Mono(cyclooctatetraenyl)samarium Complexes: the Return of the Normally "Inaccessible" Bis(trimethylsilyl)amido Derivative

M. Visseaux,*[a] A. Dormond,[a] and D. Barbier-Baudry[a]

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The complexes [(COT)Ln{N(SiMe$_3$)$_2$}(THF)] (Ln = late lanthanide metal) are readily accessible but, until now, the samarium analogue has proved elusive. The latter can be formed in solution but is easily desolvated during the isolation process, leading to a highly associated complex which is only soluble in coordinating solvents or in the presence of ancillary ligands.

Introduction

There is now a growing interest in the cyclooctatetraenyl derivatives of the metals of groups 3 and 4. As an alternative to traditional cyclopentadienyl chemistry, this ligand provides original structural features,[1a,1b] and, due to their potential for olefin[2] and lactone polymerization,[3] cyclooctatetraenyl complexes are often protected by patents. Our research has recently turned towards diene polymerization catalysed by early lanthanide metal complexes[4] and we envisaged the use of monocyclooctatetraenyl derivatives as possible starting materials for convenient catalyst precursors. During our first investigations into lanthanide chemistry, we had observed the formation of [(COT)Sm{N(SiMe$_3$)$_2$}(THF)], (COT = C_8H_8) in polar (deuterated THF) and nonpolar (deuterated benzene) solvents.[5] Therefore we were surprised when it was reported that the amido complexes [(COT)Ln{N(SiMe$_3$)$_2$}(THF)] could only be isolated for yttrium and the late lanthanide metals.[6a] For samarium, this compound could not be isolated, an unusual inverse half-sandwich complex being formed instead.[6b] Because [(COT)Sm{N(SiMe$_3$)$_2$}(THF)] could provide a good precursor for catalytically active cationic cyclooctatetraenyl species (see ref.[7] for recent results in this field), we decided to look again at the reaction of Na[N(SiMe$_3$)$_2$] with [(COT)SmCl(THF)]$_2$. In this communication we report new data leading to a better understanding of these apparently contradictory data.

Results and Discussion

All syntheses were first performed in an NMR tube and then scaled up. In a typical reaction, [(COT)SmCl(THF)]$_2$, **1** and NaN(SiMe$_3$)$_2$ were mixed in a 1/1 molar ratio in an NMR tube and C_6D_6 was added. The violet complex **1** is not soluble in benzene but, after vigorously stirring for a short time, a purple solution and a grey-brown precipitate were obtained. A set of signals clearly indicative of the presence of a mono(bistrimethylsilyl)amido complex was observed {δ = 9.17 (8 H, COT), and −2.37 [18 H, N(SiMe$_3$)$_2$]}.

Because the same compound had previously been obtained by mixing the reactants in deuterated THF and then changing the solvent for deuterated benzene,[8] the bulk synthesis of [(COT)Sm{N(SiMe$_3$)$_2$}(THF)], **2**, was performed in THF with 1/1 stoichiometric amounts of the reactants. After 16 hours stirring at room temperature, the solvent was removed and the crude product extracted with toluene. The reddish solution was slowly concentrated leaving a small crop of deep red crystals (unsuitable for X-ray analysis) and a mother liquor which, after separation of the crystals, was evaporated to dryness. Both fractions were analysed by NMR spectroscopy. The crystals were insoluble in benzene: when C_6D_6 was added to a sample of ca 5−6 mg, after smooth heating and ultrasonic stirring, a pale orange solution was obtained and a brown precipitate deposited. NMR spectroscopic analysis of the solution showed virtually only one component − the known complex Sm[N(SiMe$_3$)$_2$]$_3$ (δ = −1.57 ppm).[9] The NMR tube was then connected to a vacuum line, degassed and THF added. The precipitate immediately dissolved giving a pink-purple solution and only the signals previously observed for **2** were present.

The red solid which was obtained from the mother liquor was found, by elemental analysis, to correspond to the partially desolvated complex [(COT)Sm{N(SiMe$_3$)$_2$}(THF)$_{0.5}$]. It was only sparingly soluble in deuterated benzene and, as well as a reddish precipitate, a pale purple solution of **2** was obtained {δ (C_6D_6) = 9.19 (8 H, COT), 5.95 (4 H, THF), 2.17 (4 H, THF), −2.37 [18 H, N(SiMe$_3$)$_2$]}.

