New potentially tridentate amidinate ligand $\{o\text{-MeOC}_6H_4NC(Ph)N(SiMe_3)\}^-$. Synthesis and molecular structures of amidinate complexes of lithium $[\{o\text{-MeOC}_6H_4NC(Ph)N(SiMe_3)\}Li]_2$ and yttrium $[\{o\text{-MeOC}_6H_4NC(Ph)N(SiMe_3)\}YCl_2(THF)_2]_2$*

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The reaction of lithium silylamide $[\{o\text{-MeOC}_6H_4N(SiMe_3)\}Li(OEt_2)]_2$ with 2 equiv. of benzonitrile in THF at ~20 °C affords the lithium derivative of the new tridentate amidinate ligand $[\{o\text{-MeOC}_6H_4NC(Ph)N(SiMe_3)\}Li]_2$. The X-ray diffraction study showed that this complex has a dimeric structure due to the coordination of the N atoms and the ether group of one amidinate ligand to different Li atoms. The reaction of anhydrous YCl_3 with the resulting complex in THF gives the monoamidinate complex $[\{o\text{-MeOC}_6H_4NC(Ph)N(SiMe_3)\}YCl_2(THF)_2]_2$ regardless of the reagent ratio. The latter has a dimeric structure in the crystalline state as a result of the presence of two μ_2-bridging Cl atoms that link Y atoms. The ether groups of the amidinate ligands are not involved in the metal—ligand interaction.

Key words: rare-earth metals, amidinate ligand, lithium amidinate complexes, yttrium amidinate complexes, synthesis, structure.

The amidinate ligands $[RC(NR')_2]^-$ belonging to monoanionic four-electron ligands, in which the negative charge in delocalized over the NCN group, have attracted researchers' attention in the last three decades due to diverse coordination properties. In addition, the obvious advantages of amidinate ligands are that their electronic and steric properties can be easily modified by varying the substituents both at the N atoms and the central C atom, as well as that the starting reagents for their preparation are available and relatively cheap. Recent studies have shown the great synthetic potential of amidinate ligands in coordination chemistry of a large number of elements.[1—6] Data on amidinate ligands in organolanthanide chemistry published in the works of Edelmann[7—11] and Teuben[12—17] have greatly stimulated the development of this field and made it possible to synthesize and characterize various classes of their derivatives. Highly reactive alkyl, cationic alkyl, and hydride complexes of rare earth metals show the ability to catalyze a series of transformations of unsaturated substrates, such as polymerization of olefins[15,16] and dienes,[18] selective dimerization of monosubstituted acetylenes,[19] hydroboration,[20] hydrosilylation,[21] and hydroamination[22] of olefins.

It is known that the stability and reactivity of organic derivatives of rare earth metals are determined to a large extent by the coordinative and steric saturation of the metal coordination sphere. Therefore, considerable efforts are currently focused on searching for new types of ligand systems, which can stabilize metal complexes and provide additional ways to design the coordination environment of the central metal atom and control the reactivity.[23,24] One of approaches to this problem is based on the introduction of additional groups, which have Lewis base properties and can be coordinated to a metal atom, into the ligand system, resulting in the saturation of the coordination sphere and a change in its geometry. Several amidinate ligands containing electron-donating groups in the side chain are documented.[25—28] The aims of the present study were to design a new non-symmetrical amidinate ligand $\{o\text{-MeOC}_6H_4NC(Ph)N(SiMe_3)\}$, in which one of the N atoms contains the ether group capable of coordinating to the metal atom, as well as to synthesize lithium and yttrium complexes based on this ligand.

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* Dedicated to Academician V. N. Charushin on the occasion of his 60th birthday.

