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Synthesis, structure and reactivity of new yttrium bis(dimethylsilyl)amido and bis(trimethylsilyl)methyl complexes of a tetradentate bis(phenoxide) ligand

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Abstract

The reactions of a bulky amino-methoxy bis(phenolate) ligand H_2L with $Y(CH_2SiMe_3)_3(THF)_2$ and $Y[N(SiHMe_2)_2]_3(THF)_2$ under mild condition leads to the selective formation of the thermally stable complexes $[LY(CH_2SiMe_3)(THF)]$ (**1**) and $[LY[N(SiHMe_2)_2](THF)]$ (**2**). The X-ray structures revealed very similar binding of the [ONOO] ligand core to the metal for both complexes, which feature an octahedral geometry involving coordination of the methoxy side-arm of the ligand and of a remaining THF molecule. ¹H-NMR spectroscopy indicates that the solid state structure of **1** and **2** is retained in hydrocarbon solutions with THF coordinated to yttrium. Alkyl complex **1** showed no activity in ethylene polymerization, presumably due to the presence of coordinated THF. The amido complex **2** catalyzed sluggishly the polymerization of methyl methacrylate to give isotactic-rich PMMA but is very active for the ring-opening polymerization of ϵ -caprolactone.

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1. Introduction

Because of the permanent search for new-generation catalysts, in particular for olefin polymerization, there is currently considerable interest in developing neutral Group 3 metal complexes involving ancillary ligands other than the commonly used Cp-type ligands [1]. Much of this work has focused on polyhapto nitrogen and/or oxygen donor atom alternatives. Recent examples include scandium and yttrium complexes of benza-minidinato [2], guanidinato [3], diketiminato [4], aminotroponiminato [5], diamido [6], iminopyrrolato [7], salen [8], iminophenolato [9], and bis(phenolato) [10,11] systems. Hard, electronegative π -donor ligands such as aryloxides are particularly attractive because

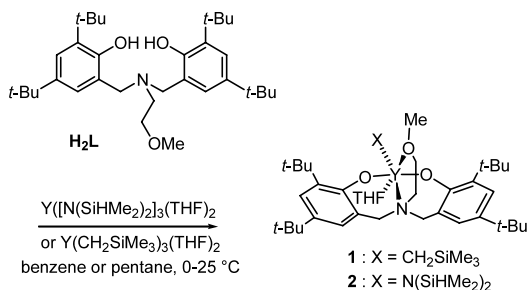
they offer strong metal–oxygen bonds that are expected to stabilize complexes of these electropositive metals. Our attention is drawn to the tetradentate bis(phenoxide) ligand H_2L (Scheme 1), which has recently given excellent performances in organo-zirconium/-hafnium and related olefin polymerization chemistry [12]. Herein we report the straightforward synthesis and structural characterization of new yttrium amido and alkyl complexes of the sterically bulky ligand H_2L . Preliminary investigations on their reactivity towards polar and non polar monomers are also described.

2. Results and discussion

It is well-documented that traditional salt metathesis reactions in lanthanide chemistry are often plagued by the formation of undesired products, such as ate-complexes and incorporation of alkali metal halide salts [8a,9]. To overcome this potential problem and to reach

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Scheme 1.

directly potentially valuable neutral complexes, we envisioned simple protonolysis reactions of lanthanide precursors with diprotonated ligand H₂L, i.e. alkane and amine eliminations (Scheme 1). Monitoring by ¹H-NMR spectroscopy showed that Y(CH₂SiMe₃)₃(THF)₂ [13] reacts selectively with one equivalent of H₂L at room temperature in benzene-*d*₆ within 1 h to give [L]Y(CH₂SiMe₃)(THF) (**1**), with concomitant release of one equivalent of SiMe₄. The synthesis was most conveniently carried out on a larger scale by generating in situ Y(CH₂SiMe₃)₃(THF)₂ from YCl₃(THF)_{3,5} and LiCH₂SiMe₃, and subsequent protonolysis with H₂L in pentane at 0 °C to give complex **1** in 70% yield. Also, to access the parent amido complex, instead of the standard alcoholysis of the bulky bis(trimethylsilyl)amido precursor Y[N(SiMe₃)₂]₃ with H₂L, which turned out problematic in some related cases [8a], we preferred the sterically less demanding bis(dimethylsilyl)amido precursor in order to favor the intramolecular approach of the second functionality of diproteo chelating ligands. As a matter of fact, the amine elimination between H₂L and Y[N(SiHMe₂)₂]₃(THF)₂ in pentane solution at room temperature leads selectively to [L]Y[N(SiHMe₂)₂](THF) (**2**) as a white, microcrystalline material in 67% isolated yield (Scheme 1). In situ monitoring by ¹H-NMR spectroscopy in benzene-*d*₆ revealed also that the reaction proceeds fast under those conditions without detection of any intermediate. Both complexes **1** and **2** were fully characterized by elemental analysis, multinuclear 1D (¹H, ¹³C{¹H}) and 2D (COSY, HMQC, HMBC) NMR spectroscopy and an X-ray diffraction study.

