Synthesis, molecular structure, and catalytic activity of borohydride complexes $[(Me_3Si)_2NC(NPr^i)_2]_2Nd(BH_4)_2Li(thf)_2$ and $[(Me_3Si)_2NC(NPr^i)_2]_2Sm(BH_4)_2Li(thf)_2$

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The reactions of lanthanide tris(borohydrides) $Ln(BH_4)_3(thf)_3$ (Ln = Sm or Nd) with 2 equiv. of lithium *N*,*N*′-diisopropyl-*N*′-bis(trimethylsilyl)guanidinate in toluene produced the $[(Me_3Si)_2NC(NPr^i)_2]Ln(BH_4)_2Li(thf)_2$ complexes (Ln = Sm or Nd), which were isolated in 57 and 42% yields, respectively, by recrystallization from hexane. X-ray diffraction experiments and NMR and IR spectroscopic studies demonstrated that the reactions afford monomeric *ate* complexes, in which the lanthanide and lithium atoms are linked to each other by two bridging borohydride groups. The complexes exhibit catalytic activity in polymerization of methyl methacrylate.

Key words: lanthanides, guanidinate ligand, N,N-ligand, borohydride ligand, synthesis, structure, polymerization, catalysis.

Lanthanide borohydride complexes of the metallocene series have been known for more than three decades.[1] Nevertheless, this class of compounds continues to attract considerable interest because of the structural diversity and high catalytic activity.[2] The borohydride groups can serve as both bridging and terminal ligands having different dentation.[3,4] Depending on the ionic radius of the central atom and its coordination environment, borohydride groups can serve as bi-,[1,3—8] tri-,[1,9] or tetradentate ligands.[3,4] A renewed interest in lanthanide borohydride complexes has been stimulated by reports on their high catalytic activity in polymerization of lactones,[10,11] methyl methacrylate,[12] and isoprene.[13] The reactivity of organic derivatives of lanthanides depends primarily on the high polarity of the metal—ligand bond and large ionic radii of Ln. Due to this, combined with a large positive charge on the metal center, these compounds are very sensitive to the degree of steric saturation of their coordination sphere. Hence, a search for new types of the coordination environment, which can stabilize lanthanide complexes and modify their reactivity and catalytic activity, is an important problem. Until recently, the range of known rare-earth metal borohydride complexes has been limited primarily to derivatives of the metallocene series.[2] The yttrium bis(amidinate) borohydride complex $[PhC(NSiMe_3)_2]_2YBH_4(thf)$ [14] and lanthanide derivatives containing the polydentate diphenoxide O,O,N,N-ligands[11,12] are the only exception. In the synthesis of new lanthanide borohydride complexes, we used tetrasubstituted guanidinate ligands, whose steric and electronic properties can easily be modified by varying substituents at the N atoms. The aim of the present study was to synthesize lanthanide bis(guanidinate) borohydride derivatives $\{(Me_3Si)_2NC(NPr^i)_2\}_2Ln(BH_4)_2Li(thf)_2$ (Ln = Sm (**1**) or Nd(**2**)) and investigate their structures and catalytic activity.

Results and Discussion

Initially, we intended to prepare borohydride complexes by the reactions of $NaBH_4$ with the corresponding bis(guanidinate) chloride derivatives $[\{(Me_3Si)_2NC(NPr^i)_2\}_2LnCl]_2$ (Ln = Nd or Sm).[15,16] The latter are easily produced in the reaction of anhydrous halides $LnCl_3$ with 2 equiv. of $\{(Me_3Si)_2NC(NPr^i)_2\}Li$, which is generated *in situ* from $[(Me_3Si)_2NLi(Et_2O)]$ and *N*,*N*-diisopropylcarbodiimide in THF (20 °C). However, it appeared that this synthetic method is inefficient, because even stirring of equimolar amounts of the starting reagents in THF at 65 °C for 24 h did not allow us to isolate lanthanide borohydride complexes in good yield. Along with the target product, the reaction mixture contained considerable amounts of the starting $[\{(Me_3Si)_2NC(NPr^i)_2\}_2LnCl]_2$ complexes. In addition, the reaction of $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ with $NaBH_4$ in hexane at room temperature followed by the treatment with dimethoxyethane and recrystallization of the reaction product from a toluene—hexane mixture afforded the samarium monoguanidinate bis(borohydride) complex $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ (**3**).[16]

