b** except for a lower degree of solvation of the lithium cations and the presence of one molecule of THF (instead of diethyl ether) directly bonded to the samarium atom. The most significant structural difference between the two compounds arises from the rather severe bending of the $O_{enolate}$-Sm-O_{thf} vector (O2-Sm-O3 150.4(2)°), since the corresponding $O_{enolate}$-Sm-O_{Et_2O} vector in complex **1b** is nearly linear.[5]

Compound 2a: The complex is dinuclear with two calix-tetrapyrrole Sm units bridged by a C_2Li_4 fragment. The calix-tetrapyrrole ligand surrounds the samarium atom by adopting the characteristic basket-like conformation providing a distorted pseudo-trigonal bipyramidal coordination geometry to the metal center (Figure 2). Two centroids of two π-bonded pyrrole rings, together with a carbon atom from the bridging carbide, define the equatorial plane. The other two nitrogen atoms of two σ-bonded pyrroles are located on the axial positions (N2-Sm1-N3 88.14(19)°, N5-Sm2-N7 163.5(2)°, N1-Sm1-C81 74.1(2)°, N5-Sm2-C82 81.2(2)°). The dinuclear structure is held together by a nearly linear C_2 unit (Sm1-C81-C82 179.3(7)°; C81-C82-Sm2 178.7(7)°), which bridges the two samarium atoms in an end-on fashion. The C−C bond length (C81−C82 1.224(10) Å) agrees well with that observed in other lanthanide carbide complexes[6, 11] and is only slightly longer than that determined in free acetylene (1.205 Å).[12] The Sm−C bond lengths (Sm1−C81 2.559(8), Sm2−C82 2.578(8) Å) are, within error limits, similar to those observed in terminally bonded and alkyl bridged Sm complexes of the same ligand system.[7, 13] The four lithium cations are located in the region between the two Sm(calix-tetrapyrrole) units forming a flattened tetrahedron bisected by the Sm-CC-Sm vector. The lithium atoms are asymmetrically side-on connected to the two carbon atoms of the C_2 unit forming both short and long Li−C bond lengths (Li1−C82 2.353(15), Li1−C81 2.530(15), Li2−C81 2.292(15), Li2−C82 2.504(15) Å). In addition, they are also connected to the pyrrole rings of two separate Sm(calix-tetrapyrrole) units (Li3−N6 2.082(16), Li2−N3 2.080(14), Li1−N8 2.099(15) Å) by both σ- and π-interactions.

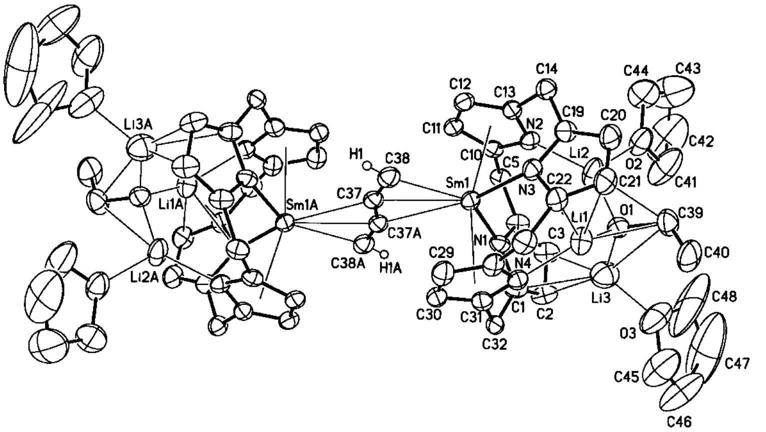


Figure 3. Thermal ellipsoid plot of **3b**. Thermal ellipsoids are drawn at the 30 % probability level. Ethyl groups were omitted for clarity.

