

Cyclooctatetraenyl complexes of the early transition metals and lanthanides VIII¹. Anionic sandwich complexes of the lanthanides containing silylated cyclooctatetraenyl ligands

Peter Poremba^a, Ulrike Reißmann^a, Mathias Noltemeyer^b, Hans-Georg Schmidt^b,
Wolfgang Brüser^a, Frank T. Edelmann^{a,*}

^a *Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, Gebäude M, D-39106 Magdeburg, Germany*
^b *Institut für Anorganische Chemie der Universität Göttingen, Tammannstr. 4, D-37077 Göttingen, Germany*

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Abstract

The new anionic sandwich complexes $[\text{Li}(\text{THF})_4][\text{Ln}(\text{COT}^*)_2]$ (1–5, Ln = Ce, Pr, Nd, Sm, Y) have been prepared by treatment of anhydrous lanthanide trichlorides with two equivalents of Li_2COT^* [$\text{COT}^* = \text{C}_8\text{H}_6(\text{SiMe}_3)_{2-1,4}$]. Ion exchange of 4 with [PPN]Cl affords the derivative [PPN][Sm(COT^{*})₂] (6). Similarly, the hexasilylated sandwich salt $[\text{K}(\text{THF})_3][\text{Tb}(\text{COT}^{*'})_2]$ (7) [$\text{COT}^{*'} = \text{C}_8\text{H}_5(\text{SiMe}_3)_{1-3,6}$] has been obtained by reacting anhydrous TbCl_3 with $\text{K}_2\text{COT}^{*'}$ in a 1:2 molar ratio. The molecular structure of 4 has been determined by X-ray diffraction. © 1997 Elsevier Science S.A.

Keywords: Sandwich complexes; Organolanthanide complexes; Cyclooctatetraenyl ligands

1. Introduction

The chemistry of rare earth cyclooctatetraenyl complexes is currently receiving renewed interest [1–3]. It is now generally recognized, that the large, flat cyclooctatetraenyl ligand ($\text{COT} = \text{C}_8\text{H}_8^{2-}$) is ideally suited to stabilize organolanthanide complexes [4]. In addition, it has been recently discovered by Schumann et al. that certain $(\text{COT})\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)$ sandwich complexes are surprisingly volatile and may be used as precursors in MOCVD processes [5,6]. In some cases, however, the synthetic value of lanthanide complexes containing the unsubstituted cyclooctatetraenyl dianion is somewhat diminished due to low solubility. This is the case for example with the polymeric lanthanide(II) derivatives $\text{Ln}(\text{COT})$ (Ln = Sm, Eu, Yb) [7,8] and the dimeric chloro complexes $[(\text{COT})\text{Ln}(\mu\text{-Cl})(\text{THF})_2]_2$ [9–12] which are only marginally soluble even in tetrahydrofuran. Interesting differences in solubility as well as structural chemistry are observed when the bulky 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand (= COT^*) is em-

ployed. This easily accessible silylated cyclooctatetraenyl ligand has been introduced into organolanthanide chemistry by Cloke et al. [13,14]. Complexes such as $[(\text{COT}^*)\text{Y}(\mu\text{-Cl})(\text{THF})_2]_2$ are much more soluble than the parent chloro complexes. The related scandium derivative $(\mu\text{-Cl})_2(\mu\text{-THF})[\text{Sc}(\text{COT}^*)]_2$ has been shown to contain an unusual semibridging THF ligand [13]. We report here the use of the COT^* ligand in the preparation of several anionic sandwich complexes of the type $[\text{Ln}(\text{COT}^*)_2]^-$ as well as the structural characterization of the samarium derivative. The cerium complex $[\text{Li}(\text{THF})_4][\text{Ce}(\text{COT}^*)_2]$ (1) had been used earlier as an intermediate in the synthesis of the silylated cerocene derivative $\text{Ce}^{\text{IV}}(\text{COT}^*)_2$, but in this case the anionic cerium(III) species was only prepared in situ and not isolated [15,16].

2. Results and discussion

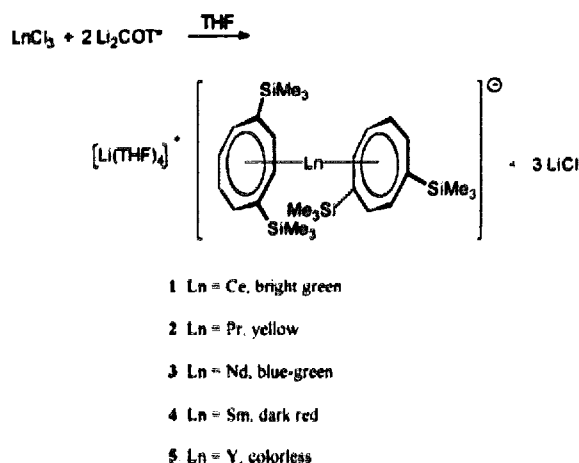
2.1. Synthesis and spectroscopic characterization

The starting material $\text{Li}_2[\text{C}_8\text{H}_6(\text{SiMe}_3)_{2-1,4}]$ (= Li_2COT^*) was prepared according to Cloke et al. [13,17] by a slightly modified in situ procedure and

* Corresponding author.

