Notes

Divalent and Mixed-Valence Samarium Clusters Supported by Dipyrrolide Ligand

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Summary: The nature of the substituents present on a dipyrrolide dianion ligand determines the assembly of Sm(II) clusters which participate to various extents in cluster formation and THF cleavage.

Introduction

Pyrrole-based polyanionic ligands have shown particular versatility in divalent samarium chemistry as possible alternatives to the traditionally used cyclopentadienyl-based systems.[1] This family of ligands is apparently capable of enhancing the strong one-electron reductant behavior of Sm(II),[2] thus making possible the occurrence of a variety of promising transformations. Macrocyclic tetrapyrrole polyanions, for example, are able to stabilize divalent samarium complexes,[3] to promote reversible coordination of ethylene,[4] and to enable dinitrogen reduction.[5] This versatility may be attributed not only to an intrinsic robustness of the ligand toward strongly reducing agents but also to its polydentate nature as well as to the ability of the pyrrole moiety to adopt either the σ or the π coordination modes. Nonetheless, limitations arise due to the invariable retention of alkali metal ions in these complexes. For this reason, we are currently focusing on di- and tripyrroles, namely, substituted di- and tripyrromethanes. We have recently described that a divalent Sm complex of the diphenyl $[Ph_2C(C_4H_3N)_2]^{2-}$ dianion affords tetrametallic reduction of dinitrogen.[6] In an attempt to obtain more information about the diversity of the reactive intermediates capable of performing these attractive transformations, we have now studied similar reactions with the newly prepared $MePhC(C_4H_3N)_2$ dianion and of the same cyclohexyl dipyrrolide ligand but *in the absence of N*$_2$.

Results and Discussion

Treatment of $SmI_2(THF)_2$ with the potassium salt of the methylphenyl dipyrromethanyl dianion under either Ar or N_2 and in THF resulted in a rapid reaction with formation of $[\{[MePhC(C_4H_3N)_2]Sm\}_5(\mu\text{-}I)][K(THF)_6]$ (**1**), which was isolated as a dark brown crystalline material (Scheme 1). This paramagnetic complex is formed by a pentanuclear anion consisting of five $\{[PhCH_3C(C_4H_3N)_2]\text{-}Sm\}$ units with the five samarium atoms pentagonally arranged around a central iodine atom. The planar pentacoordination of the iodine atom is very unusual. Each ligand bridges two samarium atoms with the pyrrole rings being in turn π-bonded to one samarium and σ-bonded to a second. As a result, each samarium atom exhibits a structure reminiscent of a bent-metallocene structure with two π-bonded rings from one ligand and two σ-bonded from another. The “Cp_2SmX_3” type of coordination around each samarium center with a severely folded SmX_3 fragment is unprecedented to the best of our knowledge. The five dipyrrole ligands are arranged such that the phenyl substituents are all oriented in the same direction, thus capping the empty coordination site about each samarium. However, the $Sm\cdots C_{Ph}$ distances, although rather short, are outside the bonding range [shortest contact: $Sm(1)\cdots C(32) = 3.194(6)$ Å]. The negative charge of the cluster is balanced by a potassium cation that is solvated by six molecules of THF and that is unconnected to the pentameric anion.

Given the similarity of the methylphenyl dipyrrolide with the diphenylmethyl or cyclohexyl ligands and that afforded dinitrogen complexes[6] and in view of the tremendous sensitivity to air and moisture of **1**, it is surprising that a dinitrogen adduct did not form upon the initial metathesis. Since previous attempts to form Sm(II) compounds of dipyrrolyl ligands via reduction of a trivalent precursor gave remarkably different results depending on the nature of both the ligand substituents and the reducing agent[6] and given the rarity of divalent

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[1] See for example: (a) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745. (b) Evans, W. J.; Forrestal, K. J.; Ansari, M. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 2180. (c) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *Inorg. Chem.* **1998**, *37*, 770. (d) Evans, W. J.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **1998**, *17*, 2103. (e) Evans, W. J.; Clark, R. D.; Ansari, M. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 9555. (f) Ihara, E.; Koyama, K.; Yasuda, H.; Kanchisa, N.; Kai, Y. *J. Organomet. Chem.* **1999**, *574*, 40. (g) Xie, Z. W.; Wang, J. W.; Zhou, Z. Y.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907. (h) Ihara, E.; Nodono, M.; Katsura, K.; Adachi, Y.; Yasuda, H.; Yamagashira, M.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *Organometallics* **1998**, *17*, 3945.

[2] For reviews on Ln(II) chemistry see: (a) Evans, W. J. *Polyhedron* **1987**, *6*, 803. (b) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (c) Edelmann, F. T. *Coord. Chem. Rev.* **1997**, *165*, 163.