The monomeric structure of **1** and **2** and the coordination of one THF unit in each complex was unequivocally established by X-ray crystallography (Figs. 1 and 2), Table 1. In the solid state, the side-arm methoxy was found to be bound to the metal center, as obvious from the Y–O(ether) distances of 2.425(4) (**1**) and 2.414(4) Å (**2**) [14]. These values are somewhat shorter than those observed for the Y–O(ether) bonds in [Y(OCH₂CH₂OMe)₃]₁₀ (average 2.52 Å) [15]. Also, these bond distances are surprisingly short in comparison to that of 2.447(3) Å observed in the analogous zirconium complex [L]Zr(CH₂Ph)₂ [12c], despite the

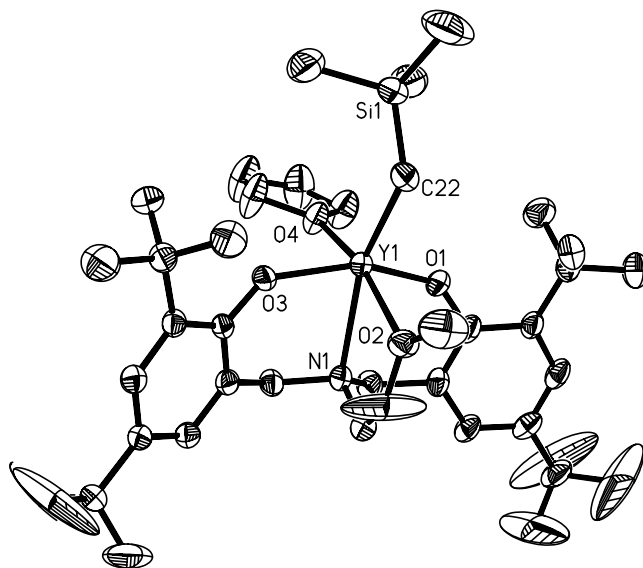


Fig. 1. ORTEP drawing of [L]Y(CH₂SiMe₃)(THF) (**1**) (ellipsoids are drawn at the 30% probability level; all hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): Y(1)–O(3), 2.127(4); Y(1)–O(1), 2.131(4); Y(1)–O(4), 2.350(4); Y(1)–O(2), 2.425(4); Y(1)–C(22), 2.431(6); Y(1)–N(1), 2.576(5); O(3)–Y(1)–O(1), 153.40(15); O(3)–Y(1)–O(4), 85.00(15); O(1)–Y(1)–O(4), 86.18(16); O(3)–Y(1)–O(2), 91.71(15); O(1)–Y(1)–O(2), 89.95(16); O(4)–Y(1)–O(2), 164.08(16); O(3)–Y(1)–C(22), 104.78(19); O(1)–Y(1)–C(22), 101.8(2); O(4)–Y(1)–C(22), 107.6(2); O(2)–Y(1)–C(22), 88.31(19); O(3)–Y(1)–N(1), 78.63(14); O(1)–Y(1)–N(1), 77.44(15); O(4)–Y(1)–N(1), 96.12(16); O(2)–Y(1)–N(1), 67.97(15); C(22)–Y(1)–N(1), 156.2(2).