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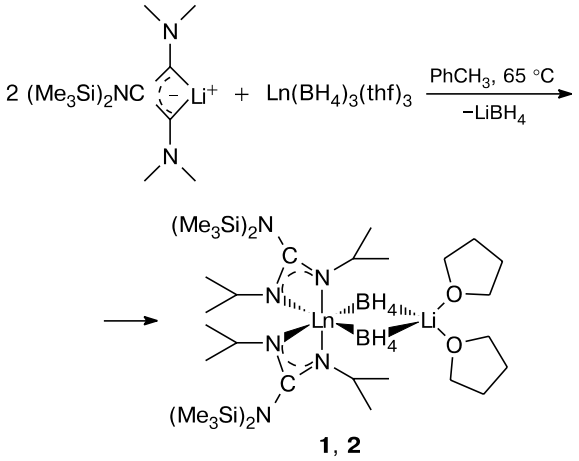
Hence, we synthesized the bis(guanidinate) borohydride complexes starting from metal tris(borohydrides) $Ln(BH_4)_3(thf)_n$.

The bis(guanidinate) borohydride complex $\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2Li(thf)_2$ (**1**) was synthesized by the reaction of samarium tris(borohydride) $Sm(BH_4)_3(thf)_3$ with 2 equiv. of $\{(Me_3Si)_2NC(NPr^i)_2\}Li$ in toluene at 65 °C. After recrystallization from hexane, compound **1** was isolated in 57% yield. The neodymium complex $\{(Me_3Si)_2NC(NPr^i)_2\}_2Nd(BH_4)_2Li(thf)_2$ (**2**) was synthesized analogously staring from $Nd(BH_4)_3(thf)_3$ in 42% yield (Scheme 1).

Scheme 1



Ln = Sm (**1**), Nd (**2**)

The proposed synthetic method affords the $\{(Me_3Si)_2NC(NPr^i)_2\}_2Ln(BH_4)_2Li(thf)_2$ complexes in virtually quantitative yields. However, their isolation in the crystalline state is complicated by very high solubility of these compounds in organic solvents.

Complexes **1** and **2** are colored crystalline compounds, which are sensitive to atmospheric oxygen and moisture and are readily soluble in ethereal solvents and aromatic and aliphatic hydrocarbons.

Transparent pale-yellow (**1**) and blue (**2**) crystals suitable for X-ray diffraction were grown by slow cooling of a concentrated hexane solution to –20 °C (complex **1**) and slow concentration at room temperature (complex **2**). The molecular structures of complexes **1** and **2** are shown in Fig. 1.

Selected bond lengths and bond angles in the structures of **1** and **2** are given in Table 1. Complex **1**, along with the diamide diamine derivative $[Sm(N_2NN^{TMS})(BH_4)_2Li]_2$,[12] is one of a few structurally characterized borohydride *ate* complexes. The X-ray diffraction study of the crystals of **1** and **2** demonstrated that the Ln and Li atoms in these *ate* complexes are linked to each other by bridging boro-