Compound 3b: The complex is a symmetry-generated dimer with each samarium atom surrounded by one calix-tetrapyrrole ligand (Figure 3). The macrocycle ligand adopts the usual conformation by arranging the four pyrrole rings in both σ- and π-bonding fashions around the samarium center (Sm1−N1 2.518(5), Sm1−N2 2.765(5), Sm1−C10 2.802(6), Sm1−C11 2.850(6), Sm1−C12 2.853(6), Sm1−C13 2.820(6) Å). On the opposite side of the cavities defined by each of the calix-tetrapyrroles, three lithium atoms, all bridged by an enolate fragment (C39−C40 1.436(10), O1−C39 1.406(8) Å), are either σ or π-bonded (Li3−C22 2.137(18), Li2−N2 1.985(13) Å) to the pyrrole rings of the ligand. One C_4H_2 moiety is located between the two metal centers, holding together the dinuclear structure. Similar to the molecular structures of $[(Cp^*_2M)_2(\mu\text{-}RC_4R)]$ (M = La, R = Ph,[14] M = Sm, R = Ph,[15] M = La, R = Me,[16] M = Ce, R = *t*Bu[16]) the four bridging carbon atoms are coplanar with the two Sm atoms (C37−C38 1.295(9), C37−C37A 1.298(14) Å). Samarium is primarily bound to the terminal carbon atom of the C_4 bridge (Sm1−C38 2.426(7), Sm1−C37 2.734(7) Å). The Sm−C bond lengths fall, within the estimated standard deviations, in the range of those found for analogous lanthanide species with substituted alkynes.[14, 16] Similar to other compounds of this type, and in contrast to the dilithiated butatrienediyl,[17] the bridging C_4 fragment is bent (C38-C37-C37A 155.0(10)°). This may be attributed to secondary interactions between samarium and the internal carbon atoms of the C_4 bridge (Sm1−C37A 3.076(7) Å), the sum of the ionic radii of which are within those expected for a Sm−C bond. The crystal structure was of sufficient quality to locate and refine the hydrogen atoms attached to the coordinated butatrienediyl group. The hydrogen atoms attached to each terminal carbon are located *trans* to one another in the SmC_4 plane and point in the opposite direction with respect to the neighboring samarium atom.

Compound 4b: The complex is also dinuclear and is formed by two identical $[(Et_8\text{-calix-tetrapyrrole})Sm[Li(thf)_2]]$ units in which one of the pyrrole rings has undergone a $\alpha \rightarrow \beta$ migration of the alkyl chain (Figure 4).

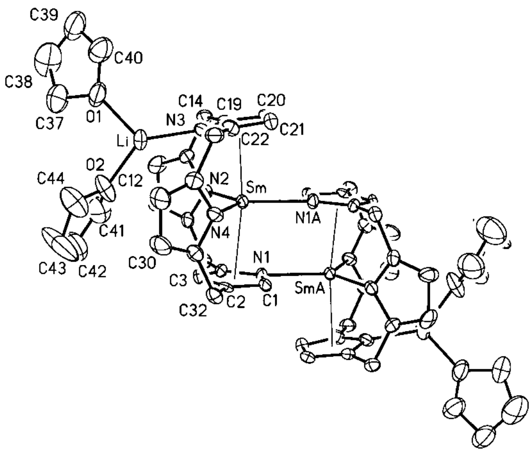


Figure 4. Thermal ellipsoid plot of **4b**. Thermal ellipsoids are drawn at the 30% probability level. Ethyl groups were omitted for clarity.

The reorganized macrocycle adopts the usual geometry with two of the four pyrrole rings in a π-coordination bonding mode with respect to Sm, while the other two are connected to samarium through Sm–N σ-bonds [Sm1–N3 2.659(6), Sm1–N1 2.781(6), Sm1–N1A 2.479(5) Å]. The nitrogen atom of the "confused" pyrrole is bonded to the samarium atom of a second identical unit, thus assembling the dinuclear structure. Two lithium cations located *trans* to one another and at opposite ends of the molecule are each σ-bonded to the N atom of one pyrrole ring (Li–N3 1.985(14) Å), which is in turn π-bonded to samarium. Two molecules of THF complete the coordination environment of each trigonal planar lithium.

