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Terphenyl Cyclooctatetraenyl Compounds of Samarium

Gerd W. Rabe,*[†] Mei Zhang-Presse,[†] Florian A. Riederer,[†] James A. Golen,[‡] Christopher D. Incarvito,[§] and Arnold L. Rheingold[||]

Technische Universität München, Anorganisch-chemisches Institut, Lichtenbergstrasse 4, 85747 Garching, Germany, Department of Chemistry, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts 02747, Department of Chemistry, Yale University, New Haven, Connecticut 06520, and Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093

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The syntheses and molecular structures of a number of terphenyl-based compounds of the lanthanide element samarium are reported. Reaction of 2 equiv of DppLi (Dpp = 2,6-diphenylphenyl) with 1 equiv of $SmCl_3$ in tetrahydrofuran at room temperature yields $(Dpp)_2SmCl(\mu\text{-}Cl)Li(THF)_3$ (**1**). The one-pot reaction of 1 equiv of K_2COT (COT^{2-} = cyclooctatetraenyl dianion) with 1 equiv $SmCl_3$ in tetrahydrofuran at room temperature followed by addition of 1 equiv of terphenyllithium salt DppLi, DmpLi (Dmp = 2,6-dimesitylphenyl), or DanipLi (Danip = 2,6-di(*o*-anisol)phenyl) produces $DppSmCOT(\mu\text{-}Cl)Li(THF)_3$ (**2**), DmpSm(THF)COT (**3**), and DanipSm(THF)COT (**4**), respectively. In the case of the Danip-based compound **4** the order of addition of reagents can be reversed producing the same compound, however, in considerably lower yield. Compound **2** can also be prepared by reaction of **1** with 1 equiv of K_2COT in tetrahydrofuran. The molecular structure of the bis(terphenyl) compound **1** exhibits a formally four-coordinate metal atom. The molecular structures of the terphenyl COT compounds **2**–**4** feature monomeric complexes which are obtained either as a lithium chloride adduct (**2**) or as tetrahydrofuran adducts (**3, 4**). In **4** the Danip ligand adopts the meso form.

Introduction

During the past decade there have been research activities in the field of terphenyl-based compounds, mostly involving p block but also some s block as well as late d block elements using a variety of different terphenyl ligand systems.[1,2] Compared with a fairly large number of known terphenyl-based compounds of the main group elements, the number of complexes of group 3 and f block elements containing terphenyl substituents as the only ancillary ligand is still relatively small. Terphenyl-based compounds have been reported for the group 3 elements scandium and yttrium as well as the lanthanide elements Sm–Lu[3–8] but not yet for the larger elements La–Nd. To date there are no published reports on terphenylactinide compounds, an area which is still to be developed.

Our efforts to develop the area of terphenyllanthanide compounds have demonstrated that a variety of monosubstituted compounds are accessible by salt metathesis reactions using different sterically demanding terphenyls such as Dmp [2,6-dimesitylphenyl][3,6,7] and Dnp [2,6-di(1-naphthyl)-phenyl][4] or the donor-functionalized ligand Danip [2,6-di-(*o*-anisol)phenyl].[5,8] We have also been investigating the reaction chemistry of Danip-based mono(terphenyl)lanthanide compounds, particularly the accessibility and structural characterization of further functionalized Danip-based compounds of general composition $DanipLnX_2$ employing

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* To whom correspondence should be addressed. E-mail: g.rabe@lrz.tum.de.
[†] Technische Universität München.
[‡] University of Massachusetts Dartmouth.
[§] Yale University.
[||] University of California at San Diego.

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both sterically encumbering mono anionic amides and alkoxides.[8]

Additionally, there are reports by Niemeyer et al. on the synthesis and structural characterization of both mono- and bis(terphenyl)lanthanide complexes of divalent ytterbium and europium containing the smallest terphenyl ligand Dpp [Dpp = 2,6-diphenylphenyl] as a supporting ligand.[9,10] Those compounds were prepared directly from the metal and Dpp iodide in tetrahydrofuran solution.

We here report our continued systematic investigations in this area of chemistry exploring the accessibility of terphenyl based lanthanide compounds vis-a-vis a dianionic ligand system, i.e. the cyclooctatetraenyl dianion, thereby providing more details on the reaction chemistry as well as structural aspects of terphenyl lanthanide compounds. We also report on the synthesis of a first example of a bis(terphenyl) compound of a trivalent lanthanide element.

