Terphenyl Ligand Systems in Lanthanide Chemistry: Use of the 2,6-Di(1-naphthyl)phenyl Ligand for the Synthesis of Kinetically Stabilized Complexes of Trivalent Ytterbium, Thulium, and Yttrium

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Received October 17, 2000

The molecular structures of terphenyl derivatives of trivalent ytterbium, thulium, and yttrium of general composition $DnpLnCl_2(THF)_2$ [Dnp = 2,6-di(1-naphthyl)phenyl] are reported. The complexes (Ln = Yb: **1**; Ln = Tm: **2**; Ln = Y: **3**) are synthesized by reaction of 1 equiv of DnpLi with 1 equiv of $LnCl_3$ (Ln = Yb, Tm, or Y) in tetrahydrofuran at room temperature in 50% yield. Attempts to prepare a Dnp scandium compound gave heterobimetallic $[(THF)_3Sc_2OCl_5Li(THF)]_2$ (**4**) in low yield. **1** crystallizes in the monoclinic space group *C*2/*c*. Crystal data for **1** at 203 K: $a = 14.333(3)$ Å, $b = 16.353(3)$ Å, $c = 12.427(2)$ Å, $\beta = 91.021(4)°$, $Z = 4$, $D_{calcd} = 1.637$ g cm^{-3}, $R_1 = 4.44\%$. **2** crystallizes in the monoclinic space group *C*2/*c*. Crystal data for **2** at 203 K: $a = 14.333(1)$ Å, $b = 16.374(2)$ Å, $c = 12.404(1)$ Å, $\beta = 90.934(2)°$, $Z = 4$, $D_{calcd} = 1.628$ g cm^{-3}, $R_1 = 3.00\%$. **3** crystallizes in the monoclinic space group *C*2/*c*. Crystal data for **3** at 203 K: $a = 14.348(3)$ Å, $b = 16.476(3)$ Å, $c = 12.356(2)$ Å, $\beta = 90.987(4)°$, $Z = 4$, $D_{calcd} = 1.441$ g cm^{-3}, $R_1 = 5.62\%$. **4** crystallizes in the monoclinic space group $P2_1/n$. Crystal data for **4** at 203 K: $a = 11.0975(9)$ Å, $b = 11.0976(9)$ Å, $c = 21.3305(18)$ Å, $\beta = 94.718(2)°$, $Z = 2$, $D_{calcd} = 1.051$ g cm^{-3}, $R_1 = 3.45\%$. Complexes **1**−**3** represent examples of novel chiral (racemic) organometallic complexes of the lanthanide elements ytterbium and thulium and the group 3 element yttrium, respectively. The molecular structures of monomeric **1**−**3** exhibit distorted trigonal−bipyramidal coordination environments at the metal center, with the two oxygen atoms of the tetrahydrofuran ligands occupying the axial positions of a trigonal−bipyramidal coordination polyeder. The molecular structure of the scandium compound **4** shows a complex polynuclear heterobimetallic arrangement.

Introduction

There is much current interest in the organometallic chemistry of the f-block elements, which is largely defined by the use of ancillary ligand systems such as cyclopentadienyl and cyclooctatetraenyl derivatives. Of particular interest and one of the challenging problems in lanthanide chemistry is the search for novel ancillary ligand systems capable of facilitating different catalytic processes.

Terphenyl ligand systems are capable of stabilizing a variety of complexes in unusual coordination geometries and bonding situations that are not readily accessible with other ligands.[1] Terphenyl-based organolanthanide complexes, however, have only recently received attention. Compared with numerous previous studies employing terphenyl ligands focusing on s-block, p-block, and late transition metal complexes,[1] the area of terphenyl-based complexes of early transition metals and lanthanides is still relatively undeveloped.

We reported earlier the synthesis and structural characterization of two novel terphenyl derivatives of the lanthanide element ytterbium, namely, $DmpYbCl_2(N\text{-}MeIm)_2(py)$ and the bis(trimethylsilyl) amide derivative $DmpYb[N(SiMe_3)_2](\mu\text{-}Cl)_2Li(THF)_2$ (Dmp = 2,6-dimesitylphenyl), thereby introducing a novel class of lanthanide complexes containing bulky terphenyl groups as the only ancillary organic ligand.[2] Another paper on this topic by Niemeyer et al. followed recently.[3] Terphenyl ligands in lanthanide chemistry were used first in complexes stabilized by two cyclopentadienyl ligands.[4] We now report our most recent investigations in this area of chemistry, thereby introducing the Dnp group [Dnp = 2,6-di(1-naphthyl)phenyl] as an ancillary organic ligand system for the strongly electropositive lanthanides and the group 3 element yttrium and providing more details on structural aspects of terphenyl-based systems of these elements.

