Synthesis, crystal structure, and reduction of bis(2-phenylindenyl)hafnium dichloride

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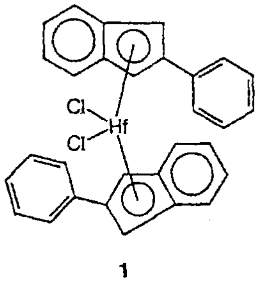
Reduction of the bent-sandwich $[\eta^5\text{-(Ph)Ind}]_2HfCl_2$ complex (1) (where (Ph)Ind is the 2-phenylindenyl anion) in a THF medium was studied by low-temperature cyclic voltammetry. Complex 1 is stable in THF at a temperature lower than −50 °C and undergoes reversible one-electron reduction to radical anion $1^{\cdot-}$. Further one-electron reduction of $1^{\cdot-}$ to dianion 1^{2-} is accompanied by the elimination of two Cl^- ions to form the bisindenyl sandwich $[\eta^5\text{-(Ph)Ind}]_2Hf$ complex (2). This complex can undergo reversible one-electron reduction to the corresponding radical anion $2^{\cdot-}$, which is stable within the cyclic voltammetry time scale. At $T \approx -30$ °C in a THF solution, complex 1 was reduced to a diamagnetic (apparently, binuclear) Hf^{III} complex, which was characterized by cyclic voltammetry. Synthesis and the crystal structure of complex 1 are reported.

Key words: metallocene complexes, bis(2-phenylindenyl)hafnium dichloride, X-ray structural analysis, cyclic voltammetry, redox properties.

Two-electron reduction of bent-sandwich metallocene dichloride complexes of Group IV is accompanied by the elimination of two chloride ions to form short-lived sandwich complexes, which have been characterized by low-temperature cyclic voltammetry.[1,2] The stability of these metallocenes is determined to a large extent by the nature of substituents in the cyclopentadienyl ligand as well as by the nature of the metal atom.[3,4] The data on sandwich and bent-sandwich complexes of Group IV with other π-ligands, in particular, with condensed polyaromatic ligands, their redox properties, and stability are scarce.[5,6] Therefore, synthesis and structural and electrochemical studies of these complexes are of obvious interest.

Recently,[7] we have characterized electrochemically *in situ* the metastable bis(2-phenylindenyl)zirconium $[\eta^5\text{-(Ph)Ind}]_2Zr$ complex, which was formed by two-electron reduction of the corresponding dichloride. In this work, we carry out a comparative study of the redox properties of bis(2-phenylindenyl)hafnium dichloride $[\eta^5\text{-(Ph)Ind}]_2HfCl_2$ (1) and study *in situ* the redox properties of the sandwich $[\eta^5\text{-(Ph)Ind}]_2Hf$ complex (2), which was generated electrochemically from 1. Synthesis and the molecular structure of complex 1, which is a highly active stereospecific catalyst for the polymerization of propylene,[8] are reported.



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Results and Discussion

Molecular structure of $[\eta^5\text{-(Ph)Ind}]_2HfCl_2$. X-ray structural analysis of a single crystal of complex 1* demonstrated that this complex is isostructural to the zirconium complex $[\eta^5\text{-(2-PhInd)}]_2ZrCl_2$ (3), which has been studied previously.[7] In the crystalline state, complex 1 occurs as two rotational isomers (Fig. 1) with respect to the Hf—ligand bond (two independent molecules in the asymmetric unit). The bond lengths and bond angles in the molecules of compound 1 are close to the corresponding values[7] in zirconium complex 3.

The molecules of compound 1 are skewed metallocenes. The X(1)—Hf(1)—X(2) and X(3)—Hf(2)—X(4) pseudobond angles, where X(1) and X(4) are the centers of the five-membered rings of the phenylindenyl ligands, are 131.7° and 132.6°, respectively. The Hf—X distances in the *syn* and *anti* isomers of 1 have close values [2.23(1) Å]. In complex 3, the corresponding

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* The coordinates of the nonhydrogen atoms, their isotropic temperature parameters, the bond lengths, and the bond angles in the structure of 1 can be obtained from M. Yu. Antipin or K. A. Lyssenko (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2161—2165, December, 1997.