A sample of analytically pure unsolvated [(COT)SmN(SiMe$_3$)$_2$]$_n$ **3**, was obtained (see experimental) by the slow evaporation of a toluene solution of **2**. The IR spectrum confirmed the absence of coordinated THF[10a,b] (no absorption in the range 1010 − 1030 cm^{-1}), and the presence of the COT^{2-} ligand (C−H bending at 719, 869 cm^{-1}).[10b,11]

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[a] Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (L.S.E.O.-U.M.R. 5632),
Faculté des Sciences Gabriel, Université de Bourgogne,
6 bd Gabriel, F-21000 Dijon, France.
E-mail: mvisseau@u-bourgogne.fr

Crystals of **2** could be obtained at low temperature, as thin foliated plates, during the concentration of a THF solution but they rapidly redissolved when the temperature was raised. Simultaneously, a colour change from pink to red, corresponding to the desolvation, was observed.

By using a nearly 1:2 molar ratio of **1** and $Na[N(SiMe_3)_2]$, the formation of an anionic compound, $[(COT)Sm\{N(SiMe_3)_2\}_2Na]$, **4**, was observed. This anionic complex is soluble in benzene and can be extracted with pentane. An analogous anionic compound containing two sterically demanding ligands, $[(COT)Ln\{CH(SiMe_3)_2\}_2Li(THF)_2]$, has also been described as being soluble in hexane.[12]

Complex **4** was not formed alone: in the benzene solution, the presence of **2** (30%) and $Sm[N(SiMe_3)_2]_3$ **(5)** (15%) was also observed {percentages estimated by integration of the (COT) and $N(SiMe_3)_2$ signals in the ^1H NMR spectrum}. In deuterated THF as solvent, the composition of the mixture was different – the presence of the less soluble $[(COT)_2SmNa]$, ($\delta = 13.21$)[10b] (10%), was also observed. The mixture contained **4** as major component (65%) and **2** (25%). The solvent was removed in vacuo and the remaining traces of coordinated solvent were eliminated by three cycles of toluene condensation and evaporation. The residue was extracted with pentane, the pentane solution transferred to another tube and pentane removed in vacuo. After addition of C_6D_6, the NMR spectrum was recorded. Signals corresponding to the half-sandwich complex[6b] were observed (10%), as well as those of **2** (25%), **4** (45%) and **5** (20%). After addition of THF, the signals of the half-sandwich complex decreased and disappeared within 12 hours.

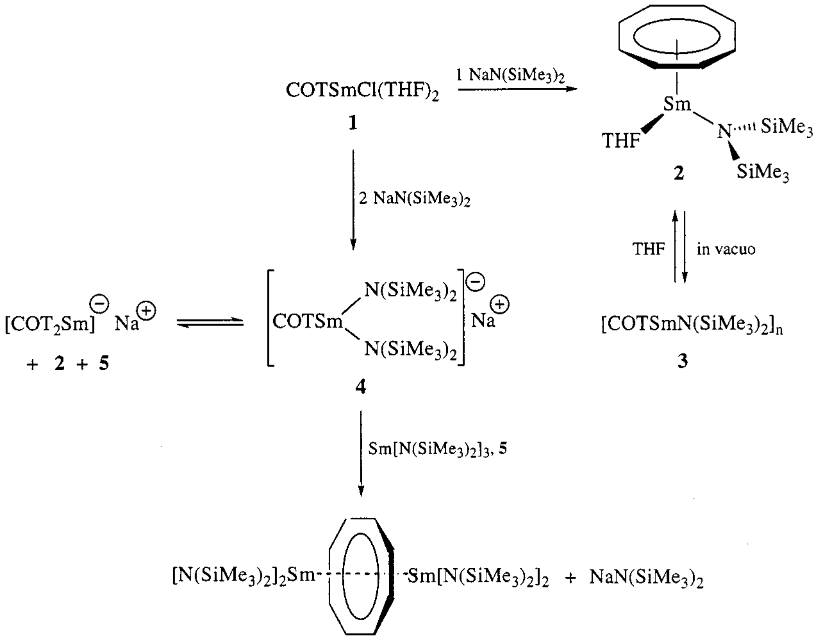
In summary, we could observe the formation of the expected $[(COT)Sm\{N(SiMe_3)_2\}(THF)]$ **(2)** when performing the reaction without an excess of amido reagent. This complex was easily desolvated, leading to an insoluble, highly associated compound $[(COT)Sm\{N(SiMe_3)_2\}]_n$ **(3)** isolated as deep red microcrystals, whose IR data are very close to those of unsolvated uranium and thorium analogues.[13] After addition of the required quantity of THF the soluble complex **2** is recovered. For the desolvated complex **3**, the saturation of the coordination sphere of the samarium ought to be completed by bridging $N(SiMe_3)_2$ groups, as commonly observed for main group derivatives,[14] or more seldom for transition metal organometallic complexes.[15] The previously described half-sandwich complex $[\{N(SiMe_3)_2\}_2Sm(COT)Sm\{N(SiMe_3)_2\}_2]$ can be obtained with a 1:2.6 molar ratio of the reactants.[6b] We could also observe the formation of this compound, in a lower yield, with a 1:2 molar ratio of the reactants. It was not stable in the presence of THF. Conproportionation-disproportionation reactions have been observed in the uranium series between an associated monocyclooctatetraenyl complex and an unsolvated homoleptic borohydride (Scheme 1).[16]

