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Donor-Functionalized Lanthanide Terphenyl Complexes: Synthesis and Structural Characterization of 2,6-Di(*o*-anisol)phenyl Compounds of Ytterbium, Yttrium, and Samarium

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The syntheses and molecular structures of a number of 2,6-di(*o*-anisol)phenyl (=Danip-) -based bis(amide) and bis(alkoxide) compounds of ytterbium, yttrium, and samarium are reported. Addtionally, NMR spectroscopic data are reported for the analogous diamagnetic yttrium compounds. Salt metathesis reaction of equimolar amounts of DanipLi and $YbCl_3$ in tetrahydrofuran at room temperature followed by addition of 2 equiv of $KN(SiMe_3)_2$ or $KN(SiHMe_2)_2$ produces $DanipYb[N(SiMe_3)_2]_2$ (**1**) and $DanipYb[N(SiHMe_2)_2]_2$ (**2**), respectively. The analogous reaction using $SmCl_3$ and $KN(SiHMe_2)_2$ produces $DanipSm[N(SiHMe_2)_2]_2$ (**3**). Reaction of DanipLi and $YbCl_3$ in tetrahydrofuran at room temperature followed by addition of 2 equiv of KO(2,6-diisopropylphenyl) produces DanipYb[O(2,6-diisopropylphenyl)]$_2$ (**4**). Our attempts to also prepare the yttrium analogue of complex **4** yielded single-crystalline material of the tetrahydrofuran adduct DanipY(THF)[O(2,6-diisopropylphenyl)]$_2$ (**5**). The molecular structures of the complexes **1**–**4** feature five-coordinate metal atoms and coordination polyhedra which can be described as distorted square-pyramidal rather than trigonal-bipyramidal, with the ipso carbon atom occupying the apical position. On the other hand, the molecular structure of the tetrahydrofuran-solvated yttrium Danip arylalkoxide compound **5** features a six-coordinate metal atom in a distorted trigonal-prismatic coordination environment. In all cases the Danip ligand system adopts the chiral (racemic) *d*,*l* form.

Introduction

There is much current interest in the chemistry of terphenyl element compounds. Still, the vast majority of terphenyl compounds are based on p block elements, followed by a number of such compounds of s block elements and some representatives of the late transition metals.[1−5] In recent years we have been investigating the coordination and reaction chemistry of terphenyl compounds of the lanthanides and group 3 elements scandium and yttrium.[6−9] We were able to demonstrate that the use of sterically demanding terphenyl groups as the only supporting ligand allows for the kinetic stabilization of novel low-coordinate complexes which are obtained by simple, straightforward salt methathesis reactions using different terphenyllithium salts and the corresponding lanthanide (Ln = Sm−Lu) or group 3 element trichlorides. Formation of mono(terphenyl) compounds is observed when employing the terphenyls Dmp (=2,6-dimesitylphenyl)[6,9] and Dnp [=2,6-di(1-naphthyl)phenyl],[7] as well as the donor-functionalized Danip [=2,6-di(*o*-anisol)phenyl].[8]

One of the problems we observed in previously studied nonfunctionalized lanthanide terphenyl systems[6,7,9] is the only

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relatively poor stability of lanthanide terphenyl compounds in the solution state, particularly in tetrahydrofuran solution at ambient temperature. Considerably more stable products were obtained with the donor-functionalized terphenyl ligand Danip,[8] a "pincer ligand" with donor groups in the ortho position of the phenyl substiutents in the 2,6-position. We were now interested in investigating the reaction chemistry of Danip-based mono(terphenyl)lanthanide compounds, particularly the accessibility and structural characterization of further functionalized Danip-based compounds. Therefore, efforts were undertaken to explore what other monoanionic ligand systems can be accommodated vis-à-vis a Danip moiety bonded to a lanthanide atom. Here we report on a simple high-yield preparation and structural characterization of a number of Danip-based monomeric bis functionalized lanthanide compounds.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk line double-manifold, high-vacuum, and glovebox (MBraun, Labmaster 130) techniques. Solvents were dried, and physical measurements were obtained by following typical laboratory procedures. DanipLi was prepared from DanipI and *n*-butyllithium in hexanes.[8,10,11] KO(2,6-diisopropylphenyl) and KN-$(SiHMe_2)_2$ were prepared by reaction of equimolar amounts of potassium hydride and the corresponding phenol or amine in hexanes at room temperature. Both potassium salts are insoluble in hexanes and toluene but soluble in tetrahydrofuran. $KN(SiMe_3)_2$ was purchased as a 0.5 M solution in toluene from Aldrich. The anhydrous halides $YbCl_3$, YCl_3, and $SmCl_3$ were purchased from Aldrich (packaged under argon in ampules) and were 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). ^{29}Si NMR spectra were referenced to tetramethylsilane.