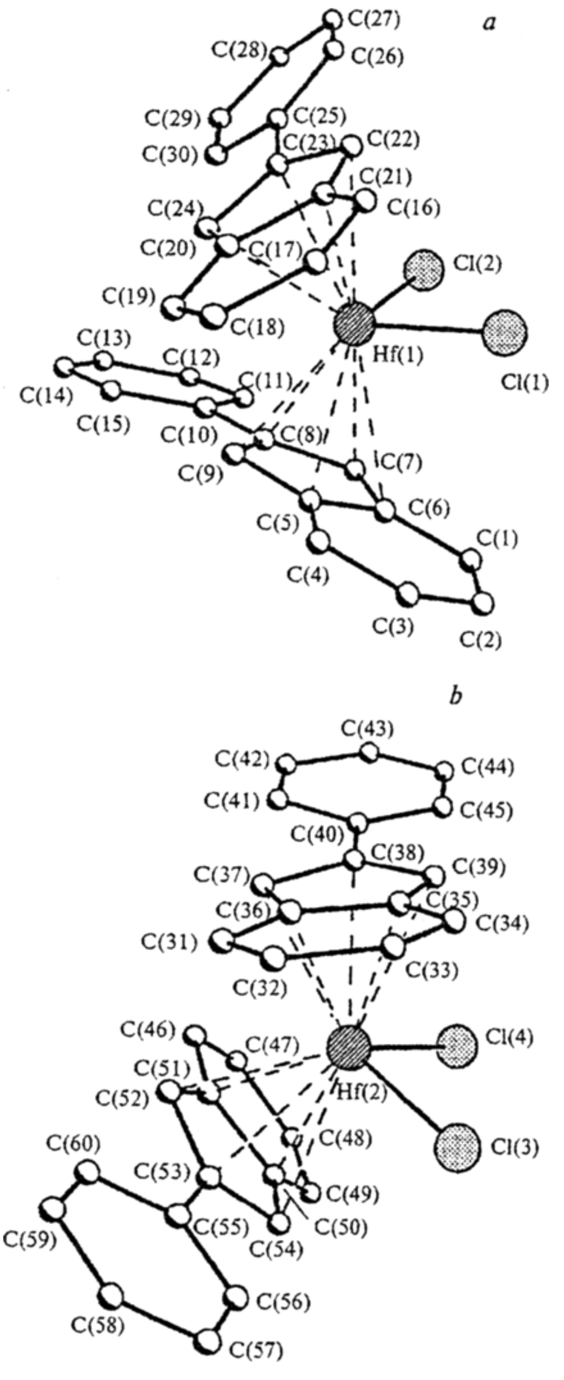

Fig. 1. Molecular structures of (*a*) *syn* and (*b*) *anti* stereoconformers of $[\eta^5\text{-(Ph)Ind}]_2\text{HfCl}_2$.

distances differ only slightly [2.235(8) and 2.246(8) Å in the *anti* and *syn* isomers, respectively].

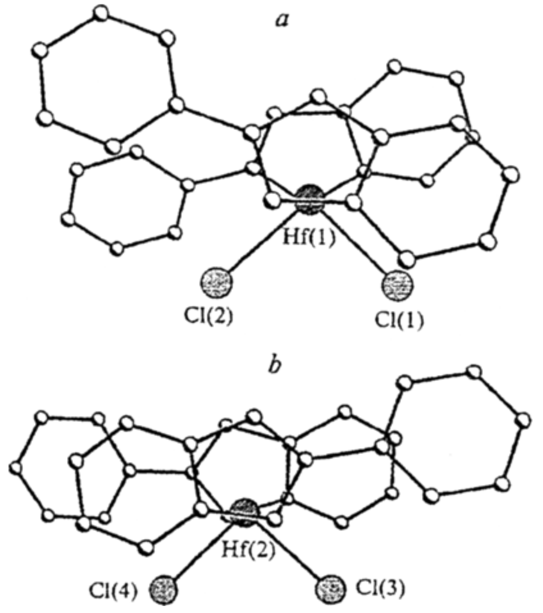

Fig. 2. Projection of the molecular structures of (*a*) *syn* and (*b*) *anti* stereoconformers of $[\eta^5\text{-(Ph)Ind}]_2\text{HfCl}_2$ onto the Cl—Hf—Cl plane.