¹ For Part VII see Ref. [31].

used without isolation. Treatment of anhydrous lanthanide trichlorides with two equivalents of Li_2COT^+ in THF solution (molar ratio 1:2) according to Eq. (1) afforded the anionic sandwich complexes $[\text{Li}(\text{THF})_4][\text{Ln}(\text{COT}^+)_2]$ (1–5, Ln = Ce, Pr, Nd, Sm, Y) in 60–70% yield:

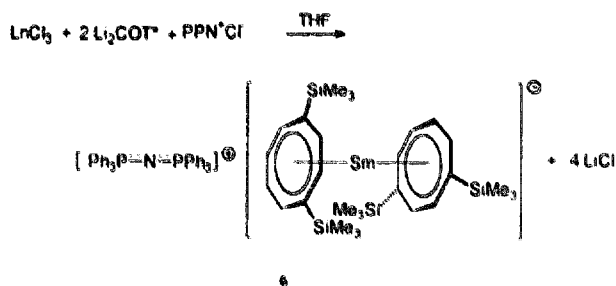


In the case of **2** a pure product was obtained only when anhydrous $\text{Pr}(\text{O}_3\text{SCF}_3)_3$ was used as a starting material instead of praseodymium trichloride. Except for the yttrium derivative **5** the new compounds exhibit the characteristic bright colors of organolanthanide complexes containing cyclooctatetraenyl ligands. They are readily soluble in toluene and moderately soluble even in hexane. This solubility behavior can be attributed to the presence of four lipophilic trimethylsilyl substituents in the molecules. As is generally observed for organolanthanide complexes, the compounds 1–5 are highly air-sensitive but thermally very robust with decomposition points above 280°C . Especially the cerium derivative **1** is vigorously air-sensitive and the bright green solid immediately turns purple in contact with traces of air (formation of neutral $\text{Ce}(\text{COT}^+)_2$ [15]). All five compounds are readily characterized by their spectroscopic data. Only mass spectrometric measurements were not helpful due to the salt-like character of the compounds. Mass spectra of **4** and **5** showed no metal-containing peaks. The IR spectra of 1–5 are almost superimposable. Strong bands around ν 1235, 919, and 840 cm^{-1} can be attributed to the SiMe_3 substituents. Broad bands at ν 1260 and 1160 as well as strong bands at 1090, 1050, 780, 750, and 735 cm^{-1} are characteristic for the COT^+ ligands. The latter three bands are due to *out-of-plane* vibrations.

NMR data confirm the presence of solvent-separated ion-pairs. In the ^1H NMR spectra the protons of the $[\text{Li}(\text{THF})_4]^+$ ions give rise to sharp resonances. Particularly strong paramagnetic shifts are observed for the ring proton resonances of **3** and **4**. For Ln = Nd (**3**) high

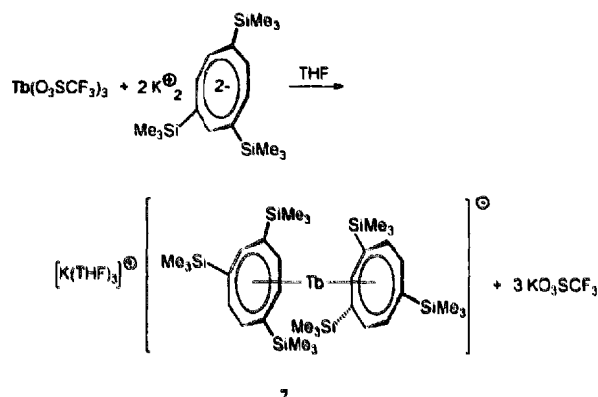
field-shifted signal are found for the ring protons at δ –7.44, –8.68, and 10.54 ppm ($\nu_{1/2}$ ca. 160–180 Hz), respectively, while the SiMe_3 peak is less influenced (δ –0.37 ppm). In the case of **3** (Ln = Sm) the SiMe_3 resonance is shifted to lower field (δ 2.62 ppm) while the signals for the ring protons appear at δ 13.35, 13.39, and 12.09 ppm ($\nu_{1/2}$ ca. 30–40 Hz). With chemical shifts in the range between –2.5 and –2.9 ppm the ^7Li resonances of **1** and **4** are not significantly different from that of the diamagnetic yttrium derivative **5**. In the case of **2** and **3** a slight shift is observed (δ 0.7 (**2**), –0.9 (**3**) ppm). ^{29}Si NMR spectra have been recorded for all five complexes, showing in each case a singlet for the SiMe_3 groups (1: δ –13.9, 2: 7.4, 3: 0.4, 4: 24.4, 5: 1.0 ppm). An interpretable $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum could be obtained only for the diamagnetic yttrium derivative **5**. Coupling with the yttrium nucleus was observed for the four ring-carbon resonances at δ 99.4, 99.3, 97.6, 97.3 ppm. The observed $^1J(^{89}\text{Y}-^{13}\text{C})$ coupling constants in the range of 1.5–2.4 Hz are typical for organoyttrium complexes containing cyclooctatetraenyl ligands [12,18,19]. Previously recorded ^{89}Y NMR resonances have been found to be in the range between δ +895 ppm (for $\text{Y}[\text{CH}(\text{SiMe}_3)_2]_3$ [20]) and ca. –200 ppm [21]. Thus, the ^{89}Y chemical shift of **5** (δ –195.5 ppm) differs only marginally from that of the parent sandwich ion in $[\text{K}(\text{THF})_3][\text{Y}(\text{COT}^+)_2]$ (δ –209.7 ppm) [22].

