

Synthesis and Structural Characterization of 2,6-Dimesitylphenyl Complexes of Scandium, Ytterbium, and Yttrium

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The molecular structures of a number of 2,6-dimesitylphenyl-based (2,6-dimesitylphenyl = Dmp) complexes of the group 3 elements scandium and yttrium as well as of the lanthanide element ytterbium are reported. Reaction of 1 equiv of DmpLi with 1 equiv of MCl₃ (M = Sc, Yb, Y) in tetrahydrofuran at room temperature followed by crystallization from toluene/hexanes at –30 °C produces DmpMCl₂(THF)₂ (M = Sc: **1**; M = Yb: **2**) and DmpMCl₂(THF)₃ (M = Y: **3**), respectively. The one-pot reaction of DmpLi with 1 equiv of YbCl₃ in tetrahydrofuran at room temperature followed by addition of 1 equiv of KO^tBu produces the heterobimetallic monoalkoxide complex DmpYb(THF)(O^tBu)(μ-Cl)₂Li(THF)₂ (**4**), which was crystallized from toluene/tetrahydrofuran (20:1) at –30 °C. Crystal data for **1**: monoclinic, *P*2₁/*n*; *T* = 203 K; *a* = 10.178(3) Å; *b* = 15.468(3) Å; *c* = 20.132(5) Å; β = 101.85(3)°; *V* = 3102.0(17) Å³; *Z*' = 4; *D*_{calcd} = 1.228 g cm⁻³; *R*₁ = 5.89%. Crystal data for **2**: monoclinic, *P*2₁/*n*; *T* = 173 K; *a* = 10.2447(7) Å; *b* = 15.5683(12) Å; *c* = 20.0979(14) Å; β = 101.749(4)°; *V* = 3238.3(5) Å³; *Z*' = 4; *D*_{calcd} = 1.485 g cm⁻³; *R*₁ = 4.32%. Crystal data for **3**: monoclinic, *P*2₁/*n*; *T* = 203 K; *a* = 15.950(3) Å; *b* = 11.865(2) Å; *c* = 18.254(3) Å; β = 92.323(3)°; *V* = 3451.9(10) Å³; *Z*' = 4; *D*_{calcd} = 1.327 g cm⁻³; *R*₁ = 4.43%. Crystal data for **4**: triclinic, *P* $\bar{1}$; *T* = 193 K; *a* = 10.2252(2) Å; *b* = 11.3497(2) Å; *c* = 18.5814(2) Å; α = 98.7353(6)°; β = 102.8964(6)°; γ = 94.8058(5)°; *V* = 2062.09(5) Å³; *Z*' = 2; *D*_{calcd} = 1.375 g cm⁻³; *R*₁ = 4.56%. The molecular structures of **1–3** feature monomeric complexes with distorted trigonal-bipyramidal (**1** and **2**) or octahedral (**3**) coordination geometry about the metal atom, with the two chlorine atoms occupying the axial positions. **4** represents the first example of an alkoxide derivative of a terphenyl lanthanide complex. The molecular structure of the ate complex **4** exhibits a heavily distorted trigonal-bipyramidal coordination polyhedron about the ytterbium atom, with one of the μ-chlorine atoms and the oxygen atom of the tetrahydrofuran ligand representing the axial positions of the trigonal-bipyramidal arrangement. A terminal alkoxide ligand is another main feature of the molecular structure of complex **4**.

Introduction

A number of structurally characterized complexes of the lanthanides bearing σ-bonded aryl groups as the only organic ligand are known,¹ but they are not as common by far as the ubiquitous π-bonded cyclopentadienyl-based lanthanide compounds. The first σ-bonded organometallic compound

of an f block element to be structurally characterized, [Li(THF)₄]⁺[Ln(2,6-Me₂C₆H₃)₄]⁻ (Ln = Yb, Lu),² was reported about 30 years ago and was obtained from an attempt to reduce bridging tendencies and isolate neutral monomeric units by using methyl groups attached to the ortho carbon atoms of the phenyl ring.

The synthesis and structural characterization of aryl lanthanide complexes is challenging because of the large ionic contribution to the metal–carbon bond in the σ-bonded

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systems of these relatively large and strongly electropositive elements and, consequently, the high reactivity of the resulting complexes. One would assume, however, that the use of large σ -bonded aryl groups would prevent attack of the highly polarized Ln–C(ipso) bond and that variously sized aryl groups could be tested to show what bulk is needed to shut down the reactivity of this particular bond.

The interest in sterically-encumbering, σ -bonded, terphenyl-element complexes arises from previous observations that such ligand systems were found to be suitable for the stabilization of main-group-element complexes in unusual coordination geometries and unprecedented bonding situations. Two recent review articles^{3,4} summarize the current knowledge about terphenyl-element complexes. Interestingly, there is no mention in these two reports on terphenyl-based compounds of either the f block elements or the early transition metals.

Our work is part of an effort to develop the chemistry of the lanthanides and group 3 elements with terphenyl ligand systems and to explore the coordination chemistry as well as the reactivity of these complexes. We reported previously the synthesis and structural characterization of novel complexes of trivalent lanthanides and also of the group 3 element yttrium containing the Dmp, Dnp, and donor-functionalized Danip ligand as the only ancillary ligand (Dmp = 2,6-dimesitylphenyl; Dnp = 2,6-di(1-naphthyl)phenyl; Danip = 2,6-di(*o*-anisyl)phenyl).^{5–7} These compounds were synthesized by simple salt metathesis reactions starting from the corresponding terphenyllithium salt and anhydrous metal trichlorides. Niemeyer et al. reported terphenyl lanthanide complexes of divalent ytterbium and europium containing the Dpp moiety (Dpp = 2,6-diphenylphenyl) as a supporting ligand.⁸ Those complexes were prepared directly from the metal and Dpp iodide in tetrahydrofuran solution.

Here we report the synthesis and structural characterization of a number of 2,6-dimesitylphenyl-based trivalent compounds of the elements scandium, ytterbium, and yttrium, thereby presenting novel low-coordinate and highly electron-deficient Dmp-based complexes of these elements and, also, the first example of a terphenyl compound of the group 3 element scandium.