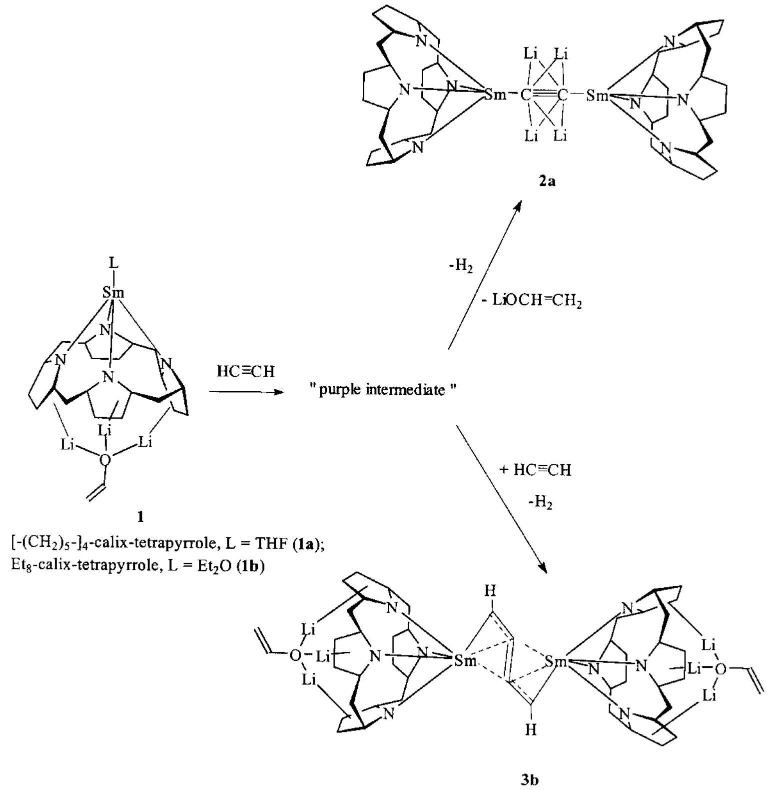
Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140254 (**1a**), 140583 (**2a**), 140584 (**3b**), 114589 (**4b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Reaction of [$Sm^{III}Cl_3(thf)_3$] with an equivalent amount of crystalline [{[(–$(CH_2)_5$–]$_4$-calix-tetrapyrrole}[Li(thf)]$_4$],[8] followed by reduction with Li under Ar and crystallization from toluene, afforded a dark green solution from which dark red crystals of the divalent samarium complex [{[–$(CH_2)_5$–}$_4$-calix-tetrapyrrole)}(thf)Sm^{II}{Li_2[Li(thf)](μ_3-OCH=CH_2)}] (**1a**) were isolated. Unfortunately, the NMR spectra were uninformative due to a combination of line broadening and extensive overlap. The presence of the lithium enolate moiety, probably arising from THF cleavage, is in line with the finding previously reported for this family of green Sm^{II} derivatives.[5] The red color of **1a** is in sharp contrast with the dark green of the octaethyl derivative **1b**, which possesses a closely related structure.[5] The possibility that **1a** might be in fact a trivalent Sm hydride, as it might be suggested by the rather severe bending of the $O_{enolate}$-Sm-O_{thf} vector (the corresponding $O_{enolate}$-Sm-O_{ether} vector of **1b** is nearly linear), is ruled out by the value of the magnetic moment in solid state which agrees rather well with that of the green **1b**.[5] Moreover, upon redissolving red single crystals of **1a** in both toluene and THF, dark green solutions were formed. At this stage, it is tempting to suggest that the anomalous color of **1a** observed in solid state is probably associated with both the lower degree of solvation of the alkali cation and consequent enhancement of π-interaction with the pyrrole rings, and/or with the structural distortion which in turn can be ascribed to solid state packing effects.

Both **1a** and **1b** react with acetylene. The exposure of a dark emerald green solution of **1a** in hexane to an excess of acetylene gas resulted in a sudden color change to dark purple. However, upon a period of minutes at room temperature the solution discolored to give a pale yellow solution from which nearly colorless crystals of a new complex [{{[–$(CH_2)_5$–]$_4$-calix-tetrapyrrole}Sm^{III}}$_2$(μ-C_2Li_4)]·Et_2O (**2a**) separated (Scheme 1). The formation of the trivalent **2a** implies the one-electron oxidation of two Sm^{II} starting complexes. Accordingly, the reaction is accompanied by evolution of nearly half an equivalent of H_2 gas per samarium atom (96% of the expected amount assuming 100% conversion was collected, measured and identified with Toepler pump/GC combined experiments).