Salts containing other cations than $[\text{Li}(\text{THF})_4]^+$ are also available as shown by the preparation of the $[\text{PPN}]^+$ derivative of the samarium sandwich anion ($\text{PPN}^+ = \text{Ph}_3\text{P}^+\text{N}^-\text{PPh}_3$). It is not even necessary to use the isolated the lithium salts as precursors. The PPN^+ derivative **6** was prepared according to Eq. (2) in a 'one pot' reaction by treatment of anhydrous SmCl_3 simultaneously with two equivalents of Li_2COT^+ and one equivalent of PPN^+Cl^- :



In the ^1H NMR spectrum of **6** the resonances of the ring protons (δ 13.79, 13.41, 12.02 ppm) and the SiMe_3 groups (δ 2.57 ppm) are very similar to those of the corresponding lithium salt **4**. The ^{29}Si signal is observed at δ 24.6 ppm and the ^{31}P resonance of the PPN^+ cation occurs at δ 24.3 ppm. IR bands at ν 1247, 910, and 835 cm^{-1} are characteristic for the SiMe_3 groups.

Similar anionic sandwich complexes are also accessible with the recently described 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl ligand (= COT^{••}). The cerium derivative $K[\text{Ce}(\text{COT}^{\bullet\bullet})_2]$ had already been used as an intermediate in the preparation of 1,1',3,3',6,6'-hexakis(trimethylsilyl)cerocene(IV) [15]. The corresponding terbium(III) complex would be of interest as a potential precursor for a molecular terbium(IV) complex. Organoterbium(IV) complexes are unknown, although, provided the right choice of ancillary ligands they might be stable, as terbium(IV) has a half-filled 4f shell. The anionic sandwich complex **7** was obtained in moderate yield by reacting anhydrous terbium(III) triflate with two equivalents of $\text{K}_2\text{COT}^{\bullet\bullet}$ (Eq. (3)):



The potassium salt **7** is thermally highly stable and decomposes slowly above 303°C. As is typical for Tb(III) complexes (f^8) [21] the ¹H NMR signals of **7** are quite broad and exhibit strong paramagnetic shifts. For example, the line width at half intensity of the ring proton resonance at δ 27.34 ppm is 780 Hz. The remaining two ring proton resonances are found at δ 52.52 and -78.84 ppm. As expected, the ²⁹Si NMR spectrum shows two signals for the trimethylsilyl substituents (δ -5.6 , 6.0 ppm). Thus far an attempted oxidation to afford neutral $\text{Tb}(\text{COT}^{\bullet\bullet})_2$ was unsuccessful. Treatment of **7** with various oxidizing agents such as AgI, AgAsF₆, XeF₂ or NO⁺BF₄⁻ only resulted in extensive decomposition and formation of insoluble materials.

2.2. Crystal structure determination of **4** [23]

Large, dark red single crystals of **3** have been obtained by slow cooling of a saturated solution in hot hexane. Table 1 contains the atomic coordinates and isotropic displacement parameters for **4**. The X-ray crystallographic investigation confirms the presence of a solvent-separated ion-pair containing a $[\text{Li}(\text{THF})_4]^+$ cation and a samarium sandwich complex as anion (Fig. 1). This is in good agreement with the O–Li–O angles,