expected major influence of effective ionic radii of the metal centers [16]. The large difference in the *trans*-influence of the THF and benzyl ligands between yttrium complexes **1/2** and the parent zirconium complex, respectively, presumably accounts for the trend observed. Thus, in both complexes **1** and **2**, the yttrium atom is six-coordinate, the ligands adopting a slightly distorted octahedral geometry with quite similar binding of the [ONOO] ligand core to the metal. The angles between the two apical oxygen and the four basal oxygen, nitrogen and carbon atoms in **1** vary from 85.00(15)° (O(3)–Y(1)–O(4)) to 104.78(19)° (O(3)–Y(1)–C(22)) and those between the two apical oxygen and the four basal oxygen and nitrogen atoms in **2** vary from 83.98(8)° (O(27)–Y(1)–O(31)) to 104.33(9)° (N(2)–Y(1)–O(31)). There is a corresponding similarity in the *trans* angles involving the basal oxygen phenoxide atoms (O–Y–O = 153.40(15)° in **1**, 153.97(8)° in **2**) and, to a lesser extent, the basal amino and functional ligands (N(1)–Y(1)–C(22) = 156.2(2)° in **1**, N(1)–Y(1)–N(2) = 165.80(9)° in **2**). The Y–O(phenoxy) bond lengths of 2.127(4) and 2.131(4) Å in **1** and 2.145(2) and 2.157(2) Å in **2** are similar to analogous bond lengths in other yttrium complexes containing these groups [8a,8b,8c,9a]. Likewise, the Y–C(alkyl) bond distance of 2.431(6) Å in **1** and the Y–N(amido) bond distance of

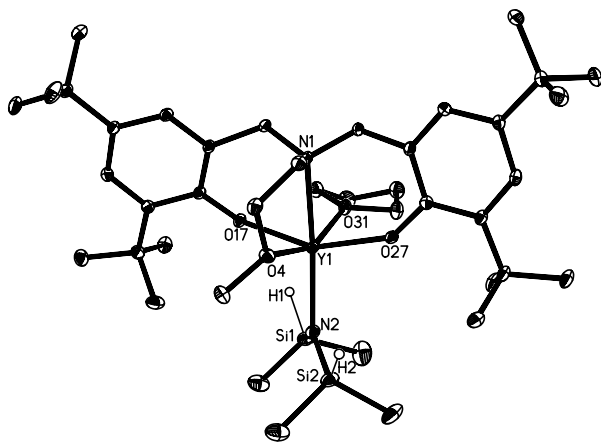


Fig. 2. ORTEP drawing of $[L]Y[N(SiHMe_2)_2](THF)$ (**2**) (ellipsoids are drawn at the 30% probability level; the solvent molecule and all hydrogen atoms, apart from those attached to Si(1) and Si(2), are omitted for clarity). Selected bond distances (Å) and angles ($^\circ$): Y(1)–O(27), 2.145(2); Y(1)–O(17), 2.157(2); Y(1)–N(2), 2.276(3); Y(1)–O(31), 2.355(2); Y(1)–O(4), 2.414(2); Y(1)–N(1), 2.533(2); O(27)–Y(1)–O(17), 153.97(8); O(27)–Y(1)–N(2), 101.87(9); O(17)–Y(1)–N(2), 103.62(9); O(27)–Y(1)–O(31), 83.98(8); O(17)–Y(1)–O(31), 84.70(8); N(2)–Y(1)–O(31), 104.33(9); O(27)–Y(1)–O(4), 96.40(8); O(17)–Y(1)–O(4), 85.25(8); N(2)–Y(1)–O(4), 98.02(9); O(31)–Y(1)–O(4), 157.09(8); O(27)–Y(1)–N(1), 77.07(7); O(17)–Y(1)–N(1), 79.51(7); N(2)–Y(1)–N(1), 165.80(9); O(31)–Y(1)–N(1), 89.70(8); O(4)–Y(1)–N(1), 68.23(7); Si(2)–N(2)–Si(1), 127.15(16); Si(2)–N(2)–Y(1), 118.45(14); Si(1)–N(2)–Y(1), 113.59(14).

2.276(3) Å in **2** are comparable to those observed in $[Y(\text{salicylaldiminato})(CH_2SiMe_2Ph)(THF)_2]$ (2.384(2) Å) [9] and $[Y(\text{salen}')\{N(SiHMe_2)_2\}(THF)]$ (2.27 Å) [8a], respectively. The Si(1)–N(2)–Si(2) bond angle of $127.15(16)^\circ$ in **2** falls in the range of values reported for “normal” Si–N–Si angles ($121.6(4)$ – $133(1)^\circ$) [17]. This argues against any significant Si–H–Y agostic interaction, consistently with the presence of a coordinated THF molecule.

