Synthesis and X-ray Crystal Structure Determination of First Examples of Donor-Functionalized Terphenyl Lanthanide Complexes

Gerd W. Rabe,*,† Christian D. Bérubé,† and Glenn P. A. Yap‡

Technische Universität München, Anorganisch-chemisches Institut, Lichtenbergstrasse 4,
85747 Garching, Germany, and Department of Chemistry, University of Ottawa,
10 Marie Curie Avenue, Ottawa, Ontario K1N 6N5, Canada

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The molecular structures of novel donor-functionalized terphenyl derivatives of trivalent ytterbium, yttrium, and samarium of composition $[\mathrm{DanipYb}(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})\mathrm{Li(THF)}]_2$ (**1**) and $[\mathrm{DanipLn}(\mu_2\text{-Cl})_2(\mu_2\text{-Cl})\mathrm{Li(THF)}_2]_2$ (Ln = Y, **2**; Ln = Sm, **3**) are reported [Danip = 2,6-di(*o*-anisol)phenyl]. The complexes are obtained from the reaction of equimolar amounts of DanipLi and LnCl_3 (Ln = Yb, Y, Sm) in tetrahydrofuran at room temperature in 60% yield. **1**·2 toluene crystallizes in the monoclinic space group $P\bar{1}$. Crystal data for **1**·2 toluene at 203 K: $a = 9.7281(9)$ Å; $b = 12.7989(12)$ Å; $c = 13.4870(12)$ Å; $\alpha = 91.553(2)°$; $\beta = 103.957(2)°$; $\gamma = 109.916(2)°$; $V = 1521.2(2)$ Å^3; $Z' = 1$; $D_{\mathrm{calcd}} = 1.615$ g cm^{-3}; R1 = 3.43%. **2**·toluene crystallizes in the monoclinic space group $P\bar{1}$. Crystal data for **2**·toluene at 203 K: $a = 10.4152(10)$ Å; $b = 12.5783(12)$ Å; $c = 14.4640(14)$ Å; $\alpha = 69.963(2)°$; $\beta = 80.900(2)°$; $\gamma = 66.603(2)°$; $V = 1633.3(3)$ Å^3; $Z' = 1$; $D_{\mathrm{calcd}} = 1.386$ g cm^{-3}; R1 = 4.07%. **3**·toluene crystallizes in the monoclinic space group $P\bar{1}$. Crystal data for **3**·toluene at 203 K: $a = 10.3457(8)$ Å; $b = 12.5658(10)$ Å; $c = 14.4365(11)$ Å; $\alpha = 70.2250(10)°$; $\beta = 81.2820(10)°$; $\gamma = 66.8330(10)°$; $V = 1623.3(2)$ Å^3; $Z' = 1$; $D_{\mathrm{calcd}} = 1.521$ g cm^{-3}; R1 = 3.40%. Complexes **1**−**3** represent first examples of donor-functionalized terphenyl complexes of the elements ytterbium, yttrium, and samarium, respectively. The molecular structures of **1**−**3** feature a “constraint geometry” type arrangement of the Danip ligand at the lanthanide atom. The complexes reported are dimeric and composed of lithium chloride bridged $\mathrm{DanipLnCl}_2$ moieties (Ln = Yb, Y, Sm), stabilized through additional coordination of two methoxy functions to the lanthanide atom.

Introduction

Although much work on organolanthanide chemistry has been published in recent years, the chemistry of low-coordinate complexes of the relatively large and strongly electropositive lanthanide cations free from stabilizing π-ligands remains poorly developed. There is much current interest in the chemistry of terphenyl ligand systems because this type of sterically demanding ligand was found to be suitable for the stabilization of main group element complexes in unusual coordination geometries and unprecedented bonding situations.[1,2]