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-3}$) for **4**. $U(\text{eq})$ is calculated as one-third of the trace of the orthogonal U_{ij} tensor

	x	y	z	$U(\text{eq})$
Sm(1)	996(1)	318(1)	2345(1)	27(1)
C(1)	-915(4)	1628(4)	3095(3)	31(1)
C(2)	25(4)	2290(4)	3010(3)	31(1)
C(3)	831(5)	2619(4)	2459(3)	35(1)
C(4)	1095(5)	2439(4)	1740(3)	33(1)
C(5)	577(5)	1834(4)	1290(3)	36(1)
C(6)	-355(5)	1201(5)	1354(3)	35(1)
C(7)	-1175(5)	894(5)	1896(3)	38(1)
C(8)	-1403(4)	1068(4)	2611(3)	33(1)
C(9)	1161(5)	-1356(4)	3334(2)	31(1)
C(10)	2051(4)	-724(4)	3420(2)	30(1)
C(11)	2990(4)	-313(4)	2986(2)	30(1)
C(12)	3378(4)	-433(4)	2270(3)	32(1)
C(13)	3030(5)	-939(4)	1712(3)	34(1)
C(14)	2140(5)	-1572(4)	1607(3)	32(1)
C(15)	1226(5)	-1948(5)	2069(3)	37(1)
C(16)	824(5)	-1867(5)	2778(3)	37(1)
Si(1)	-1653(1)	1505(1)	3998(1)	35(1)
C(17)	-3031(5)	2686(6)	4159(3)	52(2)
C(18)	-2122(6)	77(5)	4180(3)	52(2)
C(19)	-645(6)	1676(6)	4643(3)	52(2)
Si(2)	2376(2)	3138(1)	1270(1)	45(1)
C(20)	3657(6)	2051(6)	901(3)	64(2)
C(21)	1731(8)	4060(7)	550(4)	77(2)
C(22)	2866(7)	4089(6)	1846(3)	63(2)
Si(3)	3899(1)	442(1)	3471(1)	37(1)
C(23)	5064(6)	1056(6)	2887(3)	59(2)
C(24)	2956(6)	1663(6)	3999(3)	53(2)
C(25)	-4680(6)	-661(6)	4064(3)	53(2)
Si(4)	2245(2)	-1986(1)	686(1)	39(1)
C(26)	822(6)	-2398(6)	505(3)	56(2)
C(27)	3539(6)	-3231(5)	502(3)	51(2)
C(28)	2531(8)	-774(6)	65(3)	63(2)
Li(1)	-3409(8)	-3979(8)	2912(4)	39(2)
O(30)	-2958(3)	-5349(3)	2372(2)	42(1)
C(31)	-1932(6)	-5558(6)	1843(3)	56(2)
C(32)	-2388(7)	-6008(6)	1241(3)	66(2)
C(33)	-3533(7)	-6411(7)	1544(4)	69(2)
C(34)	-3604(6)	6252(5)	2300(3)	52(2)
O(40)	-5029(4)	-3936(4)	3361(2)	51(1)
C(41)	-6105(6)	-3695(6)	3032(4)	63(2)
C(42)	-7015(7)	-4260(8)	3487(5)	89(3)
C(43)	-6607(13)	-4401(17)	4115(5)	190(9)
C(44)	-5340(7)	-4270(8)	4062(4)	79(2)
O(50)	-2248(4)	-3974(3)	3529(2)	50(1)
C(51)	-2280(7)	-3193(6)	4059(4)	69(2)
C(52)	-1144(7)	-3552(6)	4375(4)	69(2)
C(53)	-609(7)	-4722(7)	4108(4)	71(2)
C(54)	-1072(6)	-4709(6)	3428(4)	61(2)
O(60)	-3323(4)	-2734(3)	2232(2)	51(1)
C(61)	-2378(8)	-2079(7)	2047(4)	80(2)
C(62)	-2458(13)	-1721(12)	1318(5)	147(6)
C(63)	-3570(8)	-1822(10)	1157(5)	98(3)
C(64)	-4041(6)	-2664(6)	1677(4)	62(2)

which are all fairly close to the tetrahedral angle. The O(50)–Li–O(60) angle, which should open up in the case of a possible interaction with the anion, is even smaller (103.2(4)°). With 187.8(1) pm the average Li–O

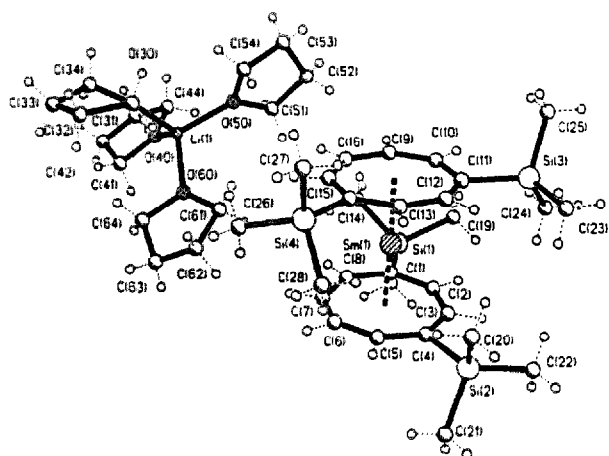


Fig. 1. Molecular structure of **4**. Selected distances (pm) and angles ($^{\circ}$) (X1A and X1B = ring centroids): Li(1)–O 187.8(1) av., Sm(1)–X1A 196.5, Sm(1)–X1B 196.6; X1A–Sm(1)–X1B 177.2, O(30)–Li(1)–O(50) 109.8(4), O(30)–Li(1)–O(40) 107.6(5), O(50)–Li(1)–O(40) 114.1(5), O(30)–Li(1)–O(60) 103.2(4), O(50)–Li(1)–O(60) 109.5(5), O(40)–Li(1)–O(60) 112.1(5).