DanipYb[N(SiMe$_3$)$_2$]$_2$ (1), DanipYb[N(SiHMe$_2$)$_2$]$_2$ (2), and DanipSm[N(SiHMe$_2$)$_2$]$_2$ (3). In the glovebox, a colorless suspension of $YbCl_3$ (279 mg, 1.0 mmol) in 10 mL of tetrahydrofuran was stirred for several hours. A freshly prepared solution of DanipLi (296 mg, 1.0 mmol) in 10 mL of tetrahydrofuran was added to the suspension. The reaction mixture was stirred for 30 min yielding a red solution. A 0.5 M toluene solution of $KN(SiMe_3)_2$ (4.0 mL, 2.0 mmol) was slowly added via syringe. After being stirred for 10 min, the obtained orange suspension was centrifuged. After removal of the mother liquor, extraction of the residues with hexanes, and centrifugation, the obtained orange solution was stored overnight at room temperature, which resulted in almost complete crystallization of **1** as a yellow microcrystalline material (470 mg, 60%). In the case of **2** a tetrahydrofuran solution of $KN(SiHMe_2)_2$ (343 mg, 2.0 mmol) was slowly added via syringe. After being stirred for 10 min, the obtained orange suspension was centrifuged. After removal of the mother liquor, extraction of the residues with hexanes, and centrifugation, the obtained orange solution was stored overnight at room temperature, which resulted in almost complete crystallization of **2** as an yellow microcrystalline material (436 mg, 60%). Bright yellow compound **3** is obtained in similar yield using $SmCl_3$ instead of $YbCl_3$. In the case of **3** the suspension of $SmCl_3$ in tetrahydrofuran was stirred overnight. After crystallization from hexanes, complexes **1**−**3** are insoluble in hexanes, soluble in aromatic solvents, and well soluble in tetrahydrofuran. We failed to obtain reasonable combustion analyses data (C, H, N) for **1**−**3**. The values obtained for both C and N were too low which can most likely be explained by incomplete combustion of the samples due to formation of SiC and SiN during the combustion process. Such incomplete combustion of lanthanide compounds, particularly with the element combination Ln/N/Si being present, is not uncommon and has been discussed earlier to explain for the observation of too low C and N values.[12−14]

1. IR (Nujol): 1576 w, 1540 w, 1259 m, 1245 s, 1208 w, 1160 m, 1113 w, 1065 w, 980 s, 951 vs, 946 vs, 869 m, 826 s, 740 s, 692 w, 661 m, 608 w, 500 w, 432 w cm^{-1}. Mp: 175−177 °C (dec).

DanipY[N(SiMe$_3$)$_2$]$_2$. ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.24 (s, 36H, Me_3Si), 3.78 (s, 6H, OMe) plus sets of signals in the aromatic region ranging from 6.65 to 7.75 ppm (11H). ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): δ 2.7 (Me_3Si), 61.8 (OMe), 120.8, 126.8, 127.2, 133.2, 138.3, 142.4, 153.7, 185.2 (d, $J_{Y-C} = 51$ Hz, ipso C). We failed to detect in the ^{13}C NMR spectrum all signals that correspond to the terphenyl ligand which is probably due to overlap of the solvent signal with some of the signals in the aromatic region. ^{29}Si NMR (C_6D_6, 79.4 MHz, 25 °C): δ −11.4 (sept, $^2J_{Si-H} = 9$ Hz).

2. IR (Nujol): 2021 vs (sh), 1789 w, 1574 m, 1548 w, 1246 vs, 1211 w, 949 vs, 942 vs, 880 vs, 869 vs, 862 vs, 832 s, 799 w, 790 w, 747 m, 745 m, 736 m, 732 m, 722 w, 698 w, 683 w, 678 w, 646 w, 630 w, 626 m, 610 m, 590 m, 578 w, 560 w, 532 w, 496 m cm^{-1}. Mp: 180−182 °C (dec).

3. IR (Nujol): 2038 vs (broad sh), 1573 w, 1546 w, 1275 s, 1242 m, 1208 w, 1158 m, 1126 w, 1067 s, 1065 s, 987 m, 884 vs, 880 vs, 837 m, 788 m, 738 vs, 722 vs, 683 m, 633 w, 589 m, 500 w, 446 w cm^{-1}. Mp: 144−146 °C (dec). The samarium compound **3** has an uninterpretable ^1H NMR spectrum.

DanipY[N(SiHMe$_2$)$_2$]$_2$. ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.18 (d, 24H, $^3J_{H-H} = 3$ Hz, Me_2Si), 3.78 (s, 6H, OMe), 4.81 (sept, 4H, $^3J_{H-H} = 3$ Hz, Si−H) plus sets of signals in the aromatic region ranging from 6.95 to 7.70 ppm (11H). ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): δ 3.0 (Me_2Si), 64.0 (OMe), 119.3, 126.5, 126.8, 132.9, 137.8, 142.7, 153.2, 186.8 (d, $J_{Y-C} = 50$ Hz, ipso C). We failed to detect in the ^{13}C NMR spectrum all signals that correspond to the terphenyl ligand which is probably due to overlap of the solvent signal with some of the signals in the aromatic region. ^{29}Si NMR (C_6D_6, 79.4 MHz, 25 °C): δ −26.1 (d, sept, $^2J_{Si-H} = 7$ Hz, $^1J_{Si-H} = 168$ Hz).