The search for stable lanthanide complexes containing novel ancillary ligand systems capable of facilitating different catalytic processes is one of the challenging problems in organolanthanide chemistry. We wanted to explore the usability of sterically encumbering terphenyl ligand systems for the synthesis of kinetically stabilized compounds of the lanthanide elements. We recently introduced lanthanide complexes with σ-bonded terphenyl ligand systems as the only ancillary organic ligand at the lanthanide atom using the Dmp (2,6-dimesitylphenyl) ligand[3] as well as the Dnp (2,6-di(1-naphthyl)phenyl) ligand.[4] Such terphenyl lanthanide compounds are readily available by a salt metathesis reaction starting from anhydrous lanthanide chlorides and terphenyl lithium salt. However, all of the terphenyl lanthanide complexes previously characterized in our laboratory were found to be of only limited stability *in solution*, particularly in tetrahydrofuran solution at ambient temperature, thereby limiting the usability of such species for further reactions. Because of these stability problems we were interested in probing the use of donor-functionalized terphenyl groups as ligand systems for the lanthanides. We therefore wanted to employ a terphenyl system with a stabilizing donor group attached to the ortho position of the aryl substituents in the 2,6-positions and decided to explore the usability of the 2,6-di(*o*-anisol)phenyl moiety (Danip) as a ligand system for the lanthanides. The two methoxy groups of the Danip ligand system can also serve as a good NMR spectroscopic “spectator ligand”, in addition to being chelating Lewis base donors. We note that the iodo derivative DanipI is easily prepared in high yield from inexpensive starting materials following the general synthetic literature procedure for the preparation of terphenyl iodides described by Hart and co-workers.[5,6]

Experimental Section

The compounds described below were handled under nitrogen using Schlenk line double manifold, high-vacuum, and glovebox (M. Braun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained following typical laboratory procedures. YbCl_3, YCl_3, and SmCl_3 were purchased from Aldrich (packaged under argon

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† Technische Universität München, Anorganisch-chemisches Institut.
‡ University of Ottawa.

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Table 1. Crystallographic Data for [DanipYb(μ_2-Cl)$_2$(μ_3-Cl)Li(THF)]$_2$·2 toluene (**1**·2 toluene) and [DanipLn(μ_2-Cl)$_2$(μ_2-Cl)Li(THF)$_2$]$_2$·toluene (Ln = Y, **2**·toluene; Ln = Sm, **3**·toluene)[a]

	1·2 toluene	**2**·toluene	**3**·toluene
formula	$C_{62}H_{66}Cl_6Li_2O_6Yb_2$	$C_{63}H_{74}Cl_6Li_2O_8Y_2$	$C_{63}H_{74}Cl_6Li_2O_8Sm_2$
fw	1479.81	1363.62	1486.50
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.7281(9)	10.4152(10)	10.3457(8)
b, Å	12.7989(12)	12.5783(12)	12.5658(10)
c, Å	13.4870(12)	14.4640(14)	14.4365(11)
α, deg	91.553(2)	69.963(2)	70.2250(10)
β, deg	103.957(2)	80.900(2)	81.2820(10)
γ, deg	109.916(2)	66.603(2)	66.8330(10)
V, Å^3	1521.2(2)	1633.3(3)	1623.3(2)
Z′	1	1	1
D_{calcd}, g cm^{-3}	1.615	1.386	1.521
temp, °C	−70(2)	−70(2)	−70(2)
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
μ(Mo Kα), cm^{-1}	33.67	20.64	20.89
R1, %	3.43	4.07	3.40
wR2, %	6.94	6.77	7.05

[a] The quantity minimized was $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0]/3$.

in ampules) and were used as received. DanipI was prepared following the general procedure for the preparation of terphenyl iodides described by Hart et al.[5,6] DanipLi was prepared following the procedure for the preparation of other base free terphenyl lithium compounds.[7,8] DanipLi is found to be completely insoluble in hexanes and aromatic solvents, but well soluble in tetrahydrofuran. NMR spectra were recorded on a JMN-GX 400 instrument. The ^{13}C NMR spectrum, recorded in THF-d_8, was referenced to the two solvent signals (67.4 and 25.2 ppm, respectively). The ^{7}Li NMR spectra were referenced to a 1 M solution of LiCl in D_2O at 25 °C.

