Lithium and lanthanum complexes with acenaphthylene dianion. Molecular structure of $[Li(Et_2O)_2]_2\{\mu_2:\eta^3[Li(\eta^3:\eta^3-C_{12}H_8)]_2\}$ complex

I. L. Fedushkin,[a]* G. V. Khoroshen´kov,[a] M. N. Bochkarev,[a] S. Mühle,[b] and H. Schumann[b]

[a]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
49 ul. Tropinina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 66 1497. E-mail: igorfed@imoc.sinn.ru
[b]*Institute of Chemistry, Berlin Technical University,*
*135 str. 17 June, D-10623 Berlin, Germany.**
Fax: +49 (30) 3142 2168

The lithium complex with the acenaphthylene dianion $[Li(Et_2O)_2]_2\{\mu_2:\eta^3[Li(\eta^3:\eta^3-C_{12}H_8)]_2\}$ (**1**) was synthesized by the reduction of acenaphthylene with lithium in diethyl ether. According to the X-ray diffraction data, compound **1** has a reverse-sandwich structure with the bridging dianion $\{\mu_2:\eta^3[Li(\eta^3:\eta^3-C_{12}H_8)]_2\}$. Two lithium atoms in complex **1** are located between two coplanar acenaphthylene ligands of the $\{\mu_2:\eta^3[Li(\eta^3:\eta^3-C_{12}H_8)]_2\}^{2-}$ dianion and are η^3-coordinated with the five- and six-membered rings. The lanthanum complex with the acenaphthylene dianion $[LaI_2(THF)_3]_2(\mu_2-C_{12}H_8)$ (**2**) was synthesized by the reduction of acenaphthylene in THF with the lanthanum(III) complex $[LaI_2(THF)_3]_2(\mu_2-C_{10}H_8)$ containing the naphthalene dianion. The ^1H NMR spectrum of complex **2** in THF-d_8 exhibits four signals of the acenaphthylene dianion, whose strong upfield shifts compared to those of free acenaphthylene indicate the dianionic character of the ligand. The highest upfield chemical shift belongs to the proton bound to the C atom on which, according to calculation, the maximum negative charge is concentrated.

Key words: lithium, lanthanum, acenaphthylene dianion, complexes, molecular structure.

Acenaphthylene is a non-alternant hydrocarbon, whose electrochemical potentials of reduction to the radical anion and dianion are equal[1] to −1.65 and −1.83 V, respectively. We have recently reported the stereoselective formation of *ansa*-metallocenes of lanthanides and calcium $(\eta^5:\eta^5-C_{24}H_{16})M(THF)_2$ (M = Sm,[2] Yb,[2] Ca[3]) by the reduction of acenaphthylene with the corresponding metals and their naphthalenides $[C_{10}H_8]^{2-}$ $M(THF)_2$, or by the exchange reaction of the corresponding diiodides $MI_2(THF)_2$ with potassium acenaphthylene $K^+[C_{12}H_8]^-$.[4] In the case of thulium, the metallocene acenaphthylene derivative $(\eta^5:\eta^5-C_{24}H_{16})TmI(THF)$ is formed by the interaction of equimolar amounts of TmI_2 and acenaphthylene.[5] In all chemical reactions listed, the radical anions formed by the one-electron reduction of acenaphthylene recombine selectively to form C_2-symmetrical *ansa*-metallocenes. The first metal complex with the acenaphthylene dianion, $[\{Li(TMEDA)\}]_2(\mu_2-\eta^3:\eta^3-C_{12}H_8)$, was synthesized[6] by the deprotonation of acenaphthene with butyllithium in hexane in the presence of TMEDA. The synthesis of the sodium complex with the acenaphthylene dianion by the reaction of metallic sodium with acenaphthylene in DME in the presence of 18-crown-6 has been described.[7] In both complexes, the metal atoms are localized symmetrically at the opposite sides of the five-membered ring and are η^3-coordinated to the latter. Such a geometry of the molecules is not consistent with the results of the MNDO calculation of the electron density distribution in the acenaphthylene dianion (Fig. 1).[7] According to the MNDO calculations, two C atoms of the six-membered rings have the maxi-