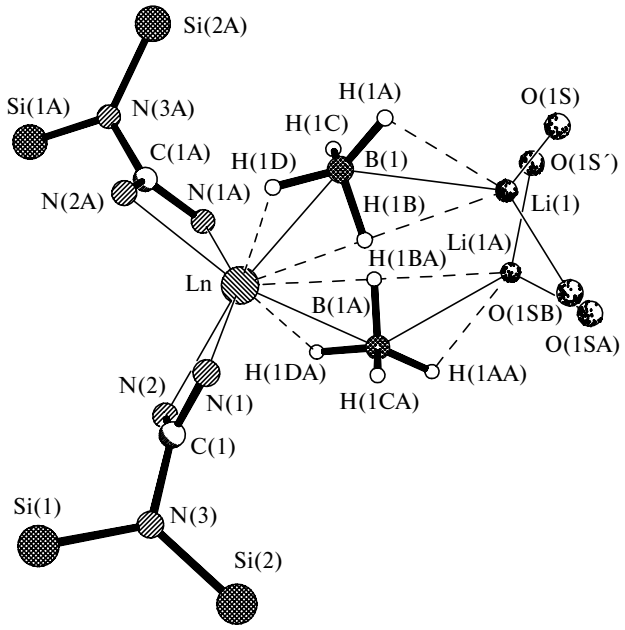


Fig. 1. Molecular structures of $(Me_3Si)_2NC(NPr^i)_2\}_2Ln(BH_4)_2$-$Li(thf)_2$ (Ln = Sm (**1**) or Nd (**2**)); the Me groups at the Si atoms and the Pr^i groups at the N atoms are omitted.

hydride groups (see Fig. 1). The $Li(thf)_2$ fragment is disordered over two positions with respect to the C_2 axis, on which the Ln atoms (Sm and Nd) are located. Three of four H atoms of the borohydride groups are bridging, two of these groups serving as μ_2-bridges, and one H atom acts as a μ_3-bridge. These data are confirmed by the IR spectra of compounds **1** and **2**, in which the BH_4 groups appear as a set of four broad bands at 2229, 2270, 2346, and 2408 cm^{-1} in the spectrum of **1** and at 2233, 2269, 2345, and 2408 cm^{-1} in the spectrum of **2** (*cf.* lit. data[2,17]).

The Sm—B distances in complex **1** (2.760(2) Å) are substantially longer than those in the bis(borohydride) complex $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ (2.607(3) and 2.615(4) Å) and shorter than those in the dinuclear

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecules **1** and **2**

Parameter	**1**	**2**
Bond	*d*/Å	
Ln(1)—N(1)	2.426(3)	2.465(3)
Ln(1)—N(2)	2.404(3)	2.447(3)
Ln(1)—B(1)	2.760(2)	2.725(2)
B(1)—Li(1)	2.481(4)	2.559(7)
N(1)—C(1)	1.299(4)	1.319(4)
N(2)—C(1)	1.329(5)	1.329(5)
Angle	ω/deg	
N(2)—Ln(1)—N(1)	54.93(8)	54.16(9)
B(1A)—Ln(1)—B(1)	89.74(6)	91.03(10)
Li(1)—B(1)—Ln(1)	124.1(1)	124.9(2)

complex $[(1,3\text{-}Bu^t_2C_5H_3)_2Sm(BH_4)]_2$ (2.833(6) and 2.882(6) Å).[3] The Sm—N distances are slightly different (2.426(3) and 2.404(3) Å), which characterizes a certain asymmetry in the coordination of the ligand. These distances are comparable with the corresponding bond lengths in the related bis(guanidinate) chloride complex $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ ($d(Sm—N)_{av}$ 2.410(5) Å).[16] In spite of the fact that the C—N bonds in the NCN fragment are also different (1.299(4) and 1.329(5) Å), they apparently characterize delocalization of the negative charge in the guanidinate ligand rather than the C—N bond alternation. The B(1)—Sm—B(1A) bond angle in **1** (89.74(6)°) is essentially smaller than the corresponding angle in the bis(borohydride) derivative $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2DME$ (102.52(13)°)[16] with terminal BH_4 ligands. The Nd—B distances in **2** (2.725(2) Å) are substantially longer than those in the bis(borohydride) complex $(C_5HPr^i_4)Nd(BH_4)_2(thf)$ (2.605(3) and 2.595(3) Å)[13] and considerably shorter than those in the dinuclear complex $[(COT)Nd(BH_4)(thf)]_2$ (COT is cyclooctatetraenyl, 2.875(6) and 2.941(6) Å).[18] The C—N distances (1.319(4) and 1.329(5) Å) in the guanidinate fragment, like those in the structure of **1**, are indicative of delocalization of the electron density. Interestingly, in spite of the larger ionic radius of Nd^{3+} (0.983 Å)[19] compared to Sm^{3+} (0.958 Å)[19] in isostructural complexes **1** and **2**, the Nd—B distance (2.725(2) Å) is substantially shorter than the analogous distance in the structure of **1** (2.760(2) Å). To the contrary, the Nd—N distances (2.465(3) and 2.447(3) Å) are longer than the Sm—N distances in the structure of **1** and are almost unproportional to the difference between the ionic radii of the Nd and Sm atoms. These characteristic features are apparently attributable to nonbonded ligand···ligand interactions in the coordination sphere of the the Ln atoms. Presumably, this is due to the smaller ionic radius of Sm and, correspondingly, the smaller size of its coordination sphere. The presence of shorter Sm—B distances compared to Nd—B (all other geometric characteristics of the complex remaining unchanged) should lead to a substantial increase in nonbonded interactions in the coordination sphere and, consequently, to destabilization of the complex. Complexes **1** and **2** differ also in that the Li(1)—B(1) distance in **1** (2.481(4) Å) is noticeably shorter than the corresponding distance in **2** (2.559(7) Å).