As in the case of complex **3** studied previously, the isomers in compound **1** differ in the mutual rotation of the phenylindenyl ligands. We use the angle at which the long axes of the 2-phenylindenyl ligands (the lines passing through the C(13) atom and the midpoint of the C(2)—C(3) bond and the C(28) atom and the midpoint of the C(17)—C(18) bond in one independent molecule; the lines passing through the C(43) atom and the midpoint of the C(32)—C(33) bond and the C(58) atom and the midpoint of the C(47)—C(48) bond in the second independent molecule) intersect as a value to describe the mutual arrangement of the ligands. The angles between the above-mentioned lines in the *syn* and *anti* isomers (with respect to the Hf—ligand bond) are 35° and 11°, respectively (Fig. 2).

The angle between the planes of the phenyl and indenyl rings in two isomers of **1** are, on the average, 12.6°. The Hf—C distances are in the range of 2.44(1)—2.63(1) Å. The remaining geometric parameters of the structure of **1** have values typical of this type of compound. The lengths of the intermolecular and intramolecular contacts correspond to the typical van der Waals distances.

Electrochemical study of complex 1. THF is one of the most convenient solvents for studying the electrochemical behavior of metallocene dichloride complexes of Group IV in a wide temperature range.[1–4] However, unlike zirconium complex **3** studied previously,[7] its hafnium analog **1** is unstable in this solvent at room temperature, which manifests itself, in particular, in the change in the color of the solution with time and in the rapid disappearance of the signals in the voltammograms. Apparently, the above-mentioned facts are due to the strong oxophilic character of complex **1** as a result of which the complex reacts with the oxygen-containing solvent. Complex **1** is quite stable in a 2,5-dimethyltetrahydrofuran medium in which the methyl

Table 1. Potentials of the peaks in the cyclic voltammograms of complexes **1** and **4**

Complex	T /°C	Peak	E^0 (E_p) /V
1	−62	D/D'	−1.78
		E	(−2.27)
		F/F'	−2.40
		F	(−2.45)
		F'	(−2.35)
4	−53	G	(−2.52)
		F'	(−2.33)

Note. The values of the potential were measured on a Pt electrode (v = 0.2 V s^{-1}) for solutions in THF/0.05 M Bu_4NPF_6 relative to a saturated calomel electrode.

substituents hinder direct contacts between the metal atom of the complex and the oxygen atom of the solvent. It is impossible to carry out electrochemical measurements in 2,5-dimethyltetrahydrofuran because tetraalkylammonium salts, which are used as the supporting electrolyte, are insoluble in this solvent. Therefore, measurements were carried out by dissolving a weighed sample of complex **1** in THF, which was preliminarily cooled to a temperature lower than −50 °C. Under these conditions, complex **1** is stable over a period large enough for measurements to be carried out, and the voltammograms show signals, which can be adequately interpreted.

As in the case of the $[\eta^5\text{-(Ph)Ind}]_2ZrCl_2$ complex (see Ref. 7), three peaks (D/D', E, and F/F')* are observed in the cyclic voltammograms of complex **1** at a temperature lower than −50 °C. The potential of these peaks (E_p or $E^0 = (E_p{}^c + E_p{}^a)/2$, where $E_p{}^c$ and $E_p{}^a$ are the potentials of cathodic and anodic peaks, respectively) are given in Table 1. The typical voltammogram of the complex at −62 °C is shown in Fig. 3 (curve *1*). All the peaks observed are diffusionally controlled ($I_p \cdot v^{-1/2}$ = const, where I_p is the peak height and v is the rate of the linear potential scan) and one-electron, because they are comparable in height to the one-electron peak of reduction of the $[\eta^5\text{-(Ph)Ind}]_2ZrCl_2$ complex recorded under identical conditions. By analogy with the redox behavior of substituted biscyclopentadienylhafnium dichlorides studied previously,[3,4] it can be concluded that the reversible or quasi-reversible pair of peaks D/D' ($\Delta E_p = E_p{}^a - E_p{}^c$ = 90 mV at −62 °C)** corresponds to the generation of radical anion $\mathbf{1}^{\cdot-}$, which is stable within the cyclic voltammetry time scale.