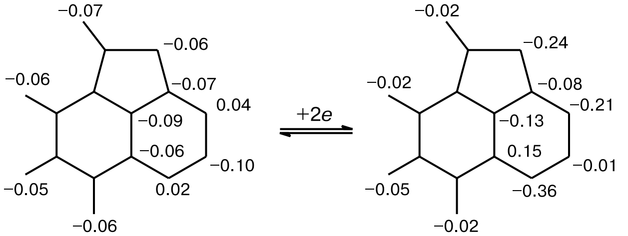


Fig. 1. Negative charge distribution in the acenaphthylene anions according to the data of the MNDO calculation.[7] The electron density values on the H atoms are presented at the left from the symmetry plane of the ligand, and those on the C atoms are shown at the right.

---

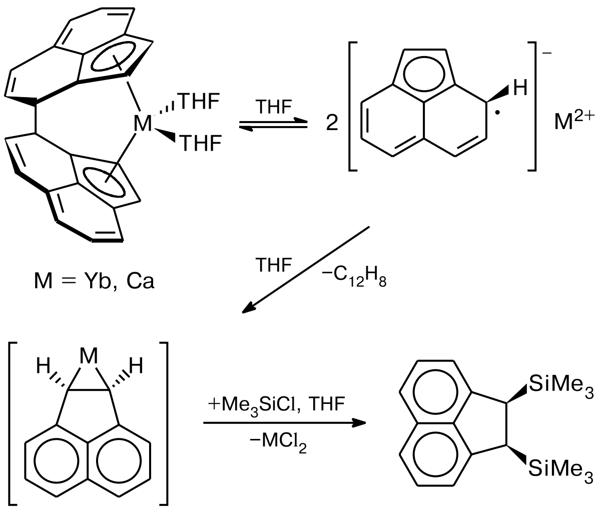
* Institut für Chemie der Technischen Universität Berlin, Straße des 17 Juni 135, D-10623 Berlin, Germany.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1286—1290, June, 2003.

mum negative charge. The C atoms of the five-membered ring have a total excess charge –0.7, and the overall charge of ten C atoms of the six-membered rings is –1.30. Another form of the acenaphthylene dianion is exemplified by the (η^2-$C_{12}H_8$)$ZrCl_2(THF)_3$ complex[3,4] in which the metal atom is bound to only two negatively charged C atoms of the five-membered ring.

The ESR study of solutions of the ytterbium and calcium acenaphthylene *ansa*-metallocene complexes (η^5:η^5-$C_{24}H_{16}$)$M(THF)_2$ (M = Yb,[2] Ca[3]) showed that the (η^5:η^5-$C_{24}H_{16}$)$M(THF)_2$ complexes (M = Yb, Ca) in a solution of THF or pyridine dissociate to the radical anions. The reaction of these complexes with trimethylchlorosilane afforded 1,2-bis(trimethylsilyl)acenaphthene.[3,4] The latter is formed by the reaction of Me_3SiCl with the acenaphthylene dianion that is produced by disproportionation of two acenaphthylene radical anions to the dianion and neutral ligand (Scheme 1).