$$[(C_8H_8)U(BH_4)_2]_n + U(BH_4)_4 \longrightarrow (BH_4)_3U(C_8H_8)U(BH_4)_3$$

$$(BH_4)_3U(C_8H_8)U(BH_4)_3 \xrightarrow{THF} [(C_8H_8)U(BH_4)_2](THF) + U(BH_4)_4(THF)_2$$

Scheme 1

Nevertheless, in the samarium series, by mixing **3** and $Sm[N(SiMe_3)_2]_3$ no such reaction occurred. It was consequently postulated that the formation of the half sandwich could occur in the alkane phase, from **4** and **5**, with elimination of $Na[N(SiMe_3)_2]$ (Scheme 2). In fact, after heating a (deuterated) benzene solution containing **4** and **5**, the half-sandwich complex was found to be the major component of the mixture.



Scheme 2. Formation of cyclooctatetraenylsilylamido derivatives

Conclusions

These experiments emphasize the great importance of the ionic strength or the polarity of the reaction medium for organolanthanide syntheses, dominated by the exchange ligand reactions. They also show the interest of using paramagnetic lanthanides for these studies: even for an element inducing a relatively small paramagnetic shift, the NMR spectra allow us to observe the different equilibria established in neutral or polar media.

Experimental Section

General: All experiments were performed with rigorous exclusion of oxygen and moisture, using a JACOMEX glovebox and vacuum line techniques. Solvents were stored over sodium-benzophenone and vacuum-transferred to reaction vessels. Deuterated solvents were distilled over Na/K alloy. NMR spectra were recorded on a Bruker AC 200 spectrometer (297 K). IR spectra were recorded in nujol mulls with a Bruker IFS/66V Spectrometer. Elemental analyses were performed with a Fisons EA 1108 CHONS apparatus. $[(COT)SmCl(THF)]_2$ **1** was prepared as previously described[10b] but with solid $K_2(COT)$ as reagent.[13] $Na[N(SiMe_3)_2]$ was purchased from Aldrich and used without further purification.

$[(COT)SmN(SiMe_3)_2(THF)]$ (2): *NMR scale*: $[(COT)SmCl(THF)]_2$ (8 mg) and $Na[N(SiMe_3)_2]$ (3 mg) were placed in an NMR tube, 0.5 mL of C_6D_6 was added and the mixture was stirred by sonication until the two solids dissolved. A purple solution of **2** and a grey-brown precipitate were obtained. *Bulk synthesis*: $[(COT)SmCl(THF)]_2$ (280 mg), and $Na[N(SiMe_3)_2]$ (118 mg), were placed in a flask connected to the vacuum line and THF (20 mL) was added by condensation. After 4 hours stirring the deep violet solution became purple. The solvent was then removed and toluene added. After filtration, the solution was condensed and red crystals deposited. They were separated, washed with toluene and dried. NMR(C_6D_6): soluble after addition of THF, exhibiting the set of signals for **2**.The mother liquor was transferred into another flask and the solvent removed in vacuo, giving a dark red solid. − ^1H NMR(C_6D_6), only partially soluble, signals of **2**: δ (C_6D_6) = 9.19 (8 H, COT), 5.95 (4 H, THF), 2.17 (4 H, THF), −2.37 [18 H, $N(SiMe_3)_2$]. − $C_{14}H_{26}NSi_2Sm(THF)_{0.5}$ (451): calcd. C 42.61, H 6.70, N 3.11; found C 42.84, H 6.31, N 3.08.