distance is shorter than that in the related cerium sandwich complex $[\text{Li}(\text{THF})_4][\text{Ce}(\text{COT})_2]$ (Li–O 193(1) pm [24]). The distances between the central Sm atom and the ring centroids in the sandwich anion are 196.5 and 196.6 pm, respectively. In $[\text{Li}(\text{THF})_4][\text{Ce}(\text{COT})_2]$ the corresponding Ce–ring centroid distance is 104.3 pm [24,25]. Taken into account a difference in ionic radii between ten-coordinated Sm^{3+} and ten-coordinated Ce^{3+} of 12 pm, the expected Sm–ring centroid distance would be 192.3 pm. The observed slight elongation of 4.3 pm certainly reflects the steric influence of the four bulky SiMe_3 substituents. With 177.2° the ring centroid–Ce–ring centroid angle is almost linear. The conformation of the anion in **4** is comparable to that in 1,1',2,2'-tetrakis(trimethylsilyl)ferrocene [26]. It deviates from the fully eclipsed conformation by 79.4° . Slight deviations from the ideal sandwich structure arise from steric interactions between opposite SiMe_3 groups, as the shortest contact (Si(2)–Si(3)) is only 553.5 pm. The *van der Waals* radius of a trimethylsilyl group is approximately 380 pm [27].

3. Experimental part

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.). All ^1H NMR spectra were measured at a temperature of 32°C . Elemental analyses:

Analytical laboratory of the Department of Inorganic Chemistry, University of Göttingen. Crystal structure determination [23]: Siemens-Stoe AED2 four-circle diffractometer, graphite-monochromated Mo- K_{α} radiation ($\lambda = 71.073$ pm), measuring temperature -120°C ; structure solution (direct methods) and refinement with SHELXTL PLUS (PC version). All non-hydrogen atoms were refined anisotropically. A semiempirical absorption correction was employed. The starting materials 1,4- $(\text{Me}_3\text{Si})_2\text{C}_8\text{H}_8$ [13,17], $\text{K}_2(\text{THF})_3(\text{COT}^{2-})$ [15], LnCl_3 (Ln = Ce, Nd, Sm, Y) [28], PPN^+Cl^- [29] and $\text{Ln}(\text{O}_3\text{SCF}_3)_3$ (Ln = Pr, Tb) [30] were prepared according to literature procedures.

3.1. Modified preparation of Li_2COT^+ [13,17]

2.00 g (8.0 mmol) of thoroughly dried 1,4-bis(trimethylsilyl)cyclooctatriene are dissolved in 100 ml THF and cooled to -78°C . 6.9 ml (16.0 mmol) of a 2.31 M solution of *n*-butyllithium in hexane are added with stirring. The mixture is allowed to warm to room temperature and stirring is continued for 15 h. The resulting solution is used directly for the following preparations.

3.2. Preparation of tetrakis(tetrahydrofuran)lithium-bis[1,4-bis(trimethylsilyl)cyclooctatetraenyl]lanthanidate(III) (general procedure)

4.0 mmol anhydrous LnCl_3 are added as a solid at room temperature to a vigorously stirred solution of 8.0 mmol Li_2COT^+ in 100 ml THF and the mixture is stirred at room temperature for 48 h, during which time LiCl precipitates as a finely divided white solid. All volatiles are removed in vacuo, the residue is extracted with 200 ml of hot toluene and filtered while hot through a thin layer of Celite filter aid. The clear filtrate is evaporated to dryness and the residue is washed with 20 ml of hexane. Drying under vacuum affords the crude product, which may be recrystallized from toluene/hexane mixtures at -20°C . Due to its enhanced solubility in hexane the cerium derivative **1** is preferentially purified by Soxhlet extraction of the crude product with hexane followed by concentration and cooling of the extract to -20°C .

3.2.1. Tetrakis(tetrahydrofuran)lithium-bis[1,4-bis(trimethylsilyl)cyclooctatetraenyl]cerate(III) (**1**)

Yield: 2.50 g (67%), bright green, highly air-sensitive solid, m.p. $> 280^{\circ}\text{C}$ (dec.). A satisfactory elemental analysis was not obtained due to the extreme air-sensitivity of **1**. $\text{C}_{44}\text{H}_{80}\text{CeLiO}_4\text{Si}_4$ (932.52). IR (Nujol) (cm^{-1}): 1406 (w), 1307 (w), 1261 (s), 1246 (vs), 1165 (w), 1091 (s br), 1047 (vs), 1043 (s sh), 1028 (w sh), 977 (m), 932 (m), 902 (m), 836 (vs), 811 (s sh), 780 (m), 749 (s), 738 (s), 682 (m), 660 (w), 635 (m), 554