[DanipYb(μ_2-Cl)$_2$(μ_3-Cl)Li(THF)]$_2$ (1). In the glovebox, a colorless suspension of $YbCl_3$ (0.26 g, 0.9 mmol) in 10 mL of tetrahydrofuran was stirred for several hours. A freshly prepared solution of DanipLi (0.27 g, 0.9 mmol) in 10 mL of tetrahydrofuran was added to the suspension. The reaction mixture was stirred for 30 min, yielding a red suspension, which was centrifuged and concentrated to incipient crystallization. Cooling to −30 °C resulted in crystallization of **1**. Removal of the mother liquor, washing with hexanes, and drying under vacuum gave **1** as an orange-red microcrystalline material (0.35 g, 60%). Analytically pure complex **1** is insoluble in hexanes, slightly soluble in aromatic solvents, and well soluble in tetrahydrofuran. **1** does not lose coordinated tetrahydrofuran upon drying under vacuum (10^{-2} mbar at room temperature).

The toluene solvate **1**·2 toluene is obtained by an alternative workup procedure: All volatiles from the reaction mixture are removed followed by extraction of the crude product using toluene and centrifugation of the obtained purple suspension. A purple product (**1**·2 toluene) slowly crystallizes from this solvent at ambient room temperature, which is (after crystallization) only sparingly soluble in toluene. Washing of the obtained crystalline material with hexanes followed by drying under vacuum over prolonged time periods leads to partial removal of the cocrystallized toluene solvent molecules. However, redissolving of the crystalline material in tetrahydrofuran followed by evaporation of solvent, washing of the obtained product with hexanes, and drying under vacuum gave complex **1**.

Colorless **2** and yellow **3** can be prepared in a similar manner using YCl_3 or $SmCl_3$, respectively, instead of $YbCl_3$. Analytically pure samples of both the yttrium complex **2** and the samarium analogue **3** are insoluble in arene solvents, but soluble in tetrahydrofuran.

1. Anal. Calcd for $C_{48}H_{50}Cl_6Li_2O_6Yb_2$: C, 44.50; H, 3.89. Found: C, 44.60; H, 3.98. IR (Nujol): 1576 w, 1546 w, 1279 m, 1248 w, 1212 m, 1168 s, 1126 m, 1114 m, 1066 m, 1045 s, 981 s, 917 m, 914 m, 889 s, 873 s, 799 m, 775 s, 772 s, 744 s, 722 s, 669 m, 632 w, 593 w, 562 w, 504 w cm^{-1}.

2. Anal. Calcd for $C_{56}H_{66}Cl_6Li_2O_8Y_2$: C, 52.90; H, 5.23. Found: C, 53.12; H, 5.35. ^{1}H NMR (C_4D_8O, 400 MHz, 25 °C): δ 3.97 (s, O−Me) plus sets of signals in the aromatic region ranging from 7.15 to 7.30 ppm and from 7.51 to 7.57 ppm. ^{7}Li NMR (C_4D_8O, 155.45 MHz, 25 °C): δ −0.1 ($\nu_{1/2}$ = 10 Hz). ^{13}C NMR (C_4D_8O, 100.4 MHz, 25 °C): δ 65.8 (br, $\nu_{1/2}$ ca. 300 Hz, *o*-Me), 121.7 (br), 125.9, 126.3, 126.6 (br), 127.5, 131.7, 140.5, 143.9, 154.7, 187.3 (br, *ipso*-C). IR (Nujol): 1574 w, 1544 w, 1279 m, 1246 w, 1212 m, 1168 m, 1126 w, 1066 m, 1044 s, 1022 s, 985 s, 917 m, 878 s, 822 w, 798 w, 775 m, 746 s, 721 m, 668 w, 632 w, 593 w, 562 w, 504 w cm^{-1}.

3. Anal. Calcd for $C_{56}H_{66}Cl_6Li_2O_8Sm_2$: C, 48.24; H, 4.77. Found: C, 48.43; H, 4.93. ^{1}H NMR (C_4D_8O, 400 MHz, 25 °C): δ 5.27 (br, $\nu_{1/2}$ = 100 Hz), 6.19 (br, $\nu_{1/2}$ = 60 Hz), 7.55 (br, $\nu_{1/2}$ = 20 Hz), 8.11 (br, $\nu_{1/2}$ = 20 Hz), 8.35 (t, J_{H-H} = 8 Hz). ^{7}Li NMR (C_4D_8O, 155.45 MHz, 25 °C): δ 1.5 ($\nu_{1/2}$ = 50 Hz). IR (Nujol): 1574 w, 1544 w, 1276 m, 1245 w, 1211 m, 1168 m, 1125 w, 1040 s, 982 s, 890 m, 822 w, 797 m, 737 s, 696 w, 632 w, 589 w, 560 w, 498 w cm^{-1}.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for Complexes 1·2 toluene, 2·toluene, and 3·toluene. Crystal, data collection, and refinement parameters are given in Table 1. No symmetry higher than triclinic was observed in the diffraction data. Solution in the centric space group option yielded chemically reasonable and computationally stable results of refinement. In each structure, the compound molecule is located at an inversion center. A coordinated tetrahydrofuran molecule in **1**·2 toluene was located disordered in two conformations with a 60/40 site occupancy distribution. A molecule of cocrystallized toluene was located in the asymmetric unit of **1**·2 toluene disordered in two positions with a 50/50 site occupancy distribution. A molecule of cocrystallized toluene was located in the asymmetric units of **2**·toluene and in the isomorphic **3**·toluene at half-occupancy disordered at an inversion center.

