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Cyclooctatetraenyl complexes of the early transition metals and lanthanides—VII. [1] polysilylated sandwich complexes of the lanthanides

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Abstract—The complexes (COT*)Ln(Cp″) [COT* = 1,4-$(Me_3Si)_2C_8H_6^{2-}$; Cp″ = 1,3-$(Me_3Si)_2C_5H_3^-$; Ln = Pr (**1**), Sm (**2**), Tb (**3**)] have been prepared in a "one pot" reaction by treatment of anhydrous lanthanide trichlorides simultaneously with equimolar amounts of Li_2COT* and LiCp″ and characterized by spectroscopic methods. © 1997 Published by Elsevier Science Ltd.

Keywords: lanthanides; organolanthanide complexes; cyclooctatetraenyl complexes; cyclopentadienyl complexes; sandwich complexes; bulky ligands.

Organolanthanide chemistry is to a large extent the chemistry of lanthanide cyclopentadienyl complexes [2–4]. One of the most useful cyclopentadienyl derivatives for the preparation of soluble, highly reactive organolanthanide complexes is the 1,3-bis(trimethylsilyl)cyclopentadienyl anion. This ligand was made popular by Lappert *et al.* [5,6]. The 1,3-$(Me_3Si)_2C_5H_3^-$ ligand (=Cp″) has been shown to be highly suitable for the synthesis of both di- and trivalent lanthanide derivatives [5–11]. Especially remarkable are the base-free metallocenes Ln$(Cp'')_2$, which have been shown to display unusual polymeric structures in the solid state [5,7,12]. The silyl-substituted counterpart in cyclooctatetraenyl chemistry is the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (=COT*). The 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand has been introduced into organolanthanide chemistry by Cloke and co-workers [13–16]. This very bulky cyclooctatetraenyl dianion often provides higher solubility and better crystallinity to organolanthanide derivatives as compared to the parent COT complexes. The preparation of organolanthanide half-sandwich complexes containing one COT* ligand is however not always straightforward, as the products are often contaminated with the anionic sandwich complexes $[Ln(COT^*)_2]^-$ [17]. We describe here the preparation and characterization of polysilylated lanthanide sandwich complexes containing both the Cp″ and COT* ligand. These represent the first examples of sandwich complexes of the type (COT)Ln(Cp) with substituted cyclooctatetraenyl ligands, whereas numerous complexes with differently substituted cyclopentadienyl rings have been reported [16].

RESULTS AND DISCUSSION

The synthetic strategy was based on the fact that the most logical precursors, i.e. the mono(COT*) lanthanide halides, have not been reported in the literature for the early and middle lanthanides. Therefore a "one pot" reaction was developed, which proved to be successful in the case of praseodymium, samarium, and terbium. This preparation involves simultaneous treatment of anhydrous lanthanide trichlorides with equimolar amounts of Li_2COT* and LiCp″ according to eq. (1). The latter two reagents are prepared by *in situ* lithiation of 1,4-bis(trimethylsilyl)cyclooctatriene and 1,3-bis(trimethylsilyl)cyclopentadiene in THF solution. The resulting solution of Li_2COT* and

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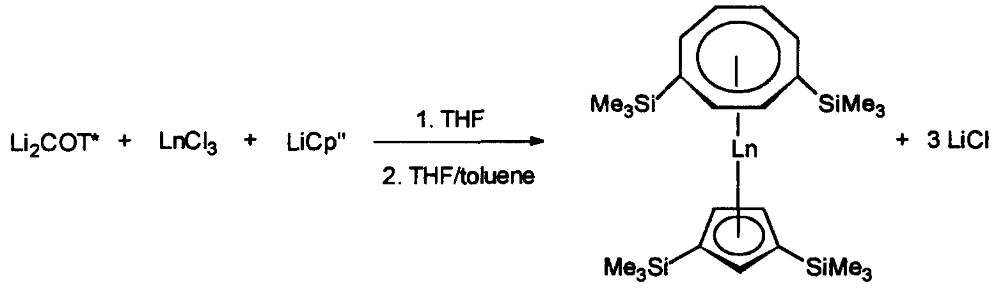

1: Ln = Pr
2: Ln = Sm
3: Ln = Tb

LiCp'' can be used directly for the reactions with lanthanide trichlorides.