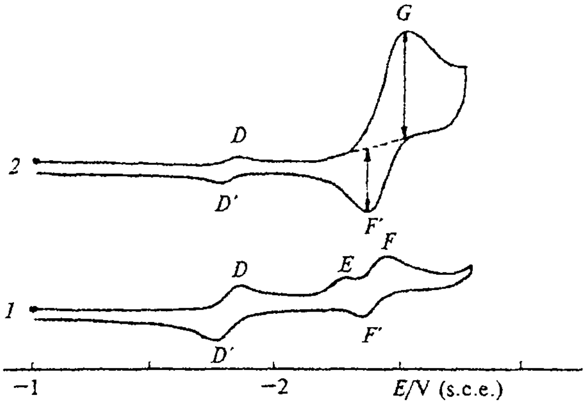

Fig. 3. Cyclic voltammograms of complex **1** in a THF/0.05 M Bu_4NPF_6 solution on a Pt electrode at v = 0.2 V s^{-1}: *1*, [**1**] = $6 \cdot 10^{-4}$ mol L^{-1}, −62 °C; and *2*, [**1**] = $1.8 \cdot 10^{-4}$ mol L^{-1}, −35 °C (recorded after 1 h).

Further reduction of $\mathbf{1}^{\cdot-}$ to dianion $\mathbf{1}^{2-}$ at the potentials of peak E is chemically irreversible and is accompanied by the elimination of two Cl^- ions to form 14-electron 2-phenyl-substituted bisindenylhafnium $[\eta^5\text{-(Ph)Ind}]_2Hf$ (**2**). At the potentials of peak F, complex **2** undergoes quasi-reversible (ΔE_p = 100 mV at −62 °C) one-electron reduction to the corresponding radical anion $\mathbf{2}^{\cdot-}$, which is stable at low temperature within the cyclic voltammetry time scale (see Fig. 3, curve *1*). Therefore, the reduction of complex **1**, like $[\eta^5\text{-(Ph)Ind}]_2ZrCl_2$ reported previously (see Ref. 7), may be represented by the following scheme:

$$\mathbf{1} \xrightleftharpoons[D/D']{e^-} \mathbf{1}^{\cdot-} \xrightarrow[-2Cl^-]{e^-} \mathbf{2} \xrightleftharpoons[F/F']{e^-} \mathbf{2}^{\cdot-}. \qquad (1)$$

The validity of the assignment of the pairs of peaks F/F' to redox process $\mathbf{2}^{0/\cdot-}$ was additionally supported by the data in Fig. 4, which shows the dependence of the values of $E^0(E_p)$ for the $[\eta^5\text{-(Ph)Ind}]_2Ni^{+/0/-}$ (see Ref. 7) and $[\eta^5\text{-(Ph)Ind}]_2M^{0/-}$ (M = Hf or Zr[7]) redox transformations on the corresponding ionization potentials of the metals (IP_j): $E^0(E_p) = -3.95 + 0.11IP_j$, and $r^2 = 0.99$. It is known[1,2,9–11] that sandwich complexes of transition metals with the same ligands are characterized by unified linear relationships between the values of E^0 of all possible redox transformations of the complexes and IP_j of the corresponding metals. The slope of these dependences is close to 0.1 V eV^{-1} regardless of the nature of the ligands, and the intercept on the axis of redox potentials is determined only by the nature of the π-ligands. Therefore, the unified linear dependence of the E^0 values of these redox transformations on the corresponding values of IP_j (with the slope equal to ~0.1 V eV^{-1}) should occur for all metals in the series of the $[\eta^5\text{-(Ph)Ind}]_2M^{+/0/-}$ redox transformations studied.