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 were refined with anisotropic displacement coefficients. All other hydrogen atoms were treated as idealized contributions.

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

Results and Discussion

[DanipYb(μ_2-Cl)$_2$(μ_3-Cl)Li(THF)]$_2$ (1) and [DanipLn(μ_2-Cl)$_2$(μ_2-Cl)Li(THF)$_2$]$_2$ (Ln = Y, 2; Ln = Sm, 3). Reaction of anhydrous $LnCl_3$ (Ln = Yb, Y, Sm) with equimolar amounts of DanipLi in tetrahydrofuran at room temperature produces tetrahydrofuran soluble complexes of composition [DanipYb-

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Table 2. Comparison of Selected Interatomic Separations (Å) and Angles (deg) of Complexes **1**−**3**

	1 (Ln = Yb)	**2** (Ln = Y)	**3** (Ln = Sm)
Ln−O(1)	2.396(3)	2.449(2)	2.520(2)
Ln−O(2)	2.353(3)	2.449(2)	2.503(2)
Ln−C(13)	2.388(4)	2.456(3)	2.489(3)
Ln−Cl	2.5750(11) [Cl(2)]	2.6433(10) [Cl(3)]	2.6959(11) [Cl(3)]
	2.5970(11) [Cl(3)]	2.6478(1) [Cl(1)]	2.7033(10) [Cl(1)]
	2.7741(10) [Cl(1)]	2.7710(8) [Cl(2)]	2.8142(9) [Cl(2)]
	2.9016(11) [Cl(1A)]	2.7748(8) [Cl(2A)]	2.8162(9) [Cl(2A)]
Li−Cl	2.421(9) [Cl(1A)]	2.336(6) [Cl(1)]	2.350(7) [Cl(1)]
	2.345(8) [Cl(2)]	2.372(5) [Cl(3A)]	2.320(6) [Cl(3A)]
	2.324(8) [Cl(3A)]		
Li−O	1.879(10) [O(3)]	1.933(6) [O(3)]	1.943(8) [O(3)]
		1.938(6) [O(4)]	1.936(7) [O(4)]
C(13)−Ln−O(1)	71.15(12)	70.02(8)	68.71(9)
C(13)−Ln−O(2)	74.71(13)	70.04(8)	69.00(9)
C(13)−Ln−Cl	141.84(11) [Cl(1)]	90.70(7) [Cl(1)]	93.95(8) [Cl(1)]
	145.27(11) [Cl(1A)]	142.23(7) [Cl(2)]	141.36(8) [Cl(2)]
	99.47(10) [Cl(2)]	141.52(7) [Cl(2A)]	140.78(8) [Cl(2A)]
	90.75(10) [Cl(3)]	93.02(7) [Cl(3)]	90.67(8) [Cl(3)]
O(1)−Ln−O(2)	143.18(10)	140.06(7)	137.71(8)
Ln−Cl−Li	87.3(2) [Cl(1)]	117.29(14) [Cl(1)]	119.67(18) [Cl(1)]
	84.5(2) [Cl(1A)]		
	93.8(2) [Cl(2)]		
	93.8(2) [Cl(3)]	119.67(15) [Cl(3)]	117.28(18) [Cl(3)]
Ln−Cl−Ln	107.92(4) [Cl(1)]	103.75(3) [Cl(2)]	102.14(3) [Cl(2)]
Cl−Li−O	121.2(5) [Cl(1A)/O(3)]	107.0(2) [Cl(1)/O(3)]	106.3(3) [Cl(1)/O(3)]
	104.2(4) [Cl(2)/O(3)]	104.6(2) [Cl(1)/O(4)]	106.2(2) [Cl(1)/O(4)]
	113.2(4) [Cl(3A)/O(3)]	106.4(2) [Cl(3A)/O(3)]	104.2(3) [Cl(3A)/O(3)]
		106.2(3) [Cl(3A)/O(4)]	107.9(3) [Cl(3A)/O(4)]
Cl−Li−Cl	97.8(3) [Cl(1A)/Cl(2)]	125.8(3)	126.1(3)
	96.0(3) [Cl(1A)/Cl(3A)]		
	124.7(4) [Cl(2)/Cl(3A)]		
O−Li−O		105.2(3)	104.2(4)
Ln−C_{ipso}−C_{ortho}	120.2(3) [C(8)]	122.65(19) [C(8)]	122.1(2) [C(8)]
	124.0(3) [C(12)]	122.7(2) [C(12)]	122.4(2) [C(12)]
C_{ipso}−C_{ortho}−$C_{ipso'}$	121.5(3) [C(7)]	120.5(3) [C(7)]	120.7(3) [C(7)]
	121.4(3) [C(14)]	120.7(3) [C(14)]	120.8(3) [C(14)]