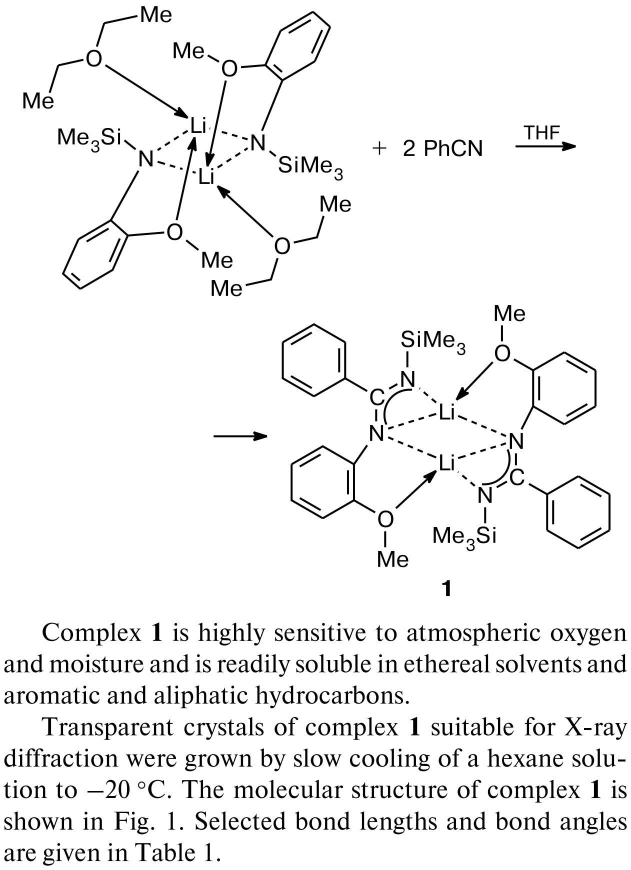
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 785—790, May, 2011.

Results and Discussion

One of facile methods for the formation of the amidinate (most often benzamidinate) moiety is based on the reaction of lithium silylamide $LiN(SiMe_3)_2$ with nitrile RC≡N,[29,30] resulting in the formation of the corresponding lithium amidinate $\{RC(NSiMe_3)_2\}Li$. This method allows one to prepare functionalized amidinate ligands containing the pyridyl and furyl moieties.[31] We used this method for the synthesis of a new potentially tridentate amidinate ligand.

It was found that the reaction of the dimeric lithium silylamide $[\{o\text{-}MeOC_6H_4N(SiMe_3)\}Li(OEt_2)]_2$ (see Ref. 32) with 2 equiv. of benzonitrile in THF at ~20 °C affords the lithium complex $[\{o\text{-}MeOC_6H_4NC(Ph)N(SiMe_3)\}Li]_2$ (**1**) containing the new amidinate ligand (Scheme 1). The reaction proceeds through the addition of lithium amide at the triple bond C≡N of benzonitrile followed by the migration of the $SiMe_3$ moiety. After the recrystallization of the reaction product from hexane, complex **1** was obtained as transparent crystals in 86% yield.

Scheme 1



1

Complex **1** is highly sensitive to atmospheric oxygen and moisture and is readily soluble in ethereal solvents and aromatic and aliphatic hydrocarbons.

Transparent crystals of complex **1** suitable for X-ray diffraction were grown by slow cooling of a hexane solution to –20 °C. The molecular structure of complex **1** is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1.

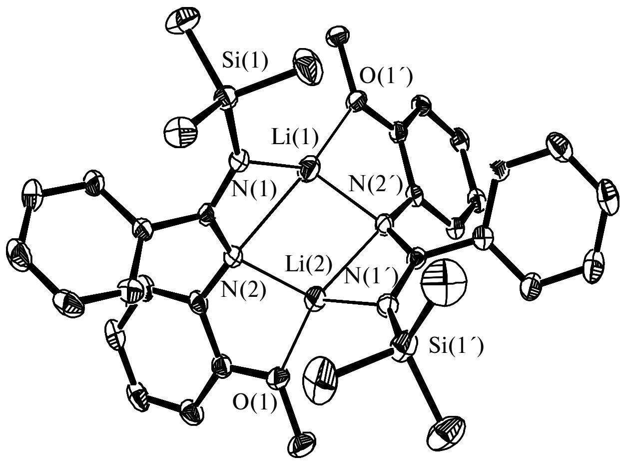


Fig. 1. Structure of complex **1**.