Despite the simplicity of the reaction implied by eq. (1), the work-up procedure and isolation of pure materials present significant problems. As mentioned above, the anionic sandwich complexes $[Ln(COT^*)_2]^-$ appear to be a "thermodynamic sink" in systems comprising Ln^{3+} ions and Li_2COT^* [17]. Initial experiments with the system $SmCl_3/Li_2COT^*/LiCp''$ showed that simple extraction of the crude reaction product with hot hexane gave $[Li(THF)_4][Sm(COT^*)_2]$ [17] as the only isolatable crystalline material. Thus $[Li(THF)_4][Sm(COT^*)_2]$ appears to be an intermediate in the "one pot" reaction. It was therefore necessary to choose conditions which allowed a ligand rearrangement to take place and at the same time the LiCl by-product to precipitate. This was finally achieved by continuously diminishing the polarity of the reaction medium by slow addition of toluene to a concentrated THF solution of the reaction product. In the last step small amounts of remaining $[Ln(COT^*)_2]^-$ impurities were removed by recrystallization from hexane. In this manner the complexes **1**–**3** could be isolated as pure materials. In the case of Ce and Nd the method failed as $[Li(THF)_4][Ce(COT^*)_2]$ and $[Li(THF)_4][Nd(COT^*)_2]$ [17,18] were the only isolatable products.

The new compounds are air-sensitive but thermally very stable with melting points in the range 233–248°C. They are highly soluble in THF and toluene and moderately soluble in hexane. The EI mass spectra of all three compounds show the molecular ion besides characteristic fragment peaks. Molecular or fragment ions due to $Ln(Cp'')_3$ [10,11], which would imply the presence of $Ln(Cp'')_3/[Li(THF)_4][Ln(COT^*)_2]$ mixtures, are not observed. A strong IR band at ν 1260–1240 is attributed to the $SiMe_3$ substituents. The ^1H NMR spectra of **1**–**3** confirm the presence of the base-free sandwich complexes $(COT^*)Ln(Cp'')$ (Ln = Pr,Sm,Tb). All proton resonances are strongly influenced by the paramagnetism of the central lanthanide ions, especially in the case of the terbium derivative **3**. The ^1H-NMR spectrum of **3** also displays significant line-broadening. The ^{29}Si NMR spectra are also consistent with the proposed structure. They exhibit only two resonances which can be attributed to the trimethylsilyl substituents on the two ring systems.

The variable-temperature ^1H NMR spectrum of **2** was studied in order to gain insight into possible intramolecular interactions between the two bulky ligands (Fig. 1).

Due to its half intensity signal 1 can be unambiguously assigned to the single H-2 proton of the Cp'' ligand, while a definite assignment of the remaining resonances 2–5 (each corresponding to two ring pro-

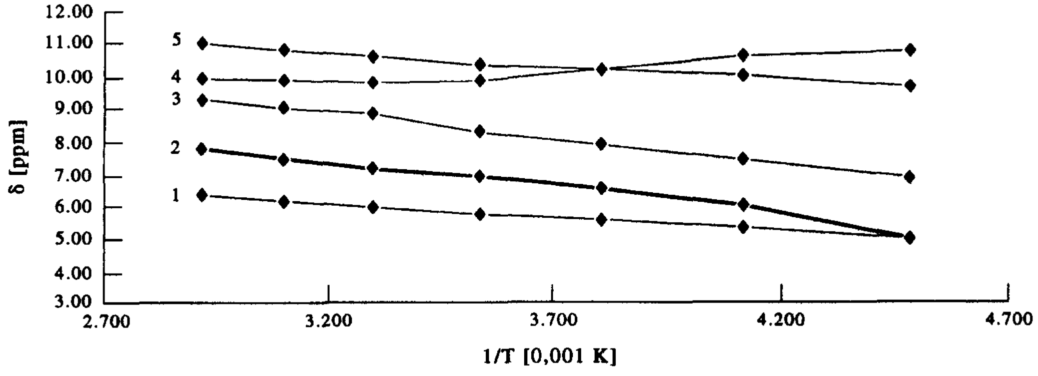

Fig. 1. Variable-temperature ^1H NMR spectrum of **2**.