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. $YbCl_3$, $TmCl_3$, YCl_3, and $ScCl_3$ were purchased from Aldrich (packaged under argon in ampules) and were used as received. DnpI was prepared following the general procedure for the preparation of terphenyl iodides described by Hart et al.[5,6] DnpLi[7] was prepared following the procedure for the preparation of DmpLi.[8] In contrast to hexane-soluble DmpLi,

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10.1021/ic001148m CCC: $20.00

Table 1. Crystallographic Data for $DnpYbCl_2(THF)_2$ (**1**), $DnpTmCl_2(THF)_2$ (**2**), $DnpYCl_2(THF)_2$ (**3**), and $[(THF)_3Sc_2OCl_5Li(THF)]_2$ (**4**)[a]

complex	1	2	3	4
formula	$C_{34}H_{33}Cl_2O_2Yb$	$C_{34}H_{33}Cl_2O_2Tm$	$C_{34}H_{33}Cl_2O_2Y$	$C_{32}H_{64}Cl_{10}Li_2O_{10}Sc_4$
fw	717.54	713.43	633.41	1157.05
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)
a, Å	14.333(3)	14.333(1)	14.348(3)	11.0975(9)
b, Å	16.353(3)	16.374(2)	16.476(3)	11.0976(9)
c, Å	12.427(2)	12.404(1)	12.356(2)	21.3305(18)
β , deg	91.021(4)	90.934(2)	90.987(4)	94.718(2)
V, $Å^3$	2912.3(9)	2910.7(5)	2920.6(10)	2618.1(4)
Z	4	4	4	2
D_{calcd}, g cm^{-3}	1.637	1.628	1.441	1.468
temp, °C	−70(2)	−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)	Mo Kα (λ = 0.71073 Å)
μ(Mo Kα), cm^{-1}	34.24	32.61	22.10	10.51
R_1, %	4.44	3.00	5.62	3.45
wR_2, %	8.37	5.63	10.13	7.16

[a] The quantity minimized was $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R_1 = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_0, 0]/3$.

DnpLi is found to be completely insoluble in hexanes and aromatic solvents but well-soluble in tetrahydrofuran.

$DnpYbCl_2(THF)_2$ (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 DnpLi (0.30 g, 0.9 mmol) in 10 mL of tetrahydrofuran was added to the suspension, the reaction mixture was stirred for 30 min yielding an orange suspension, and the suspension was centrifuged. All volatiles were removed under vacuum, the residues were extracted with toluene/tetrahydrofuran (2:1), and they were centrifuged. Cooling of the solution to −30 °C resulted in crystallization of **1**. Removal of the mother liquor and washing of the obtained product with hexanes and toluene followed by drying under vacuum gave **1** as an orange microcrystalline material (0.29 g, 50%). Analytically pure complex **1** is insoluble in hexanes and aromatic solvents but soluble in tetrahydrofuran. **1** does not lose coordinated tetrahydrofuran after being dried under vacuum (10^{-2} mbar at room temperature). Colorless complexes **2** and **3** can be prepared in a similar manner using $TmCl_3$ or YCl_3, respectively, instead of $YbCl_3$.

1. Anal. Calcd for $C_{34}H_{33}Cl_2O_2Yb$: C, 56.91; H, 4.64. Found: C, 56.65; H, 4.53. IR (Nujol): 1592 (w), 1234 (w), 1176 (w), 1169 (w), 1094 (m), 1007 (s), 974 (m), 920 (w), 852 (s), 798 (s), 786 (s), 744 (m), 731 (m), 669 (w), 660 (w), 628 (w), 618 (m), 581 (w) cm^{-1}. mp: 185 °C dec.

2. Anal. Calcd for $C_{34}H_{33}Cl_2O_2Tm$: C, 57.24; H, 4.66. Found: C, 57.01; H, 4.50. IR (Nujol): 1592 (w), 1573 (w), 1234 (w), 1177 (w), 1169 (w), 1093 (m), 1007 (s), 973 (m), 918 (w), 853 (s), 798 (s), 786 (s), 744 (m), 731 (m), 669 (w), 660 (w), 628 (w), 618 (m), 580 (w) cm^{-1}. mp: 182 °C dec.