The structure of **2a**, as revealed by an X-ray diffraction analysis has some interesting structural analogies with the



1

[-$(CH_2)_5$-]$_4$-calix-tetrapyrrole, L = THF (**1a**); Et_8-calix-tetrapyrrole, L = Et_2O (**1b**)

Scheme 1. Synthesis of **2a** and **3b**; organic substituents (either Et or –$(CH_2)_5$–) and thf coordintated to the Li atoms have been omitted for clarity.

encapsulated dinitrogen complex[4] of the same ligand system. Even in this case, the C_2 unit is encapsulated within a Sm_2Li_4 cluster. Different from N_2, however, the C_2 unit is placed end-on with respect to the two Sm centers and side-on with respect to the four lithium cations, which define a flattened tetrahedron rather than a square plane. The side-on arrangement of the four lithium cations around the C_2 unit is curiously asymmetric and is in striking contrast to the symmetry of the $Sm_2Li_4N_2$ cluster. Also in contrast to the encapsulated dinitrogen complex, the C–C bond length is very short and is indicative of minimal extent of acetylene reduction. The light color of **2a**, as well as magnetic susceptibility data (μ_{eff} = 2.37 μ_B per dimer) also confirms the presence of two trivalent Sm centers and are consistent with the presence of an intact C–C triple bond.

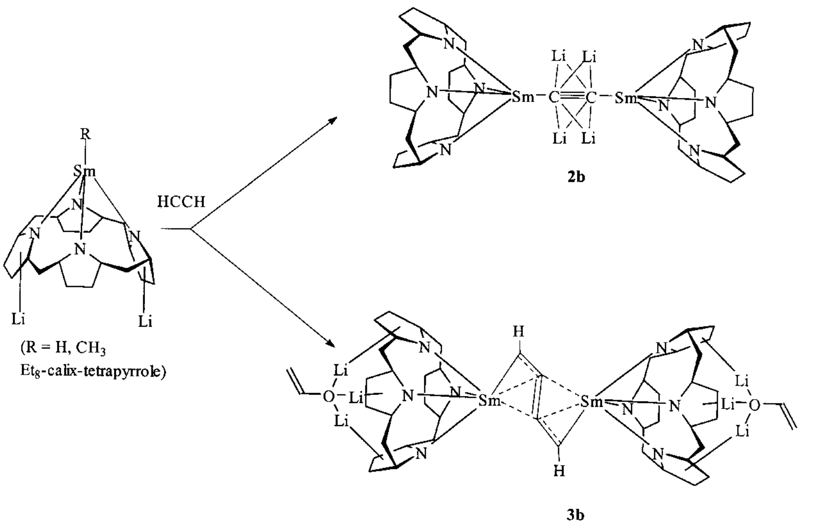
A reaction carried out under identical conditions but with the ethyl derivative [{(Et$_8$-calix-tetrapyrrole)(Et$_2$O)}Sm^{II}-{[Li(thf)]$_2$[Li(thf)$_2$](μ_3-OCH=CH$_2$)}][5] (**1b**) also resulted in an instant color change from green to dark purple-red. In this case, however, an intense light-red color persisted and cherry-red crystals of a new compound formulated as [{[(Et$_8$-calix-tetrapyrrole)Sm^{III}{Li[Li(thf)]$_2$(μ_3-OCH=CH$_2$)}}$_2$(μ,η^2,η'^2-HC=C=C=CH)] (**3b**) were isolated in good yield and analytically pure form from diethyl ether (Scheme 1). The complex formally arises from the coupling of two acetylene molecules and release of H_2 (93% of the stoichiometric amount was recovered with a Toepler pump from the reaction mixture).

Surprisingly, the two reactions proceeded selectively towards the formation of compounds **2a** and **3b** regardless of variations in solvent or temperature. In either case, it was not possible to isolate the purple intermediate even by carrying out reactions at –78 °C, nor did we observe evidence for the presence of other compounds in the reaction mixtures. Neither **2a** nor **3b** showed signs of reactivity with H_2, while both were found to be stable at 70 °C for a few days.

Considering the close steric and electronic similarity between the two calix-tetrapyrrole ligands, the only explanation for the diversity of the reaction pathways relies on kinetic factors. We tentatively propose that the formation of the two compounds results from two different reaction pathways (dehydrogenation versus coupling) of the same intermediate. Evidently the nature of the substituents plays an important role in modifying the activation energies of the two competitive processes, thus determining in the end the nature of the final product. The situation is closely reminiscent of the behavior of the same divalent samarium compounds with ethylene[5] to the extent that the degree of reversibility of ethylene fixation is extremely sensitive to the nature of the ligand substituents. Whereas labile fixation always occurred when R = {–(CH$_2$)$_5$–}$_{0.5}$, more robust ethylene complexation were observed when R = Et.