(μ_2-Cl)$_2$(μ_3-Cl)Li(THF)]$_2$ (**1**) and [DanipLn(μ_2-Cl)$_2$(μ_2-Cl)Li(THF)$_2$]$_2$ (Ln = Y, **2**; Ln = Sm, **3**), respectively, in 60% yield. Formation of mono terphenyl substituted complexes was also observed using at least 2 equiv of DanipLi. Under inert gas, compounds **1**−**3** are stable in toluene/tetrahydrofuran solutions at ambient temperature over prolonged time periods (several days) without noticeable decomposition. This observation is in contrast to the only limited stability of previously reported non-donor-functionalized terphenyl lanthanide species in solution at room temperature.[3,4] Single-crystalline material of toluene solvates of all three compounds suitable for X-ray diffraction studies was obtained after several days at ambient temperature from saturated solutions of compounds **1**−**3** in tetrahydrofuran layered with toluene inside a glovebox. We note that we did not manage to obtain single-crystalline material of compounds **1**−**3** directly from tetrahydrofuran, only from tetrahydrofuran/toluene mixtures.

The molecular structures of **1**−**3** feature dimeric centrosymmetric heterobimetallic cage-like frameworks consisting of two lanthanide centers, two lithium atoms, and six chlorine atoms. The solid state structures are composed of lithium chloride adducts of DanipLnCl$_2$ moieties (Ln = Yb, Y, Sm) stabilized through additional coordination of two methoxy functions to the lanthanide center, thereby resulting in a "constraint geometry" type arrangement of the Danip ligand at the lanthanide atom. Depending on the size of the lanthanide metal employed, one or two tetrahydrofuran molecules coordinate to each of the lithium atoms in **1**−**3**.

The molecular structure of the ytterbium complex **1** (Figure 1) shows a formally seven-coordinate ytterbium atom surrounded by four chlorine atoms, two methoxy functions [O(1)−Yb−O(2) = 143.18(10)°], and an ipso carbon atom. The ligands are arranged in a heavily distorted pentagonal-bipyramidal fashion about the lanthanide atom, with atoms Cl(2) and Cl(3) occupying the axial positions of the coordination polyhedron [Cl(2)−Yb−Cl(3) = 168.74(3)°]. The two ytterbium atoms are bridged by two μ_3-bonded chlorine atoms as well as two (μ_2-Cl)−Li(THF)−(μ_2-Cl) units. The Yb−Cl distances range from 2.5750(11) Å [Cl(2)] to 2.9016(11) Å [Cl(1A)], with the two Yb−(μ_2-Cl) distances being clearly shorter than the two Yb−(μ_3-Cl) distances (Table 2). The formally four-coordinate lithium atom shows Li−Cl distances of 2.324(8) Å [Cl(3A)], 2.345(8) Å [Cl(2)], and 2.421(9) Å [Cl(1A)] as well as a Li−O(THF) distance of 1.879(10) Å.