The 10 π aromatic cyclooctatetraenyl dianion ($=COT^{2-}$) is the second most important ligand in organolanthanide chemistry, next to the cyclopentadienyl and the pentamethylcyclopentadienyl anion, which clearly dominate the area of organolanthanide chemistry.[11-13] The first report on a rare-earth element containing the COT^{2-} ligand was in 1969 by Hayes and Thomas.[14] The reaction of COT with metallic europium or ytterbium in liquid ammonia was described to produce mono-COT lanthanide complexes of composition $(COTLn)_x$. Other reports followed on COT compounds of the lighter and middle rare-earth elements of composition $COTLnCl(THF)_x$ ($x = 1$ or 2) and COT_2LnK, which were synthesized by reaction of 1 or 2 equiv of K_2COT with the corresponding lanthanide trichloride.[15-18] Mono-COT lanthanide(III) complexes represent the largest and most thoroughly studied group of rare-earth COT compounds.[11-13] We note that there is a report on a lanthanide aryl COT compound of the element lutetium using the internally chelating [(dimethylamino)methyl]phenyl ligand.[19] However, there are so far no reports on terphenyl COT compounds of the lanthanides.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk double-manifold, high-vacuum, and glovebox (MBraun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained by following typical laboratory procedures. Cyclooctatetraen was purchased from Aldrich and purified prior to use by drying over molecular sieves followed by three freeze−pump−thaw cycles and, finally, vacuum transfer. DppLi,[20] DmpLi,[21] DanipLi,[5,22] and K_2COT[23,24] were prepared according to the literature. K_2COT was not isolated but used in situ. $SmCl_3$ was purchased from Aldrich (packaged under argon in ampules) and was used as received. NMR spectra were recorded on a JMN-GX 400 instrument. ^{13}C NMR spectra were referenced to the solvent signals (benzene-d_6, 128.0 ppm; THF-d_8, 67.4 and 25.2 ppm, respectively).

$(Dpp)_2SmCl(\mu\text{-}Cl)Li(THF)_3$ (1). In the glovebox, a colorless suspension of $SmCl_3$ (257 mg, 1.0 mmol) in 5 mL of tetrahydrofuran was stirred overnight. Addition of a freshly prepared solution of (2,6-diphenylphenyl)lithium (472 mg, 2.0 mmol) in 5 mL of tetrahydrofuran gave a bright yellow solution. The reaction mixture was stirred for 30 min and was centrifuged. All volatiles were removed, and the residues were washed with hexanes. A couple of milliliters of toluene were added to the residues first, followed by stepwise addition of small amounts of tetrahydrofuran (upon stirring) until the residues were dissolved. The obtained solution was centrifuged, layered with a small portion of hexanes, and cooled to −30 °C. Repeated layering with additional small portions of hexanes over a period of several days resulted in almost quantitative crystallization of **1**. Removal of the mother liquor followed by drying under vacuum gave bright yellow **1** as a crystalline material (542 mg, 60%). Analytically pure **1** is insoluble in hexanes and only sparingly soluble in aromatic solvents but well soluble in tetrahydrofuran. Solutions of **1** in toluene or tetrahydrofuran at room temperature decompose slowly but appear to be unchanged over longer time periods if stored at −25 °C.

Anal. Calcd for $C_{48}H_{50}Cl_2LiO_3Sm$: C, 63.84; H, 5.58. Found: C, 63.62; H, 5.43. Mp: 84−86 °C (dec). ^1H NMR (C_4D_8O, 400 MHz, 25 °C): δ 5.00 (br s, 4H), 5.35 (br s, 2H), 7.24 (br s, 2H), 7.56 (br s, 1H), 8.28 (br s, 4H). We failed to detect any signals in the ^{13}C NMR spectrum in tetrahydrofuran-d_8 solution. We note that **1** is not sufficiently stable in THF solution at ambient temperature to allow for long time runs.