tons) to one or the other ring system cannot be made. The strong deviations from linearity suggest the presence of a complicated equilibrium between several conformations (Fig. 2). A plausible explanation is the large difference in the radii of the two ring systems, which causes repulsion between opposite $SiMe_3$ groups. As a consequence, conformation **I**, which was shown to be the preferred conformation in the homoleptic sandwich complexes $Fe(Cp'')_2$ [19] and $[Li(THF)_4][Sm(COT^*)_2]$ [17], becomes less favorable. A possible relief of this steric congestion may come from a ring slippage process as illustrated by conformation **II** (Fig. 2). An analogous reduction in hapticity of the cyclopentadienyl ring has already been shown to occur in $(C_{13}H_9)_2Sm(THF)_2$ ($C_{13}H_9$ = fluorenyl) [20], and a related fluxionality involving η^3-coordinated intermediates was reported for the "open cyclopentadienyl" complex tris(2,4-dimethylpentadienyl)samarium(III) [21]. The other energetically more favorable conformation **III** could easily be adopted *via* the η^3-intermediate **II**. The combination of a Cp″ and a COT* ligand around a lanthanide center seems to be the upper limit of steric congestion at least for the middle and late lanthanides. This was shown by an unsuccessful attempt to prepare an analogue of **2** with the use of the even bulkier 1,3,5-tris(trimethylsilyl)cyclooctatetraenyl ligand (= COT**). Treatment of anhydrous $SmCl_3$ simultaneously with KCp″ and K_2COT^{**} gave a product mixture containing $Sm(Cp'')_3$. The target molecule (COT**)Sm(Cp″) appears to be unstable due to severe steric crowding.

EXPERIMENTAL

All reactions were carried out under rigorous exclusion of air and moisture using standard Schlenk line and dry-box techniques. Solvents were carefully dried over Na/benzophenone and freshly distilled under N_2 prior to use. IR spectra: Perkin-Elmer spectrometer 180 and Bio-Rad FTS 7, Nujol mulls between KBr disks. ^1H NMR spectra: Bruker WP 80 SY and Bruker AM-250 (250 MHz, TMS ext., 32°C). ^{29}Si NMR spectra: Bruker AM-250 (79.460 MHz, TMS, 32°C). Elemental analyses: Analytical laboratory of the Department of Inorganic Chemistry, University of Göttingen. The starting materials 1,4-$(Me_3Si)_2C_8H_8$ [14] 1,3-$(Me_3Si)_2C_5H_4$ [22] and $LnCl_3$ (Ln = Pr,Sm,Tb) [23] were prepared according to literature procedures.

Preparation of a THF solution of [1,4-*bis*(*trimethylsilyl*)*cyclooctatetraenyl*]*dilithium and* 1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl-lithium*

2.00 g (8.0 mmol) 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene and 1.69 cm^3 (1.68 g, 8.0 mmol) 1,3-bis(trimethylsilyl)-2,4-cyclopentadiene were dissolved in 70 cm^3 THF and cooled to −78°C. 10.44 cm^3 (24 mmol) of a 2.30 M solution of *n*-butyllithium in hexane were added *via* syringe. The mixture was allowed to warm up to room temperature and was stirred for 15 h while being connected with a pressure release valve. The resulting greenish-brown solution was used directly for further reactions.