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

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

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

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

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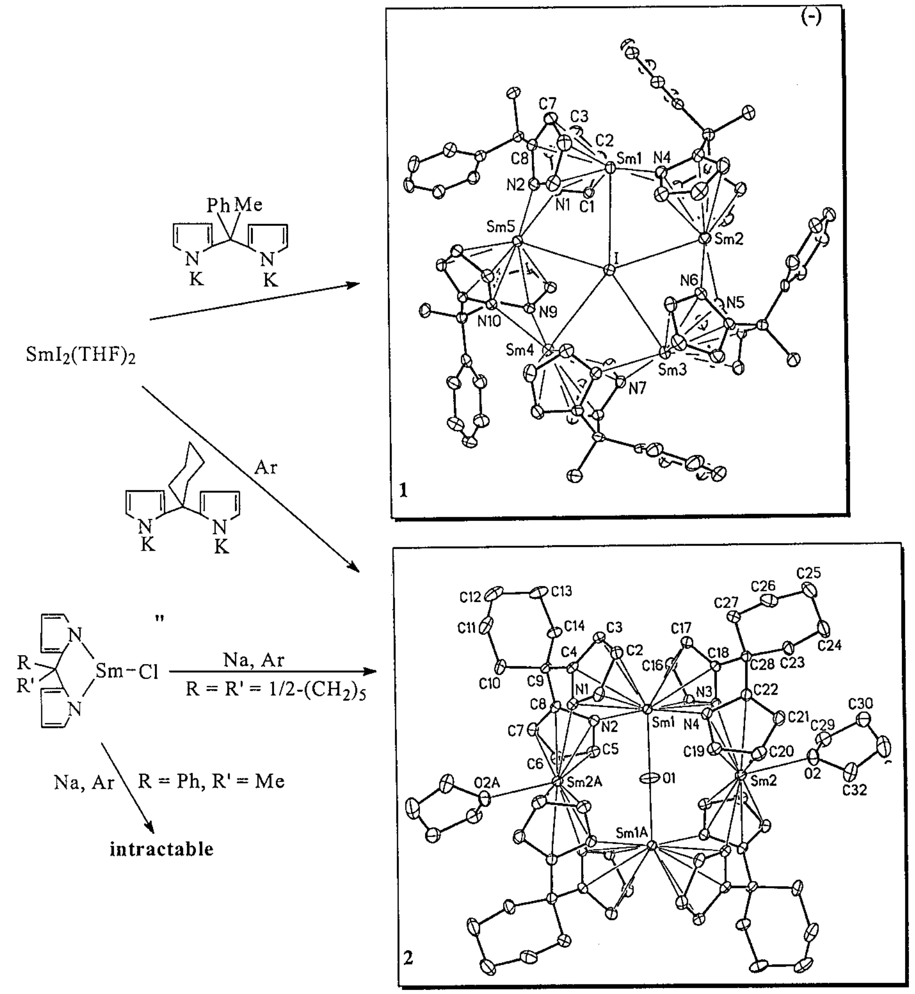
Scheme 1. Thermal Ellipsoids of 1 and 2 Are Drawn at the 30% Probability Level



lanthanide clusters,[7] we have also explored similar reductions of trivalent precursors but *avoiding the presence of dinitrogen*. Unfortunately, only intractable materials have been obtained under a variety of reaction conditions and reducing agents in the case of the Me/Ph derivative. Conversely, reduction with Na metal of a trivalent "{[Cy(C_4H_3N)$_2$]Sm}Cl" precursor *under Ar*- afforded a dark purple-red solution which produced crystals of {[Cy(C_4H_3N)$_2$]Sm}$_4$(μ-O) (**2**) (Scheme 1). The very same product was also obtained in comparable yield via reaction of $SmI_2(THF)_2$ with the potassium salt of the cyclohexyl dipyrrolyl dianion. The connectivity of complex **2,** as indicated by an X-ray crystal structure determination, revealed a tetramer formed by four {-[Cy(C_4H_3N)$_2$]Sm} units arranged to form a tetrametallic planar core. Also in this case, four ligands bridge the four metal centers adopting both the σ- and π-bonding modes. In contrast to **1**, however, the metallocenic-type structure of each samarium is realized with two π-bonded pyrrolyl rings from two different ligands rather than from the same ligand. A single oxygen atom, located in the center of the plane, bridges two of the samarium atoms in a linear fashion, thus forming a mixed-valent Sm(II)/Sm(III) cluster.