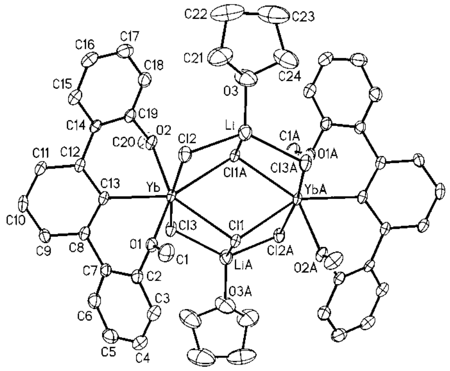

Figure 1. ORTEP diagram of [DanipYb(μ_2-Cl)$_2$(μ_3-Cl)Li(THF)]$_2$ (**1**) showing atom-labeling scheme; thermal ellipsoids at the 30% level.

The ytterbium−C(ipso) distance of 2.388(4) Å in formally seven-coordinate **1** is shorter than the corresponding distance

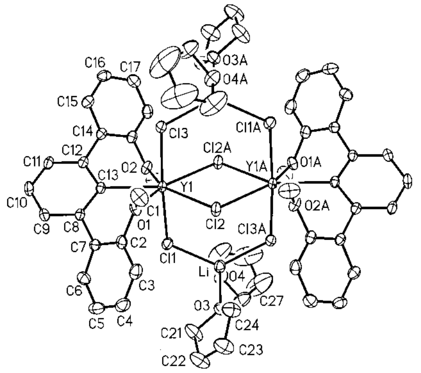

Figure 2. ORTEP diagram of [DanipY(μ_2-Cl)$_2$(μ_2-Cl)Li(THF)$_2$]$_2$ (**2**) showing atom-labeling scheme; thermal ellipsoids at 30% level.

in hexa-coordinate DmpYbCl$_2$(N-MeIm)$_2$(py) [2.447(9) Å].[3] The Yb−C(ipso) separation in **1** can also be favorably compared with the corresponding distances in formally four-coordinate DmpYb[N(SiMe$_3$)$_2$](μ-Cl)$_2$Li(THF)$_2$ [2.403(4) Å],[3] in the bis-(cyclopentadienyl) derivative (C$_5$H$_4$Me)$_2$YbDmp [2.410(3) Å],[9] and in Ph$_3$Yb(THF)$_3$ [2.39(1), 2.40(1), and 2.43(1) Å].[10] Further comparisons can be made with the average terminal Yb(III)−C distance in the mixed-valent ytterbium complex Ph$_2$(THF)Yb(μ-Ph)$_3$Yb(THF)$_3$ [2.42 Å].[11]

The Yb−O distances of 2.396(3) Å [O(1)] and 2.353(3) Å [O(2)] in complex **1** can be compared with distances in other donor-functionalized ytterbium(III) systems stabilized by a chelating uncharged methoxy function; e.g., Yb−O(OMe) distances of 2.456(6) and 2.482(6) Å are reported for [Cp′$_2$Yb-(μ-OCH$_2$CHMeOMe)]$_2$.[12]

The molecular structures of the colorless yttrium derivative **2** (Figure 2) and the isomorphous yellow samarium compound **3** feature centrosymmetric heterobimetallic arrangements similar to that found in complex **1**. Despite the fact that the ionic radius of an yttrium(III) cation is only slightly larger than that of an ytterbium(III) cation for a given coordination number,[13] the solid state structures adopted by complexes **1** and **2** differ. One additional molecule of tetrahydrofuran coordinates to each of the lithium atoms in both the yttrium derivative **2** and the samarium compound **3**, but not to the lanthanide atoms. As a consequence, the four-coordinate lithium atoms in complexes **2** and **3** are bonded to only two chlorine atoms, while the lithium atoms in complex **1** are in close contact with three chlorine atoms. The remaining two chlorine atoms in complexes **2** and **3**, namely, Cl(2) and Cl(2A), bridge the two lanthanide atoms in a μ_2-fashion. The different bonding modes of the lithium atoms in both types of complexes are illustrated in Figure 3. While both the Yb−Cl(3)−Li(A) and the Yb−Cl(2)−Li angle in **1** are 93.8(2)°, the Ln−Cl(1)−Li and Ln−Cl(3)−Li(A) angles in **2** and **3** are 117.29(14)° and 119.67(15)° [**2**] and 119.67(18)° and 117.28(18)° [**3**], respectively. In complex **1**, the lithium atom deviates 1.08(5) Å from the plane described by the two lanthanide atoms and chlorine atoms Cl(2), Cl(2A), Cl(3), and Cl(3A), but only 0.18(1) Å in **2** and 0.24(1) Å in **3**, respectively, from the corresponding plane formed by the two lanthanide atoms and the chlorine atoms Cl(1), Cl(1A), Cl(3), and Cl(3A).