DanipYb[O(2,6-diisopropylphenyl)]$_2$ (4) and DanipY(THF)-[O(2,6-diisopropylphenyl)]$_2$ (5). In the glovebox, a colorless suspension of $YbCl_3$ (279 mg, 1.0 mmol) in 10 mL of tetrahydrofuran was stirred for several hours. A freshly prepared solution of DanipLi (296 mg, 1.0 mmol) in 10 mL of tetrahydrofuran was added to the suspension. The reaction mixture was stirred for 30 min yielding an orange-red solution. A solution of KO(2,6-diisopropylphenyl) (433 mg, 2.0 mmol) in tetrahydrofuran was slowly added via pipet. After being stirred for 10 min, the obtained yellow suspension was centrifuged. After removal of all volatiles and

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Table 1. Crystallographic Data for DanipYb[N(SiMe$_3$)$_2$]$_2$ (**1**), DanipYb[N(SiHMe$_2$)$_2$]$_2$ (**2**), DanipSm[N(SiHMe$_2$)$_2$]$_2$ (**3**), DanipYb[O(2,6-diisopropylphenyl)]$_2$ (**4**), and DanipY(THF)[O(2,6-diisopropylphenyl)]$_2$ (**5**)[a]

param	**1**	**2**	**3**	**4**	**5**
formula	$C_{32}H_{53}N_2O_2Si_4Yb$	$C_{28}H_{45}N_2O_2Si_4Yb$	$C_{28}H_{45}N_2O_2Si_4Sm$	$C_{44}H_{51}O_4Yb$	$C_{48}H_{59}O_5Y$
fw	783.16	727.06	704.37	816.89	804.86
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	22.208(4)	16.5309(16)	16.4865(15)	22.6759(16)	9.2978(10)
b, Å	11.803(3)	10.1709(10)	10.2719(9)	12.3333(9)	19.631(2)
c, Å	14.182(2)	21.603(2)	21.860(2)	17.6237(12)	24.810(3)
α, deg					87.042(2)
β, deg	93.870(14)	109.313(2)	109.324(2)	128.0890(10)	84.740(2)
γ, deg					81.056(2)
V, Å^3	3708.6(12)	3427.8(6)	3493.4(5)	3879.2(5)	4451.3(8)
Z	4	4	4	4	4
D(calcd), g cm^{-3}	1.403	1.409	1.339	1.399	1.201
temp, °C	70(2)	70(2)	70(2)	70(2)	70(2)
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ(Mo Kα), cm^{-1}	26.80	28.93	18.43	24.51	13.53
R$_1$, %	5.11	2.20	4.09	1.84	5.35
wR$_2$, %	11.34	6.24	8.56	4.74	8.86

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

extraction of the residues with hexanes followed by repeated centrifugation (over a period of a couple of hours), the obtained yellow solution was stored overnight at room temperature, which resulted in almost complete crystallization of **4** as a bright yellow microcrystalline material (490 mg, 60%). After crystallization from hexanes, complex **4** is insoluble in hexanes, soluble in aromatic solvents, and well soluble in tetrahydrofuran. Colorless DanipY[O(2,6-diisopropylphenyl)]$_2$ was prepared in a similar manner. In contrast to the ytterbium compound **4** the crude product of the yttrium analogue is insoluble in hexanes. We failed to crystallize the yttrium compound from toluene but managed to obtain crystalline material of the tetrahydrofuran adduct **5** from a toluene solution in the presence of small amounts of tetrahydrofuran. The obtained crystalline material rapidly desolvates when exposed to vacuum, thereby preventing further characterization of **5**. According to ^{1}H and ^{13}C NMR data a completely desolvated compound is obtained of composition DanipY[O(2,6-diisopropylphenyl)]$_2$.

4. Anal. Calcd for $C_{44}H_{51}O_4Yb$: C, 64.69; H, 6.29. Found: C, 64.51; H, 6.10. IR (Nujol): 1926 w, 1893 w, 1645 w, 1585 m, 1262 s, 1258 s, 1252 s, 1205 m, 1170 m, 1103 s, 1040 m, 1016 w, 968 m, 886 s, 860 s, 825 w, 806 m, 796 m, 774 m, 751 s, 743 m, 694 s, 614 w, 570 m, 539 w, 510 m, 439 w, 430 w cm^{-1}. Mp: 245−248 °C (dec).

DanipY[O(2,6-diisopropylphenyl)]$_2$. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 1.18 (d, 24H, $^3J_{H-H}$ = 7 Hz, Me$_2$C), 3.06 (sept, 4H, $^3J_{H-H}$ = 7 Hz, C−H), 3.42 (s, 6H, OMe) plus sets of signals in the aromatic region ranging from 6.87 to 7.70 ppm (17H). ^{13}C NMR (C$_6$D$_6$, 100.4 MHz, 25 °C): δ 24.0 (Me$_2$C), 27.2 (C−H), 65.3 (OMe), 118.1, 122.3, 123.0, 126.4, 127.9, 128.1, 128.5, 132.7, 136.4, 138.7, 143.7, 152.0, 158.1 (d, $^1J_{C-H}$ = 5 Hz), 183.6 (d, J_{Y-C} = 53 Hz).