Given the presence of four heavy atoms in **2**, the possibility that the central atom might be a nitride could not be conclusively ruled out according to X-ray and analytical data alone. Nonetheless, not even traces of NH_3 could be detected during degradation experiments. This, in addition to the fact that reduction carried out *under an argon atmosphere* also yielded **2**, dismisses the possibility that **2** might in fact be a nitride species.

The presence of the oxygen atom in **2** is likely to have arisen from cleavage of THF, a process which is well-documented in lanthanide chemistry.[8] The presence of propylene and ethylene in the reaction mixture was clearly identified in the GC−MS of the mother solution. While ethylene is commonly formed during THF-cleavage process, the presence of propylene is surprising and indicates the presence of a complex reaction pathway.

The variety of transformations we are currently experiencing in the chemistry of low-valent samarium complexes supported by a dipyrrolide ligand system is primarily dependent on relatively minor changes of the organic groups attached to the carbon atoms bridging the two pyrrolyl rings. This behavior may be related to

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(7) See for example: (a) Bottomley, D. E.; Paez, P. S.; White, J. *J. Organomet. Chem.*, **1985**, *291*, 35. (b) Constantine, S. P.; DeLima, G. M.; Hitchcock, P. B.; Keates, J. M.; Lawless, G. A. *J. Chem. Soc. Chem. Commun.* **1996**, 2421.

(8) (a) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3967. (b) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2641. (c) Aspinall, H. C.; Tillotson, M. R. *Inorg. Chem.* **1996**, *35*, 2163. (d) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291.

steric factors or, more likely, to the modification of the metal redox potential via modification of its interaction with the pyrrole rings. This striking sensitivity is reminiscent of that observed with calix-tetrapyrrole samarium derivatives[3−5] except that in the dipyrrole systems the effect is considerably more enhanced. Further synthetic work is in progress.

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_2O_3 under an inert atmosphere prior to use, degassed in vacuo, and transferred and stored under inert atmosphere. Methylphenyl dipyrromethane and cyclohexyl dipyrromethane were prepared by slightly modifying the literature procedure described for the diphenyl derivative.[9] $SmCl_3(THF)_3$[10] and $SmI_2(THF)_2$[11] were prepared according to literature procedures. C_6D_6 and THF-d_8 were dried over Na/K alloy, vacuum-transferred into ampules, and stored under nitrogen prior to use. Infrared spectra were recorded on a Mattson 3000 FTIR 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), and corrections for underlying diamagnetism were applied to the data.[12,13] Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer

Preparation of $[\{[MePhC(C_4H_3N)_2]Sm\}_5(\mu\text{-}I)][K(THF)_6]$ (1). Solid KH (0.2 g, 5.0 mmol) was added to a solution of methylphenyl dipyrromethane (0.6 g, 2.5 mmol) in 75 mL of THF, resulting in immediate effervescence. The suspension was stirred at room temperature for 20 min until an appreciable amount of microcrystalline solid had accumulated and the gas evolution stopped. The addition of $SmI_2(THF)_2$ (1.3 g, 2.4 mmol) resulted in an immediate color change to dark purple-brown. After stirring at room temperature under N_2 for 24 h and removal of KI by filtration, the solution was concentrated to about 25 mL. Addition of toluene (25 mL) and standing at room temperature for 2 weeks resulted in precipitation of dark brown crystals of **1** (0.5 g, 0.2 mmol, 42%). Anal. Calcd (Found) for $C_{104}H_{118}N_{10}O_6I\,KSm_5$: C 49.53 (49.60), H 4.72 (4.32), N 5.55 (5.49). IR (Nujol mull, cm^{-1}) ν: 3084(w), 3088(w), 1691(w), 1595(w), 1487(m), 1462(vs), 1420(w), 1377(s), 1284(w), 1259(m), 1170(m), 1151(w), 1101(m), 1052(m), 1034(s), 1024(s), 939(m), 895(w), 802(w), 746(vs), 702(s), 877(w), 834(m), 580(s). $\mu_{eff} = 5.15\ \mu_B$.