$DppSmCOT(\mu\text{-}Cl)Li(THF)_3$ (2). In the glovebox, a colorless suspension of $SmCl_3$ (257 mg, 1.0 mmol) in 5 mL of tetrahydrofuran was stirred overnight. A freshly prepared solution of K_2COT (1.0 mmol) in 5 mL of tetrahydrofuran was added to the suspension. The reaction mixture was stirred for 30 min yielding a purple suspension. A freshly prepared solution of DppLi (236 mg, 1.0 mmol) in tetrahydrofuran was slowly added via syringe. After being stirred for 10 min, the obtained red suspension was centrifuged and the mother liquor was removed. Washing of the residues with hexanes followed by extraction with toluene in the presence of a couple of drops tetrahydrofuran, centrifugation of the obtained red solution, and cooling to −25 °C resulted in crystallization of **2**. Removal of the mother liquor and drying under vacuum gave dark red **2** as microcrystalline material (447 mg, 60%). Analytically pure **2** is insoluble in hexanes, only sparingly soluble in aromatic solvents, but well soluble in tetrahydrofuran.

Anal. Calcd for $C_{38}H_{45}ClLiO_3Sm$: C, 61.47; H, 6.11. Found: C, 61.25; H, 6.04. Mp: 119−120 °C (dec). ^1H NMR (C_4D_8O, 400 MHz, 25 °C): δ 5.89 (d, $J_{H-H} = 7$ Hz, 4H), 6.00−6.05 (m, 6H),

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Table 1. Crystallographic Data for $(Dpp)_2SmCl(\mu\text{-}Cl)Li(THF)_3$ (**1**), $DppSmCOT(\mu\text{-}Cl)Li(THF)_3$ (**2**), DmpSm(THF)COT (**3**), and DanipSm(THF)COT (**4**)[a]

param	1	2	3	4
formula	$C_{48}H_{50}Cl_2LiO_3Sm$	$C_{38}H_{45}ClLiO_3Sm$	$C_{36}H_{41}OSm$	$C_{32}H_{33}O_3Sm$
fw	903.07	742.48	640.04	615.93
space group	$P2_1/c$	$P2_1/n$	Pbca	Pbca
a, Å	12.055(3)	12.7753(8)	14.1920(9)	8.3673(11)
b, Å	19.984(5)	16.8698(10)	14.9607(9)	19.780(3)
c, Å	18.316(4)	16.9344(11)	28.2053(18)	32.181(4)
β, deg	103.154(4)	103.4950(10)		
V, Å^3	4296.6(17)	3548.9(4)	5988.6(6)	5326.1(12)
Z	4	4	8	8
D_{calcd}, g cm^{-3}	1.396	1.390	1.420	1.536
temp, °C	−50(2)	−126(2)	−55(2)	−123(2)
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
$\mu_{MoK\alpha}$, cm^{-1}	15.30	17.63	19.87	22.36
GOF	1.049	1.042	1.186	1.055
R_1, % (obsd)	3.48	3.44	6.66	2.85
wR_2, % (all data)	9.28	8.72	15.00	7.47

[a] The quantity minimized was $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R_1 = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2Fc^2 + \max(F_o, 0]/3$.

7.48 (d, J_{H-H} = 7 Hz, 2H), 8.03 (t, J_{H-H} = 7 Hz, 1H), 9.51 (s, COT, 8H). ^{13}C NMR (C_4D_8O, 100.4 MHz, 25 °C): δ 78.6 (COT), 115.2, 123.8, 125.0, 126.7, 127.6, 145.3, 157.7. The signal corresponding to the ipso carbon atom could not be located, presumably due to the direct neighborhood of the paramagnetic samarium atom.

DmpSm(THF)COT (3) and DanipSm(THF)COT (4). In the glovebox, a colorless suspension of $SmCl_3$ (257 mg, 1.0 mmol) in 5 mL of tetrahydrofuran was stirred overnight. A freshly prepared solution of K_2COT (1.0 mmol) in 5 mL of tetrahydrofuran was added to the suspension. The reaction mixture was stirred for 30 min yielding a purple suspension. A freshly prepared solution of DmpLi (320 mg, 1.0 mmol) or DanipLi (296 mg, 1.0 mmol), respectively, in tetrahydrofuran was slowly added via syringe. After being stirred for 15 min, the obtained red suspension was centrifuged and the mother liquor was removed. Washing of the residues with hexanes followed by extraction with toluene, centrifugation of the obtained red solution, and cooling to −25 °C resulted in crystallization of **3** and **4**, respectively. Removal of the mother liquor and drying under vacuum gave red **3** and **4**, respectively, as microcrystalline material (**3**, 384 mg, 60%; **4**, 370 mg, 60%). Analytically pure **3** and **4** are insoluble in hexanes but soluble in aromatic solvents and quite soluble in tetrahydrofuran.