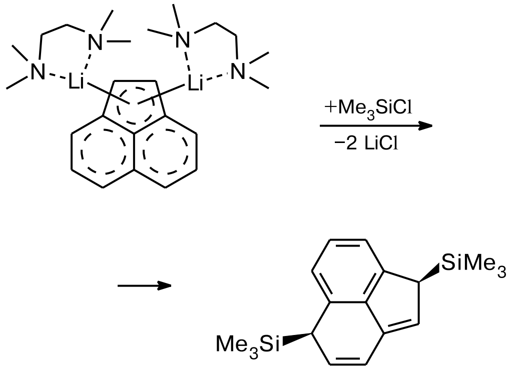
Scheme 1



At the same time, the reaction of acenaphthylene dilithium salt [{Li(TMEDA)}]$_2$(μ_2-η^3:η^3-$C_{12}H_8$) with trimethylchlorosilane in hexane afforded 1,6-bis(trimethylsilyl)-1,6-dihydroacenaphthylene (Scheme 2).[8] The result of this reaction agrees with the data of the quantum-chemical calculations of the negative charge distribution in the acenaphthylene dianion[7]: the trimethylsilyl electrophile attacks positions 1 and 4 of the acenaphthylene dianion on which the negative charge is concentrated. No characteristics (and, first of all, spectroscopic) of the metal complexes with the acenaphthylene dianions have been obtained up to presently, except for the structural data.

The purpose of this work is the synthesis of new metal complexes with the acenaphthylene dianion and the study of their spectroscopic and structural characteristics.

Scheme 2



Results and Discussion

Synthesis and structure of lithium complex with acenaphthylene dianion. The reduction of acenaphthylene with metallic lithium to the dianion occurs readily at room temperature in Et_2O. The reaction does not need excess lithium and under strictly aprotic and anaerobic conditions affords the [Li(Et_2O)$_2$]$_2${μ_2:η^3[Li(η^3:η^3-$C_{12}H_8$)]$_2$} complex (**1**) in high yield even at the stoichiometric ratio of the reactants. Upon removal of the solvent from the reaction mixture, compound **1** is crystallized as large black rectangular crystals, which are ignited in air. A solution of complex **1** in Et_2O is dichroic (green—red). Compound **1** is barely insoluble in toluene and hexane but is well soluble in DME and THF. According to the X-ray diffraction data, the molecule of complex **1** contains two dianionic acenaphthylene ligands and four Li atoms, two of which coordinate the Et_2O molecules (Fig. 2). The main bond lengths in molecule **1** are presented in Table 1. The molecule has the inversion center localized in the middle of the section connecting the Li(2) and Li(2´) atoms. Thus, the molecule contains two geometrically equivalent [(Et_2O)$_2$Li($C_{12}H_8$)Li] units. As a whole, a molecule of compound **1** can be considered as a reverse-sandwich complex similar to the known[6] lithium complex [{Li(TMEDA)}]$_2$(μ_2-η^3:η^3-$C_{12}H_8$).

As in the [{Li(TMEDA)}]$_2$(μ_2-η^3:η^3-$C_{12}H_8$) complex, the Li(1) atom in molecule **1** has three short contacts with the C(1), C(2), and C(3) atoms. These distances in complexes **1** and [{Li(TMEDA)}]$_2$(μ_2-η^3:η^3-$C_{12}H_8$) are 2.351(4), 2.241(4), 2.359(4) Å and 2.27(2), 2.18(3), 2.24(2) Å, respectively. The Li(2) atom, similarly to the second Li atom in the [{Li(TMEDA)}]$_2$(μ_2-η^3:η^3-$C_{12}H_8$) complex, also coordinates three C atoms of the five-membered ring but with the displacement toward the C(4) atom (see Fig. 2). The projections of the Li atom to the plane of the acenaphthylene ligand in complex **1** are shown in Fig. 3.