$[(COT)Sm[N(SiMe_3)_2]_n$ (3): $[(COT)SmCl(THF)]_2$ **1** (240 mg) and $Na[N(SiMe_3)_2]$ (101 mg) were placed in a flask connected to the vacuum line and THF (20 mL) was added by condensation. After 20 minutes stirring at ambient temperature, the mixture was heated at reflux for 5 minutes to give a deep purple solution, with some remaining violet crystals of **1** and a greyish precipitate. The volatiles were then removed in vacuo and toluene(20 mL) was added. After stirring for a short time, the mixture was allowed to stand overnight to allow the precipitation of the sodium salt and other insolubles. After filtration the solution was very slowly evaporated to dryness, at ambient temperature, leaving **3** as deep red microcrystals. Yield ca 65%. − IR (nujol): $\tilde{\nu}$ = 1254 (s) cm^{-1}, 1241(s), 986 (vs), 869 (s), 840 (s), 822 (s), 770 (m), 719 (s), 663 (m). − $C_{14}H_{26}NSi_2Sm$ (414.9): calcd. C 40.53, H 6.32, N 3.38; found C 40.37, H 6.17, N 3.39. No melting point was observed up to 210 °C. A slow decomposition occurred, shown by the formation of a colourless solid.

Formation of Adducts

THF Adduct: In the glove box 6 mg of **3** were introduced into an NMR tube and C_6D_6 added. No colour developed in solution after vigorous shaking. The solvent was frozen, the tube connected to the vacuum line, evacuated, and then THF was added at ambient temperature. The purple colour of **2** appeared on melting of the solvent and no precipitate was observed.

Nitrile Adduct: 6 mg of **3** were introduced into an NMR tube and C_6D_6 added. After addition of 7 mg (3 eq) of 2,4,6,trimethylbenzonitrile an orange solution was obtained. − ^1H NMR: δ = 9.13 (8 H, COT), −2.24 {(18 H, $N(SiMe_3)_2$}, 6.32, 2.31 and 1.78 (nitrile).

$(COT)Sm[N(SiMe_3)_2]_2Na$ (4) and Half-Sandwich Complex: In an NMR tube were placed 8 mg of **1** and 7 mg of $NaN(SiMe_3)_2$. C_6D_6 (0.5 mL) was added and after a few minutes of gentle heating, the ^1H NMR spectrum of the resulting orange solution was recorded. − ^1H NMR (C_6D_6) **4**: δ = 8.47 (8 H, COT), 3.75 (4 H, THF), 1.48 (4 H, THF), −1.56 [36 H, $N(SiMe_3)_2$] (the integration of the $N(SiMe_3)_2$ signal indicated the presence of overlapped **5**); **2**: δ = 9.19 (8 H, COT) −2.41 [18 H, $N(SiMe_3)_2$]; δ = 9.25 (8 H) and −2.23 (72 H) (traces < 3%), tentatively attributed to the half-sandwich complex The latter signals disappeared after 12 h. After changing the solvent, **4**: δ (C_4D_8O) = 8.63 (8 H) −1.75 (36 H); **2**: δ = 9.57 (8 H) −1.21(18 H); δ = 13.2 $(COT)_2SmNa$. − The tube was then pumped dry, toluene added by condensation and then removed, and pentane (1 mL) added. After stirring for five minutes and decanting, the pentane solution was transferred into another tube, the volatiles were evacuated and C_6D_6 was added: δ(C_6D_6) = 9.27 (4 H, COT), −2.24 [36 H, $N(SiMe_3)_2$], half-sandwich complex; **2**: δ = 9.06 (8 H, COT) −2.50 [18 H, $N(SiMe_3)_2$]; **4**: δ = 8.35 (8 H) and −1.64 [36 H, $N(SiMe_3)_2$]; **5**: δ = −1.56. After addition of a tenfold excess of THF, an NMR spectrum was immediately recorded. The intensities of the signals of **2** and of the half-sandwich complex had significantly decreased (by 50%). C_6D_6 was added to the pentane-insoluble residue, which was sparingly soluble in benzene. The NMR spectrum was identical to the earlier one except that **2** was present only in trace amounts (<1%). − **3** (8 mg), **5** (8 mg) and 0.5 mL of C_6D_6 were added to an NMR tube. The tube was vigorously stirred then subjected to sonication. Only **5** was present in the solution. After addition of $NaN(SiMe_3)_2$, **3** disappeared and the solution was found to contain **4** and **5**. After a few minutes of gentle heating, the ^1H NMR spectrum of the orange solution was recorded. Compounds **4**, **5** and the half-sandwich complex (27, 17 and 56%, respectively) were present.

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