3. Anal. Calcd for $C_{36}H_{41}OSm$: C, 67.56; H, 6.46. Found: C, 67.35; H, 6.27. Mp: 130−140 °C (dec). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.92 (br, THF, 4H), 2.16 (s, *p*-Me, 6H), 2.21 (s, *o*-Me, 12H), 4,51 (br, THF, 4H), 6.29 (s, 4H), 6.50 (d, J_{H-H} = 7 Hz, 2H), 7.58 (t, J_{H-H} = 7 Hz, 1H), 9.28 (s, COT, 8H). ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): δ 22.2 (*o*-Me), 25.9 (*p*-Me), 29.9 (THF), 75.3 (THF), 83.9 (COT), 117.9, 134.8, 135.9, 150.9. We failed to detect in the ^{13}C NMR spectrum all aromatic signals of the terphenyl moiety which is probably due to overlap of the solvent signal with some of the signals. Also, the signal corresponding to the ipso carbon atom could not be located, presumably due to the direct neighborhood of the paramagnetic samarium atom.

4. Anal. Calcd for $C_{32}H_{33}O_3Sm$: C, 62.40; H, 5.40. Found: C, 62.23; H, 5.28. Mp: 180−185 °C (dec). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.69 (br s, OMe, 6H), 1.46 (s, THF, 4H), 3.67 (s, THF, 4H), 9.07 (s, COT, 8H) plus sets of signals in the aromatic region ranging from 6.31 to 8.03 ppm (11H). ^{1}H NMR (C_4D_8O, 400 MHz, 25 °C): δ −1.38 (br s, OMe, 6H), 10.37 (s, COT, 8H) plus sets of signals in the aromatic region ranging from 6.94 to 7.55 ppm (11H). We note that the chemical shift of the signal corresponding to the methoxy functions is concentration dependent. A ^{13}C-solution NMR spectrum of **4** could not be obtained because of the limited solubility of analytically pure **4** in benzene solution and limited stability in THF solution.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for Complexes 1−4. Crystal, data collection, and refinement parameters are given in Table 1. Data were collected on a Bruker AXS CCD system or a modified Siemens-Bruker Apex AXS CCD system. The systematic absences in the diffraction data are uniquely consistent for the reported space groups. All crystals were mounted on glass fibers with Paratone-N oil and cooled to indicated temperatures. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. SADABS absorption corrections were applied to all data sets. All non-hydrogen atoms except those exhibiting disorder were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. In **1**, carbon atoms C(37) and C(38) of one tetrahydrofuran ligand were disordered over two positions at 0.51 occupancy and carbon atom C(41) of another tetrahydrofuran molecule at 0.41 occupancy. These atoms were refined isotropically. Carbon atom C(40) exhibited a high thermal parameter, but its disorder could not be modeled. In **2**, the carbon atom pairs C(29), C(30) and C(31), C(33) and C(37), C(38) of the tetrahydrofuran ligands were disordered with occupancy 0.53, 0.56, and 0.40, respectively. These atoms were refined isotropically. Residual electron density for **1**−**3** were less than 1 e/A^3 and were within 1 Å of the samarium atoms. In **4**, residual electron density of 1.11 and 1.05 e/A^3 were found at 0.86 and 0.84 Å from the samarium atom.

All software and sources of the scattering factors are contained in SHELXTL (5.10) program library (G. M. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

$(Dpp)_2SmCl(\mu\text{-}Cl)Li(THF)_3$ (1). Reaction of 2 equiv of DppLi with 1 equiv of $SmCl_3$ in tetrahydrofuran solution at ambient temperature produces a heterobimetallic bis(terphenyl) compound of composition $(Dpp)_2SmCl(\mu\text{-}Cl)Li(THF)_3$ (**1**). It is noteworthy that **1** is also obtained using a 1:1 stoichiometry of reagents, leaving 0.5 equiv of unreacted $SmCl_3$ as a side product. The crude product of compound **1**