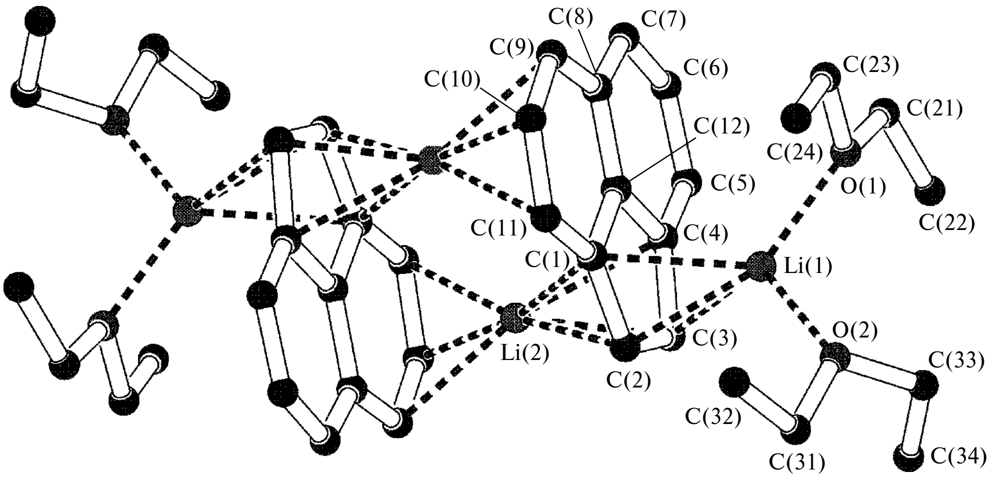


Fig. 2. Molecular structure of the $[Li(Et_2O)_2]_2\{\mu_2:\eta^3[Li(\eta^3:\eta^3\text{-}C_{12}H_8)]_2\}$ complex (**1**). Hydrogen atoms are not shown. The main bond lengths are presented in Table 1.

Table 1. Main interatomic distances (*d*) in complex **1**

Bond	*d*/Å	Bond	*d*/Å
Li(1)—O(1)	1.983(4)	Li(1)—O(2)	2.002(4)
Li(1)—C(1)	2.351(4)	Li(1)—C(2)	2.241(4)
Li(1)—C(3)	2.359(4)	Li(1)—C(4)	2.564(4)
Li(1)—C(12)	2.517(4)	Li(2)—C(2)	2.213(4)
Li(2)—C(1)	2.418(4)	Li(2)—C(4)	2.329(4)
Li(2)—C(3)	2.174(4)	Li(2)—C(9)*	2.276(4)
Li(2)—C(12)	2.465(4)	Li(2)—C(11)*	2.356(4)
Li(2)—C(10)*	2.196(4)	Li(2)—C(1)*	2.607(4)
Li(2)—C(8)*	2.557(4)	Li(2)......Li(2)*	2.955(7)
Li(2)—C(12)*	2.651(4)	C(2)—C(3)	1.443(3)
C(1)—C(2)	1.417(3)	C(4)—C(5)	1.440(3)
C(3)—C(4)	1.427(3)	C(1)—C(12)	1.441(3)
C(4)—C(12)	1.428(3)	C(5)—C(6)	1.374(3)
C(1)—C(11)	1.453(3)	C(7)—C(8)	1.405(3)
C(6)—C(7)	1.411(3)	C(8)—C(12)	1.428(3)
C(8)—C(9)	1.436(3)	C(10)—C(11)	1.384(3)
C(9)—C(10)	1.410(3)		

* The coordinates of atoms were obtained from the coordinates of the corresponding basis atoms using the symmetry transform $1 - x, -y, -z + 1$.

The Li(2)—C(2), Li(2)—C(3), and Li(2)—C(4) distances are 2.213(4), 2.174(4), and 2.329(4) Å, respectively. A distinctive feature of the structure of complex **1** is that the Li(2) atom also coordinates three C atoms of one of the six-membered rings. The distances from the Li(2) atom to the C(9´), C(10´), and C(11´) atoms are 2.276(4), 2.196(4), and 2.356(4) Å, respectively. In fact, the Li(2) atom is localized between the C(9´) and C(11´) atoms on which, according to the calculation data, the negative charge of the six-membered rings of the acenaphthylene dianion is concentrated. Note that in the alkaline metal (Li and Na) complexes with the fluoranthene, *viz.*, $[\{Li(DME)\}]_2(\mu_2\text{-}\eta^3:\eta^3\text{-}C_{16}H_{10})$, $[\{Na(DME)\}]_2(\mu_2\text{-}\eta^6:\eta^6\text{-}C_{16}H_{10})$, and $[\{Na(diglym)\}]_2(\mu_2\text{-}\eta^3:\eta^6\text{-}C_{16}H_{10})$, the cations coordinate the six-membered rings of the naphthalene moiety of the dianion in all the cases.[7]