Decomposition of complex **1** in a THF solution at room temperature is accompanied by destruction of the sandwich structure. However, at T from −30 to −40 °C, the peaks of reduction of the initial dichloride (D/D'

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* For convenience, the notaion of the peaks used previously[7] is retained.

** Because of the high resistance of a solution of the supporting electrolyte at low temperature, the value of ΔE_p for the undoubtedly reversible ferrocene$^{0/+}$ redox pair is 85 mV under these conditions.

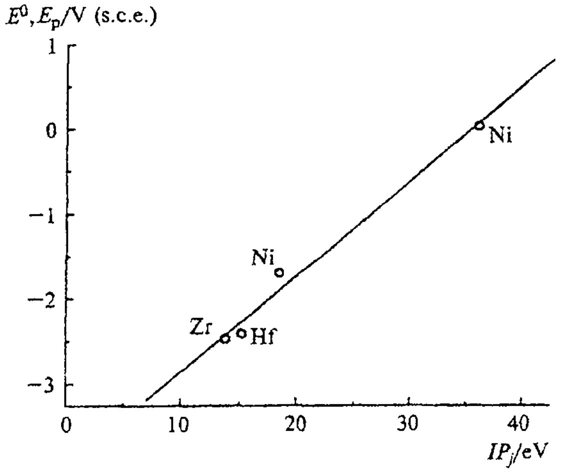

Fig. 4. Dependence between the values of the standard potential (E^0) and the reduction peak potential (E_p) for the sandwich bis(2-phenylindenyl) complexes and the corresponding ionization potentials of the metals.

and *E*) gradually disappear in 1 h, and virtually one pair of peaks (cathodic peak *G* and anodic peak *F'*, see Fig. 3, curve *2*) persists in the voltammograms. This pair of peaks characterizes a new compound, which was formed from **1**.

This behavior distinguishes essentially complex **1** from the metallocene dichloride complexes of Group IV studied previously,[3,4,7] and suggests that complex **1** was transformed into the previously unknown complex in a THF medium. In this complex, the metal atom is in the lower valence state than Hf^{IV}, which is evidenced by the substantially more negative potential of peak *G* compared to the pair of peaks *D*/*D'* of the initial dichloride (see Table 1). This result is rather unexpected because the data on spontaneous (in the absence of a reducing agent) reduction of bent-sandwich complexes of Group IV metals are unavailable in the literature.

All the aforesaid gave impetus to the isolation of the product, which was formed upon prolonged (>10 days) storage of a solution of complex **1** in THF at −30 °C. Based on the data of elemental analysis for chlorine, the Hf/Cl ratio in the pale-yellow product is equal to unity, which, apparently, indicates that the degree of oxidation of Hf in the complex is +3. Although we failed to obtain single crystals and carry out an X-ray structural analysis, it is believed that the complex has the dimeric $\{[(Ph)Ind]_2HfCl\}_2$ structure (**4**). First, the product isolated is diamagnetic, which is typical of dimeric metallocene monochloride complexes of Zr^{III} [12–14] and Hf^{III}.[14] Second, the results of electrochemical studies of complex **4** reported below is indirect evidence of its dimeric structure.

Because the compound obtained is moderately stable in THF at −20 °C, electrochemical measurements were carried out at *T* from −55 to −45 °C. Under these conditions, complex **4** is stable in a solution of the supporting electrolyte, and the single pair of peaks *G* and *F'* (ΔE_p = 190 mV at −53 °C) is observed in its voltammograms. This pair of peaks is identical to the pair *G*/*F'* observed previously in the voltammograms of complex **1** measured after storage of the latter at low temperature for 1 h (see Fig. 3, curve *2*), and, therefore, it is omitted in Fig. 3. At first glance, the pair of peaks *F*/*F'* for complex **1** is analogous to the pair of peaks *G*/*F'* for complex **4**. However, two essential differences between these pairs occur. First, the values of ΔE_p for pairs *F*/*F'* and *G*/*F'* are 100 and 190 mV, respectively. Second, the ratio of the heights of peaks *F*/*F'* is equal to unity, as it must for the reversible one-electron process, whereas the height of peak *G* is always two times as large as that of peak *F'* (see Fig. 3, curve *2*) at all the temperatures used and at all the rates of the potential scan. All the above unambiguously indicates that peak *G* for complex **4** is two-electron, and it is a superposition of two peaks, which correspond to different electrode processes.