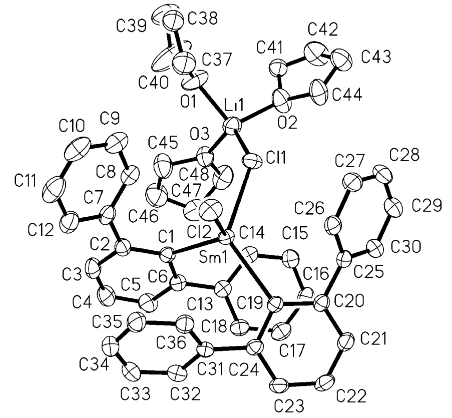

Figure 1. ORTEP diagram of $(Dpp)_2SmCl(\mu\text{-}Cl)Li(THF)_3$ (**1**), showing the atom labeling scheme. Thermal ellipsoids are at the 30% level. Disordered carbon atoms as well as hydrogen atoms were omitted for clarity.

slowly dissolves in toluene after dropwise addition of small amounts of tetrahydrofuran. Cooling of a toluene/tetrahydrofuran solution to −30 °C and repeated layering with small portions of hexanes (over several days) results in almost complete crystallization of yellow **1**. Analytically pure **1** is only sparingly soluble in toluene but quite soluble in tetrahydrofuran. Solutions of **1** in toluene or tetrahydrofuran at ambient temperature decompose slowly forming a colorless precipitate (presumably lithium chloride). We note that we failed to isolate any characterizable material from the remaining mother liquor. On the other hand, solutions of compound **1** show no visible signs of decomposition in both solvents at −30 °C, even over prolonged time periods.

The molecular structure of **1** (Figure 1) shows a samarium atom surrounded by two σ-bonded Dpp ligands and two chlorine atoms. In contrast to **1** all previously structurally characterized samarium terphenyl compounds were monosubstituted.[5,7,8] The Sm−C(ipso) distances [Sm−C(1) = 2.476(3) Å; Sm−C(19) = 2.489(3) Å] are somewhat shorter than the value found in the six-coordinate mono(terphenyl) compound $DmpSmCl_2(N\text{-}MeIm)_2THF$ [2.536(7) Å],[7] as one would expect in light of the lower coordination number at the metal atom in **1**. The coordination geometry about the metal atom can best be described as a distorted tetrahedron with interligand angles ranging from 99.00(3)° [Cl(1)−Sm(1)−Cl(2)] to 124.45(7)° [C(19)−Sm(1)−Cl(1)]. Besides the two Sm−C(ipso) distances the next closest Sm−C distances are to two ortho carbon atoms of phenyl rings in the 2,6-position belonging to different terphenyl moieties, namely atom C(36) [3.127(3) Å] and atom C(14) [3.151(3) Å]. As a consequence, both Dpp ligands are slightly tilted, as can be seen by inspecting the Sm(1)−C(*ipso*)−C(*ortho*) angles [124.9(2) and 116.7(2)° for the Dpp ligand containing atom C(1), 123.46(18)° and 118.14(19)° for the other]. The C(*ipso*)−C(*ortho*)−C(*ipso′*) angles are 119.2(3) and 117.9(2)° for the Dpp ligand containing atom C(1) [118.5(2) and 116.9(2)° for the other Dpp moiety]. The four dihedral angles between the central phenyl rings of the two Dpp ligands and the aryl rings in the 2,6-position are within a narrow range [40.8° (C(7−12)) and 42.6° (C(13−18)) for the Dpp ligand containing atom C(1), 39.3° (C(25−30)) and 42.5° (C(31−36)) for the other]. Atom Cl(1) is bridging with an Sm(1)−Cl(1)−Li(1) angle of 134.07(17)° while atom Cl(2) is a terminal chloride ligand. The bridging Sm−Cl distance [2.6673(9) Å] is only slightly longer than the terminal one [2.6174(9) Å]. The lithium atom in **1** is four-coordinate with a Li···Cl distance of 2.329(6) Å and Li−O distances ranging from 1.913(7) to 1.947(7) Å. Further interatomic distances and angles of **1** can be derived from Table 2.