(m), 468 (m), 377 (vs). ^1H NMR (CD_3CN): δ 3.79 (m, 16 H, THF), 3.38 (br, $\nu_{1/2} = 22$ Hz, 4 H, ring-H), 2.74 (br, $\nu_{1/2} = 20$ Hz, 40 H, ring-H + SiMe_3), 2.43 (br, $\nu_{1/2} = 20$ Hz, 4 H, ring-H), 1.81 (m, 16 H, THF) ppm. ^7Li NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ -2.5 (s, $\nu_{1/2} = 4$ Hz) ppm. ^{29}Si NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ -13.9 (s br, $\nu_{1/2} = 17$ Hz) ppm.

3.2.2. Tetrakis(tetrahydrofuran)lithium-bis[1,4-bis(trimethylsilyl)cyclooctatetraenyl]praseodymate(III) (2)

In this case the general procedure did not yield a pure product and therefore it was modified as follows: A suspension of 8.6 g (14.6 mmol) anhydrous $\text{Pr}(\text{O}_3\text{SCF}_3)_3$ in 50 ml THF is added at 0°C to a stirred solution of freshly prepared Li_2COT^+ (29.1 mmol) in 40 ml THF and the brown reaction mixture is stirred for 3 d at room temperature. After evaporation to dryness the residue is extracted with 100 ml of boiling toluene and filtered while hot. Removal of the solvent followed by recrystallization of the crude product from 50 ml of hexane affords 9.2 g (68%) of a yellow solid, which decomposes above 351°C . Found: C, 54.8; H, 8.2. $\text{C}_{44}\text{H}_{80}\text{LiO}_4\text{PrSi}_4$ (933.3) calcd.: C, 56.6; H, 8.6%. IR (Nujol) (cm^{-1}): 1941 (m), 1627 (m), 1236 (vs), 1174 (vs), 1062 (vs), 977 (m), 895 (vs), 839 (s), 649 (vs), 591 (m), 555 (m), 518 (s), 405 (vs), 353 (vs), 334 (vs), 307 (vs). ^1H NMR (C_6D_6): δ 6.00 (m, 16 H, THF), 2.71 (m, 16 H, THF), -5.60 (s, 36 H, SiMe_3), -6.58 bis -8.19 (m, 12 H, ring-H) ppm. ^7Li NMR (toluene- d_8): δ 0.7 (s br, $\nu_{1/2} = 21$ Hz) ppm. ^{29}Si NMR (toluene- d_8): δ 7.4 (s) ppm.

3.2.3. Tetrakis(tetrahydrofuran)lithium-bis[1,4-bis(trimethylsilyl)cyclooctatetraenyl]neodymate(III) (3)

Yield: 2.32 g (62%), blue-green crystals, m.p. $> 300^\circ\text{C}$ (dec.). Found: C, 54.5; H, 8.3. $\text{C}_{44}\text{H}_{80}\text{LiNdO}_4\text{Si}_4$ (936.6) calcd.: C, 56.4; H, 8.6%. IR (Nujol) (cm^{-1}): 1402 (w), 1308 (w), 1262 (s), 1247 (vs), 1209 (w), 1177 (w sh), 1148 (w sh), 1093 (s br), 1049 (vs), 1029 (s sh), 979 (m), 933 (m), 899 (m), 835 (vs), 810 (s sh), 785 (m sh), 750 (s), 734 (s), 682 (m), 658 (w sh), 635 (m), 555 (m), 513 (m), 459 (w), 350 (s). ^1H NMR (CD_3CN): δ 3.68 (m, 16 H, THF), 1.82 (m, 16 H, THF), -0.37 (s, 36 H, SiMe_3), -7.44 (br, $\nu_{1/2} = 168$ Hz, 4 H, ring-H), -8.68 (br, $\nu_{1/2} = 180$ Hz, 4 H, ring-H), -10.54 (br, $\nu_{1/2} = 161$ Hz, 4 H, ring-H) ppm. ^7Li NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ -0.9 (s br, $\nu_{1/2} = 13$ Hz) ppm. ^{29}Si NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ 0.4 (s) ppm.