The presence of the Li atom in molecule **1** is confirmed by the ^{7}Li NMR method. In the ^{7}Li NMR spectrum of paramagnetic complex **1**, the Li atoms are observed as a singlet at δ −0.63, which confirms the existence of the compound as the *ate* complex. The presence of the only signal in the ^{11}B NMR spectrum (at δ −51.17) is indicative of the presence of the samarium bis(guanidinate) borohydride complex with equivalent borohydride groups.

As expected, the signals in the ^{1}H NMR spectrum (benzene-d_6, 20 °C) of weakly paramagnetic complex **1** (μ_{eff} = 1.3—1.9 μ_B)[20] are slightly broadened and shifted compared to those in the spectra of diamagnetic derivatives.[21,22] The guanidinate ligands are observed as the following set of signals: a singlet at δ_H 1.42 corresponding to the protons of the Me group of the $N(SiMe_3)_2$ fragment and a doublet (J_{H-H} = 6.4 Hz) at δ_H 0.29 corresponding to the Me protons of the isopropyl groups. The signal for the methine protons of the isopropyl groups (δ_H = 3.22) partially overlaps with the signal for the β-methylene protons of the THF molecule (δ_H = 3.32). The α-methylene protons are characterized by a broadened singlet at δ_H 1.26. The protons of the BH_4 groups give a broad singlet in a range from −3.5 to −4.8 ppm. In the ^{13}C NMR spectrum, the guanidinate fragments are observed as one set of signals, which is indicative of the equivalence of both ligands.

The catalytic activity of complexes **1** and **2** in polymerization of methyl methacrylate (MMA) was studied at room temperature both in a block and in a toluene solution. After the addition of solid complexes **1** and **2** (0.2 mol.%) to MMA, vigorous exothermic polymerization started. After 10—15 min, the reaction mixture solidified. However, the degree of conversion was at most 50% even after 48 h. Hence, all catalytic experiments were carried out in a toluene solution (C_{MMA} = 4.61 mol L^{-1}, $C_{cat} = 9.2 \cdot 10^{-3}$ mol L^{-1}, $C_{cat} : C_{MMA}$ = 1 : 500). In the reaction with the use of complex **1**, the degree of conversion of 77% was achieved within 3 h. The resulting polymer has the average molecular weight M_w = 199900, M_n = 20100, and a rather high polydispersity index (M_w/M_n = 9.95). The NMR spectroscopic experiments show that a heterotactic polymer is formed, with syndiotactic triads slightly predominating. The percentages of iso-, hetero-, and syndiotactic triads were 22, 31, and 47%, respectively. In the presence of complex **2**, polymerization under analogous conditions proceeds slightly more slowly, and the degree of conversion is 52% after 3 h. The resulting polymer is characterized by a substantially lower molecular weight and a narrower molecular weight distribution (M_w = 21400, M_n = 8500, M_w/M_n = 2.52). The percentages of iso-, hetero-, and syndiotactic triads estimated by the NMR method were 44, 41, and 15%, respectively. The polymer can also be characterized as heterotactic but with a predominance of isotactic triads. Based on the initial region of the kinetic curve of polymerization measured by the dilatometric method (up to the degree of conversion of 20%), the samarium complex exhibits higher activity compared to the neodymium analog.