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 following typical laboratory procedures. DmpLi was prepared according to the literature.⁹ The anhydrous halides ScCl₃, YCl₃, and YbCl₃ were purchased from

Aldrich (packaged under argon in ampules) and were used as received. KO^tBu was purchased from Aldrich and was sublimed prior to use. NMR spectra were recorded on a JMN-GX 400 instrument. ¹³C NMR spectra were referenced to the solvent signals (benzene-*d*₆: 128.0 ppm; THF-*d*₈: 67.4 and 25.2 ppm).

DmpScCl₂(THF)₂ (1), DmpYbCl₂(THF)₂ (2), and DmpYCl₂(THF)₃ (3). In the glovebox, addition of a solution of 2,6-dimesitylphenyllithium⁹ (0.42 g, 1.3 mmol) in 5 mL of tetrahydrofuran to a colorless suspension of ScCl₃ (0.20 g, 1.3 mmol) (YbCl₃: 0.35 g (1.3 mmol); YCl₃: 0.25 g (1.3 mmol)) in 5 mL of tetrahydrofuran gave a colorless (YbCl₃: red) suspension. The reaction mixture was stirred for 30 min (ScCl₃: 5–10 min) and centrifuged. All volatiles were removed, and the residues were washed with hexanes, extracted with toluene, centrifuged, layered with hexanes, and cooled to –30 °C, which resulted in crystallization of **1**, **2**, or **3**. Removal of the mother liquor followed by washing the crystals with hexanes and drying them under vacuum gave **1** as colorless microcrystalline material in relatively poor yield (approximately 20–30%), **2** as a purple microcrystalline material (0.45 g, 50%), and **3** as a colorless microcrystalline material (0.45 g, ca. 50%). We note that in some cases the attempted synthesis of **1** failed completely. This result was typically the case when the reaction mixture in tetrahydrofuran solution was stirred longer than 30 min. The limited stability of **1** in tetrahydrofuran is probably due to C–H bond activation occurring in tetrahydrofuran solution. Complexes **1–3** are only sparingly soluble in hexanes but are very soluble in aromatic solvents and in tetrahydrofuran. **1** and **2** do not desolvate upon drying under vacuum (10^{–2} mbar at room temperature). We failed to obtain correct combustion analysis data (C, H) for complex **3**, which is most likely due to partial desolvation of the sample when dried under vacuum. Elemental analysis data (C, H) as well as integration data from the ¹H NMR spectrum recorded in deuterated benzene are consistent with the composition DmpYCl₂(THF)_{*x*} (*x* = 2–2.5).

1: Anal. Calcd for C₃₂H₄₁Cl₂O₂Sc: C, 67.02; H, 7.21. Found: C, 66.80; H, 7.03. ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 1.15 (THF, 8H), 2.19 (s, 6H, *p*-Me), 2.57 (s, 12H, *o*-Me), 3.76 (THF, 8H), 6.90 (s, 4H), 6.91 (d, ³*J*_{H–H} = 7 Hz, 2H), 7.29 (t, ³*J*_{H–H} = 7 Hz, 1H). ¹H NMR (C₄D₈O, 400 MHz, 25 °C): δ 2.23 (s, 12H, *o*-Me), 2.31 (s, 6H, *p*-Me), 6.57 (d, ³*J*_{H–H} = 7 Hz, 2H), 6.91 (s, 4H), 7.04 (t, ³*J*_{H–H} = 7 Hz, 1H). ¹³C NMR (C₆D₆, 100.4 MHz, 25 °C): δ 21.1 (*p*-Me), 22.3 (*o*-Me), 25.2 (THF), 74.9 (THF), 126.2, 127.4, 128.7, 135.8, 138.9, 142.1, 144.9. ¹³C NMR (C₄D₈O, 100.4 MHz, 25 °C): δ 21.2 (*p*-Me), 22.2 (*o*-Me). IR (Nujol): 1906 (w), 1848 (w), 1729 (w), 1607 (m), 1542 (m), 1296 (m), 1243 (w), 1172 (m), 1098 (m), 1071 (w), 1035 (m), 997 (vs), 953 (m), 924 (m), 849 (vs), 798 (s), 729 (vs), 696 (m), 673 (m), 575 (m), 556 (m), 546 (m), 510 (w), 503 (w), 467 (w), 450 (w) cm^{–1}.

2: Anal. Calcd for C₃₂H₄₁Cl₂O₂Yb: C, 54.78; H, 5.89. Found: C, 54.52; H, 5.75. IR (Nujol): 1608 (w), 1541 (w), 1296 (w), 1230 (w), 1169 (m), 1093 (m), 1073 (m), 1042 (vs), 1018 (s), 953 (w), 912 (m), 850 (vs), 799 (s), 728 (s), 693 (m), 673 (w), 574 (w), 558 (w), 546 (w), 447 (m) cm^{–1}.

3: ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 1.25 (THF, ca. 8H), 2.17 (s, 6H, *p*-Me), 2.51 (s, 12H, *o*-Me), 3.71 (THF, ca. 8H), 6.90 (s, 4H), 6.96 (d, ³*J*_{H–H} = 7 Hz, 2H), 7.33 (t, ³*J*_{H–H} = 7 Hz, 1H). ¹H NMR (C₄D₈O, 400 MHz, 25 °C): δ 2.20 (s, 12H, *o*-Me), 2.27 (s, 6H, *p*-Me), 6.43 (d, ³*J*_{H–H} = 7 Hz, 2H), 6.81 (s, 4H), 6.93 (t, ³*J*_{H–H} = 7 Hz, 1H). ¹³C NMR (C₆D₆, 100.4 MHz, 25 °C): δ 21.4 (*p*-Me), 22.4 (*o*-Me), 25.6 (THF), 72.2 (br, THF), 125.9, 127.6, 129.3, 136.0, 138.5, 142.8, 148.6, 182.7 (*ipso*-C, ¹*J*_{C–Y} = 56 Hz). ¹³C NMR (C₄D₈O, 100.4 MHz, 25 °C): δ 20.2 (*p*-Me), 21.3 (*o*-Me), 182.3 (*ipso*-C, ¹*J*_{C–Y} = 56 Hz). IR (Nujol): 1607 (w), 1541