3. Anal. Calcd for $C_{34}H_{33}Cl_2O_2Y$: C, 64.47; H, 5.25. Found: C, 64.28; H, 5.17. IR (Nujol): 1591 (w), 1574 (w), 1541 (w), 1234 (w), 1204 (w), 1175 (w), 1092 (w), 1008 (s), 974 (w), 910 (w), 853 (s), 806 (s), 798 (s), 786 (s), 730 (m), 720 (m), 670 (w), 660 (w), 627 (w), 618 (m), 580 (w), 568 (w) cm^{-1}. mp: 173 °C dec. A ^{13}C-solution NMR spectrum of **3** in THF-d_8 could not be obtained because of the limited solubility and stability of analytically pure **3** in THF solution over prolonged time periods at ambient temperature.

4. Anal. Calcd for $C_{32}H_{64}Cl_{10}Li_2O_{10}Sc_4$: C, 33.22; H, 5.58. Found: C, 33.02; H, 5.40.

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. The systematic absences in the diffraction data are consistent for the space groups *Cc* and *C*2/*c* for **1**−**3** and, uniquely, for the space group $P2_1/n$ for **4**. *E*-statistics, as well as the value of *Z* and the molecular 2-fold in **1**−**3**, suggested the centrosymmetric option, *C*2/*c*, for **1**−**3** that 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 molecules in **1**−**3**, respectively, are located at a 2-fold rotation axis. The molecule in **4** is located at an inversion center. All nonhydrogen atoms were refined with anisotropic displacement coefficients. All other hydrogen atoms were treated as idealized contributions.

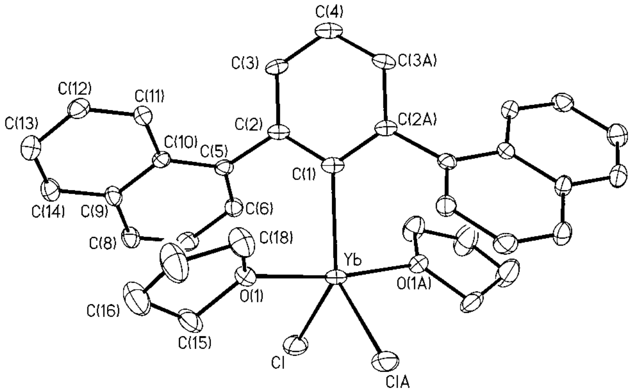

Figure 1. ORTEP diagram of $DnpYbCl_2(THF)_2$ (**1**) showing atom-labeling scheme. Thermal ellipsoids at 30% level. Hydrogen atoms were omitted for clarity.

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

$DnpLnCl_2(THF)_2$ (Ln = Yb: 1; Ln = Tm: 2; Ln = Y: 3). Reaction of $LnCl_3$ (Ln = Yb, Tm, Y) with 1 equiv of DnpLi[7] at room temperature produces tetrahydrofuran-soluble complexes of general composition $DnpLnCl_2(THF)_2$ (Ln = Yb, orange **1**; Ln = Tm, colorless **2**; Ln = Y, colorless **3**) in 50% yield. Formation of monoterphenyl-substituted complexes was also observed using 2 or more equiv of DnpLi. Crystals of **1**−**3** suitable for X-ray diffraction studies were obtained by slow evapoation of toluene/tetrahydrofuran solutions at ambient temperature. A main feature of the isomorphous molecular structures of **1**−**3** (Figure 1), respectively, is a metal atom in a distorted trigonal−bipyramidal coordination environment. The axial positions of the trigonal bipyramid are occupied by two oxygen atoms of the tetrahydrofuran ligands, while the two chlorine atoms are in the equatorial positions. The Yb−C interatomic separation of 2.395(8) Å in penta-coordinate **1** is slightly shorter than the corresponding distance in hexa-