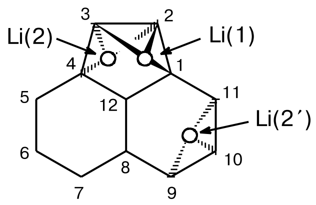


Fig. 3. Arrangement of the Li atoms relatively to the plane of the acenaphthylene ligand in the $[Li(Et_2O)_2]_2\{\mu_2:\eta^3[Li(\eta^3:\eta^3\text{-}C_{12}H_8)]_2\}$ complex (**1**).

Lanthanum complex with acenaphthylene dianion. The lanthanide complexes containing the naphthalene dianion are convenient reactants for the synthesis of new organic derivatives of these metals. The potential of reduction of naphthalene to the radical anion is much more negative (−2.6 V)[1] than that in the case of acenaphthylene (−1.65 V).[1] This allowed us to use the reduction of acenaphthylene with the lanthanum complex containing the naphthalene dianion $[LaI_2(THF)_3]_2(\mu_2\text{-}\eta^4:\eta^4\text{-}C_{10}H_8)$ for the synthesis of the lanthanum complex with the acenaphthylene dianion.[9] Naphthalene is substituted by acenaphthylene in the complex by the reaction of $[LaI_2(THF)_3]_2(\mu_2\text{-}\eta^4:\eta^4\text{-}C_{10}H_8)$ with the equimolar amount of acenaphthylene. The resulting lanthanum complex with the acenaphthylene dianion $[LaI_2(THF)_3]_2(\mu_2\text{-}C_{12}H_8)$ (**2**) is crystallized from the reaction mixture as dark green, almost black crystals. The ^{1}H NMR spectrum of complex **3** in a THF solution exhibits only four signals of protons of the acenaphthylene ligand (Fig. 4), indicating the symmetrical arrangement of the $[LaI_2(THF)_3]^+$ cations relatively to the acenaphthylene dianion. The

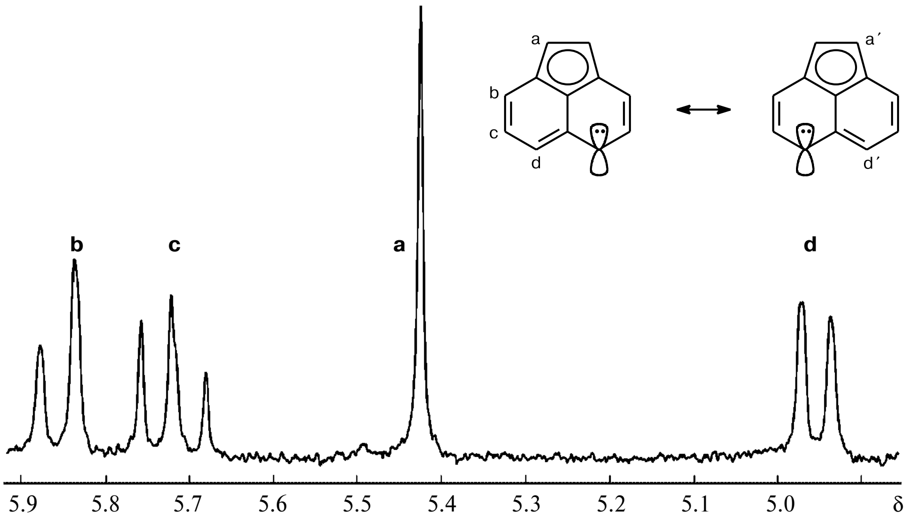


Fig. 4. ^1H NMR spectrum of complex **2** (200 MHz, THF-d_8, 295 K). The region of THF signals is not shown.

strong upfield shift of the proton signals confirms the dianionic character of the ligand. The ^1H NMR spectrum of complex **2** demonstrates the greatest shift for H(4), which indicates a considerable effective negative charge on the C(4) atom. This fact agrees completely with the results of calculation of the electron density distribution in the acenaphthylene dianion.[7] Based on the symmetrical pattern of the NMR spectrum, we can assume that in complex **2**, as in the $[\{Li(TMEDA)\}]_2(\mu_2\text{-}\eta^3\text{:}\eta^3\text{-}C_{12}H_8)$ complex, the $[LaI_2(THF)_3]^+$ cations are localized at the opposite sides of the five-membered ring. X-ray diffraction analysis was carried out to establish the structure of complex **2**. Unfortunately, a low quality of the experimental structural data obtained did not provide a reliable structural information for molecule **2**.