The yttrium alkyl complex **1** and its amido analogue **2** proved remarkably stable in hydrocarbon solutions. No decomposition was observed after several days at room temperature in benzene and a few hours at 60°C in toluene. The minor asymmetry observed within the crystal structures is lost in solution at room temperature as only one set of resonances for a symmetrically coordinated ligand is observed in the $^1\text{H-NMR}$ spectra of **1** and **2** in benzene- d_6 . All ligand and THF peaks are resolved singly and sharply with their expected coupling patterns (see Section 3). Those corresponding to the methoxy group were found, respectively, at δ 2.88 and δ 2.84, shifted upfield from that in the free ligand (δ 2.99), confirming that the six-coordinated geometry observed in the solid state is retained in solution. Also, the resonances corresponding to the bound THF were found, respectively, at δ 3.87 and 1.27 (**1**) and δ 3.84 and 1.18 (**2**), shifted from free THF. Immediate exchange of coordinated THF occurred when the spectra

were recorded in THF- d_8 , consistent with the existence of an equilibrium involving THF dissociation fast on both the chemical and NMR time scales. However, for both the alkyl and amido complexes, neither pumping of solids under high vacuum for prolonged periods nor repeated stripping of toluene solutions yielded the corresponding THF-free complexes, indicating that THF coordination in **1** and **2** is rather strong.

Preliminary investigations were carried out to explore the reactivity of the new complexes towards polar and non polar monomers. Yttrium alkyl **1** was found inefficient for the polymerization of ethylene; insignificant gas consumption was noticed when **1** was exposed at 20°C under 4 atm of C_2H_4 for 2 h and no polymer could be precipitated after quenching. Such inactivity likely arises from the presence of a THF ligand which, as aforementioned, has the tendency to remain within the coordination sphere of the complex and might thus block the “active-site”. Other alkoxy and diamido yttrium alkyl complexes that possess THF ligands have been also reported to exhibit comparable inactivity towards ethylene (olefins) [6b,18]. Complex **1** did not catalyze the polymerization of methyl methacrylate (MMA) either but this could be achieved with the amido complex **2** (Table 2). Noteworthy is the formation of isotactic-rich poly(MMA), up to 71% at the *mm* diad level at 0°C , though modest activities were observed. Sluggish polymerizations of MMA were also observed on increasing the temperature to 50°C or using THF as solvent. On the other hand, the amido complex **2** is a highly active catalyst for the ring-opening polymerization of ϵ -caprolactone (CL). Mixtures of catalyst and monomer at room temperature in ratios ranging from 1:200 to 1:400, in bulk or in toluene solutions, led to immediate precipitation of poly(CL), with quantitative conversion within 1 min. The polymers formed were recovered as white solids and had weight-average molecular weights in the range 50 000–82 000 and a polydispersity of 2.4–4.1.

In conclusion, we have prepared via convenient and high yielding σ -bond metathesis protocols new thermally stable organoyttrium complexes incorporating the bis(phenolato) ligand L, which are neutral analogues of cationic Group 4 metal systems. Current efforts are focused on the synthesis of base-free analogues of these compounds.

3. Experimental

3.1. General considerations

All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (toluene, pentane) were freshly distilled from Na/K alloy under nitrogen and degassed

thoroughly by freeze–thaw–vacuum cycles prior to use. Deuterated solvents (benzene-*d*₆, toluene-*d*₈, THF-*d*₈; >99.5% D, Eurisotop) were freshly distilled from sodium/potassium amalgam under argon and degassed prior to use. Ligand H₂L [12c] and yttrium precursors Y(CH₂SiMe₃)₃(THF)₂ [13] and Y[N(SiHMe₂)₂]₃(THF) [19] were prepared following literature procedures. MMA (99%, Aldrich) and ε-caprolactone (CL) (99%, ACROS) were vacuum distilled over CaH₂ and stored at –20 °C under argon. NMR spectra were recorded on Bruker AC-200 and AC-300 spectrometers in Teflon-valve NMR tubes. ¹H and ¹³C chemical shifts are reported in ppm versus SiMe₄ and were determined by reference to the residual solvent peaks. Assignment of signals was made from ¹H–¹H COSY, ¹H–¹³C HMQC and HMBC NMR experiments. Coupling constants are given in Hertz. Elemental analyses were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations. Size exclusion chromatography (SEC) of poly(MMA) and poly(CL) samples was performed in THF at 20 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer, a DAD-UV detector and Waters styragel columns (HR2, HR3, HR4, HR5E) or PL-GEL Mixte B and 100A columns. The number-average molecular masses (*M*_n) and polydispersity index (*M*_w/*M*_n) of the resultant polymers were calculated with reference to a polystyrene calibration. Microstructure of poly(MMA)s was measured by ¹H-NMR spectroscopy at 23 °C in CDCl₃.