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coordinate DmpYbCl_2(*N*-MeIm)$_2$(py) [2.447(9) Å].[1] 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],[1] in the bis(cyclopentadienyl) derivative (C_5H_4Me)$_2$YbDmp [2.410(3) Å],[4] as well as in Ph_3Yb(THF)$_3$ [2.39(1), 2.40(1), and 2.43(1) Å].[9] 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].[10] The Tm−C(ipso) distance of 2.413(3) Å in **2** matches, e.g., the corresponding distances in Ph_3Tm(THF)$_3$ [2.421(6), 2.425(6), and 2.416(7) Å][11] within the error limits of the determinations, while the corresponding distance in the yttrium derivative **3** [2.436(6) Å] can be compared, e.g., with the Y−C(ipso) distance of 2.41(2) Å in $Cp_2YC_6H_4$-*o*-CH_2NMe_2.[12] The Cl−Yb−Cl angle of 98.89(8)° as well as the O−Yb−O angle of 172.3(2)° in **1** document the deviation from ideal trigonal−bipyramidal coordination polyeder. The observation of such a heavily distorted coordination geometry in penta-coordinated **1**−**3** can mostly be ascribed to the steric demands of the Dnp ligand. The torsion angle of O(1)−Yb−C(1)−C(2) is 56.1°, and the dihedral angle between the mean planes of the naphthyl ligand and the central, metalated phenyl ring is 56.0°, thereby resulting in an arrangement of the terphenyl substituent that is somewhat reminiscent of a two-bladed propellor. Furthermore, complexes of general composition DnpLnCl_2(THF)$_2$ are chiral with both enantiomers being equally present in the packing diagram. The arrangement of the two naphthyl groups in **1**−**3** is such that both outer phenyl rings of the naphthyl group are turned away from the metal center. This arrangement differs from that found in the solid state structure of previously characterized DnpLi(THF)$_2$[7] in which both outer phenyl rings of the naphthyl substituents point toward the metal center. The two different arrangements of the naphthyl substituents of the Dnp ligand adopted in the solid state demonstrate that this particular terphenyl ligand system possesses stereochemical flexibility. Besides the lanthanide−ipso-carbon distance in DnpLnCl_2(THF)$_2$ [2.395(8) (**1**), 2.413(3) (**2**), and 2.436(6) Å (**3**), respectively], there are weak secondary interactions between the metal atom and carbon atoms C(6) and C(5) at a distance of 3.292(8) [C(6)] and 3.481(8) Å [C(5)] in complex **1** [3.285(3) and 3.490(3) Å for the corresponding carbon atoms in **2**, 3.283(6) and 3.496(6) Å in **3**]. These distances represent the next closest metal−carbon distances and originate from those phenyl rings of the naphthyl substituents attached to the 2,6-position of the central, metalated phenyl ring. Further details on interatomic separations and angles of complexes **1**−**3** can be derived from Table 2.

[(THF)$_3$$Sc_2OCl_5$Li(THF)]$_2$ (4). We were interested in probing the accessibility of Dnp compounds of other lanthanide or group 3 metals. As part of this effort, equimolar amounts of DnpLi and $ScCl_3$ were reacted in tetrahydrofuran at room temperature. The obtained colorless crude product was extracted using toluene and was centrifuged. Slow evaporation of the obtained colorless toluene solution in a glovebox at ambient temperature gave colorless crystals of **4** suitable for an X-ray diffraction study in an approximate yield of 10%.