$DppSmCOT(\mu\text{-}Cl)Li(THF)_3$ (2). The one-pot reaction of 1 equiv of K_2COT and 1 equiv of $SmCl_3$ in tetrahydrofuran at room temperature followed by addition of 1 equiv of DppLi yields tetrahydrofuran-soluble $DppSmCOT(\mu\text{-}Cl)Li(THF)_3$ (**2**). The dark red compound **2** can also be prepared by an alternative route, i.e. reaction of $(Dpp)_2SmCl(\mu\text{-}Cl)Li(THF)_3$ and 1 equiv of K_2COT in tetrahydrofuran. Interestingly, the tris(tetrahydrofuran)lithium chloride moiety of **1** is retained in the course of the reaction, while 1 equiv of KCl and 1 equiv of "KDpp" are eliminated. We note that previous studies by Power et al. have shown that terphenyl compounds of the heavier alkali metals sodium and potassium are very reactive and undergo C−H activation by metalation of solvents yielding the protonated terphenyl.[25] The first route appears to be the method of choice because compound **2** is obtained in higher yield. Furthermore, no purification of the intermediate **1** is necessary. As a side product, varying amounts of the known bis-COT sandwich compound $[Li(THF)_3\{\mu\text{-}(\eta^2{:}\eta^8\text{-}COT)\}Sm(\eta^8\text{-}COT)]$[26] are obtained in both cases, which is tetrahydrofuran soluble and is formed by a ligand redistribution reaction in which the terphenyllithium salt solely functions as the lithium source.

The Sm−C(ipso) distance in **2** [2.509(3) Å; Figure 2] is only slightly longer than the two Sm−C(ipso) distances in **1** [2.476(3) and 2.489(3) Å, respectively]. As was found in **1**, besides the Sm−C(ipso) distance there are secondary Sm−C(terphenyl) interactions with two ortho carbon atoms of phenyl rings in the 2,6-position, namely atom C(16) [3.211(3) Å] and atom C(26) [3.223(3) Å]. The dihedral angles between the central phenyl ring of the Dpp ligand and the aryl rings in the 2,6-position are 42.9° (C(15−20)) and 36.4° (C(21−26)). The Sm−C(COT) distances (average: 2.62 Å) are within the expected range.[26] The Sm−Cl−Li angle in **2** of 134.40(17)° can favorably be compared with the corresponding angle in **1**, while the bridging Sm−Cl distance of 2.7414(9) Å is slightly longer than the value found in **1** [2.6673(9) Å]. Further interatomic distances and angles of **2** can be derived from Table 2.

DmpSm(THF)COT (3) and DanipSm(THF)COT (4). Similar to the preparation of **2**, the toluene-soluble Dmp-based compound **3** can be prepared from the one-pot reaction of K_2COT, $SmCl_3$, and DmpLi in tetrahydrofuran at ambient temperature. An alkali halide-free, neutral compound is obtained with the samarium atom being complexed by one molecule of tetrahydrofuran. We note that our attempts to reverse the order of addition of reagents resulted in exclusive formation of the known bis-COT sandwich compound

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Table 2. Comparison of Selected Interatomic Separations (Å) and Angles (deg) of **1**−**4**[a]

param	1	2	3	4
Sm−C(ipso)	2.476(3) [C(1)]	2.509(3)	2.529(7)	2.543(3)
	2.489(3) [C(19)]			
Sm−C(COT)		2.597(4) [C(6)]	2.570(10) [C(8)]	2.631(3) [C(6)]
		2.602(4) [C(5)]	2.585(9) [C(7)]	2.641(3) [C(5)]
		2.603(4) [C(3)]	2.604(9) [C(5)]	2.641(3) [C(4)]
		2.611(4) [C(2)]	2.606(10) [C(1)]	2.660(3) [C(7)]
		2.616(4) [C(7)]	2.609(9) [C(6)]	2.672(3) [C(3)]
		2.616(4) [C(4)]	2.610(10) [C(4)]	2.703(3) [C(8)]
		2.661(4) [C(1)]	2.636(11) [C(2)]	2.721(3) [C(2)]
		2.663(4) [C(8)]	2.673(10) [C(3)]	2.759(3) [C(1)]
Sm−Cnt		1.889(7)	1.885(10)	1.948(7)
Sm−Cl	2.6174(9) [Cl(2)]	2.7414(9)		
	2.6673(9) [Cl(1)]			
Sm−O			2.444(5)	2.535(2) [O(3)]
				2.5436(19) [O(2)]
				2.576(2) [O(1)]
Li−Cl	2.329(6)	2.327(7)		
Li−O	1.913(7) [O(3)]	1.904(7) [O(1)]		
	1.923(7) [O(2)]	1.916(7) [O(3)]		
	1.947(7) [O(1)]	1.921(7) [O(2)]		
Sm−C_{ipso}−C_{ortho}	116.7(2) [C(6)]	119.2(2) [C(14)]	108.7(5) [C(10)]	122.30(19) [C(10)]
	124.9(2) [C(2)]	121.3(2) [C(10)]	136.0(6) [C(14)]	123.13(19) [C(14)]
	118.14(19) [C(24)]			
	123.46(18) [C(20)]			
C_{ipso}−C_{ortho}−C_{ipso}	117.9(2) [C(13)]	117.0(3) [C(15)]	116.0(6) [C(24)]	119.8(3) [C(15)]
	119.2(3) [C(7)]	117.8(3) [C(21)]	119.1(6) [C(15)]	120.5(3) [C(22)]
	116.9(2) [C(31)]			
	118.5(2) [C(25)]			
Cnt−Sm−C(ipso)		132.2(2)	141.6(4)	124.2(4)
Cnt−Sm−O			122.4(4)	115.6(2) [O(3)]
				127.0(2) [O(1)]
				129.3(2) [O(2)]