Preparation of $\{[Cy(C_4H_3N)_2]Sm\}_4(\mu\text{-}O)$ (2). Method A. Addition of NaH (0.8 g, 33.3 mmol) to a solution of cyclohexyl dipyrromethane (3.7 g, 17.3 mmol) in THF (150 mL) and stirring for 1 h at room temperature resulted in the formation of a significant amount of microcrystalline solid. Subsequent treatment with $SmCl_3(THF)_3$ (7.6 g, 16.1 mmol) yielded a yellow suspension, which was stirred for 1 h at room temperature. The suspension was thoroughly degassed, and metallic sodium (0.37 g, 16.2 mmol) was introduced under an Ar atmosphere with a catalytic amount of naphthalene (0.06 g, 0.5 mmol). Stirring for an additional 16 h at room temperature produced a deep purple-red solution, which was filtered to remove insoluble solid. Concentration to small volume (50 mL) followed by layering with hexanes (50 mL) and standing at room temperature for 4 days resulted in the separation of crystals of **2** (1.8 g, 1.0 mmol, 26%). IR ν: 3087(w), 2729(w), 2671(w), 1626(w), 1462(s), 1427(s), 1402(w), 1377(s), 1350(w), 1298(m), 1281(m), 1261(s), 1232(w), 1213(w), 1192(m), 1153(vs), 1122(vs), 1095(vs), 1068(vs), 1038(vs), 960(m), 895(s), 870(m), 829(m), 802(m), 769(vs), 740(vs), 688(w), 631(m). Anal. Calcd (Found) for $C_{72}H_{96}N_8O_5Sm_4$: C 49.27 (48.37), H 5.51 (5.32), N 6.38 (6.59). $\mu_{eff} = 8.57\ \mu_B$.

Table 1. Crystal Data and Structure Analysis Results

	1	2
formula	$C_{104}H_{118}IKN_{10}O_6Sm_5$	$C_{72}H_{96}N_8O_5Sm_4$
fw	2521.83	1754.97
space group	P2(1)/n	*C*2/*c*
a (Å)	13.949(2)	23.116(4)
b (Å)	22.679(4)	11.836(2)
c (Å)	31.193(3)	24.932(4)
β (deg)	94.22(1)	96.820(2)
V (Å^3)	9841(2)	6773(2)
Z	4	4
radiation (Kα, Å)	0.71073	0.71073
T (K)	203(2)	203(2)
D_{calcd} (g cm^{-3})	1.702	1.721
μ_{calcd} (cm^{-1})	3.351	3.473
F_{000}	4968	3488
R, $R_w{}^2$,[a] GoF	0.0315, 0.0519, 1.004	0.0364, 0.0899, 1.005

[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)

1	2
Sm(1)−I = 3.5321(6)	Sm(1)−O(1) = 2.1844(4)
Sm(2)−I = 3.526(1)	Sm(1)−N(1) = 2.672(3)
Sm(3)−I = 3.535(1)	Sm(1)−N(2) = 2.507(4)
Sm(4)−I = 3.517(1)	Sm(1)−N(3) = 2.658(3)
Sm(5)−I = 3.5566(6)	Sm(1)−N(4) = 2.546(4)
Sm(1)−N(1) = 2.799(3)	Sm(1)···Sm(2) = 3.730(4)
Sm(1)−N(2) = 2.820(3)	Sm(1)−C(2) = 2.850(4)
Sm(1)−C(1) = 2.928(4)	Sm(2)−O(1) = 3.028(1)
Sm(1)−N(4) = 2.627(3)	Sm(2)−O(2) = 2.609(3)
Sm(1)···Sm(2) = 4.195(1)	Sm(1)−O−Sm(1A) = 179.1(2)
Sm(1)···Sm(5) = 4.169(1)	N(1)−Sm(1)−N(3) = 172.74(10)
Sm(1)···C(32) = 3.194(6)	Sm(1)−N(3)−Sm(2) = 88.59(10)
Sm(1)···C(31) = 3.469(6)	
Sm(1)···C(27) = 3.514(7)	
Sm(1)−I−Sm(2) = 144.467(10)	
Sm(1)−I−Sm(5) = 72.048(8)	
Sm(1)−N(1)−Sm(5) = 101.34(10)	

Method B. A solution of cyclohexyl dipyrromethane (3.9 g, 18.2 mmol) in THF (100 mL) under Ar was treated with KH (1.5 g, 37.0 mmol). Stirring proceeded for 30 min at room temperature until the effervescence stopped and an appreciable amount of colorless crystalline material accumulated. Subsequent addition of $SmI_2(THF)_2$ (9.4 g, 17.2 mmol) resulted in a rapid reaction with a color change to deep purple-red. After stirring for 16 h at room temperature followed by filtration to remove a significant amount of light-colored solid, the solution was concentrated to 50 mL. Layering with hexanes (25 mL) and standing at room temperature for 2 days yielded purple-red crystals of **2** (1.5 g, 0.8 mmol, 20%).

X-ray Crystallography. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to

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

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[13] Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Selectionnes, Diamagnetisme, Paramagnetism, Relaxation Paramagnetique*; Masson: Paris, 1957.

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.[14]

Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with difference Fourier syntheses, and refinedwith full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement. 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 distances and angles are given in Table 2.

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Supporting Information Available: Crystallographic data (excluding structure factors) and extensive tables of bond distance and angles for **1** and **2**.

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