The X-ray diffraction study showed that lithium amidinate complex **1** has a dimeric structure due to the coordination of the N atoms of the NCN group and the O atoms of the ether groups of one ligand to different Li atoms. It is interesting that, in spite of the presence of diethyl ether molecules in the starting amide and the occurrence of the reaction in THF, complex **1** does not contain coordinated donor solvent molecules. The coordination sphere of the Li atoms in complex **1** is formed by three N atoms of two amidinate moieties and the O atom of the ether group, resulting in the formal coordination number 4. It should be noted that the coordination of the amidinate moieties to the Li atom in the structure of **1**, as opposed to derivatives of benzamidinate ligands,[27] is strongly distorted, and the Li—N bond lengths in the metallacycles LiNCN are substantially different: Li(1)—N(1), 1.963(3) Å; Li(1)—N(2), 2.401(3) Å; Li(2)—N(2′), 2.025(2) Å; Li(2)—N(1′), 1.973(2) Å. The Li—O bond lengths are 1.957(3) and 1.914(2) Å.

In the ^1H NMR spectrum of complex **1** (C_6D_6, 20 °C), the protons of the trimethylsilyl group appear as a singlet at δ 0.22, a singlet at δ 3.31 is assigned to the protons of the methoxy group, and signals for aromatic protons appear as a multiplet in low field (δ 6.34—7.49). In the ^{13}C NMR spectrum, the signal for the quaternary C atom of the amidinate moiety is observed in the characteristic region at δ 176.8, the signal for the C atoms of the trimethylsilyl

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **1**

Bond	*d*/Å	Angle	ω/deg
Li(1)—N(1)	1.963(3)	N(1)—Li(1)—N(2′)	137.08(14)
Li(1)—N(2)	2.401(3)	O(1′)—Li(1)—N(2)	83.30(10)
Li(1)—N(2′)	2.025(2)	N(1)—Li(1)—N(2)	62.29(8)
Li(1)—O(1′)	1.957(3)	N(2′)—Li(1)—N(2)	100.32(11)
Li(2)—N(2)	2.014(2)	Li(2)—N(2)—Li(1)	70.75(9)
Li(2)—N(2′)	2.160(3)	O(1)—Li(2)—N(1′)	121.12(13)
Li(2)—N(1′)	1.973(2)	O(1)—Li(2)—N(2)	84.50(10)
Li(2)—O(1)	1.914(2)	O(1)—Li(2)—N(2′)	142.63(13)

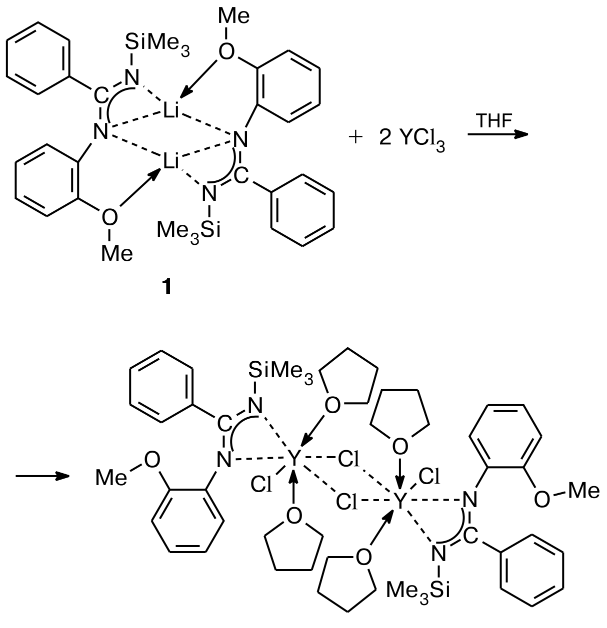
groups appear at δ 1.7, and the signal for the C atoms of the methoxy group is observed at δ 54.3. In the IR spectrum, the intense absorption band of C≡N at 2300 cm^{-1} is absent; instead, the absorption band at 1620 cm^{-1} assigned to the double bond of the amidinate moiety appears.