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Table 1. Crystallographic Data for DmpMCl₂(THF)₂ (M = Sc: **1**; M = Yb: **2**), DmpYCl₂(THF)₃ (**3**), and DmpYb(THF)(O^tBu)(μ-Cl)₂Li(THF)₂ (**4**)^a

complex	1	2	3	4
formula	C ₃₂ H ₄₁ Cl ₂ O ₂ Sc	C ₃₂ H ₄₁ Cl ₂ O ₂ Yb	C ₃₆ H ₄₉ Cl ₂ O ₃ Y	C ₄₀ H ₅₈ Cl ₂ LiO ₄ Yb
fw	573.51	701.59	689.56	853.74
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n	P1
a, Å	10.178(3)	10.2447(7)	15.950(3)	10.2252(2)
b, Å	15.468(5)	15.5683(12)	11.865(2)	11.3497(2)
c, Å	20.132(5)	20.0979(14)	18.254(3)	18.5814(2)
β, deg	101.85(3)	101.749(4)	92.323(3)	102.8964(6)
V, Å ³	3102.0(17)	3138.3(5)	3451.9(10)	2062.09(5)
Z'	4	4	4	2
D _(calcd) , g cm ⁻³	1.228	1.485	1.327	1.375
T, °C	-70(2)	-100(2)	-70(2)	-80(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα), cm ⁻¹	4.35	31.76	18.77	24.33
R1, %	5.89	4.32	4.43	4.56
wR2, %	14.38	9.74	7.51	17.39

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

(w), 1202 (w), 1168 (m), 1102 (w), 1038 (vs), 1008 (s), 955 (w), 917 (m), 890 (s), 849 (vs), 800 (s), 765 (w), 728 (vs), 690 (m), 577 (w), 549 (w), 466 (m) cm⁻¹.

DmpYb(THF)(O^tBu)(μ-Cl)₂Li(THF)₂ (4**).** In the glovebox, addition of a solution of 2,6-dimesitylphenyllithium⁹ (0.42 g, 1.3 mmol) in 5 mL of tetrahydrofuran to a colorless suspension of YbCl₃ (0.35 g, 1.3 mmol) in 5 mL of tetrahydrofuran followed by addition of 1 equiv of KO^tBu (0.14 g, 1.3 mmol) in 5 mL of tetrahydrofuran gave a yellow-orange suspension. The reaction mixture was stirred for 30 min and centrifuged. The solvent was removed, and the residues were washed with hexanes, dissolved in toluene/tetrahydrofuran (20:1), and centrifuged. Cooling to -30 °C resulted in crystallization of **4**. Removal of the mother liquor followed by drying under vacuum gave **4** as a bright yellow microcrystalline material (0.56 g, 50%). Analytically pure **4** is insoluble in hexanes and aromatic solvents but is very soluble in tetrahydrofuran. **4** does not desolvate upon drying under vacuum (10⁻² mbar at room temperature). Anal. Calcd for C₄₀H₅₈Cl₂LiO₄Yb: C, 56.27; H, 6.85. Found: C, 56.06; H, 6.80. IR (Nujol): 2356 (m), 2342 (m), 1912 (w), 1852 (w), 1792 (w), 1723 (w), 1610 (m), 1538 (w), 1207 (s), 1093 (m), 1015 (vs), 848 (s), 800 (m), 777 (w), 728 (s), 674 (m), 575 (w), 548 (w), 522 (m), 477 (m) cm⁻¹.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for Complexes 1–4. Crystal data, data collection, and refinement parameters are given in Table 1. The systematic absences in the diffraction data are uniquely consistent for the reported space groups for **1–4**. The structures were solved using direct methods, were completed by subsequent difference Fourier syntheses, and were refined by full-matrix, least-squares procedures. *SADABS* absorption corrections were applied to all data sets. In the molecular structure of **1**, the coordinated tetrahydrofuran molecule with oxygen atom O(2) is disordered at two positions that are roughly along the Sc(1)–O(2) axis and have 70/30 refined-site occupancies. One of the carbon atoms, C(31), of a tetrahydrofuran molecule in the isomorphous structure **2** is disordered over two positions with 75/25 site-occupancy distributions. All non-hydrogen atoms, except the disordered carbon atom C(31') of **2**, were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to C(30) of **2** were omitted because of the disorder. All other hydrogen atoms were treated as idealized contributions.

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

Results and Discussion

DmpMCl₂(THF)_x (M = Sc: **1; M = Yb: **2**; M = Y: **3**).** Reaction of MCl₃ (M = Sc, Yb, Y) with 1 equiv of DmpLi⁹ in tetrahydrofuran solution at room temperature produces toluene-soluble complexes of general composition DmpMCl₂(THF)_x [M = Sc (**1**), Yb (**2**): $x = 2$; M = Y (**3**): $x = 3$]. Crystals of **1–3** that were suitable for X-ray diffraction studies were obtained from toluene solutions that were layered with hexanes and stored at -30 °C. Neither the scandium compound **1** nor the ytterbium compound **2** lose coordinated solvent molecules when they are dried under vacuum, on the basis of integration data from the ¹H NMR spectrum of **1** in deuterated benzene as well as combustion analysis data (C, H) of **1** and **2**. The yttrium compound **3** becomes partially desolvated when it is dried under vacuum, yielding a product of composition DmpYCl₂(THF)_x ($x = 2–2.5$) on the basis of elemental analysis data (C, H) as well as integration data from the ¹H NMR spectrum recorded in deuterated benzene.

While **2** and **3** are obtained from this salt metathesis reaction in relatively good yield (ca. 50%), **1** is obtained in poor yield (approximately 20–30%). This observation can most likely be attributed to C–H bond activation occurring in tetrahydrofuran solution. As a matter of fact, ¹H NMR spectroscopic investigations of the reaction mixture clearly revealed the presence of a significant amount of the protonated terphenyl DmpH (that was identified by comparison with an authentic sample), in addition to two signals in a 2:1 ratio in the alkyl region of the proton NMR spectrum that indicate the presence of DmpScCl₂(THF)₂. Formation of DmpD was observed when deuterated tetrahydrofuran was used as a solvent for the reaction. No reaction was observed in aromatic solvents or hexanes instead of tetrahydrofuran for the reaction of DmpLi with ScCl₃, YbCl₃, or YCl₃, respectively.