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for Complexes 1−5. Crystal, data collection, and refinement parameters are given in Table 1. The systematic absences in the diffraction data are uniquely consistent for the reported space group for **2** and **3** and consistent for the space groups Cc and $C2/c$ for **1** and **4**. No symmetry higher than triclinic was observed for **5**. The E-statistics suggested the centrosymmetric option, $C2/c$, for **1** and **4** and $P\bar{1}$ for **5**, which yielded chemically reasonable and computationally stable results of refinement. 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. The compound molecule was located at a 2-fold axis in **1** and **4**. One isopropyl moiety in **4** was located rotationally disordered with a roughly 50/50 refined site occupancy distribution. Two symmetry unique but chemically identical compound molecules were located in the asymmetric unit of **5**. In **2** and **3** the hydrogen atoms on the silicon atoms were located from a difference map and refined. 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

We previously reported the synthesis of the donor-functionalized terphenyllithium salt DanipLi[8,10,11] Danip as well as its reaction with different lanthanide trichlorides (Ln = Sm, Y, Yb) which produces two different types of lithium chloride adducts of composition [DanipLn(μ_2-Cl)$_2$(μ_3-Cl)-Li(THF)]$_2$ (Ln = Yb) or [DanipLn(μ_2-Cl)$_2$(μ_2-Cl)Li(THF)$_2$]$_2$ (Ln = Sm, Y), depending on the size of the metal atom being employed.[8] The molecular structures of these compounds are comprised of dimeric cagelike arrangements.

We here report the one-pot reaction of DanipLi with LnCl$_3$ (Ln = Sm, Y, Yb) and 2 equiv of different sterically encumbering potassium amide or alkoxide compounds yielding novel neutral and low-coordinate unsolvated bis substituted compounds of general composition DanipLnX$_2$ in good yield. The obtained compounds are toluene soluble, and under exclusion of air and moisture, toluene solutions of the presented compounds show no visible signs of decomposition over several days at ambient temperature. Single-crystalline material of compounds **1**−**4** was obtained by extraction of the obtained crude products with hexanes and slow evaporation of the obtained solutions at room temperature. We note that after crystallization from hexanes compounds **1**−**4** are insoluble in hexanes but soluble in toluene. In the case of the tetrahydrofuran solvate **5** single-crystalline material was obtained by slow evaporation of a toluene solution in the presence of a small amount of tetrahydrofuran. Our repeated

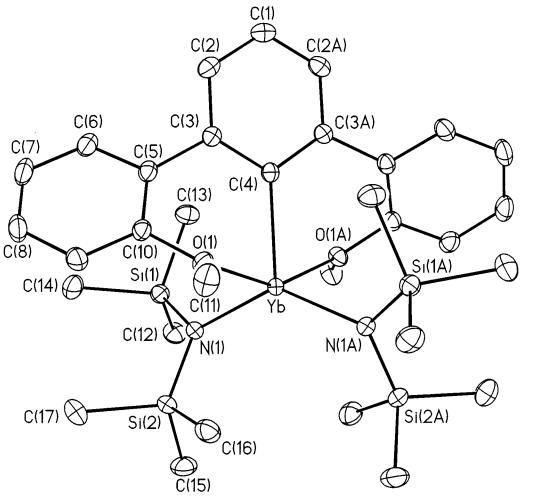

Figure 1. ORTEP diagram of DanipYb[N(SiMe$_3$)$_2$]$_2$ (**1**) showing the atom-labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

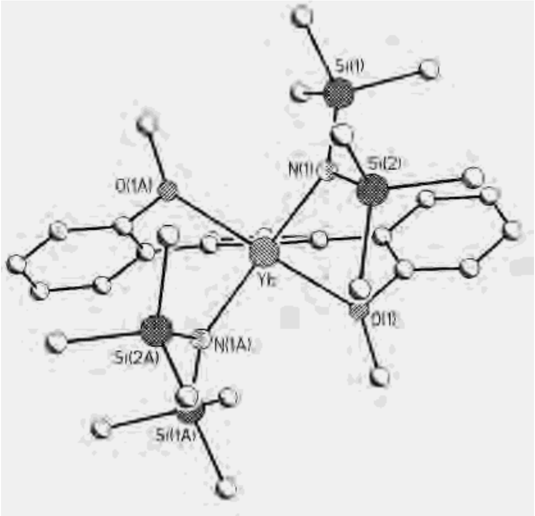

Figure 2. Side view of complex **1** viewed along the Yb···C(ipso) vector.

attempts to obtain crystalline material of hexane-insoluble DanipYb[O(2,6-diisopropylphenyl)]$_2$ from toluene in the absence of tetrahydrofuran gave amorphous material only. According to ^{1}H and ^{13}C NMR data compound **5** becomes readily and completely desolvated when dried under vacuum.