[a] Cnt = centroid.

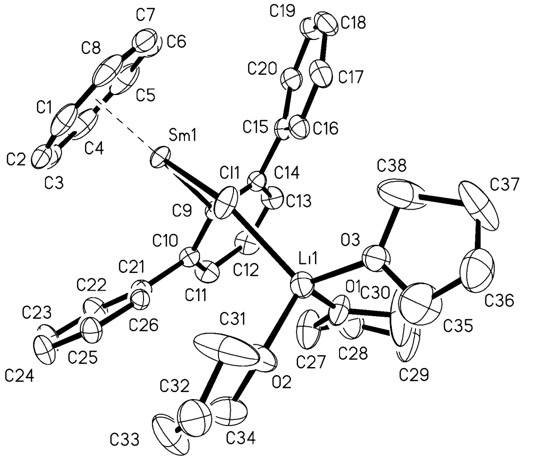

Figure 2. ORTEP diagram of DppSmCOT(μ-Cl)Li(THF)$_3$ (**2**), showing the atom labeling scheme. Thermal ellipsoids are at the 30% level. Disordered carbon atoms as well as hydrogen atoms were omitted for clarity.

[Li(THF)$_3${μ-(η^2:η^8-COT)}Sm(η^8-COT)],[26] as was observed in the case of compound **2**.

The Danip-based compound **4** is prepared as well in a one-pot synthesis. As was found in the case of compound **3**, a toluene-soluble neutral tetrahydrofuran solvate and not an anionic "ate" complex is obtained. We were able to demonstrate that in the case of the synthesis of compound **4** the order of addition of reagents can actually be reversed. **4** can be separated from small amounts of tetrahydrofuran-soluble side-product [Li(THF)$_3${μ-(η^2:η^8-COT)}Sm(η^8-COT)] by extraction of the crude product with toluene. We note that toluene solutions of **4** show a pronounced tendency at room temperature to decompose forming the above-mentioned anionic COT sandwich compound, which precipitates as an orange-brown powder. Additionally, it needs to be mentioned that our previous attempts to synthesize a mixed terphenyl COT compound using lanthanide ions smaller than samarium failed. In all cases an anionic bis-COT sandwich compounds was obtained as the only isolable product.[27,28]

The molecular structures of both **3** and **4** (Figures 3 and 4) are comprised of one η^8-bonded COT ligand and one σ-bonded terphenyl moiety, as well as a tetrahydrofuran ligand. While in all compounds reported in this paper the terphenyl moieties are not or only slightly tilted, the Dmp ligand in **3** is considerably tilted with Sm−C(ipso)−C(ortho) angles of 108.7(5)° [C(10)] and 136.0(6)° [C(14)]. In addition, besides the Sm−C(ipso) distance of 2.529(7) Å the next closest Sm···C(terphenyl) distances are to three phenyl carbon atoms of one mesityl ring, namely 3.071(7) Å [C(24)], 3.243(7) Å [C(25)], and 3.269(7) Å [C(10)], which documents the presence of a weak allyl-like electrostatic interaction between the samarium atom, one of the ortho carbon atoms of the central phenyl ring, and the ipso and one of the ortho carbon atoms of one of the mesityl rings. A similar asymmetric but still different arrangement of the Dmp ligand was previously observed in the molecular structure of Cp$_2$-