After removal of tetrahydrofuran, **1** can be crystallized (in the absence of tetrahydrofuran) from a toluene solution that is layered with hexanes and stored at -30 °C. The observation of slow decomposition of solutions of a single crystalline material of **1** in tetrahydrofuran is in good agreement with a previous report on the poor stability of Ph₃Sc(THF)₂ in

solution.¹⁰ Using deuterated benzene as a solvent for the ^{13}C NMR spectroscopic investigation (an overnight run), no decomposition of **1** was observed. The signal corresponding to the ipso carbon atom in the ^{13}C NMR spectrum was not detected, which is most likely due to the neighboring ^{45}Sc nucleus (100% natural abundance; $I = 7/2$). A similar observation was previously made in the case of the ipso carbon atom in $\text{Ph}_3\text{Sc}(\text{THF})_2$.¹⁰ Because of the above-mentioned limited stability and gradual decomposition of **1** in tetrahydrofuran over longer times, only the two signals corresponding to the ortho and para methyl carbon atoms could definitely be assigned in the ^{13}C NMR spectrum obtained using this solvent.

While the Dmp-based ytterbium and yttrium compounds (**2** and **3**) are considerably more stable in tetrahydrofuran at ambient temperature than is the scandium complex **1**, we note that we are still unable to report a complete set of ^{13}C NMR signals of **3** in tetrahydrofuran because of the limited stability and solubility in this solvent at longer times (an overnight run) at ambient temperature. As a result of the partial decomposition of the sample, only the signals corresponding to the ipso carbon atom and the two types of methyl groups can definitely be assigned. However, using benzene instead of tetrahydrofuran as a solvent for the NMR spectroscopic investigation, a complete set of signals was obtained. We note that such stability problems in tetrahydrofuran at ambient temperature were also observed in the case of the above-mentioned Dnp-based complexes.⁶

A point that needs to be mentioned here is that in the case of the previously reported Dnp-based complexes⁶ (Dnp = 2,6-di(1-naphthyl)phenyl) we failed to isolate a Dnp scandium compound. A terphenyl-free decomposition product (i.e., a tetrahydrofuran-solvated dimeric lithium chloride adduct of Sc_2OCl_4) was isolated instead.⁶ On the other hand, the synthesis and structural characterization of the Dnp-based ytterbium, thulium, and yttrium analogues were found to be feasible. Using the 2,6-dimesitylphenyl ligand system, however, we also managed to obtain a terphenyl compound of the relatively small group 3 element scandium, namely, **1**.

The synthesis of Dmp complexes of the larger lanthanide elements as well as of the group 3 element lanthanum was also attempted by reacting equimolar amounts of DmpLi with the corresponding anhydrous lanthanide trichloride in tetrahydrofuran at room temperature. Reproducibly, a productive outcome of these salt metathesis reactions was found in the case of samarium and smaller lanthanide elements (Gd–Lu) (i.e., terphenyl lanthanide complexes were isolated). In all cases (except for ytterbium), the lack of crystalline material suitable for X-ray diffraction studies prevented a definite characterization of the obtained materials. On the other hand, in cases involving the lanthanide element neodymium or larger metals such as lanthanum, quantitative formation of DmpH was observed reproducibly, which most likely was due to C–H bond activation. Formation of DmpD

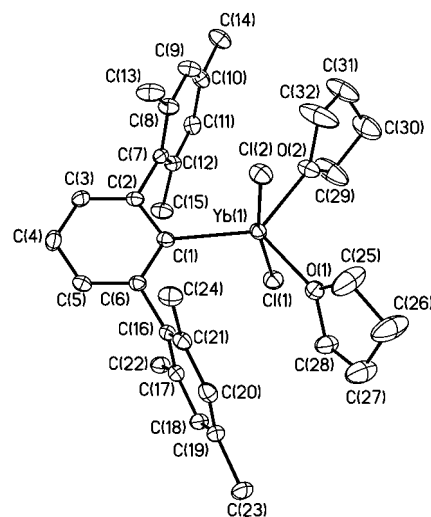


Figure 1. ORTEP diagram of DmpYbCl₂(THF)₂ (**2**) showing the atom-labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms and the minor disordered contributor carbon atom, C(31'), were omitted for clarity.

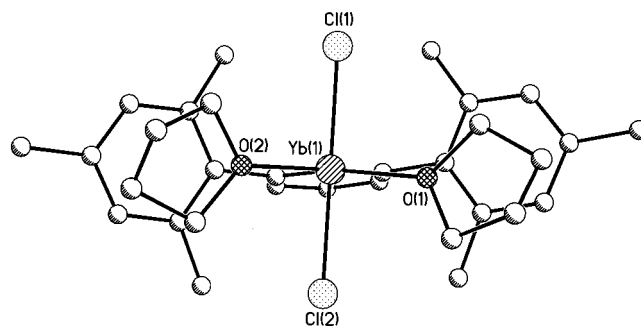


Figure 2. Ball-and-stick drawing of the molecular structure of **2** viewed along the Yb(1)···C(1)···C(4) vector.

was observed when the reaction was carried out in deuterated tetrahydrofuran, but we failed to isolate any characterizable lanthanide species. Our attempts to synthesize Dmp-based compounds of the larger lanthanides using, for example, aromatic solvents instead of tetrahydrofuran failed (no reaction).

The observation of a different outcome for the lanthanide elements samarium and neodymium is indeed surprising because the difference in ionic radii between samarium(III) and neodymium(III) is only 0.02 Å for a given coordination number.¹¹ The observation that the accessibility of terphenyl lanthanide complexes depends on the ionic radius of the lanthanide cation employed was previously found when the Dnp⁶ and also the Danip⁷ ligand systems were employed as ancillary ligand systems for the stabilization of lanthanide complexes.