Hence, we found in this work the first complex of the rare-earth element with the acenaphthylene dianion and measured the NMR spectra for the acenaphthylene dianion. The lithium complex with the acenaphthylene dianion obtained has a unique reverse-sandwich structure.

Experimental

All procedures on the synthesis and isolation of the complexes were carried out *in vacuo* or under dry nitrogen using the Schlenk technique. Diethyl ether and THF were dehydrated, stored above sodium benzophenone ketyl, and taken for reactions by recondensation *in vacuo*. Acenaphthylene (75%, Aldrich) was sublimed at 80 °C, 10^{-1} Torr to remove impurities and enhance its content to 85% (acenaphthene admixture 10—15%). The amount of acenaphthylene and the yields of the products are indicated in the procedures of syntheses as based on neat acenaphthylene. The IR spectrum of complex **2** was recorded for a suspension in Nujol. IR spectra were obtained on a Specord M-80 spectrometer. NMR spectra were recorded on a Bruker ARX-400 instrument in THF-d_8 at 20 °C, and chemical shifts are presented in δ (ppm) and were measured relatively to those of the residual protons and ^{13}C isotopes of deuterated solvents.

Bis(acenaphtylene)tetrakis(diethyl etherate)tetralithium (1). A mixture of acenaphthylene (1.0 g, 6.57 mmol) and lithium (0.092 g, 13.25 mg-atom) in Et_2O (40 mL) was magnetically stirred until lithium was completely dissolved. After the solution was stored for 1 day, it was decanted from a precipitate and slowly (during 5—6 h) concentrated by the removal of the solvent at ~20 °C. A minor amount of the remaining solution was decanted from the precipitated crystals, which were washed with cold Et_2O vapor and dried *in vacuo* with short evacuation at ~20 °C. Complex **1** was obtained as black crystals in 66% yield (1.37 g), m.p. >60 °C (decomp.). Since compound **1** is highly sensitive to air oxygen and moisture, we failed to obtain satisfactory elemental analysis data.

(Acenaphthylene)hexakis(tetrahydrofuranate)tetraiodolanthanum (2). A solution of acenaphthylene (0.75 g, 4.93 mmol) in THF (20 mL) was added to a suspension of the $[LaI_2(THF)_3]_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-}C_{10}H_8)$ complex (prepared *in situ* from $LaI_3(THF)_3$ (7.8 g, 10.6 mmol), lithium (0.074 g, 10.6 mg-atom), and naphthalene (2.35 g, 12.2 mmol)) in THF (50 mL). A blue precipitate of the $[LaI_2(THF)_3]_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-}C_{10}H_8)$ complex dissolved in several seconds to form a dark red-brown solution. The solution was concentrated to 30 mL by the removal of the solvent *in vacuo* to form black crystals of complex **2**. After decanting the solution, compound **2**·2THF was obtained in 57% yield (4.32 g), m.p. > 100 °C (decomp.). Found (%): La, 19.22; I, 32.11. $C_{44}H_{72}I_4O_8La_2$ (1514.48 g mol^{-1}). Calculated (%): La, 18.35; I, 33.52. ^1H NMR (200 MHz), δ: 4.93 (d, 2 H, H(4), J = 7.0 Hz); 5.43 (s, 2 H, H(1)); 5.72 (dd, 2 H, H(3), J = 8.0 Hz, 7.0 Hz); 5.87 (d, 2 H, H(2), J = 8.0 Hz). ^{13}C NMR (50 MHz), d: 138.4, 130.7, 126.0, 107.3, 103.0, 99.3. IR, ν/cm^{-1}: 1175 w, 1145 w, 1025 s, 870 s, 820 s, 795 s, 765 s, 735 v.s, 715 v.s.