3.2. Synthesis of [L]Y(CH₂SiMe₃)(THF) (1)

3.2.1. NMR scale reaction

To a solution of Y(CH₂SiMe₃)₃(THF)₂ (0.031 g, 0.06 mmol) in benzene-*d*₆ (ca. 0.5 ml) in an NMR tube was added H₂L (0.032 g, 0.06 mmol) at room temperature (r.t.). The tube was vigorously shaken and left at r.t. After 1 h, the reaction was checked by ¹H-NMR spectroscopy, which indicated complete and selective conversion of the ligand and starting yttrium alkyl to complex 1.

3.2.2. Preparative scale reaction

To a stirred solution of Y(CH₂SiMe₃)₃(THF)₂ (0.148 g, 0.30 mmol) in pentane (5 ml) was added at 0 °C a solution of H₂L (0.153 g, 0.30 mmol) in pentane (5 ml). The solution was stirred for 2 h at 0 °C and volatiles were removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving 1 as a colorless powder (0.16 g, 70%). Single crystals suitable for X-ray diffraction were grown from pentane at –35 °C. ¹H-NMR (300 MHz, C₆D₆): δ 7.59 (d, 2H, *J*_{HH} = 2.5, ArH), 7.08 (d, 2H, *J*_{HH} = 2.5, ArH), 3.87 (br, 4H, α-CH₂ THF), 3.76 (d, 2H, *J*_{HH} = 12.5, ArCH₂), 2.92 (d, 2H, *J*_{HH} = 12.5, ArCH₂), 2.88 (s,

3H, OCH₃), 2.44 (t, 2H, *J*_{HH} = 5.3 Hz, CH₂O), 2.21 (t, 2H, *J*_{HH} = 5.3, NCH₂), 1.80 (s, 18H, C(CH₃)₃), 1.46 (s, 18H, C(CH₃)₃), 1.27 (br, 4H, β-CH₂ THF), 0.49 (s, 9H, Si(CH₃)₃), –0.40 (d, 2H, *J*_{YH} = 3.1, CH₂SiMe₃). ¹³C{¹H}-NMR (75 MHz, C₆D₆): δ 161.38, 136.59, 136.40, 125.40, 124.21, 123.90, (s, Ar–C), 73.84 (s, CH₂OMe), 70.66 (s, α-CH₂ THF), 64.65 (s, CH₂Ar), 61.09 (s, OCH₃), 49.09 (s NCH₂), 35.39 (s, CMe₃), 34.04 (s, CMe₃), 32.05 (s, (CH₃)₃), 30.11 (s, (CH₃)₃), 24.92 (s, β-CH₂ THF), 24.70 (d, *J*_{CY} = 46.4 Hz, YCH₂), 4.64 (s, Si(CH₃)₃). Anal. Calc. for C₄₁H₇₀NO₄SiY: C, 64.97; H, 9.31; N, 1.85. Found: C, 65.11; H, 9.65; N, 1.74%.

3.3. Synthesis of [L]Y[N(SiHMe₂)₂](THF) (2)

To a stirred solution of Y[N(SiHMe₂)₂]₃(THF)₂ (0.189 g, 0.30 mmol) in pentane (5 ml) was added a solution of H₂L (0.153 g, 0.30 mmol) in pentane (5 ml) at r.t. After stirring 2 h at r.t., a white precipitate formed. To ensure complete reaction, the mixture solution was stirred for additional 10 h. The solid was then filtered out yielding 2 as a white powder (0.163 g, 67%). Single crystals suitable for X-ray diffraction study were grown from pentane at –35 °C. ¹H-NMR (300 MHz, C₆D₆): δ 7.60 (d, 2H, *J*_{HH} = 2.5, ArH), 7.10 (d, 2H, *J*_{HH} = 2.3, ArH), 5.14 (m, 2H, SiH), 3.87 (d, 2H, *J*_{HH} = 12.5, overlap with THF signal, ArCH₂), 3.84 (b, 4H, α-CH₂ THF), 2.97 (d, 2H, *J*_{HH} = 12.5, ArCH₂), 2.84 (s, 3H, OCH₃), 2.71 (t, 2H, *J*_{HH} = 5.2, NCH₂), 2.31 (t, 2H, *J*_{HH} = 5.2, CH₂O), 1.79 (s, 18H, C(CH₃)₃), 1.47