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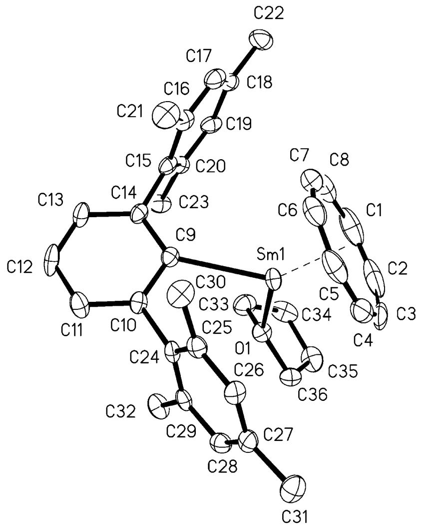

Figure 3. ORTEP diagram of DmpSm(THF)COT (**3**), showing the atom labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

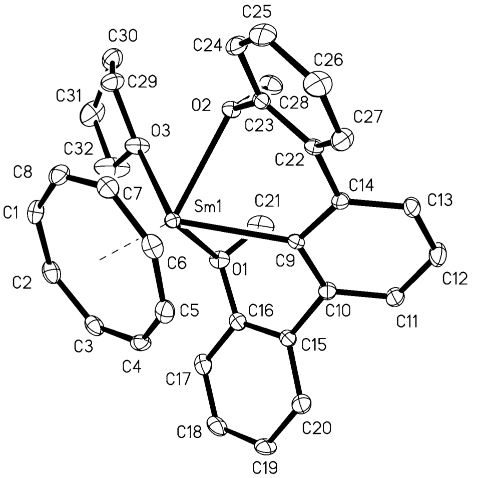

Figure 4. ORTEP diagram of DanipSm(THF)COT (**4**), showing the atom labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

SmDmp, which shows Sm−C(ipso) distances of 2.560(8) and 2.536(9) Å for both independent molecules.[29] However, other than in the molecular structure of **3**, in the case of the molecular structure of Cp$_2$SmDmp the allyl-type arrangement is between the samarium atom and the ipso carbon atom and the two ortho carbon atoms of one of the mesityl rings.[29] Other than in the molecular structures of **1** and **2**, in **3** the central phenyl ring of the terphenyl moiety and the two mesityl rings are arranged in an almost rectangular fashion with dihedral angles of 86.5° (C(15−20)) and 79.5° (C(24−29)), respectively. Further interatomic distances and angles of **3** can be derived from Table 2.

In the molecular structure of compound **4** for the first time the Danip ligand is seen to adopt the meso form, presumably as a result of steric crowding at the metal atom, while in all previously reported Danip-based terphenyllanthanide compounds the Danip ligand adopts the chiral (racemic) *d*,*l* form.[5,8] This view is further supported by the observation of both Sm−C(ipso)−C(ortho) angles being larger than 120° [122.30(19) and 123.13(19)°, respectively]. The dihedral angles between the central phenyl ring and the two aryl rings in the 2,6-position of 50.2° [C(15−20)] and 48.7° [C(22−27)], respectively, are considerably larger than the corresponding angles in complexes **1**−**3**. Both the Sm−C(ipso) [2.543(3) Å] and the Sm−Cnt distance [1.948(7) Å] are noticeably longer than the same distances in **2** and **3** (see Table 2). Also, the Sm−O(THF) distance in Danip-based **4** [2.535(2) Å] is considerably longer than the same distance in the Dmp-based complex **3** [2.444(5) Å]. An observation that can be explained by the higher coordination number at the metal atom in **4**. Further interatomic distances and angles of **4** can be derived from Table 2.

Conclusions

Our work demonstrates that a number of novel terphenyl-based lanthanide COT compounds of the element samarium are accessible by simple straightforward salt metathesis reaction starting from K$_2$COT, SmCl$_3$, and the corresponding terphenyllithium salt. The compounds are obtained either as anionic "ate" complexes (**1** and **2**) or as neutral tetrahydrofuran solvates (**3** and **4**). In **4** the Danip ligand adopts the meso form, while all previously reported Danip-based lanthanide compounds show the chiral (racemic) *d*,*l* conformation. Also, the synthesis and structural characterization of the first bis(terphenyl) compound of a trivalent lanthanide element is reported. Our work gives more insight into structural aspects as well as the reactivity of terphenyl-based lanthanide compounds. Further reactivity studies with these compounds are currently being undertaken.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of (Dpp)$_2$SmCl(μ-Cl)Li(THF)3 (**1**), DppSmCOT(μ-Cl)Li(THF)$_3$ (**2**), DmpSm(THF)COT (**3**), and DanipSm(THF)COT (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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