The formation of an intense purple color observed during the first minutes of the reaction time clearly indicates the formation of an intermediate species. Quenching of the purple solution by addition of D_2O did not give appreciable amount of DH; this suggests that the purple intermediate is perhaps a simple coordination adduct and not an hydride as we initially thought. In an attempt to gain insight on the nature of other important reaction intermediates, we have explored the reactivity of the recently prepared trivalent samarium hydride and alkyl calix-tetrapyrrole derivatives[7] with acetylene. Treatment of either [(Et$_8$-calix-tetrapyrrole)(thf)Sm^{III}{(μ-H)-[Li(thf)]$_2$}] or [(Et$_8$-calix-tetrapyrrole)(CH$_3$)Sm^{III}{[Li(thf)]$_2$-[Li(thf)$_2$](μ_3-Cl)}] with H-C≡C-H resulted in rapid reactions from which similar mixtures of the two complexes in similar ratios, the colorless [{(Et$_8$-calix-tetrapyrrole)Sm^{III}}$_2$(μ-Li$_4$C$_2$)] (**2b**) and the bright-red [{(Et$_8$-calix-tetrapyrrole)Sm^{III}{Li-[Li(thf)]$_2$(μ_3-OCH=CH$_2$)}}$_2$(μ,η^2,η'^2-HC=C=C=CH)] (**3b**), were obtained in crystalline form (Scheme 2). Even in this case the reaction was very sensitive to the nature of the ligand substituents. Similar to the case of the reaction of Sm^{II} complexes with acetylene, the formation of **3b**, which results from partial dehydrogenation and dimerization of two acetylene molecules, was observed only in the case where R = Et.

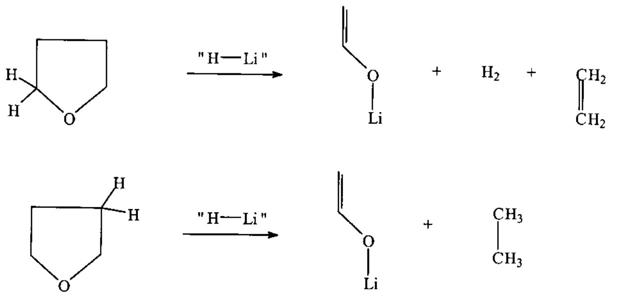
Similar to the case of **1a**, the ^{1}H NMR spectrum of **2a** was uninformative due to line broadness and extensive signal overlap. Conversely, the line sharpness and separation made possible a complete assignment of the spectral features of the ethyl derivatives. In the case of **2b**, the ^{1}H NMR spectrum showed two rather broad signals reminiscent of poorly solved doublets, which arise from the pyrrole C–H groups. The presence of two non-equivalent rings is consistent with the solid state crystal structure showing two π-bonded and two σ-bonded pyrrole rings. The eight ethyl substituents attached to the ring featured three distinct sets of resonances. The four ethyl groups pointing away from the molecular core generate one set, while the other four pointing inward form two distinct



Scheme 2. Synthesis of **2b** and **3b**; ethyl groups and thf coordintated to the Li atoms have been omitted for clarity.

sets. Each set of signals is characterized by a diastereotopic CH_2 group featuring two widely separated signals appearing either as pseudo-quadruplets or multiplets. The methyl groups feature instead broad singlets. A rather sharp pseudo-triplet was observed only in the case of one group of two ethyl groups. This non-equivalency of the eight ethyl groups and the enhanced diastereotopism of the CH_2 groups is very strange. The molecule has an idealized C_{2v} symmetry, thus the methylene protons, which comprise an AB spin system, should provide eight resonances of 2H each. Similarly, four resonances of 6H each should be expected for the methyl groups. The fact that we observed five methylene resonances in the ratio 2:2:4:4:4 may be attributed to accidental line overlap or to the fact that the molecule undergoes some motion at that particular temperature. Temperature variation gave a complex spectral modification indicative of fluxional behavior, but the complete interpretation is still not possible at this stage. Although we are unable to provide a non-speculative explanation of this behavior, we observe that it is a recurrent feature among trivalent samarium compounds of this particular ligand system.[5] The ^1H NMR spectrum of **3b** showed only one pyrrole signal and only two sets of ethyl groups each consisting of three broad multiplets, one for the methyl groups and one for each of the two diastereotopic methylene hydrogens.