Therefore, the use of guanidinate ligands allows the synthesis of the reactive lanthanide bis(guanidinate) borohydride derivatives $[(Me_3Si)_2NC(NPr^i)_2]Ln(BH_4)_2Li(thf)_2$, which are efficient catalysts for polymerization of MMA.

Experimental

The complexes were synthesized under conditions precluding exposure to atmospheric oxygen and moisture with the use of the standard Schlenk technique. Tetrahydrofuran, hexane, and toluene were dried over sodium benzophenone ketyl, thoroughly degassed, and condensed under vacuum into a reaction tube immediately before use. The IR spectra were recorded on a Specord M-80 instrument as deaerated Nujol mulls. The ^{1}H, ^{7}Li, ^{11}B, and ^{13}C NMR spectra were measured on a Bruker DPX 200 instrument (20 °C, benzene-d_6). The chemical shifts are given on the δ scale relative to the known shifts of the residual protons of the deuterated solvents. The molecular weight distribution was determined on a Waters gel permeation chromatograph equipped with a R-403 (Waters) differential refractometer as the detector with the use of THF as the eluent. The calibration was performed with the use of narrow-disperse polystyrene standards. Anhydrous $LnCl_3$,[23] $(Me_3Si)_2NLi(Et_2O)$,[24] and $Ln(BH_4)_3(thf)_n$ [25] were synthesized according to known procedures. *N*,*N*′-Diisopropylcarbodiimide and $NaBH_4$ were commercial reagents (Acros). *N*,*N*′-Diisopropylcarbodiimide was used after drying with A4 molecular sieves and condensation under vacuum; $NaBH_4$ was used without additional purification.

Bis[*N*,*N*-diisopropyl-*N*′-bis(trimethylsilyl)guanidinato]-di(tetrahydroborato)bis(tetrahydrofuran)lithiumsamarium(III), $\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(\mu^3\text{-}BH_4)_2Li(thf)_2$ (1). The $Sm(BH_4)_3(thf)_3$ compound (0.51 g, 1.23 mmol) was added to a solution of lithium guanidinate, which was prepared by the reaction of $(Me_3Si)_2NLi(Et_2O)$ (0.61 g, 2.53 mmol) with *N*,*N*′-diisopropylcarbodiimide (0.32 g, 2.54 mmol) in toluene (50 mL). The reaction mixture was stirred at 65 °C for 14 h, the resulting solution was filtered, and the solvent was removed under vacuum at room temperature. After recrystallization of the residue from hexane, pale-yellow crystals of **1** were obtained in a yield of 0.65 g (57%). Found (%): C, 44.69; H, 9.27; Sm, 16.70. $C_{34}H_{88}B_2N_6O_2Si_4Sm$. Calculated (%): C, 45.18; H, 9.73; Sm, 16.64. IR, ν/cm^{-1}: 2408, 2346, 2270, 2229, 1638, 1323, 1253, 1178, 1049, 956, 920, 880, 835, 758, 684, 658. ^{1}H NMR, δ: −(4.80—3.50) (br.s, 8 H, BH_4); 0.29 (d, 24 H, $CH(C\underline{H}_3)_2$, J_{H-H} = 6.4 Hz); 1.26 (br.s, 8 H, THF): 1.42 (c, 36 H, $N(SiMe_3)_2$); 3.22 (m, 4 H, $C\underline{H}(CH_3)_2$); 3.32 (br.s, 8 H, THF). ^{13}C NMR, δ: 3.8 ($N(SiMe_3)_2$); 22.7 (β-CH_2, THF); 26.2 ($CH(\underline{C}H_3)_2$); 44.3 ($\underline{C}H(CH_3)_2$); 67.9 (α-CH_2, THF); 207.5 (CN_3). ^{7}Li NMR, δ: −0.63 (c, $Li(THF)_2$). ^{11}B NMR (20 °C, benzene-d_6), δ: −51.17 (c, $Li(BH_4)_2$).