DanipYb[N(SiMe$_3$)$_2$]$_2$ (1). The molecular structure of compound **1** (Figure 1) features a C_2-symmetric five-coordinate ytterbium complex in a distorted square-pyramidal coordination environment with the ipso carbon atom occupying the apical position. The Danip ligand adopts the chiral (racemic) *d*,*l* form (Figure 2). The Yb−N distance [2.241(5) Å] is, e.g., somewhat longer than the corresponding distances in the as well five-coordinate amide compounds tris((2,6-diisopropylphenyl)amido)bis(tetrahydrofuran)-ytterbium (average 2.17 Å)[15] and {(Me$_3$Si)$_2$N]$_2$Yb(THF)(μ-Cl)}$_2$ [2.174(5) and 2.108(5) Å, respectively].[16] The Yb−N distance in **1** is shorter than the Yb−O distance [2.376(4) Å], and the C−Yb−N angle [112.54(12)°] is considerably larger than the C−Yb−O angle [76.38(19)°]. The distortion from an ideal square-pyramidal coordination polyhedron can also be seen by inspecting the two trans and the two cis interligand angles which belong to the base of the square pyramid. The O−Yb−O angle [152.8(2)°] is larger than the N−Yb−N angle [134.9(2)°], and the two O−Yb−N angles are 91.31(15) and 99.07(15)°, respectively. The Yb−N−Si angles in **1** are 123.9(2)° [Si(1)] and 115.9(2)° [Si(2)]. However, a closer inspection of the metal···carbon distances reveals that there are no "agostic" interactions present, which is noteworthy taking into consideration the low coordination number of the ytterbium atom. Except for the Yb−C(ipso) distance [2.350(8) Å], there are no Yb···carbon distances shorter than 3.0 Å and the closest Yb···C(SiMe$_3$) distance is 3.334(8) Å [C(16)]. Further interatomic separations and angles of the molecular structure of **1** can be derived from Table 2.

We note that our attempts to also crystallize the corresponding yttrium and samarium compound from different solvent combinations yielded amorphous material only.

DanipYb[N(SiHMe$_2$)$_2$]$_2$ (2) and DanipSm[N(SiHMe$_2$)$_2$]$_2$ (3). We were interested in investigating how the molecular structure of Danip-based lanthanide bis(amide) compounds would vary when using amide ligands with different steric demands. We therefore decided to employ the slightly smaller bis(dimethylsilyl)amide ligand. The amine is commercially available and was first introduced as a ligand in lanthanide chemistry by Anwander and Herrmann.[17]

The Yb−C, Yb−N, and Yb−O distances in **2** can favorably be compared, within the error limits of determination, with the corresponding distances in compound **1**. Besides the Yb−C(ipso) distance [2.377(2) Å] all other Yb···C distances in **2** are clearly longer than 3.0 Å. As one would expect, the N−Yb−N angle of 118.85(9)° in **2** is considerably smaller than the corresponding angle in **1** [134.9(2)°]. An observation which can most likely be attributed to the different steric demand of both ligand systems. On the other hand, the C−Yb−O and O−Yb−O angles do not differ much in both compounds (see Table 2). The Yb−N−Si angles in **2** are within the expected range [Si(1), 113.79(12)°; Si(2), 118.95(12)°; Si(3), 111.46(12)°; Si(4), 120.14(13)°]. The four Si−H hydrogen atoms were located from a difference map and refined. The relatively long Yb···H(Si−H) distances [H(1), 3.30(2); H(2), 3.39(2); H(3), 3.25(2); H(4), 3.40(2) Å] indicate that there is no "agostic" interaction present despite the relatively low coordination number at the metal atom.

Since we did not detect any "agostic" interactions in the solid-state structure of compound **2**, we continued our investigations by choosing a metal of larger size. Previous investigations from our laboratory[6−9] have shown that lanthanide terphenyl compounds are accessible for the smaller lanthanide elements and that, so far, the largest

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Table 2. Comparison of Selected Interatomic Separations (Å) and Angles (deg) of Complexes **1**−**5**