Molecular Structures of Complexes 1–3. One main feature of the molecular structures of isomorphous **1** and **2** (Figures 1 and 2) is a metal atom in a distorted trigonal-bipyramidal coordination environment with the axial positions of the coordination geometry being occupied by two chlorine atoms while the two oxygen atoms of the tetrahydrofuran ligands occupy two of the equatorial positions. To

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Table 2. Comparison of Selected Interatomic Separations (Å) and Angles (deg) of Complexes **1–4**

complex	1 (M = Sc)	2 (M = Yb)	3 (M = Y)	4 (M = Yb)
M–O	2.162(2) (O(1))	2.266(4) (O(1))	2.345(2) (O(3))	1.965(5) (O(1))
	2.168(2) (O(2))	2.288(4) (O(2))	2.370(2) (O(2))	2.315(5) (O(2))
M–Cl	2.4219(13) (Cl(1))	2.5121(16) (Cl(1))	2.5645(10) (Cl(1))	2.6202(19) (Cl(1))
	2.4040(13) (Cl(2))	2.5295(16) (Cl(2))	2.5917(10) (Cl(2))	2.595(2) (Cl(2))
M–C _{ipso}	2.247(3)	2.358(6)	2.478(3)	2.425(6)
M···C _{ipso'}	3.450(3) (C(21))	3.438(6) (C(7))	3.610(3) (C(6))	3.371(6) (C(7))
C–M–O	3.481(3) (C(6))	3.553(6) (C(16))	3.761(3) (C(22))	3.693(6) (C(16))
	124.79(11) (O(1))	123.21(17) (O(1))	175.81(10) (O(1))	115.7(2) (O(1))
C–M–Cl	129.02(11) (O(2))	129.87(18) (O(2))	111.78(10) (O(2))	90.55(19) (O(2))
			104.44(10) (O(3))	
O–M–O	91.61(9) (Cl(1))	96.93(14) (Cl(1))	94.60(8) (Cl(1))	135.45(16) (Cl(1))
	95.48(9) (Cl(2))	93.84(14) (Cl(2))	96.47(8) (Cl(2))	98.17(15) (Cl(2))
Cl–M–Cl	106.11(10)	106.87(17)	143.76(8) (O(2)/O(3))	86.5(2)
			72.01(8) (O(1)/O(3))	
O–M–Cl			71.85(8) (O(1)/O(2))	
			168.84(3)	82.84(7)
M–C _{ipso} –C _{ortho}	172.89(4)	169.22(6)	83.42(6) (O(1)/Cl(1))	108.28(16) (O(1)/Cl(1))
	87.93(8) (O(1)/Cl(1))	87.50(12) (O(1)/Cl(1))	86.19(6) (O(2)/Cl(1))	85.14(13) (O(2)/Cl(1))
C _{ipso} –C _{ortho} –C _{ipso'}	87.18(8) (O(2)/Cl(1))	86.55(11) (O(2)/Cl(1))	92.21(7) (O(3)/Cl(1))	97.08(16) (O(1)/Cl(2))
	88.43(8) (O(1)/Cl(2))	86.84(12) (O(1)/Cl(2))	85.62(6) (O(1)/Cl(2))	167.97(14) (O(2)/Cl(2))
C _{ipso} –C _{ortho} –C _{ipso'}	87.97(8) (O(2)/Cl(2))	86.33(11) (O(2)/Cl(2))	88.42(6) (O(2)/Cl(2))	
			86.37(7) (O(3)/Cl(2))	
M–C _{ipso} –C _{ortho}	122.4(2) (C(10))	120.7(4) (C(2))	120.4(2) (C(10))	117.2(5) (C(2))
	121.5(2) (C(14))	122.7(4) (C(6))	125.8(4) (C(14))	127.6(4) (C(6))
C _{ipso} –C _{ortho} –C _{ipso'}	121.0(3) (C(14)/C(21))	119.5(5) (C(2)/C(7))	123.3(3) (C(10)/C(6))	120.3(6) (C(6)/(C16))
	121.8(3) (C(10)/C(6))	120.9(5) (C(6)/C(16))	123.3(3) (C(14)/C(22))	120.0(6) (C(2)/(C7))

the best of our knowledge, only two other scandium complexes bearing σ -bonded aryl groups have been structurally characterized thus far.^{10,12} The scandium–C(ipso) (2.247(3) Å) as well as the two Sc–O distances (2.162(2) and 2.168(2) Å) in five-coordinate **1** can favorably be compared to the corresponding distances in these two compounds, namely, the five-coordinate ScPh₃(THF)₂ (av Sc–C(ipso) = 2.250(4) Å; av Sc–O = 2.183(2) Å)¹⁰ and the borata-benzene complex (C₅H₅B–Ph)ScPh₂(THF) (Sc–C(ipso) = 2.214(3) and 2.231(3) Å; Sc–O = 2.125(2) Å),¹² allowing for expected changes attributable to variations in the coordination numbers. There are relatively short interatomic separations between the scandium atom of **1** and both ipso mesityl carbon atoms (i.e., 3.450(3) Å (C(21)) and 3.481(3) Å (C(6))).

In the isomorphous structure of the ytterbium analogue **2**, the Yb–C interatomic separation of 2.358(6) Å is significantly shorter than the corresponding distance in six-coordinate DmpYbCl₂(*N*-MeIm)₂(py) (2.447(9) Å)⁵ but is only slightly shorter than the Yb–C distance of 2.395(8) Å in five-coordinate DnpYbCl₂(THF)₂.⁶ The Yb–C(ipso) distance in **2** can also be compared to those of other ytterbium(III) aryl complexes (e.g., the corresponding distances in formally four-coordinate DmpYb[N(SiMe₃)₂](μ -Cl)₂Li(THF)₂, 2.403(4) Å;⁵ in seven-coordinate [DanipYb(μ -Cl)₂(μ -Cl)Li(THF)₂], 2.388(4) Å;⁷ in the bis(cyclopentadienyl) derivative (C₅H₄Me)₂YbDmp, 2.410(3) Å;¹³ in six-coordinate Ph₃Yb(THF)₃, 2.39(1), 2.40(1), and 2.43(1) Å;¹⁴ and also the