To study the coordination of the new tridentate amidinate ligand to a metal atom with a larger ionic radius (in our case, the Y atom), we investigated the reaction of anhydrous YCl_3 with complex **1** in THF at ~20 °C. It was found that this reaction affords exclusively the monoamidinate derivative regardless of the reagent molar ratio (YCl_3 : **1** = 1 : 1 and 2 : 1). Evidently, the size of the amidinate ligand prevents the simultaneous coordination of two moieties to one Y atom. The removal of THF, the extraction of the reaction product with toluene, and the separation of a LiCl precipitate followed by recrystallization from THF allowed us to isolate the complex $[\{o\text{-}MeOC_6H_4NC(Ph)N(SiMe_3)\}YCl_2(THF)_2]_2$ (**2**) in 69% yield (Scheme 2).

Transparent crystals of complex **2** suitable for X-ray diffraction study were prepared by slow evaporation of a solution of complex **2** in THF to –20 °C. The molecular structure of complex **2** is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 2.

The X-ray diffraction study showed that compound **2** has a dimeric structure due to the μ_2-bridging coordination of two Cl atoms to two Y atoms, whereas two other Cl atoms are terminal. Complex **2** is neutral and does not contain LiCl in the form of the ate complex. The coordination sphere of the Y atom is formed by two N atoms of the amidinate moiety, three Cl atoms, and two O atoms of THF molecules, resulting in the coordination number 7 for the Y atom. According to the X-ray diffraction data, the O atom of the ether group in complex **2** is not coordinated to the Y atom. The bridging Y—Cl bonds in the structure of **2** (2.7262(6), 2.7765(6), 2.7764(6) Å) are, as expected, substantially longer than the terminal bonds (2.5082(6) Å); their lengths are comparable with the average length of the bridging bonds in the seven-coordinate complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)(\mu\text{-}Cl)]_2$ (2.736(2) Å).[33] The Y—N bond lengths in the metallacycle YNCN (2.384(2) and 2.375(2) Å) are in the range

Scheme 2



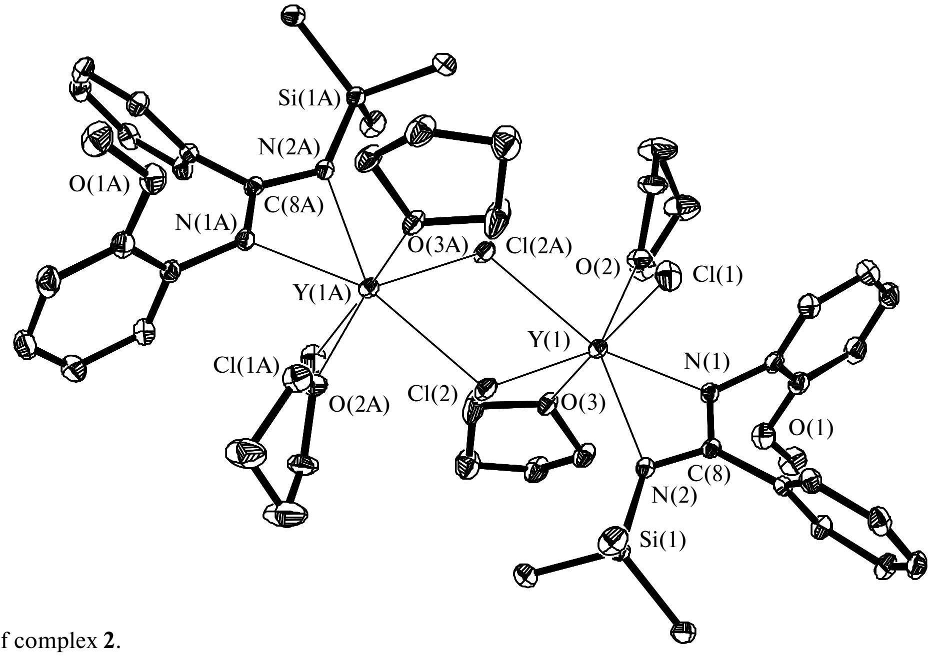


Fig. 2. Structure of complex **2**.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **2**