X-ray diffraction study of the $[Li(Et_2O)_2]_2\{\mu_2\text{:}\eta^3[Li(\eta^3\text{:}\eta^3\text{-}C_{12}H_8)]_2\}$ complex (1). Diffraction data for complex **1** were obtained on a Siemens SMART CCD diffractometer (ω scan mode, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. Corrections for absorption were not applied. The structure was solved by the direct method using the SHELXS-97 program[10] followed by refinement by the full-matrix least-squares method against F^2 using the SHELXL-97 program.**[11]** All non-hydrogen atoms were refined in the anisotropic approximation. Hydrogen atoms were placed in the idealized positions (U_{iso} = 0.08 Å^3). The PLATON program**[12]** was used for analysis of the geometric parameters of the structure of complex **1**. Crystallographic data, parameters of the X-ray diffraction experiment and refinement: crystal size 0.64×0.34×0.26 mm^3, monoclinic crystal system, space group $P2_1/n$, a = 8.25390(10), b = 15.0395(3), c = 14.86090(10) Å, β = 95.4080(10)°, V = 1836.54(4) Å^3, Z = 2, d_{calc} = 1.137 • 10^3 kg m^{-3}, μ = 0.069 mm^{-1}, $F(000)$ = 680, 1.93° $\leq \theta \leq$ 27.50°, $-9 \leq h \leq 10$, $-19 \leq k \leq 16$, $-17 \leq l \leq 19$, total number of reflections 13457, number of independent reflections 4221 [R_{int} = 0.0614], 4221 reflections with $I > 2\sigma(I)$, 221 refined parameters, GOOF(F^2) = 1.035, final parameters R ($R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$): R_1 = 0.0615, wR_2 = 0.1496, ratio of the maximum residual electron density (e Å^{-3}) to the minimum density 0.995/−1.274. The coordinates of atoms are deposited with the Cambridge Structural Data Bank.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32631) and the Alexander von Humboldt Stiftung (FRG).

References

1. E. de Boer, *Adv. Organomet. Chem.*, 1964, **2**, 115.
2. I. L. Fedushkin, S. Dechert, and H. Schumann, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 561.
3. I. L. Fedushkin, T. V. Petrovskaya, M. N. Bochkarev, S. Dechert, and H. Schumann, *Angew. Chem., Int. Ed.*, 2001, **40**, 2474.
4. I. L. Fedushkin, Yu. A. Kurskii, V. I. Nevodchikov, M. N. Bochkarev, S. Mühle, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 151 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 160].
5. I. L. Fedushkin, M. N. Bochkarev, S. Dechert, and H. Schumann, *Chem.-Eur. J.*, 2001, **7**, 3558.
6. W. E. Rhine, J. H. Davis, and G. Stucky, *J. Organomet. Chem.*, 1977, **134**, 139.
7. H. Bock, C. Arad, and Ch. Näther, *J. Organomet. Chem.*, 1996, **520**, 1.
8. M. Laguerre, G. Felix, J. Dunogues, and R. Calas, *J. Org. Chem.*, 1979, **44**, 4275.
9. I. L. Fedushkin, M. N. Bochkarev, H. Schumann, L. Esser, and G. Kociok-Kohn, *J. Organomet. Chem.*, 1995, **489**, 145.
10. G. M. Sheldrick, *Program for Crystal Structure Solution*, Universität Göttingen, Göttingen, 1990.
11. G. M. Sheldrick, *Program for Crystal Structure Refinement,* Universität Göttingen, Göttingen, 1997.
12. A. L. Spek, *Acta Crystallogr.*, 1990, **A 46**, C-34.

Received October 25, 2002;
in revised form February 6, 2003