param	**1** (Ln = Yb)	**2** (Ln = Yb)	**3** (Ln = Sm)	**4** (Ln = Yb)	**5** (Ln = Y)
Ln−C	2.350(8)	2.377(2)	2.484(4)	2.379(3)	2.474(3) [Y(1)]/2.468(3) [Y(2)]
Ln−N	2.241(5)	2.213(2) [N(1)] 2.204(2) [N(2)]	2.313(3) [N(1)] 2.303(3) [N(2)]		
Ln−O	2.376(4)	2.4050(18) [O(1)] 2.3898(18) [O(2)]	2.512(3) [O(1)] 2.496(3) [O(2)]	2.3172(13) [O(1)] 2.0634(13) [O(2)]	2.393(2) [O(1)]/2.397(2) [O(6)] 2.434(2) [O(2)]/2.413(2) [O(7)] 2.127(2) [O(3)]/2.122(2) [O(8)] 2.111(2) [O(4)]/2.100(2) [O(9)] 2.439(2) [O(5)]/2.458(2) [O(10)]
C−Ln−N	112.54(12)	122.75(9) [N(1)] 118.16(9) [N(2)]	122.74(13) [N(1)] 117.98(13) [N(2)]		
C−Ln-O	76.38(10)	74.49(7) [O(1)] 75.18(7) [O(2)]	71.66(11) [O(1)] 72.85(11) [O(2)]	76.94(3) [O(1)] 114.72(4) [O(2)]	76.07(9) [O(1)]/74.42(9) [O(6)] 72.61(9) [O(2)]/73.49(9) [O(7)] 105.30(9) [O(3)]/106.99(9) [O(8)] 109.90(9) [O(4)]/105.35(9) [O(9)] 142.64(9) [O(5)]/144.69(9) [O(10)]
N−Ln−N	134.9(2)	118.85(9)	119.07(13)		
O−Ln−O	152.8(2)	149.67(6)	144.51(9)	153.89(7) [O(1)/O(1A)] 130.55(8) [O(2)/O(2A)] 102.32(5) [O(1)/O(2)] 88.60(5) [O(1)/O(2A)]	147.67(7) [O(1)/O(2)]/147.74(8) [O(6)/O(7)] 82.04(7) [O(1)/O(3)]/82.51(7) [O(6)/O(8)] 87.25(7) [O(1)/O(4)]/90.24(8) [O(6)/O(9)] 140.38(7) [O(1)/O(5)]/140.33(7) [O(6)/O(10)] 113.76(8) [O(2)/O(3)]/109.93(8) [O(7)/O(8)] 95.87(8) [O(2)/O(4)]/95.15(9) [O(7)/O(9)] 71.88(7) [O(2)/O(5)]/71.91(8) [O(7)/O(10)] 139.37(8) [O(3)/O(4)]/143.46(8) [O(8)/O(9)] 79.04(7) [O(3)/O(5)]/78.77(7) [O(8)/O(10)] 84.99(7) [O(4)/O(5)]/84.64(7) [O(9)/O(10)]
O−Ln−N	91.31(15) [O(1)/N(1)] 99.07(15) [O(1)/N(1A)]	107.20(7) [O(1)/N(1)] 92.98(8) [O(1)/N(2)] 89.68(8) [O(2)/N(1)] 100.78(8) [O(2)/N(2)]	108.61(11) [O(1)/N(1)] 93.96(11) [O(1)/N(2)] 90.41(11) [O(2)/N(1)] 102.70(12) [O(2)/N(2)]		
$Ln-C_{ipso}-C_{ortho}$	122.5(3)	122.30(17) [C(8)] 121.42(17) [C(12)]	122.3(3) [C(8)] 121.5(3) [C(12)]	121.72(12)	121.8(2) [C(8)]/122.3(2) [C(56)] 122.3(2) [C(12)]/122.0 (2) [C(60)]
$C_{ipso}-C_{ortho}-C_{ipso'}$	121.3(5)	121.7(2) [C(8)/C(7)] 121.5(2) [C(12)/C(14)]	121.8(4) [C(8)/C(7)] 121.3(4) [C(12)/C(14)]	121.58(18)	122.3(3) [C(8)/C(7)]/122.7(3) [C(56)/C(55)] 122.4(3) [C(12)/C(14)]/121.9(3) [C(60)/C(62)]

lanthanide element that yields stable terphenyl compounds is samarium. The molecular structure of the samarium analogue **3** is isomorphic with the ytterbium compound **2**. The Sm−N distances in **3** [2.303(3) and 2.313(3) Å, respectively] are in the same range as those in the as well five-coordinate $Sm[N(SiHMe_2)_2]_3(THF)_2$ [2.302(3), 2.327(2), and 2.330(3) Å].[18] The N−Ln−N angles in both the ytterbium compound **2** [118.85(9)°] and the samarium analogue **3** [119.07(13)°] are found to be very similar. The Sm−N−Si angles in **3** [Si(1), 111.77(19)°; Si(2), 116.99(18)°, Si(3), 110.11(18)°; Si(4), 117.3(2)°] can be favorably compared with the corresponding angles in **2**. As was found in the molecular structure of **2**, there are no Sm···H(Si−H) distances in **3** that are significantly shorter than 3.0 Å [H(1), 3.01(2); H(2), 3.23(2); H(3), 3.04(2); H(4), 3.14(2) Å]. Again, this excludes the presence of an "agostic" interaction in compound **3**. Additionally, as one would expect, there are no Sm···C distances shorter than 3.0 Å, besides the Sm−C(ipso) distance at 2.484(4) Å. The next closest Sm···C distance is 3.271(8) Å [C(19)], and the nearest interaction with one of the methyl groups on the silicon atoms is 4.627(8) Å [C(22)]. The Si−N−Si angles in the bis(dimethylsilyl) derivatives **2** [Si(1)−N(1)−Si(2), 127.25(14)°; Si(3)−N(2)−Si(4), 128.30(14)°] and **3** [Si(1)−N(1)−Si(2), 131.2(2)°; Si(3)−N(2)−Si(4), 132.5(2)°] are somewhat larger than the corresponding angle in the bis(trimethylsilyl) compound **1** [Si(1)−N(1)−Si(2), 120.1(3)°]. Further bond distances and angles of both compounds **2** and **3** are provided in Table 2.

DanipYb[O(2,6-diisopropylphenyl)]$_2$ (4) and DanipY(THF)[O(2,6-diisopropylphenyl)]$_2$ (5). We were interested in the accessibility of other derivatives of general composition $DanipLnX_2$ and therefore decided to employ a moderately sterically demanding aryloxide ligand, i.e., the 2,6-diisopropylphenoxide ligand, vis-à-vis a Danip moiety. This particular aryloxide ligand was employed first as an ancillary ligand system for the lanthanides in the early nineties by Clark and co-workers.[19,20] As was found in the case of the Danip-based bis(amide) compounds **1**−**3**, the molecular structure of the as well five-coordinate bis(alkoxide) compound **4** (Figure 4) features a distorted square-pyramidal coordination environment about the metal atom. Besides the Yb−C(ipso) distance [2.379(3) Å] all other Yb···C distances in **4** are clearly longer than 3.0 Å. The Yb−O(OMe) distance [2.3172(13) Å] in **4** is noticeably shorter than in the bis(amide) compounds **1** [2.376(4) Å] and **2** [2.4050(18) and 2.3898(18) Å, respectively]. The Yb−O(aryloxide) distance [2.0634(13) Å] is approximately 1/10 of an angstrom longer than the Yb−O(*tert*-butoxide) distance in the as well five-coordinate terphenyl mono(alkoxide) compound $DmpYb(THF)(O^tBu)(\mu\text{-}Cl_2)Li(THF)_2$ [1.965(5) Å], which is so far the only other reported terphenyl-based lanthanide alkoxide compound.[9] This observation presumably is as a result of the increased steric crowding at the metal atom. The Yb−O(aryloxide) distance of 2.0634(13) Å in **4** can further be compared, e.g., with the metal−O(aryloxide) distances in the