3.2.4. Tetrakis(tetrahydrofuran)lithium-bis[1,4-bis(trimethylsilyl)cyclooctatetraenyl]samarate(III) (4)

Yield: 2.62 g (70%), dark red crystals, m.p. $> 290^\circ\text{C}$ (dec.). Found: C, 54.6; H, 8.2. $\text{C}_{44}\text{H}_{80}\text{LiO}_4\text{Si}_4\text{Sm}$ (942.8) calcd.: C, 56.1; H, 8.6%. IR (Nujol) (cm^{-1}): 1309 (m), 1261 (s), 1247 (s), 1175 (w), 1158 (w), 1092 (s br), 1055 (vs), 1025 (s), 981 (w), 934 (m), 909 (m),

835 (vs), 802 (m), 782 (m sh), 749 (m), 731 (m), 692 (s), 682 (m sh), 663 (w), 634 (m), 560 (w), 515 (w), 463 (w), 341 (s). EI-MS (70 eV) m/z (rel. int.%): 248 [$\text{C}_8\text{H}_6(\text{SiMe}_3)_2$, 9], 233 [$\text{C}_8\text{H}_6(\text{SiMe}_3)_2-\text{CH}_3$, 2], 160 [$\text{C}_8\text{H}_6\text{SiMe}_3$, 31], 146 [Si_2Me_6 , 20], 73 [SiMe_3 , 100]. ^1H NMR (CD_3CN): δ 13.85 (br, $\nu_{1/2} = 37$ Hz, 4 H, ring-H), 13.39 (br, $\nu_{1/2} = 39$ Hz, 4 H, ring-H), 12.09 (br, $\nu_{1/2} = 33$ Hz, 4 H, ring-H), 3.69 (m, 16 H, THF), 2.62 (s, 36 H, SiMe_3), 1.93 (m, 16 H, THF) ppm. ^7Li NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ -2.9 (s br, $\nu_{1/2} = 53$ Hz) ppm. ^{29}Si NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ 24.4 (s br, $\nu_{1/2} = 30$ Hz) ppm.

3.3. Tetrakis(tetrahydrofuran)lithium-bis[1,4-bis(trimethylsilyl)cyclooctatetraenyl]yttriate(III) (5)

Yield: 2.55 g (72%), colorless crystals, m.p. $> 310^\circ\text{C}$ (dec.). Found: C, 58.6; H, 8.2. $\text{C}_{44}\text{H}_{80}\text{LiO}_4\text{Si}_4\text{Y}$ (881.3) calcd.: C, 60.0; H, 9.1%. IR (Nujol) (cm^{-1}): 1400 (w), 1307 (w), 1261 (s), 1247 (vs), 1169 (w sh), 1155 (w sh), 1091 (s br), 1050 (vs), 1022 (br sh), 979 (m), 934 (m), 901 (m), 831 (vs br), 824 (s sh), 801 (m sh), 780 (m sh), 750 (s), 739 (s), 732 (s), 682 (m), 660 (w sh), 636 (m), 553 (m), 510 (m), 463 (w), 360 (vs). EI-MS (70 eV) m/z (rel. int.%): 248 [$\text{C}_8\text{H}_6(\text{SiMe}_3)_2$, 4], 233 [$\text{C}_8\text{H}_6(\text{SiMe}_3)_2-\text{CH}_3$, 4], 160 [$\text{C}_8\text{H}_6\text{SiMe}_3$, 10], 146 [Si_2Me_6 , 20], 73 [SiMe_3 , 100]. ^1H NMR (CD_3CN): δ 6.17–5.87 (m, 12 H, ring-H), 3.65 (m, 16 H, THF), 1.81 (m, 16 H, THF), 0.41 (s, 36 H, SiMe_3) ppm. ^7Li NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ -2.8 (s, $\nu_{1/2} = 5$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 99.4 (d, $^1J(^{89}\text{Y}-^{13}\text{C}) = 2.4$ Hz, ring-C), 99.3 (d, $^1J(^{89}\text{Y}-^{13}\text{C}) = 1.9$ Hz, ring-C), 97.6 (d, $^1J(^{89}\text{Y}-^{13}\text{C}) = 1.5$ Hz, ring-C), 97.3 (d, $^1J(^{89}\text{Y}-^{13}\text{C}) = 2.1$ Hz, ring-C), 68.4 (s, THF), 26.2 (s, THF), 1.3 (s, SiMe_3) ppm. ^{29}Si NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ 1.0 (s) ppm. ^{89}Y NMR ($\text{THF}/\text{C}_6\text{D}_6$): δ -195.5 (s, $\nu_{1/2} = 5$ Hz) ppm.

3.4. [Bis(triphenylphosphine)immonium][bis[1,4-bis(trimethylsilyl)cyclooctatetraenyl]samarate(III)] (6)

0.770 g (3.0 mmol) anhydrous SmCl_3 and 1.72 g (3.0 mmol) PPN^+Cl^- are added successively to a stirred solution of Li_2COT^+ (6.0 mmol) in 100 ml THF and the resulting deep red solution is stirred for 24 h at room temperature. All volatiles are evaporated in vacuo, the oily residue is extracted with 200 ml of hot toluene and filtered while hot through a thin layer of Celite filter aid. The clear filtrate is evaporated to dryness and the residue is redissolved in 50 ml acetonitrile. The solution is concentrated to a total volume of ca. 10 ml. Cooling to -20°C (24 h) affords 0.44 g (12%) **5** as dark red crystals. M.p. 236°C . Found: C, 64.2; H, 6.0; N, 1.4. $\text{C}_{64}\text{H}_{78}\text{NP}_2\text{Si}_4\text{Sm}$ (1186.0) calcd.: C, 64.8; H, 6.6; N, 1.2%. IR (Nujol) (cm^{-1}): 1582 (w), 1538 (w), 1440 (vs), 1417 (m), 1335 (m), 1309 (m), 1261 (s),