Bond	*d*/Å	Angle	ω/deg
Y(1)—O(2)	2.3664(14)	O(2)—Y(1)—O(3)	87.98(6)
Y(1)—O(3)	2.3729(16)	O(2)—Y(1)—N(2)	131.87(6)
Y(1)—N(2)	2.3748(17)	O(3)—Y(1)—N(2)	85.21(6)
Y(1)—N(1)	2.3839(17)	O(2)—Y(1)—N(1)	75.44(6)
Y(1)—Cl(1)	2.5802(6)	O(3)—Y(1)—N(1)	85.43(6)
Y(1)—Cl(2)	2.7262(6)	N(2)—Y(1)—N(1)	56.55(6)
Y(1)—C(8)	2.746(2)	N(2)—Y(1)—Cl(1)	96.54(5)
Y(1)—Cl(2A)	2.7765(6)	N(1)—Y(1)—Cl(1)	90.52(5)
Cl(2)—Y(1A)	2.7764(6)	Y(1)—Cl(2)—Y(1A)	107.071(18)
N(1)—C(8)	1.326(3)	N(1)—C(8)—N(2)	115.80(18)
N(2)—C(8)	1.335(3)	C(8)—N(1)—Y(1)	90.89(12)

characteristic of yttrium derivatives with guanidinate and amidopyridinate ligands.[34] The C—N bond lengths in the amidinate moiety are equivalent: C(8)—N(1), 1.326(3) Å; C(8)—N(2), 1.335(3) Å. This is indicative of delocalization of the negative charge in the NCN group.

In the ^1H NMR spectrum of complex **2** (C_6D_6, 20 °C), the singlet at δ 0.25 corresponds to protons of the trimethylsilyl group, the β-protons of four THF molecules appear as a singlet at δ 1.40, and the protons of the methoxy group together with the α-protons of four THF molecules give a singlet at δ 3.70 The aromatic protons appear as a set of low-field signals (δ 6.20—7.21).

With the aim of synthesizing alkyl complexes of yttrium in the tridentate amidinate ligand environment, we performed the reactions of complex **2** with Me_3SiCH_2Li and MeLi (in the presence of TMEDA). The reaction of complex **2** with Me_3SiCH_2Li was carried out at 0 °C; the reaction with MeLi was performed in diethyl ether in the presence of TMEDA at 0 °C. The occurrence of the transformations was evidenced by the precipitation of LiCl. However, we failed to isolate the corresponding alkyl derivatives. Soluble reaction products were brown oily liquids of unknown composition.

To sum up, we found that the reaction of lithium silylamide $[\{o\text{-}MeOC_6H_4N(SiMe_3)\}Li(OEt_2)]_2$ with 2 equiv. of benzonitrile in THF at ~20 °C affords the lithium derivative of the new tridentate amidinate ligand $[\{o\text{-}MeOC_6H_4NC(Ph)N(SiMe_3)\}Li]_2$ (**1**). The reaction of anhydrous YCl_3 with complex **1** in THF gives the monoamidinate complex $[\{o\text{-}MeOC_6H_4NC(Ph)N(SiMe_3)\}YCl_2(THF)_2]_2$ (**2**) regardless of the reagent ratio. Complex **2** has a dimeric structure in the crystalline state due to the presence of two μ_2-bridging Cl atoms that link Y atoms. The ether groups of the amidinate ligands are not involved in the metal—ligand interaction.