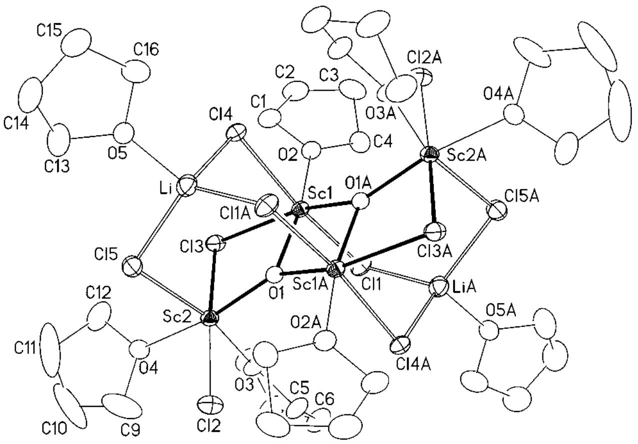

Figure 2. Molecular diagram of [(THF)$_3$$Sc_2OCl_5$Li(THF)]$_2$ (**4**) showing atom-labeling scheme. Thermal ellipsoids at 30% level. Hydrogen atoms were omitted for clarity. Carbon and oxygen atoms are depicted as boundary ellipsoids. Lithium and chlorine atoms are depicted as ellipsoids with principal axes. Scandium atoms are depicted as ellipsoids with shaded segments. Closed thick bonds highlight the four-step ladder framework of the central molecular core. Open bonds, together with the closed thick bonds, describe two interpenetrating adamantane-type frameworks. Selected interatomic separations (Å) and angles (deg): Sc(1)−O(1A) = 2.0006(16), Sc(1)−O(1) = 2.0427(17), Sc(1)−O(2) = 2.2274(18), Sc(1)−Cl(1) = 2.5107(8), Sc(1)−Cl(3) = 2.6130(8), Sc(1)−Cl(4) = 2.5103(8), Sc(1)···Sc(1A) = 3.0774(10), Sc(1)···Sc(2) = 3.3964(7), Sc(2)−O(1) = 1.9742(16), Sc(2)−O(3) = 2.1928(18), Sc(2)−O(4) = 2.2265(18), Sc(2)−Cl(2) = 2.4114(9), Sc(2)−Cl(3) = 2.5606(8), Sc(2)−Cl(5) = 2.4843(8), Li−O(5) = 1.933(5), Li−Cl(1A) = 2.368(5), Li−Cl(4) = 2.348(5), Li−Cl(5) = 2.364(5) Å; O(1)−Sc(1)−O(1A) = 80.88(7), O(1)−Sc(1)−O(2) = 166.35(7), O(2)−Sc(1)−O(1A) = 112.71(7), Cl(1)−Sc(1)−Cl(3) = 90.51(3), Cl(1)−Sc(1)−Cl(4) = 165.69(3), Cl(3)−Sc(1)−Cl(4) = 86.78(3), O(1)−Sc(1)−Cl(1) = 95.83(5), O(1)−Sc(1)−Cl(3) = 79.88(5), O(1)−Sc(1)−Cl(4) = 97.51(5), O(1A)−Sc(1)−Cl(1) = 93.06(5), O(1A)−Sc(1)−Cl(3) = 160.59(5), O(1A)−Sc(1)−Cl(4) = 94.13(5), O(2)−Sc(1)−Cl(1) = 82.67(5), O(2)−Sc(1)−Cl(3) = 86.56(5), O(2)−Sc(1)−Cl(4) = 83.14(5), O(1)−Sc(2)−O(3) = 100.15(7), O(1)−Sc(2)−O(4) = 167.39(7), O(3)−Sc(2)−O(4) = 79.78(7), Cl(2)−Sc(2)−Cl(3) = 171.22(3), Cl(2)−Sc(2)−Cl(5) = 94.83(3), Cl(3)−Sc(2)−Cl(5) = 93.36(3), O(1)−Sc(2)−Cl(2) = 100.01(5), O(1)−Sc(2)−Cl(3) = 82.45(5), O(1)−Sc(2)−Cl(5) = 94.74(5), O(3)−Sc(2)−Cl(2) = 87.00(5), O(3)−Sc(2)−Cl(3) = 84.27(5), O(3)−Sc(2)−Cl(5) = 164.46(5), O(4)−Sc(2)−Cl(2) = 92.59(6), O(4)−Sc(2)−Cl(3) = 85.00(6), O(4)−Sc(2)−Cl(5) = 84.72(6), O(5)−Li−Cl(1A) = 109.7(2), O(5)−Li−Cl(4) = 108.3(2), O(5)−Li−Cl(5) = 102.8(2), Cl(1A)−Li−Cl(4) = 102.37(18), Cl(1A)−Li−Cl(5) = 117.7(2), Cl(4)−Li−Cl(5) = 115.7(2), Li−Cl(1A)−Sc(1A) = 101.82(12), Li−Cl(4)−Sc(1) = 98.53(12), Li−Cl(5)−Sc(2) = 100.84(12)°.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complexes **1**−**3**

complex	**1** (Ln = Yb)	**2** (Ln = Tm)	**3** (Ln = Y)
Ln−Cl	2.4996(16)	2.5143(8)	2.5528(14)
Ln−O(1)	2.282(4)	2.298(2)	2.322(3)
Ln−C(1)	2.395(8)	2.413(3)	2.436(6)
Ln···C(5)	3.481(8)	3.490(3)	3.496(6)
Ln···C(6)	3.292(8)	3.285(3)	3.283(6)
Ln···H(6)	3.02(2)	3.05(2)	3.03(2)
C(1)−Ln−O(1)	86.13(10)	86.02(5)	86.02(8)
C(1)−Ln−Cl	130.56(4)	130.40(2)	130.11(3)
Cl−Ln−Cl(A)	98.89(8)	99.20(4)	99.78(7)
O(1)−Ln−O(1A)	172.3(2)	172.04(9)	172.03(16)