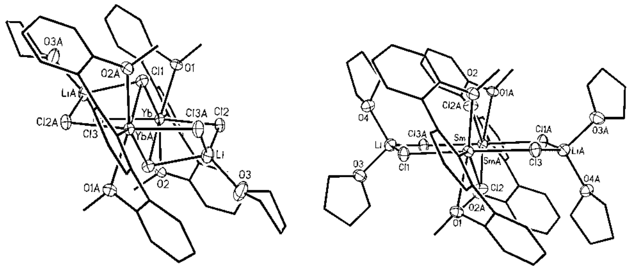

Figure 3. Side views of compounds **1** (left) and **3** (right) showing both molecules in similar orientations.

A closer inspection of the two different types of bridging chlorine atoms in isomorphous **2** and **3** shows that the Ln−Cl distances involving atoms Cl(2) and Cl(2A) which bridge the two lanthanide atoms are approximately 0.11−0.13 Å longer than the Ln−Cl distances involving atoms Cl(3) and Cl(1) (Table 2).

In complexes **1**−**3** the dihedral angles between the central, metalated phenyl ring and the two phenyl rings in the 2,6-positions are 37.3° (**1**), 41.8° (**2**), and 43.6° (**3**) [involving the anisol substituent containing atom O(1)] and 40.0° (**1**), 38.9° (**2**), and 40.0° (**3**) [involving the anisol substituent containing atom O(2)] (Figure 3).

Further details on interatomic separations and angles of complexes **1**−**3** can be derived from Table 2.

Finally, we note that the synthesis of Danip scandium, neodymium, and lanthanum complexes was also attempted by reacting equimolar amounts of DanipLi with the corresponding anhydrous metal trichlorides in tetrahydrofuran solution at room temperature. However, we repeatedly failed to isolate any characterizable metal-containing species. This observation is indeed surprising since the difference in ionic radii between samarium(III) and neodymium(III) is only 0.02 Å for a given coordination number.[13] In the case of ScCl$_3$, polymerization of tetrahydrofuran was observed. On the other hand, complexes **1**−**3** can be synthesized reproducibly in good yield. The observation that the accessibility of terphenyl lanthanide complexes depends on the ionic radius of the lanthanide cation employed was previously found in the case of the Dnp ligand system.[4]

Conclusions

Our work introduces the Danip moiety as an ancillary ligand system for the lanthanide elements ytterbium and samarium as well as the group 3 element yttrium, thereby providing easy access to a novel class of donor-functionalized terphenyl based "constraint geometry" type complexes and providing bonding parameters for this class of compounds. The complexes reported in this work are found to be considerably more stable in the solution state than other previously characterized terphenyl lanthanide systems. Two similar, but still slightly different, types of solid state structures are observed, depending on the ionic radius of the metal employed. Also, we were able to demonstrate that the Danip ligand system allows for an easy ^{1}H NMR spectroscopic characterization of the diamagnetic yttrium compound because of the presence of a spectator group, i.e., the methoxy function, which could be useful, e.g., when studying processes catalyzed by terphenyl based lanthanide complexes. Further investigations on the reaction chemistry as well as catalytic properties of these systems are currently underway.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[\mathrm{DanipYb}(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})\mathrm{Li(THF)}]_2\cdot$2 toluene (**1**·2 toluene) and $[\mathrm{DanipLn}(\mu_2\text{-Cl})_2(\mu_2\text{-Cl})\mathrm{Li(THF)_2}]_2\cdot$toluene (Ln = Y, **2**·toluene; Ln = Sm, **3**·toluene). This material is available free of charge via the Internet at http://pubs.acs.org.

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