average terminal Yb(III)–C distance in the mixed-valent ytterbium complex Ph₂(THF)Yb(μ -Ph)₃Yb(THF)₃, 2.42 Å¹⁵). The Cl–Yb–Cl angle of 169.22(6)° in five-coordinate **1** matches the Cl–Yb–Cl angle of 169.70(8)° in six-coordinate DmpYbCl₂(*N*-MeIm)₂(py),⁵ while the O–Yb–O angle of 106.87(17)° in **1** differs from the N(*N*-MeIm)–Yb–N(*N*-MeIm) angle of 144.3(3)° in six-coordinate DmpYbCl₂(*N*-MeIm)₂(py). The Cl–Yb–Cl as well as the O–Yb–O angle in **2** documents the deviation from ideal trigonal-bipyramidal coordination geometry, which probably results from the steric requirements of the Dmp ligand. The arrangement of the terphenyl substituent in **2** is almost coplanar with the two tetrahydrofuran ligands (Figure 2). Besides the lanthanide–ipso carbon distance in DmpYbCl₂(THF)₂ (2.358(6) Å), there are short interatomic separations between the metal atom and both ipso mesityl carbon atoms (3.553(6) Å C(16) and 3.438(6) Å C(7)). Other interatomic distances and angles of **1** and **2** can be derived from the data in Table 2.

As a result of the steric requirements of the Dmp ligand, the molecular structure of yttrium complex DmpYCl₂(THF)₃ (**3**) features an yttrium atom in a heavily distorted octahedral coordination environment. The L–Y–L(trans) angles are 175.81(10)° (C(1)–Y(1)–O(1)), 143.76(8)° (O(2)–Y(1)–O(3)), and 168.84(3)° (Cl(1)–Y(1)–Cl(2)), while the L–Y–L(cis) angles range from 71.85(8)° (O(1)–Y(1)–O(2)) to 111.78(10)° (C(1)–Y(1)–O(2)). On the basis of the interligand angles, the axial positions in the coordination polyhedron in **3** can be assigned to the ipso carbon atom as well as to the oxygen atom O(1) (Figures 3 and 4). Additionally, the molecular structure of **3** can be described as the mer isomer.

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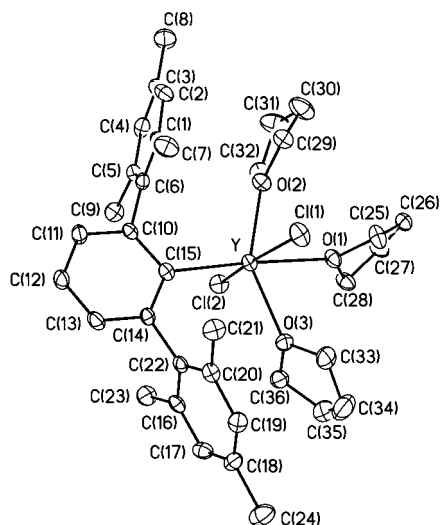


Figure 3. ORTEP diagram of $\text{DmpYCl}_2(\text{THF})_3$ (**3**) showing the atom-labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

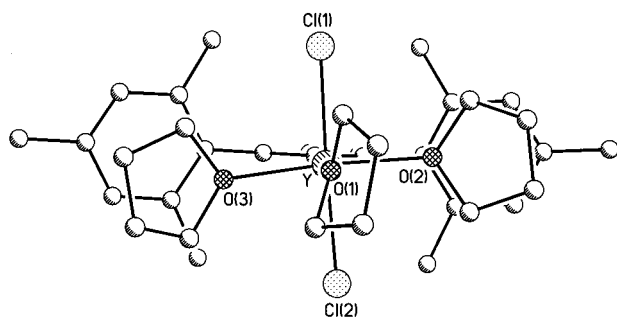


Figure 4. Ball-and-stick drawing of the molecular structure of **3** viewed along the $\text{O}(1)\cdots\text{Y}\cdots\text{C}(15)$ vector.

A closer inspection of the $\text{Y}-\text{O}(\text{THF})$ distances reveals that the $\text{Y}-\text{O}(1)$ distance, in which the $\text{Y}-\text{O}(1)$ component is trans to the terphenyl ligand, is significantly longer (approximately 0.2 Å) than the remaining two $\text{Y}-\text{O}$ distances (Table 2). This observation can possibly be attributed to a trans-directing influence of the anionic Dmp ligand. An alternative view is that the steric bulk and attendant bending-back of the other two THF ligands results in the “backing off” of the trans THF moiety.

As one would expect for metal complexes with different coordination numbers at the metal atom, the $\text{Y}-\text{C}(\text{ipso})$ distance (2.478(3) Å), the two shorter $\text{Y}-\text{O}$ distances (2.345(2) and 2.370(2) Å), and also the two $\text{Y}-\text{Cl}$ distances (2.5645(10) and 2.5917(10) Å) in six-coordinate **3** are slightly but noticeably longer than the corresponding distances in previously reported five-coordinate $\text{DnpYCl}_2(\text{THF})_2$ ($\text{Y}-\text{C} = 2.436(6)$ Å; $\text{Y}-\text{O} = 2.322(3)$ Å; $\text{Y}-\text{Cl} = 2.5528(14)$ Å).⁶ Further comparisons of the $\text{Y}-\text{C}(\text{ipso})$ distance in **3** can be made with seven-coordinate $[\text{DanipY}(\mu_2\text{-Cl})_2(\mu_2\text{-Cl})\text{-Li}(\text{THF})_2]_2$ (2.456(3) Å).⁷ To the best of our knowledge, these are the only other structurally characterized terphenyl compounds of the group 3 element yttrium. Further interatomic distances and angles of **3** can be derived from Table 2.