[1,4-*Bis*(*trimethylsilyl*)*cyclooctatetraenyl*][1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*praseodymium*(*III*) (**1**)

1.98 g (8.0 mmol) $PrCl_3$ were added with stirring to a solution of 8.0 mmol Li_2COT^* and 8.0 mmol LiCp″ in 70 cm^3 THF. After stirring at room temperature for 15 h the reaction mixture turned yellow and a finely divided white precipitate (LiCl) had formed. The solution was concentrated *in vacuo* to a total volume of *ca* 10 cm^3, over a period of 6 h slowly diluted with 150 cm^3 of toluene and stirred for another 15 h. All volatiles were removed *in vacuo*, the oily residue redissolved in 120 cm^3 toluene and stirred for another 15 h. The resulting solution was heated to boiling and filtered while hot through a thin layer of Celite filter aid. Evaporation of the clear filtrate to dryness afforded a yellow, somewhat sticky solid, which was recrystallized from 30 ml hexane (−25°C) and dried *in vacuo* to give 1.58 g (2.6 mmol, 33%) (**1**) as a yellow, microcrystalline solid. M.p. 248°C.

IR (KBr): ν = 1413 w, 1307 w, 1261 s, 1247 vs, 1209

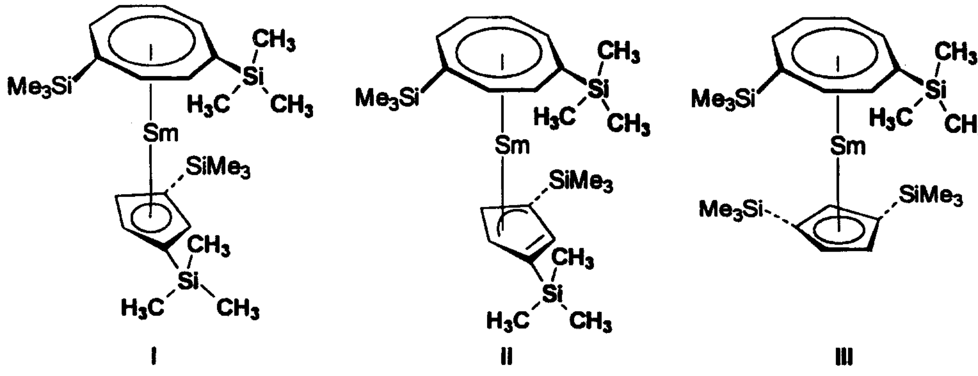

Fig. 2. Proposed conformational changes in **2**.

w, 1170 w sh, 1100 br s sh, 1078 vs, 1048 vs, 1034 br s sh, 978 w, 899 w, 839 vs, 829 vs, 816 s sh. 776 m, 751 vs, 738 s, 686 m, 666 w, 635 m, 556 m, 513 m, 486 s, 361 s cm^{-1}. MS/EI: *m*/*z* (% rel. int.) 598 [M$^+$, 100], 525 [M$^+$-Me, 6], 389 [(COT*)Pr$^+$, 14], 349 [(Cp″)Pr$^+$, 10], 315 [(COT*)Pr$^+$-SiMe$_3$, 10], 248 [(COT*)$^+$, 3], 210 [Cp″H$^+$, 8], 160 [(COT*)$^+$-SiMe$_3$-Me, 7], 73 [SiMe$_3^+$, 58%). ^{1}H NMR (C$_6$D$_6$): $\delta = 7.46$ (br, $\nu_{1/2} = 90$ Hz, 18 H, SiMe$_3$), 0.09 (br, $\nu_{1/2} = 98$ Hz, 18 H, SiMe$_3$), -1.92 (s, 2 H, Ring-H), -1.98 (s br, $\nu_{1/2} = 21$ Hz, 2 H, ring-H), -3.52 (s, $\nu_{1/2} = 7$ Hz, 1 H, Cp″-ring-H), -10.08 (s, $\nu_{1/2} = 20$ Hz, 2 H, ring-H), -10.96 (s, $\nu_{1/2} = 30$ Hz, 2 H, ring-H) ppm. ^{29}Si NMR (THF/C$_6$D$_6$): $\delta = -1.8$ (s), -12.9 (s) ppm. C$_{25}$H$_{45}$PrSi$_4$ (598.9): calcd. C, 50.1 (found 49.7); H, 7.6 (7.9).