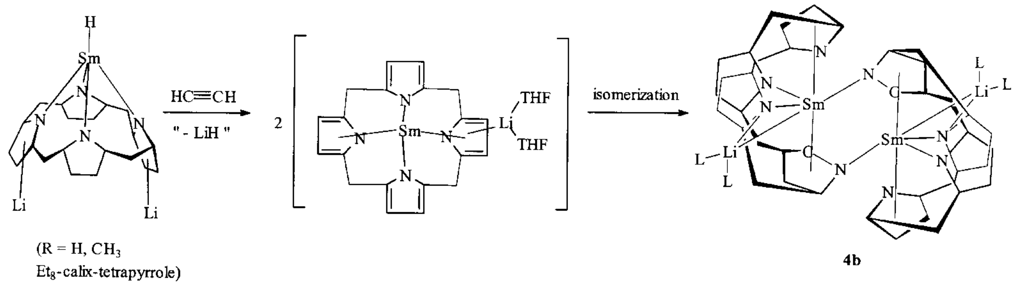
The fact that the same products obtained from the reaction of the divalent samarium compounds with acetylene were also obtained by using Sm^{III} precursors is in agreement with the idea that a trivalent Sm-hydride might be involved in the reactivity of divalent samarium with acetylene. However, the formation of **3b** from the trivalent Sm–R [R = H, CH_3] implies the presence of Li(enolate). In contrast to the Sm^{II} reagents, this moiety is *absent* in the samarium hydride and methyl starting compounds. The Li(enolate) unit typically arises from THF cleavage achieved through either radical or anionic attack on the THF α-hydrogen or β-carbon atoms (Scheme 3). Both processes afford, in addition to the enolate anion, a mixture of ethylene/H_2 or ethane, respectively. These products are found rather frequently altogether as a result of lack of selectivity in reaction mixtures in which THF cleavage occurs. The THF cleavage process also may be favored by the coordination of Lewis acids to the oxygen atom. Evidently the trivalent Sm–R [R = H, Me] compounds used in this work cannot be responsible per se for the formation of the two enolate anions present in **3b**, since both are stable in THF for a few days even at higher temperatures. The process leading to the formation of **2** also cannot be responsible, since the two lithium atoms present in the structure of the Sm–R reagents must be retained in the structure of **2a**, **b** and therefore cannot be made available for the THF cleavage process. Thus, the presence of the enolate fragment in **3b** implies that another product must be formed during the reaction with acetylene. In other words, the reaction must necessarily lead to the formation of another species in which both the hydride (or alkyl group) and the lithium cation are devoted to form Li(enolate).



Scheme 3. Lithium enolate generated by either radical of anionic reaction mechanism.

A third product (**4b**) was isolated in low yield (7%) from the mother liquor of the reaction of [(Et$_8$-calix-tetrapyrrole)(thf)Sm^{III}{(μ-H)[Li(thf)]$_2$}] with acetylene (Scheme 4). Its structure, as indicated by X-ray analysis (Figure 4), is unique in the sense that the ligand has undergone of a $\alpha \rightarrow \beta$ migration of the alkyl chain. The ^1H NMR spectrum is characterized by the expected high asymmetry as reflecting from the solid state structure. The eight C-H protons of the four pyrrole rings form six rather broad singlets. The ethyl groups form four sets of ligands ascribed to four, two, one, and one ethyl groups, respectively. Even in this case, each set of signals formed by each ethyl group features two diastereotopic hydrogens for the ethyl methylene group. The methyl groups formed six separate resonances.

The reorganized calix-tetrapyrrole macrocyle of **4b** has been recently prepared by Sessler[18b] and it is reminiscent of the "N-confused" porphyrins[19] isolated by Furuta[20] and Latos et al.;[21] the rational synthesis was achieved more recently by Dolphin et al.[22] Given the low yield, the possibility that the presence of the N-confused calix-tetrapyrrole may be caused in this case by adventitious (yet reproducible) carrying on from the original ligand preparation cannot be completely excluded. However, it should be reiterated that **4b** was isolated after *four* subsequent reactions, and purification of *three* different precursors. Thus,



Scheme 4. Complexation of **4b**.