Interestingly, in the previously reported five-coordinate molecular structures of terphenyl lanthanide complexes containing the Dnp ligand of general composition DnpLnCl_2 -

$(\text{THF})_2$ ($\text{Ln} = \text{Yb}, \text{Tm}, \text{Y}$; $\text{Dnp} = 2,6\text{-di}(1\text{-naphthyl})\text{phenyl}$),⁶ the coordination geometry about the metal atom is also distorted trigonal-pyramidal, as it is in **1** and **2**, but with the axial positions of the trigonal-bipyramidal coordination geometry being occupied by two oxygen atoms of the tetrahydrofuran ligands, while the chlorine atoms are in the equatorial positions. The observation of differently arranged coordination geometries in these two different types of five-coordinate terphenyl lanthanide complexes is most likely due to the different steric demand of the Dmp versus the Dnp ligand system. We also note that in the case of the Dnp system the molecular structures of the ytterbium and the yttrium complex are isomorphous, while the Dmp-based **2** ($\text{M} = \text{Yb}$) and **3** ($\text{M} = \text{Y}$) show different coordination geometries and coordination numbers at the metal atom for these two elements that have only slightly different ionic radii.¹¹

We previously obtained a six-coordinate complex of composition $\text{DmpYbCl}_2(\text{N-MeIm})_2(\text{py})$ ⁵ from the reaction of YbCl_3 with DmpLi by using a mixture of different bases (tetrahydrofuran/pyridine/*N*-methylimidazole) in the crystallization process. The structure of this complex is somewhat reminiscent of the solid-state structure adopted by the yttrium compound **3**. One of the interesting features of the molecular structure of $\text{DmpYbCl}_2(\text{N-MeIm})_2(\text{py})$ is the fact that a complex is formed with two different types of nitrogen bases bonded to the six-coordinate metal center and that significantly different $\text{Yb}-\text{N}$ distances are found for the two different types of nitrogen bases. The two *N*-methylimidazole ligands occupy the equatorial positions ($\text{Yb}-\text{N}(\text{N-MeIm}) = 2.412(8)$ and $2.434(8)$ Å), and the weaker base (the pyridine ligand) is in the axial position and is trans to the Dmp ligand ($\text{Yb}-\text{N}(\text{py}) = 2.624(7)$ Å). The observation of significantly different $\text{Yb}-\text{N}$ distances may again, as was discussed earlier in this work, be attributed to a trans-directing influence of the Dmp substituent. In light of the molecular structure of six-coordinate $\text{DmpYbCl}_2(\text{N-MeIm})_2(\text{py})$, the observed formation of the only five-coordinate bis(tetrahydrofuran) adduct **2** in the absence of classical Lewis bases other than tetrahydrofuran is somewhat surprising. This observation can possibly be explained by the different basicity of tetrahydrofuran versus pyridine and *N*-methylimidazole.

DmpYb(THF)(*O*^tBu)(μ -Cl)₂Li(THF)₂ (4**).** We were interested in testing the stability of the Dmp–Ln framework in the presence of other functional groups. Therefore, we decided to evaluate the *tert*-butoxide ligand as a coligand vis-à-vis a Dmp group. Metal alkoxides are of importance as useful “sol–gel” precursors.¹⁶ We previously managed to synthesize and characterize a Dmp-based ytterbium monoamide derivative, $\text{DmpYb}[\text{N}(\text{SiMe}_3)_2](\mu\text{-Cl})_2\text{Li}(\text{THF})_2$, which was obtained from the one-pot reaction of YbCl_3 , DmpLi , and $\text{KN}(\text{SiMe}_3)_2$.⁵

Reaction of 1 equiv of 2,6-dimesitylphenyllithium⁹ with 1 equiv of YbCl_3 in tetrahydrofuran at room temperature followed by addition of 1 equiv of KO^tBu produces the

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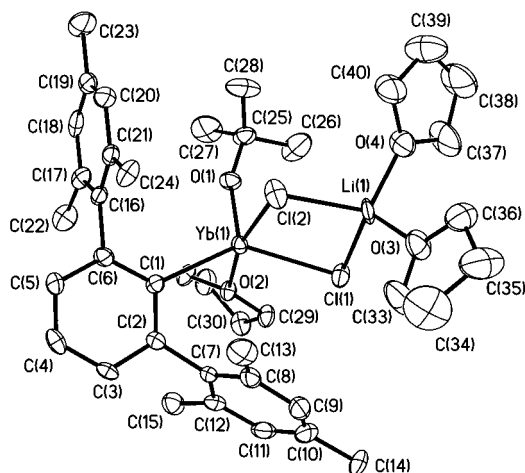


Figure 5. ORTEP diagram of $\text{DmpYb}(\text{THF})(\text{O}^t\text{-Bu})(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**4**) showing the atom-labeling scheme. Thermal ellipsoids are at the 30% level. Hydrogen atoms were omitted for clarity.

heterobimetallic monoalkoxide derivative $\text{DmpYb}(\text{THF})(\text{O}^t\text{-Bu})(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**4**) in a one-pot synthesis in 50% yield. Crystalline material of the bright-yellow ate complex **4** that was suitable for an X-ray diffraction study was obtained from toluene/tetrahydrofuran (20:1) at -30°C . On the basis of elemental analysis data (C, H), drying **4** under vacuum (10^{-2} mbar, at room temperature) for several hours does not lead to partial loss of the coordinated tetrahydrofuran molecules. Also, our attempts to prepare the bis(alkoxide) Dmp-Yb derivative using 2 equiv of KO^tBu failed, which can most likely be attributed to a sterically overcrowded situation at the ytterbium atom. We also attempted the synthesis of a bis(alkoxide) compound by reacting isolated $\text{DmpYbCl}_2(\text{THF})_2$ with 2 equiv of KO^tBu in tetrahydrofuran at room temperature but failed to isolate any characterizable lanthanide species. It is interesting to note that we made a similar observation earlier when the synthesis of a bis(amide) compound starting from isolated $\text{DmpYbCl}_2(\text{THF})_2$ and 2 equiv of $\text{KN}(\text{SiMe}_3)_2$ was attempted.⁵

The molecular structure of **4** (Figure 5) features a five-coordinate ytterbium atom in a heavily distorted trigonal-bipyramidal coordination environment and a bent terminal-alkoxide moiety ($\text{Yb}(1)\text{-O}(1)\text{-C}(25) = 157.9(6)^\circ$; $\text{O}(1)\text{-C}(25) = 1.411(9)\text{ \AA}$). In contrast to the molecular structure of the previously reported four-coordinate ytterbium bis(trimethylsilyl) amide derivative $\text{DmpYb}[\text{N}(\text{SiMe}_3)_2](\mu\text{-Cl})_2\text{Li}(\text{THF})_2$,⁵ additional coordination of one tetrahydrofuran molecule to the ytterbium atom is found in the case of the alkoxide derivative **4**, a result which can most likely be attributed to the different steric demands of the *tert*-butoxide and bis(trimethylsilyl) amide ligands.