Bis[*N*,*N*-diisopropyl-*N*′-bis(trimethylsilyl)guanidinato]-di(tetrahydroborato)bis(tetrahydrofuran)lithiumneodymium(III), $\{(Me_3Si)_2NC(NPr^i)_2\}_2Nd(\mu^3\text{-}BH_4)_2Li(thf)_2$ (2). The $Nd(BH_4)_3(thf)_3$ compound (0.56 g, 1.38 mmol) was added to a solution of lithium guanidinate, which was prepared by the reaction of $(Me_3Si)_2NLi(Et_2O)$ (0.67 g, 2.78 mmol) with *N*,*N*′-diisopropylcarbodiimide (0.35 g, 2.78 mmol) in toluene (50 mL). The reaction mixture was stirred at 65 °C for 14 h, the resulting solution was filtered, and the solvent was re-

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

Parameter	**1**	**2**
Molecular formula	$C_{34}H_{88}B_2LiN_6O_2Si_4Sm$	$C_{34}H_{88}B_2LiN_6NdO_2Si_4$
Molecular weight	904.37	898.26
Crystal system	Trigonal	
T/K	150(2)	100(2)
Space group	$P3_22_1$	
a,*b*/Å	14.0719(4)	14.0587(3)
c/Å	24.347(1)	24.240(1)
α,β/deg	90	
γ/deg	120	
V/Å	4175.3(2)	4149.0(2)
Z	3	
ρ/g cm^{-3}	1.079	1.079
μ/mm^{-1}	1.170	1.055
F(000)	1443	1437
Crystal dimensions/mm	0.20×0.18×0.15	0.45×0.21×0.16
θ-Scan range/deg	1.87—25.00	2.37—24.99
Ranges of indices of measured reflections	$-16 \le h \le 16$ $-16 \le k \le 16$ $-28 \le l \le 28$	
Number of observed reflections	33152	32720
Number of independent reflections (R_{int})	4880 (0.0242)	4841 (0.0291)
Goodness-of-fit on F^2	1.101	1.108
R_1/wR_2 ($I > 2\sigma(I)$)	0.0685/0.1880	0.0478/0.1278
R_1/wR_2 (based on all reflections)	0.0694/0.1883	0.0492/0.1293
Absolute structural factor	0.001(30)	0.001(15)
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	1.609/−1.103	1.444/−0.571

moved under vacuum at ~20 °C. After recrystallization of the residue from hexane, blue crystals of **2** were obtained in a yield of 0.52 g (42%). Found (%): C, 45.03; H, 9.61; Nd, 16.47. $C_{34}H_{88}B_2N_6NdO_2Si_4$. Calculated (%): C, 45.49; H, 9.80; Nd, 16.06. IR, ν/cm^{-1}: 2408, 2345, 2269, 2233, 1640, 1321, 1254, 1167, 1049, 955, 921, 880, 841, 757, 687, 656.

Standard experiments on polymerization of MMA in the presence of complexes 1 and 2. A solution of complex **1** (0.021 g, 0.023 mmol) in toluene (0.5 mL) was added to a solution of MMA (1.15 g, 11.50 mmol) in toluene (2 mL) and placed in a thermostat at 20 °C. After 3 h, the reaction tube was opened, air was admitted into the tube, and one drop of MeOH was added. The solution was filtered to separate hydrolysis products of the catalyst. Then the polymer was precipitated by hexane, filtered off, washed with methanol and hexane, and dried to constant weight under vacuum at ~20 °C. Poly(methyl methacrylate) was isolated in a yield of 0.88 g.

X-ray diffraction study. X-ray diffraction data sets for complexes **1** and **2** were collected on a Smart Apex diffractometer (Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator). The structures of complexes **1** and **2** were solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} using the SHELXTL program package.[26] Absorption corrections were applied using the SADABS program.[27] All nonhydrogen atoms were refined with anisotropic displacement parameters. The H atoms in complexes **1** and **2** were positioned geometrically and refined using a riding model, except for the H atoms at the B(1) atom, which were located in difference electron density maps and refined with fixed isotropic thermal parameters (0.08 Å^2). The disordered Li atom in the complex was refined with an occupancy of 0.5. The C(2S), C(3S), and C(4S) atoms of the THF molecule are not disordered, whereas the O(1S) and C(1S) atoms in the structures of **1** and **2** are disordered over two positions, C(1S′) and O(1S′), respectively, and were refined with an occupancy of 0.5. The crystallographic parameters and the X-ray diffraction data collection and refinement statistics for complexes **1** and **2** are given in Table 2. The atomic coordinates were deposited with the Cambridge Structural Database.