[1,4-*Bis*(*trimethylsilyl*)*cyclooctatetraenyl*][1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*samarium*(*III*) (**2**)

Starting from 2.05 g SmCl$_3$ the synthetic procedure was essentially the same as with PrCl$_3$. After evaporation of the final toluene solution the oily, red residue was redissolved in 40 cm^3 hexane and the solution was kept at -25°C for 7 d. Decanting of the supernatant and washing the crystals with 5 cm^3 of cooled (-78°C) hexane afforded a first crop of **2** (0.76 g). Concentration of the mother liquid to a total volume of 20 cm^3 followed by cooling to -25°C (7d) afforded a second portion. The combined yield was 1.12 g (1.84 mmol, 23%). The bright red crystals melt at 223°C.

IR (KBr): $\nu = 1404$ w, 1315 w, 1268 s, 1248 vs, 1211 w, 1173 w sh, 1160 m sh, 1102 br s, 1078 vs, 1046 vs, 1022 br s, 981 m, 922 s, 835 br vs, 818 br vs sh, 778 m sh, 750 s, 737 m sh, 689 m, 636 s, 554 w, 519 w, 473 s, 390 s, 364 s cm^{-1}. MS/EI: *m*/*z* (% rel. int.) 609 [M$^+$, 88], 400 [(COT*)Sm$^+$, 20], 360 [(Cp″)Sm$^+$, 18], 326 [(COT*)Sm$^+$-SiMe$_3$, 8], 248 [(COT*)$^+$, 1], 209 [(Cp″)$^+$, 5], 160 [(COT*)$^+$-SiMe$_3$-Me, 7], 146 [Si$_2$Me$_6^+$, 22], 73 [SiMe$_3^+$, 100%]. ^{1}H-NMR (toluene-*d*$_8$): 343 K: $\delta = 10.99$ (s, $\nu_{1/2} = 7$ Hz, 2 H), 9.95 (s, $\nu_{1/2} = 9$ Hz, 2 H), 9.31 (s, $\nu_{1/2} = 19$ Hz, 2 H), 7.81 (s, $\nu_{1/2} = 20$ Hz, 2 H), 6.34 (s, $\nu_{1/2} = 7$ Hz, 1 H), 0.64 (s, 18 H, SiMe$_3$), -0.14 (s, 18 H, SiMe$_3$) ppm; 323 K: $\delta = 10.80$ (s, $\nu_{1/2} = 7$ Hz, 2 H), 9.87 (s, $\nu_{1/2} = 9$ Hz, 2 H), 9.02 (s, $\nu_{1/2} = 17$ Hz, 2 H), 7.48 (s, $\nu_{1/2} = 18$ Hz, 2 H), 6.16 (s, $\nu_{1/2} = 7$ Hz, 1 H), 0.68 (s, 18 H, SiMe$_3$), -0.13 (s, 18 H, SiMe$_3$) ppm; 303 K: $\delta = 10.58$ (s, $\nu_{1/2} = 8$ Hz, 2 H), 9.82 (s, $\nu_{1/2} = 10$ Hz, 2 H), 8.67 (s, $\nu_{1/2} = 18$ Hz, 2 H), 7.16 (s, $\nu_{1/2} = 19$ Hz, 2 H), 5.93 (s, $\nu_{1/2} = 7$ Hz, 1 H), 0.70 (s, 18 H, SiMe$_3$), -0.18 (s, 18 H, SiMe$_3$) ppm. 283 K: $\delta = 10.36$ (s, $\nu_{1/2} = 7$ Hz, 2 H), 9.90 (s, $\nu_{1/2} = 8$ Hz, 2 H), 8.30 (s, $\nu_{1/2} = 15$ Hz, 2 H), 6.95 (s, $\nu_{1/2} = 17$ Hz, 2 H), 5.77 (s, $\nu_{1/2} = 7$ Hz, 1 H), 0.68 (s, 18 H, SiMe$_3$), -0.23 (s, 18 H, SiMe$_3$) ppm. 263 K: $\delta = 10.22$ (s, $\nu_{1/2} = 10$ Hz, 4 H), 7.82 (s, $\nu_{1/2} = 18$ Hz, 2 H), 6.52 (s, $\nu_{1/2} = 19$ Hz, 2H), 5.59 (s, $\nu_{1/2} = 9$ Hz, 1 H), 0.68 (s, 18 H, SiMe$_3$), -0.31 (s, 18 H, SiMe$_3$) ppm; 243 K: $\delta = 10.63$ (s, $\nu_{1/2} = 15$ Hz, 2 H), 10.07 (s, $\nu_{1/2} = 11$ Hz, 2 H), 7.46 (s, $\nu_{1/2} = 14$ Hz, 2 H), 5.58 (s, $\nu_{1/2} = 21$ Hz, 2 H), 5.36 (s, $\nu_{1/2} = 7$ Hz, 1 H), 0.64 (s, 18 H, SiMe$_3$), -0.44 (s, 18 H, SiMe$_3$) ppm; 223 K: $\delta = 10.79$ (s br, $\nu_{1/2} = 33$ Hz, 2 H), 9.77 (s, $\nu_{1/2} = 14$ Hz, 2 H), 6.94 (s, $\nu_{1/2} = 19$ Hz, 2 H), 5.07 (s, $\nu_{1/2} = 20$ Hz, 2 H), 0.64 (s, 18 H, SiMe$_3$), -0.52 (s, 18 H, SiMe$_3$) ppm. ^{29}Si NMR (THF/C$_6$D$_6$): $\delta = 17.3$ (s), -1.8 (s) ppm. C$_{25}$H$_{45}$Si$_4$Sm (608.3): calcd. C, 49.3 (found 47.0); H, 7.5 (7.3).