In the molecular structure of **4**, atoms O(2) and Cl(2) represent the axial positions of the trigonal-bipyramidal arrangement about the lanthanide atom ($\text{O}(2)\text{-Yb}(1)\text{-Cl}(2) = 167.97(14)^\circ$). Other interligand angles about the lanthanide center, including either atoms O(2) or Cl(2), range from $82.84(7)^\circ$ ($\text{Cl}(1)\text{-Yb}(1)\text{-Cl}(2)$) to $98.17(15)^\circ$ ($\text{C}(1)\text{-Yb}(1)\text{-Cl}(2)$). All other interligand angles involving only atoms from the equatorial sites (C(1), O(1), and Cl(1) as well as Yb(1)) deviate noticeably from the ideal 120° angle

($\text{O}(1)\text{-Yb}(1)\text{-Cl}(1) = 108.28(16)^\circ$, $\text{O}(1)\text{-Yb}(1)\text{-C}(1) = 115.7(2)^\circ$, and $\text{C}(1)\text{-Yb}(1)\text{-Cl}(1) = 135.45(16)^\circ$).

The $\text{Yb}(1)\text{-C}(1)$ separation ($2.425(6)\text{ \AA}$) can favorably be compared to the corresponding distances in previously reported 2,6-dimesitylphenyl derivatives of trivalent ytterbium.^{5,13} The $\text{Yb-O}(\text{alkoxide})$ distance of $1.965(5)\text{ \AA}$ is, as one would expect, significantly shorter than the $\text{Yb-O}(\text{THF})$ interatomic separation of $2.315(5)\text{ \AA}$. It is also shorter than the corresponding terminal Yb-O distances in divalent $(\text{THF})_2\text{Yb}(\text{O}^t\text{Bu})_2$ ($2.092(14)$ and $2.07(2)\text{ \AA}$).¹⁷ Given the fact that Y^{3+} and Yb^{3+} cations have a similar radial size,¹¹ further comparisons can be made (e.g., with the terminal $\text{Y-O}(\text{alkoxide})$ distances of $1.995(10)$ and $2.018(9)\text{ \AA}$ reported for $[\text{Cp}^*\text{Y}(\mu\text{-O}^t\text{Bu})(\text{O}^t\text{Bu})_2]$.¹⁸ The Yb-Cl distances in **4** ($2.595(2)$ and $2.620(2)\text{ \AA}$) are slightly longer than the corresponding distances in the bis(trimethylsilyl) amide derivative $\text{DmpYb}[\text{N}(\text{SiMe}_3)_2](\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ ($2.5467(11)$ and $2.5596(12)\text{ \AA}$, respectively).⁵ These results can be explained in terms of the higher coordination number at the lanthanide atom in the case of the alkoxide derivative. While the $\text{Yb}(1)\text{-C}(1)\text{-C}(2)$ and $\text{Yb}(1)\text{-C}(1)\text{-C}(6)$ angles in **2** at $120.7(4)$ and $122.7(4)^\circ$, respectively, are very similar (within the error limits), the corresponding angles ($117.2(5)$ and $127.6(4)^\circ$, respectively) in the alkoxide derivative **4** show that the Dmp substituent is tilted, with the side of the Dmp ligand facing the *tert*-butoxide moiety showing the larger $\text{M-C}_{\text{ipso}}\text{-C}_{\text{ortho}}$ angle and also the longer $\text{M}\cdots\text{C}_{\text{ipso}'}$ distance (see Table 2). The two Li-Cl distances in the ate complex **4** are $2.344(15)$ (Cl(1)) and $2.330(13)\text{ \AA}$ (Cl(2)), and the Li-O distances are $1.904(17)$ (O(3)) and $1.906(15)\text{ \AA}$ (O(4)), with a Cl-Li-Cl angle of $95.1(4)^\circ$ and a O-Li-O angle of $105.9(7)^\circ$. A listing of additional relevant interatomic separations and angles is given in Table 2.

Conclusions

A synthetic approach to terphenyl-based metal complexes of general composition $\text{DmpMCl}_2(\text{THF})_x$ is reported from a simple salt metathesis reaction using a terphenyllithium salt and anhydrous metal trichlorides. Our work (a) gives further insight into the structural aspects and reactivity of Dmp-based lanthanide complexes and (b) demonstrates that a stable heterobimetallic Dmp-Ln system containing a terminal alkoxide moiety as a coligand is accessible. So far, only mono substitution of the halogen atoms in 2,6-dimesitylphenyl-based ytterbium(III) complexes appears to be feasible using bulky alkali metal substrates (e.g., KO^tBu and $\text{KN}(\text{SiMe}_3)_2$). Our work also shows that, interestingly, two different types of trigonal-bipyramidal arrangements are found in complexes of composition $\text{RYbCl}_2(\text{THF})_2$ ($\text{R} = \text{Dmp}$ or Dnp) with respect to the arrangement of axial and equatorial ligands. This observation is probably due to the different steric requirements of the two terphenyl ligands. The potential of these $\text{DmpMCl}_2(\text{THF})_x$ -type complexes for further derivatization reactions and possible catalytic ap-

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plications of these complexes and their derivatives is still to be explored.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $\text{DmpScCl}_2(\text{THF})_2$ (**1**), $\text{DmpYbCl}_2(\text{THF})_2$ (**2**), $\text{DmpYCl}_2(\text{THF})_3$ (**3**), and $\text{DmpYb}(\text{THF})(\text{O}^i\text{Bu})(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**4**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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