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(18) Rabe, G. W.; Yap, G. P. A. *Z. Kristallogr.*−*New Cryst. Struct.* **2000**, *215*, 457.

(19) Clark, D. L.; Watkin, J. G.; Huffman, J. C. *Inorg. Chem.* **1992**, *31*, 1556.

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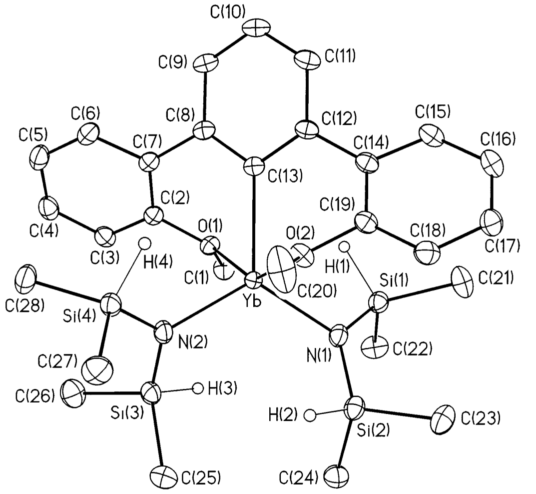

Figure 3. ORTEP diagram of DanipYb[N(SiHMe$_2$)$_2$]$_2$ (**2**) showing the atom-labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

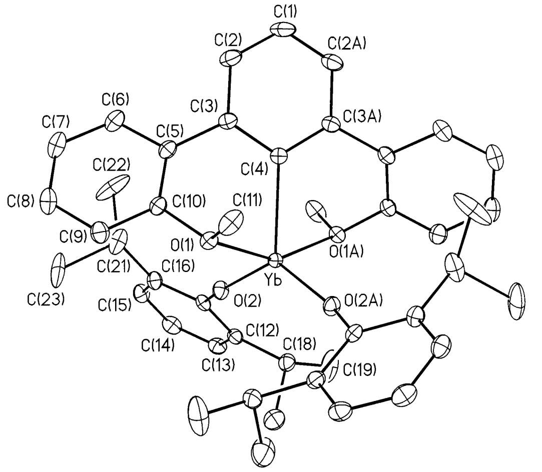

Figure 4. ORTEP diagram of DanipYb[O(2,6-diisopropylphenyl)]$_2$ (**4**) showing the atom-labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

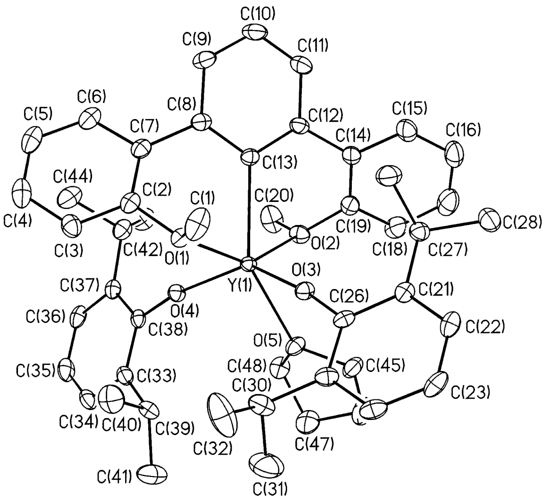

Figure 5. ORTEP diagram of DanipY(THF)[O(2,6-diisopropylphenyl)]$_2$ showing the atom-labeling scheme. Only one of the two independent molecules (**5a**) is shown. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

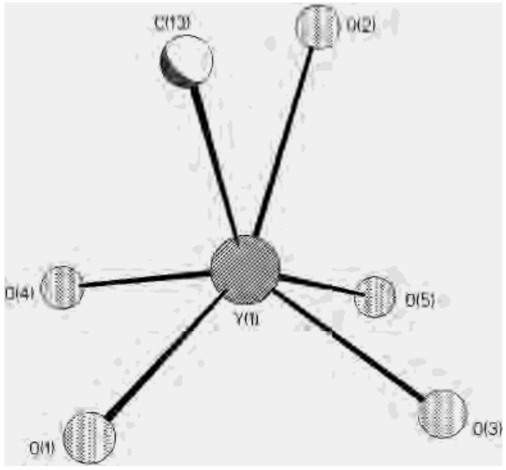

Figure 6. Central core of **5a** showing the distorted trigonal-prismatic coordination polyhedron.