Experimental

All operations associated with the synthesis and isolation of the products were carried out in evacuated glassware with the use of standard Schlenk technique. Tetrahydrofuran was dried with potassium hydroxide followed by distillation over sodium benzophenone ketyl. Hexane and benzene were dried by refluxing and distillation over metallic Na; C_6D_6 was dried with metallic Na, degassed, and condensed *in vacuo*. Lithium amide $[\{o\text{-}C_6H_4OMeN(SiMe_3)\}Li(OEt_2)]_2$ (see Ref. 32) and anhydrous YCl_3 (see Ref. 35) were prepared according to known procedures. *o*-Anisidine and benzonitrile are commercial reagents (Acros). *o*-Anisidine was dried with calcium hydride, distilled, and stored in an evacuated container. Benzonitrile was distilled, dried over molecular sieves, and stored in an evacuated container.

The IR spectra were recorded on a Bruker-Vertex 70 instrument. Samples of the compounds were prepared under dry argon as Nujol mulls. The ^1H, ^{13}C, and ^7Li NMR spectra were recorded on Bruker DPX 200 and 400 instruments (20 °C). The chemical shifts (ppm) are given with respect to the known shifts of the residual protons of deuterated solvents.

Bis[(*N*-trimethylsilyl-*N*´-*o*-methoxyphenylbenzamidinato)lithium], $[\{o\text{-}MeOC_6H_4NC(Ph)N(SiMe_3)\}Li]_2$ (1). A solution of PhCN (0.25 g, 2.40 mmol) in THF (3 mL) was added to a solution of $[\{o\text{-}C_6H_4OMeN(SiMe_3)\}Li(OEt_2)]_2$ (0.67 g, 1.2 mmol) in THF (30 mL). The reaction mixture was stirred at ~20 °C for 24 h. Then THF was removed, and the oily residue was dissolved in hexane. After cooling of the concentrated hexane solution to –20 °C, transparent crystals of complex **1** were obtained in a yield of 0.68 g (86%). Found (%): C, 66.73; H, 6.77; N, 9.03. $C_{17}H_{21}LiN_2OSi$. Calculated (%): C, 67.08; H, 6.95; N, 9.20. ^1H NMR (C_6D_6), δ: 0.22 (s, 18 H, $SiMe_3$); 3.31 (s, 6 H, OMe); 6.33 (m, 2 H, C_6H_4); 6.54 (m, 4 H, PhCN); 6.61 (m, 2 H, PhCN); 7.00 (d, 6 H, C_6H_4); 7.47 (d, 4 H, PhCN). ^{13}C NMR (C_6D_6), δ: 1.7 ($SiMe_3$); 54.3 (OMe); 109.2, 118.1, 121.1, 124.4, 141.5, 149.9 (C_6H_4); 126.7, 126.9, 127.1, 127.8 (Ph); 176.8 (NCN). ^7Li NMR (C_6D_6), δ: 5.06. IR (Nujol), ν/cm^{-1}: 1633 (w), 1517 (s), 1242 (s), 1105 (m), 964 (s), 852 (s), 765 (m).