The molecular structure of complex **4** (Figure 2) can best be described as a dimeric lithium−chloride adduct of $ScOCl_4$, which is complexed by tetrahydrofuran. It is comprised of a rather complex framework exhibiting two types of hexacoordinate scandium atoms in different coordination environ-

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ments. Main features of the molecular structure of heterobimetallic complex **4** are (i) a heavily distorted transoid four-step ladder framework consisting of the four scandium atoms, the two bridging oxygens, and two chlorine atoms bridging scandium atoms and (ii) a heavily distorted adamantane-type structural motif per half molecule that is formed by three scandium atoms, two bridging oxygen atoms, four bridging chlorine atoms, and a lithium atom. Sc(1) is surrounded by two μ-oxide ligands, one tetrahydrofuran molecule, and three μ-chloride ligands. On the other hand, Sc(2) is complexed by one of the μ-oxide ligands, two tetrahydrofuran, one terminal chlorine, and two bridging chlorine atoms. As one would expect, the Sc−μ-oxygen distances match within the error limits of the determinations [Sc(1)−O(1) = 2.0427(17) Å; Sc(1)−O(1A) = 2.0006(16) Å; Sc(2)−O(1) = 1.9742(16) Å]. They are significantly shorter than the Sc−O(THF) separations [Sc(1)−O(2) = 2.2274(18) Å; Sc(2)−O(3) = 2.1928(18) Å; Sc(2)−O(4) = 2.2265(18) Å]. The Sc−Cl distances range from 2.4114(9) to 2.6130(8) Å, with the terminal Sc(2)−Cl(2) distance being the shortest and the two Sc−Cl distances involving Cl(3), which bridges the two scandium atoms, being the longest [Sc(1)−Cl(3) = 2.6130(8) Å; Sc(2)−Cl(3) = 2.5606(8) Å]. The deviation of the coordination environments of the two scandium atoms from ideal octahedral coordination geometry is most readily seen by inspecting the interligand angles. The cis interligand angles of Sc(1) range from 79.88(5) to 112.71(7)° [79.78(7) to 100.15(7)° for Sc(2)], while the trans interligand angles are 160.69(5), 165.69(3), and 166.35(7)° for Sc(1) and 164.46(5), 167.39(7), and 171.22(3)°, respectively, for Sc(2). The coordination geometry of the lithium atom deviates from the ideal tetrahedral coordination polyeder with interligand angles ranging from 102.37(18) to 117.7(2)°. Further details on interatomic separations and angles of **4** can be derived from the figure caption of Figure 2.

We note that the origin of the two μ-oxide ligands in complex **4**, as well as the mechanism of its formation, is not clear. The possibility of trace amounts of water being present in the solvents used cannot be ruled out completely. Another possibility is that a Dnp−scandium complex is formed first, followed by a more complex reaction involving C, H activation, and THF deoxygenation. An inspection of the mother liquor by GC/MS spectroscopy, however, clearly showed the presence of the parent hydrocarbon DnpH but not of ethylene (as a product from a THF cleavage reaction). Another possible source for the μ-oxide ligands could be scandium oxochloride (as a contamination of $ScCl_3$). We also note that formation of complex **4** from the toluene cut of this reaction is reproducible, however, in only relatively poor yield. Complex **4** is, after crystallization from toluene, no longer toluene soluble.

We also attempted the synthesis of Dnp−samarium, −neodymium, and −lanthanum complexes by reacting equimolar amounts of DnpLi with the corresponding anhydrous lanthanide trichloride in tetrahydrofuran at room temperature. Formation of DnpH was observed in all cases; however, we failed to isolate any characterizable lanthanide species, other than in the case of the reaction of DnpLi with $ScCl_3$, which yielded complex **4**.

Conclusions

Our work introduces the Dnp ligand system as an ancillary ligand system for the lanthanide elements ytterbium and thulium as well as the group 3 element yttrium, thereby providing easy access to a novel class of chiral (racemic) terphenyl-based−lanthanide complexes. Further investigations on the reaction chemistry as well as catalytic properties of these systems are currently underway.

Acknowledgment. We are thankful for financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Leonhard-Lorenz Foundation. Generous support from Professor H. Schmidbaur is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $DnpLnCl_2(THF)_2$ (Ln = Yb: **1**; Ln = Tm: **2**; Ln = Y: **3**) and $[(THF)_3Sc_2OCl_5Li(THF)]_2$ (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC001148M