[1,4-*Bis*(*trimethylsilyl*)*cyclooctatetraenyl*][1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*terbium*(*III*) (**3**)

This compound was prepared in an analogous manner from 8.0 mmol Li$_2$COT**, 8.0 mmol LiCp″ and 2.12 g (8.0 mmol) TbCl$_3$. 1.78 g (2.8 mmol, 35%) of **3** were isolated as a bright yellow, pyrophoric solid. M.p. 239°C.

IR (KBr): $\nu = 1405$ w, 1306 m, 1261 vs, 1248 vs, 1191 m, 1144 m sh, 1093 br vs, 1079 vs, 1049 vs, 1025 br vs, 979 w, 934 m, 892 w sh, 836 br vs, 801 br vs, 783 s sh, 750 s, 739 s, 732 br m sh, 683 m, 636 s, 553 w, 511 w, 462 w, 425 s cm^{-1}. MS/EI: *m*/*z* (% rel. int.) 407 [(COT*)Tb$^+$, 4], 350 [(COT*)Tb$^+$-MeSiCH$_2$, 14], 336 [(COT*)Tb$^+$-SiMe$_3$, 16], 295 [(Cp″)Tb$^+$, 5], 207 [(COT*)$^+$-C$_3$H$_5$, 28], 202 [(COT*)$^+$-2Me-CH$_4$, 23], 161 [(COT*)$^+$-SiMe$_4$, 16], 73 [SiMe$_3^+$, 100%]. ^{1}H NMR (C$_6$D$_6$): $\delta = 76.32$ (s br, $\nu_{1/2} = 1200$ Hz, 36 H, SiMe$_3$), 66.68 (s br, $\nu_{1/2} = 70$ Hz, 1 H, Cp″-H), 57.92 (s br, $\nu_{1/2} = 126$ Hz, 2 H), 9.63 (s br, $\nu_{1/2} = 140$ Hz, 2 H), 6.03 (s br, $\nu_{1/2} = 160$ Hz, 4 H) ppm. ^{29}Si NMR (THF/C$_6$D$_6$): $\delta = 32.4$ (s br, $\nu_{1/2} = 30$ Hz), 31.7 (s br, $\nu_{1/2} = 28$ Hz) ppm.

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