assuming that the formation of **4b** is indeed triggered by the reaction with acetylene, questions arise about the factors that promoted the isomerization of the macrocycle with consequent assembly of the dinuclear structure. At this stage we cannot offer a detailed explanation for the formation of **4b**. However, the possibility that the rearrangement could be triggered by reversible attack on the pyrrole β-hydrogen by one strongly basic function (perhaps a vinyl formed through the insertion of acetylene into the Sm–H bond) followed by chain shifting can be confidently ruled out. The recently characterized trivalent [(calix-tetrapyrrole)Sm-vinyl] complex, isostructural with the methyl derivative used in this work, rather produces a Sm^{II} species upon room temperature thermal decomposition.[7] Thus, we can only observe at this stage that the formation of **4b** from the hydride samarium complex during the reaction with acetylene implies the *formal* dissociation of a LiH unit followed by ring reorganization. A "LiR" [R = H, alkyl] unit is precisely what is necessary for the cleavage of a THF molecule and the formation of the Li(enolate) present in **3b**, as well as balancing the overall stoichiometry of the reaction.

Acknowledgement

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[1] a) W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 3728; b) W. J. Evans, L. A. Hughes, D. K. Drummond, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1986**, *108*, 1722; c) W. J. Evans, D. K. Drummond, *J. Am. Chem. Soc.* **1988**, *110*, 2772; d) W. J. Evans, D. K. Drummond, S. G. Bott, J. L. Atwood, *Organometallics* **1986**, *5*, 2389; e) W. J. Evans, J. W. Grate, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 405; f) W. J. Evans, S. L. Gonzales, J. W. Ziller, *J. Am. Chem. Soc.* **1991**, *113*, 9880; g) W. J. Evans, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1988**, *110*, 6877; h) W. J. Evans, J. T. Leman, J. W. Ziller, *Inorg. Chem.* **1996**, *35*, 4283.

[2] T. Dubé, S. Conoci, S. Gambarotta, G. P. A. Yap, G. Vasapollo, *Angew. Chem.* **1999**, *111*, 3890; *Angew. Chem. Int. Ed.* **1999**, *38*, 3657.

[3] J. Guan, T. Dubé, S. Gambarotta, G. P. A. Yap, *Organometallics*, in press.

[4] J. Jubb, S. Gambarotta, *J. Am. Chem. Soc.* **1994**, *116*, 4477.

[5] T. Dubé, S. Gambarotta, G. P. A. Yap, *Angew. Chem.* **1999**, *111*, 1507; *Angew. Chem. Int. Ed.* **1999**, *38*, 1432.

[6] W. J. Evans, G. W. Rabe, J. W. Ziller, *J. Organomet. Chem.* **1994**, *483*, 21.

[7] T. Dubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 121.

[8] W. H. Brown, B. J. Hutchinson, M. H. McKinnon, *Can. J. Chem.* **1971**, *49*, 4017.

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

[10] R. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33.

[11] M. St. Clair, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1991**, *10*, 525.

[12] J. Overend, H. W. Thompson, *Proc. R. Soc. A.* **1956**, *234*, 306.

[13] T. Dubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 817.

[14] C. M. Forsyth, S. P. Nolan, C. L. Stern, T. J. Marks, *Organometallics* **1993**, *12*, 3618.

[15] a) W. J. Evans, R. A. Keyer, J. W. Ziller, *Organometallics* **1993**, *12*, 2618; b) W. J. Evans, R. A. Keyer, J. W. Ziller, *Organometallics* **1990**, *9*, 2628.

[16] H. J. Heers, J. Nijhoff, J. H. Teuben, *Organometallics* **1993**, *12*, 2609.

[17] W. Neugebauer, G. A. P. Geiger, A. J. Kos, J. J. Stezowski, P. v. R. Schleyer, *Chem. Ber.* **1985**, *118*, 1504.

[18] a) S. Depraetere, M. Smet, W. Dehaen, *Angew. Chem.* **1999**, *111*, 3556; *Angew. Chem. Int. Ed.* **1999**, *38*, 3359, and references therein; b) P. A. Gale, J. L. Sessler, *Chem. Commun.* **1998**, 1, and references therein.

[19] J. L. Sessler, *Angew. Chem.* **1994**, *106*, 1410; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1348.

[20] H. Furuta, T. Asano, T. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 767.

[21] P. J. Chmielewski, L. Latos-Grazynski, K. Rachlewicz, T. Glowiak, *Angew. Chem.* **1994**, *106*, 805; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 779.

[22] B. Y. Liu, C. Bruckner, D. J. Dolphin, *Chem. Commun.* **1996**, 2141.

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