Bis[(*N*-trimethylsilyl-*N*´-*o*-methoxyphenylbenzamidinato)(dichlorido)di(tetrahydrofuran)yttrium], $[\{o\text{-}MeOC_6H_4NC(Ph)N(SiMe_3)\}YCl_2(THF)_2]_2$ (2). A solution of **1** (0.524 g, 1.72 mmol) in THF (50 mL) was added to a suspension of anhydrous YCl_3 (0.336 g, 1.72 mmol) in THF (10 mL). The reaction mixture was stirred at ~20 °C for 24 h. Then THF was removed *in vacuo*, the solid reside was extracted with toluene, and the extract was filtered to separate LiCl. Toluene was removed by condensation *in vacuo*, and the solid residue was dried *in vacuo* to constant weight. The recrystallization of the solid residue from THF gave yellow crystals of **2** in a yield of 0.71 g (69%). Found (%): C, 49.60; H, 6.05; N, 4.39; Y, 14.90. $C_{50}H_{74}Cl_4N_4O_6Si_2Y_2$. Calculated (%): C, 49.92; H, 6.20; N, 4.66; Y, 14.78. ^1H NMR (C_6D_6), δ: 0.24 (s, 18 H, SiMe); 1.38 (s, 16 H, β-CH_2, THF); 3.70 (br.s, 22 H, 16 H, α-CH_2, THF and 6 H, *o*-$C_6H_4(O\underline{Me})$); 6.20 (d, 1 H, C_6H_4); 6.32 (d, 2 H, *o*-C_6H_4); 6.49 (m, 5 H, *o*-C_6H_4); 6.88 (s, 7 H, Ph); 7.21 (s, 3 H, Ph). ^{13}C NMR (pyridine-d_5), δ: 2.1, 3.6 ($SiMe_3$); 25.8 (β-CH_2, THF); 55.8 (*o*-$C_6H_4(O\underline{Me})$); 67.9 (α-CH_2, THF); 113.1, 121.8, 124.0, 128.0, 128.5, 130.5, 136.8, 139.6, 152.0, 156.0 (C_6H_4, Ph); 158.6 (NCN). IR (Nujol), ν/cm^{-1}: 1626 (w), 1245 (m), 1182 (m), 1043 (s), 1013 (s), 856 (s), 677 (m).

X-ray diffraction study. X-ray diffraction study of complex **1** was performed at 100 K on a SMART APEX II CCD diffractometer (λ(Mo-Kα) = 0.71072 Å, ω-scanning technique). The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement pa-

Table 3. Crystallographic parameters and the X-ray data collection and refinement statistics for complexes **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{17}H_{21}LiN_2OSi$	$C_{50}H_{74}C_{l4}N_4O_6Si_2Y_2$
Molecular weight	304.39	1202.94
Space group	P21/*c*	P21/*n*
a/Å	15.6597(8)	9.8406(5)
b/Å	11.7281(6)	13.6738(8)
c/Å	19.6459(10)	21.6449(12)
α/deg	90.00	90
β/deg	91.3356(10)	93.4160(10)
γ/deg	90.00	90
V/Å^{-3}	3607.2(3)	2907.3(3)
Z	4	2
d_{calc}/g cm^{-3}	1.121	1.374
μ/mm^{-1}	1.31	2.258
θ-Scan range, deg	1.30—29.00	1.76—27.00
Number of measured reflections	36030	18552
Number of reflections with $I > 2\sigma(I)$	9590	4987
R_{int}	0.0310	0.0311
GOOF (F^2)	1.036	1.006
R_1 ($I > 2\sigma(I)$)	0.0413	0.0340
ωR_2 (all data)	0.1253	0.0521
Residual electron density (max/min)/e Å^{-3}	0.390/–0.239	0.660/–0.323

rameters for all nonhydrogen atoms based on F^2_{hkl}. The hydrogen atoms were positioned geometrically and refined isotropically with fixed thermal parameters $U_{\text{iso}} = 1.2C_{\text{iso}}$. An analysis of difference electron density maps showed that one of $SiMe_3$ groups in the structure of **1** is disordered over two positions with equal occupancy. The positions of the carbon atoms of the disordered group were refined anisotropically with the Si—C bond lengths and anisotropic displacement parameters restrained to be equal (Eadp instructions). The calculations were carried out with the use of the SHELXTL 5.10^2 program package.[36]

The X-ray diffraction study of complex **2** was performed on a SMART APEX I diffractometer (graphite monochromator, Mo-Kα radiation, φ—ω-scanning technique) at 100 K. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms based on F^2_{hkl}. The hydrogen atoms were positioned geometrically and refined using a riding model. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[36] The absorption correction was applied with the use of the Sadabs program.[37] Principal crystallographic parameters and the X-ray data collection and structure refinement statistics for complexes **1** and **2** are given in Table 3.*

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 08-03-00391 and 11-03-00555).

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* Additional crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC 818268 and 818269) and can be obtained, free of charge, on application to www.ccdc.cam.uk/data_request/cif.

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Received December 22, 2010;
in revised form March 22, 2011