Table 1
Summary of crystallographic data

	1	2·0.5pentane
Formula	C ₄₁ H ₇₀ NO ₄ SiY	C _{43.5} H ₇₉ N ₂ O ₄ Si ₂ Y
Crystal size (mm)	0.12 × 0.20 × 0.26	0.05 × 0.10 × 0.16
<i>M</i> _r (g mol ^{–1})	757.98	839.18
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.2553(2)	11.18130(10)
<i>b</i> (Å)	19.3870(3)	15.4103(2)
<i>c</i> (Å)	35.0029(6)	15.7042(2)
α (°)	90	99.3330(10)
β (°)	90	98.7160(10)
γ (°)	90	101.3630(10)
<i>V</i> (Å ³)	8995.1(2)	2570.27(5)
<i>Z</i>	8	2
<i>D</i> _{calc.} (g cm ^{–3})	1.119	1.084
<i>T</i> (K)	200(2)	100(2)
θ Range (°)	2.10–26.01	2.91–33.14
μ (mm ^{–1})	1.359	1.217
Reflections measured	15 611	48 698
Independent reflections	8707	19 104
Reflections with <i>I</i> > 2σ(<i>I</i>)	4313	12 313
Parameters	433	490
Goodness of fit	1.009	1.053
<i>R</i> _{int} [<i>I</i> > 2σ(<i>I</i>)]	0.0824	0.0737
w <i>R</i> ₂	0.1747	0.1605

Table 2
Polymerization of MMA promoted by **2**^a

<i>T</i> (°C)	<i>t</i> (h)	Yield (%)	<i>M_n</i> ^b 10 ³	<i>M_w</i> / <i>M_n</i> ^b	Tacticity ^c		
					<i>rr</i>	<i>mr</i>	<i>mm</i>
0	7	5	25.8	1.70	18	11	71
25	5	5	15.7	1.37	23	15	61

^a [MMA]/[**2**] = 500; 1:1 v/v toluene/MMA solutions.

^b Average number molecular mass and polydispersity as determined by GPC.

^c Determined by ¹H-NMR in CDCl₃.

(s, 18H, C(CH₃)₃), 1.18 (m, 4H, β-CH₂ THF), 0.49 (d, 12H, *J*_{HH} = 3.0 Hz, HSi(CH₃)₂). ¹H-NMR (300 MHz, THF-*d*₈): δ 7.19 (d, 2H, *J*_{HH} = 2.5, ArH), 6.91 (s br, 2H, ArH), 4.90 (m, 2H, SiH), 4.00 (d, 2H, *J*_{HH} = 12.5, ArCH₂), 3.58 (4H, α-CH₂ THF, overlap with solvent resonances), 3.26 (m, 7H, ArCH₂, OCH₃, NCH₂), 2.70 (t, 2H, *J*_{HH} = 5.2, CH₂O), 1.73 (m, 4H, β-CH₂ THF, overlap with solvent resonances), 1.48 (s, 18H, C(CH₃)₃), 1.26 (s, 18H, C(CH₃)₃), 0.15 (d, 12H, *J*_{HH} = 3.0 Hz, HSi(CH₃)₂). ¹³C{¹H}-NMR (75 MHz, C₆D₆): 161.38, 136.53, 125.40, 124.11, (s, Ar-C), 73.11 (s, CH₂OMe), 70.96 (s, α-CH₂ THF), 64.54 (s, CH₂Ar), 60.43 (s, OCH₃), 49.57 (s NCH₂), 35.46 (s, CMe₃), 34.04 (s, CMe₃), 32.06 (s, (CH₃)₃), 30.30 (s, (CH₃)₃), 24.95 (s, β-CH₂ THF), 4.22 (s, Si(CH₃)₂). Anal. Calc. for C₄₁H₇₃N₂O₄Si₂Y: C, 61.32; H, 9.17; N, 3.49. Found: C, 61.74; H, 9.36; N, 3.36%.

3.4. X-ray crystallography

Suitable single crystals of compounds **1** and **2** were mounted onto glass fibers using the “oil-drop” method. Diffraction data were collected using a NONIUS Kappa CCD diffractometer with graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). Crystal structures were solved by means of direct methods, remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on *F*² (programs SHELXS-97 and SHELXL-97) [20]. Many hydrogen atoms could be found from the Fourier difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. The cell of **2** was found to contain one molecule of crystallization pentane. Crystal data and details of data collection and structure refinement are given in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Data Center, CCDC No. 209841 and 209842 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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