1247 (vs), 1115 (vs), 1096 (s sh), 1052 (vs), 1025 (s), 981 (m), 934 (s), 910 (m), 835 (vs), 802 (s), 794 (s sh), 749 (s), 721 (vs), 692 (s), 678 (m sh), 634 (m), 535 (vs), 500 (s), 450 (w), 394 (w). $^1\text{H NMR}$ (CD_3CN): δ 13.79 (br, $\nu_{1/2} = 33$ Hz, 4 H, ring-H), 13.41 (br, $\nu_{1/2} = 36$ Hz, 4 H, ring-H), 12.02 (br, $\nu_{1/2} = 33$ Hz, 4 H, ring-H), 7.82–7.37 (m, 30 H, Ph), 2.57 (s, 36 H, SiMe_3) ppm. $^{29}\text{Si NMR}$ ($\text{THF}/\text{C}_6\text{D}_6$): δ 24.6 (s br, $\nu_{1/2} = 30$ Hz) ppm. $^{31}\text{P NMR}$ (CD_3CN): δ 24.3 (s) ppm.

3.5. [Tris(tetrahydrofuran)potassium][bis[1,3,6-tris(trimethylsilyl)cyclooctatetraenyl]terbate(III)] (7)

2.46 g (4.0 mmol) $\text{K}_2\text{COT}^{2+}$ (as the tris(THF) solvate) and 1.21 g (2.0 mmol) $\text{Tb}(\text{O}_3\text{SCF}_3)_3$ are dissolved in 60 ml THF and stirred for 24 h at room temperature. All volatiles are evaporated in vacuo, the oily residue is extracted with 80 ml of hot toluene and filtered while hot through a thin layer of Celite filter aid. The clear filtrate is evaporated to dryness and the residue is washed with 30 ml hexane. Drying under vacuum (6 h) affords 0.58 g (28%) of pyrophoric, colorless, microcrystalline solid. M.p. 303°C (dec.). A satisfactory elemental analysis was not obtained due to the pyrophoric nature of 6. $\text{C}_{46}\text{H}_{88}\text{KO}_3\text{Si}_6\text{Tb}$ (1055.7). IR (Nujol) (cm^{-1}): 1404 (w), 1309 (w), 1260 (s), 1247 (vs), 1166 (w), 1153 (w), 1090 (s br), 1048 (s br), 976 (m), 933 (m), 902 (m), 835 (vs), 812 (s sh), 778 (m), 748 (s), 737 (s), 684 (m), 659 (w), 635 (m), 553 (m), 518 (m), 468 (m), 377 (s). $^1\text{H NMR}$ (CD_3CN): δ 89.73 (s, $\nu_{1/2} = 165$ Hz, 18 H, 6,6'- SiMe_3), 82.50 (s, $\nu_{1/2} = 170$ Hz, 36 H, 1,1',3,3'- SiMe_3), 52.53 (s, $\nu_{1/2} = 200$ Hz, 2 H, COT^{2+} -2-H), 27.34 (br, $\nu_{1/2} = 280$ Hz, 4 H, ring-H), 3.74 (m, 12 H, THF), 2.09 (m, 12 H, THF), = 78.84 (br, $\nu_{1/2} = 270$ Hz, 4 H, ring-H) ppm. $^{29}\text{Si NMR}$ ($\text{THF}/\text{C}_6\text{D}_6$): δ = 5.6 (s), = 6.0 (s) ppm.

3.6. Crystal data of 4

$\text{C}_{44}\text{H}_{80}\text{LiO}_4\text{Si}_4\text{Sm}$ (942.8); crystal dimensions: 0.6 × 0.6 × 0.2 mm; triclinic, $P\bar{1}$, $a = 1143.4(2)$, $b = 1176.0(2)$, $c = 1970.0(4)$ pm; $\alpha = 87.16(3)$, $\beta = 81.97(3)$, $\gamma = 78.50(3)^\circ$; $V = 2.5697(8)$ nm³; $d_{\text{calc}} = 1.218$ g cm⁻³; $Z = 2$, $\mu(\text{Mo K}\alpha) = 1.271$ mm⁻¹; 6711 measured and 6708 symmetry-independent reflexions; 6705 reflexions observed with $F \geq 3\sigma(F)$; 499 refined parameters; $2\theta_{\text{max}} = 45^\circ$; goodness-of-fit: 1.030; $R = 0.0452$; max/min residual electron intensity 1470/–1789 e nm⁻³.

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