The spectroscopic and X-ray diffraction studies were carried out at the Analytical Center of the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences.

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References

1. T. J. Marks and G. W. Grynkewich, *Inorg. Chem.*, 1976, **6**, 1302.
2. M. Ephritikhine, *Chem. Rev.*, 1997, **97**, 2193.
3. Y. K. Gun´ko, B. M. Bulychev, G. L. Soloveichik, and V. K. Belsky, *J. Organomet. Chem.*, 1992, **424**, 289.
4. E. B. Lobkovsky, Y. K. Gun´ko, B. M. Bulychev, G. L. Soloveichik, and V. K. Belsky, *J. Organomet. Chem.*, 1991, **424**, 289.
5. H. Schumann and W. Genthe, *J. Organomet. Chem.*, 1983, **213**, C7.
6. H. Schumann, W. Genthe, N. Brunks, and J. Pickardt, *Organometallics*, 1982, **1**, 1194.
7. D. Deng, X. Zheng, C. Qian, J. Sun, and L. Chang, *J. Organomet. Chem.*, 1994, **466**, 95.
8. H. Schumann, M. R. Keitsch, J. Demtschuk, and S. Mühle, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1811.
9. M. Mancini, P. Bougeard, R. C. Burns, M. Mlekuz, B. G. Sayer, J. I. A. Thompson, and J. McGlinchey, *J. Inorg. Chem.*, 1984, **23**, 1082.
10. I. Pallard, A. Soum, and S. M. Guillaume, *Chem. Eur. J.*, 2004, **10**, 4054.
11. F. Bonnet, A. R. Cowley, and P. Mountford, *Inorg. Chem.*, 2005, **44**, 9046.
12. F. Bonnet, A. C. Hilier, A. Collins, S. R. Dubberley, and P. Monutford, *Dalton Trans.*, 2005, 421.
13. D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann, and M. Visseaux, *Eur. J. Inorg. Chem.*, 2000, 2333.
14. R. Duchateau, C. T. van Wee, A. Meetsma, P. Th. Van Duijnen, and J. H. Teuben, *Organometallics*, 1996, **15**, 2279.
15. Y. Yao, Y. Luo, J. Chen, Z. Zhang, Y. Zhang, and Q. Shen, *J. Organomet. Chem.*, 2003, **679**, 229.
16. A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, G. K. Fukin, E. A. Fedorova, and M. N. Bochkarev, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2433 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2511].
17. T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.
18. S. M. Cendrowski-Guillaume, M. Nierlich, M. Lance, and M. Ephritikhine, *Organometallics*, 1998, **17**, 786.
19. R. D. Schannon, *Acta Crystallogr.*, 1976, **A32**, 751.
20. W. J. Evans and M. A. Hozbor, *J. Organomet. Chem.*, 1987, **326**, 299.
21. A. A. Trifonov, E. A. Fedorova, G. K. Fukin, and M. N. Bochkarev, *Eur. J. Inorg. Chem.*, 2004, 4396.
22. A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov, and V. N. Glushakova, *Chemistry, Eur. J.*, 2006, **12**, 5320.
23. M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, 1962, **24**, 387.
24. L. E. Manzer, *Inorg. Chem.*, 1978, **17**, 1552.
25. U. Mirsaidov, I. B. Shaimuradov, and M. Khikmatov, *Zh. Neorg. Khim.,* 1986, **31**, 1321 [*J. Inorg. Chem. USSR*, 1986, **31** (Engl. Transl.)].
26. G. M. Sheldrick, *SHELXTL*, *v. 6.12*, *Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 2000.
27. G. M. Sheldrick, *SADABS*, *v. 2.01*, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, Wisconsin, USA, 1998.

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