as well five-coordinate lutetium compound Lu[O(2,6-diisopropylphenyl)]$_3$(THF)$_2$ (average 2.044 Å),[20] taking into consideration the slightly smaller ionic radius of lutetium(III).[21] The ytterbium aryloxide moieties in **4** are slightly bent [Yb−O(2)−C(17), 159.04(12)°], as was previously observed in the case of tris(2,6-diisopropylphenoxide) compounds of the lanthanides.[20] The 2,6-diisopropylphenyl moieties are not tilted [O(2)−C(17)−C(12), 119.68(16)°; O(2)−C(17)−C(16), 120.22(17)°]. While the O(OMe)−Yb−O(OMe) angles in the bis(amide) compound **1** [152.8(2)°] and in the bis(alkoxide) derivative **4** [153.89(7)°] are very similar, the O(aryloxide)−Yb−O(aryloxide) angle in **4** [130.55(8)°] is somewhat smaller than the N−Yb−N angle [134.9(2)°] in **1**.

We were interested in investigating how differences in the size of the metal atom would affect the molecular structure of compound **4**. In the case of the bis(dimethylsilyl) compounds **2** and **3** the same structural type was observed for metals of different size. And in the case of the bis(trimethylsilyl)amide analogues of compound **1** but with yttrium and samarium instead of ytterbium we failed to obtain single crystalline material. Interestingly, in the molecular structure of the yttrium bis(alkoxide) compound **5** (Figure 5) additional coordination of one molecule of tetrahydrofuran is observed, resulting in a coordination polyhedron which can be described as distorted trigonal-prismatic rather than octahedral (Figure 6) since there is no interligand angle about the metal atom close to 180°. Two chemically identical independent molecules are found in the unit cell of compound **5**. The largest interligand angles about the metal atom are those involving the two methoxy functions, namely 147.67(7)° [**5a**, O(1)−Y(1)−O(2)] and 147.74(8)° [**5b**, O(6)−Y(2)−O(7)]. The Y−O(THF) distance [**5a**, 2.439(2) Å; **5b**, 2.458(2) Å] is considerably longer than the Y−O(aryloxide) distances [**5a**, 2.111(2) and 2.127(2) Å; **5b**, 2.100(2) and 2.122(2) Å] but can favorably compared with the Y−O(OMe) distances ranging from 2.393(2) to 2.434(2) Å. The smallest O(THF)−Y−O angle is with one of the O(OMe) atoms [O(2), 71.88(7)° (**5a**); O(7), 71.91(8)° (**5b**), respectively]. Both the Y−O(OMe) and the Y−O(aryloxide) distances in

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(21) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

5 are slightly longer (see Table 2) than the corresponding distances in the ytterbium bis(aryloxide) compound **4**, as one would expect on the basis of Shannon's radii[21] for a molecular structure with a coordination number 6 instead of 5 at the metal atom and a slightly larger metal atom, i.e., yttrium instead of ytterbium. While the O(aryloxide)−Y−O(aryloxide) angles [**5a**, 139.37(8)°; **5b**, 143.46(8)°] are larger than the corresponding angle in **4** [130.55(8)°], the O(OMe)−Y−O(OMe) angles [**5a**, 147.67(7)°; **5b**, 147.74(8)°] are noticeably smaller than the same angle in **4** [153.89(7)°]. As was found in the molecular structure of compound **4**, the yttrium aryloxide moieties in **5** are slightly bent [**5a**, 168.98(18) and 169.62(19)°; **5b**, 165.87(19) and 171.77(19)°] but to a smaller extent than in **4** [159.04(12)°]. Again, as in **4**, the 2,6-diisopropylphenyl moieties are not tilted. Further interatomic separations and angles of **4** and both independent molecules of **5** can be derived from Table 2.

Conclusion

Our work demonstrates that a number of novel low-coordinate monomeric bis(amide) and bis(arylalkoxide) compounds of Danip-based lanthanide systems (Ln = Yb, Y, Sm) are easily accessible in good yield via simple salt metathesis reaction in a one-pot synthesis. Our work gives further insight into structural aspects as well as the reactivity of Danip-based lanthanide complexes. Under exclusion of air and moisture the compounds are remarkably stable in the solution state, in contrast to previously reported non-functionalized lanthanide terphenyl compounds which were of only limited stability, particularly in tetrahydrofuran solution at room temperature. The molecular structures of compounds **1**−**4** exhibit square-pyramidal coordination environments about the metal atom. Except for the yttrium bis(alkoxide) compound **5** all presented complexes are free of coordinating Lewis bases such as tetrahydrofuran. In all molecular structures that are reported in this paper, the Danip ligand adopts the chiral (racemic) *d*,*l* form. The usability of these compounds for, e.g., catalytic applications for a variety of transformations is currently under investigation.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of DanipYb[N($SiMe_3$)$_2$]$_2$ (**1**), DanipYb[N($SiHMe_2$)$_2$]$_2$ (**2**), DanipSm[N($SiHMe_2$)$_2$]$_2$ (**3**), DanipYb[O(2,6-diisopropylphenyl)]$_2$ (**4**), and DanipY(THF)[O(2,6-diisopropylphenyl)]$_2$ (**5**). This material is available free of charge via the Internet at http://pubs.acs.org.

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