It is known[3] that $(Cp_2MCl)_2$ dimers and the corresponding metallocenes Cp_2M of Group IV are reduced at close values of the potentials although reduction of dimers occurs somewhat readily. On this basis and assuming that complex **4** has a dimeric structure and that one molecule of sandwich complex **2** is generated by one-electron irreversible reduction of **4**, the fact that the ratio of the heights of peaks *G*/*F'* in the voltammograms of complex **4** is equal to 2 can be explained. The mechanism of reduction of this complex at the potentials of peak *G* can be represented by the *ECE* scheme (*E* and *C* are the electrochemical and chemical stages, respectively):

$$\mathbf{4} \xrightarrow{e^-} \text{Products} + \mathbf{2} \xrightleftharpoons[F']{e^-} \mathbf{2}^{\cdot -}. \qquad (2)$$

If Scheme 2 is true, it is apparent that because of the close values of the potentials of one-electron reduction of dimer **4** and sandwich complex **2**, cathodic peak *G* and the corresponding anodic peak *F'* in the voltammograms of complex **4** should be two-electron and one-electron, respectively, *i.e.*, the ratio of the heights of peaks *G*/*F'* is 2. Moreover, the value of ΔE_p for the pair of peaks *G*/*F'* of complex **4** should be larger than that for the pair of peaks *F*/*F'* of complex **1**. All the aforesaid actually occurs (see above), and it is believed with certainty that the scheme of reduction of complex **4** is adequately described by Eq. (2) on the assumption that **4** has a binuclear structure.

The mechanism of chemical reduction of complex **1** to **4** in a THF medium is still not clearly understood. However, it can be suggested that because of the oxophilic character, 16-electron coordinatively unsaturated complex **1** attacks the solvent (THF) molecule at the oxygen atom, apparently, with cleavage of the C—O bond. This is supported, in particular, by the fact that complex **1** is quite stable even at room temperature in a solution in dimethyltetrahydrofuran, whose methyl groups hinder the attack at the oxygen atom. Radical particles, which are formed as a result of cleavage of the C—O bond, may appear to be rather strong reducing agents capable of reducing, at least partially, Hf^{IV} to Hf^{III}.

Experimental

Toluene and THF freshly distilled over $LiAlH_4$ were used for preparing complex **1**. All procedures were carried out under a pure dry argon atmosphere using the Schlenk technique.

Synthesis of $[\eta^5\text{-(Ph)Ind}]_2HfCl_2$ (1). One equivalent of Bu^nLi (3 mL, 2 mol L^{-1} in hexane, 6 mmol) was added dropwise with continuous stirring at −50 °C to a suspension of 2-phenylindene (2-PhIndH, 1.146 g, 6 mmol) in toluene (10 mL), which contained a small amount of THF. The yellow-orange solution of 2-PhIndLi was slowly heated and kept at ~20 °C for 2 h. Then the solution was added dropwise with continuous stirring to a suspension of $HfCl_4$ (Aldrich, 0.96 g, 3 mmol) in toluene (50 mL) at −15 °C. The temperature of the reaction mixture was raised to ~20 °C, and the solution was stirred for 16 h until the pale precipitate of $HfCl_4$ was completely dissolved. The reaction mixture was a lemon-yellow solution with a large amount of a yellow precipitate. The solvent was removed by distillation *in vacuo*, and $[\eta^5\text{-(Ph)Ind}]_2HfCl_2$ was extracted repeatedly with toluene. The extracts were combined, concentrated by removing a portion of the solvent *in vacuo*, and cooled to −30 °C. The crystals that formed were washed with cold pentane and dried *in vacuo*. The yield of compound **1** was 1.43 g (75%). The data of elemental analysis correspond to molecular formula **1**. Single crystals suitable for X-ray structural study were obtained by recrystallization of **1** from a 1:1 (volume) toluene : THF mixture. To perform X-ray structural analysis, a crystal of **1** of dimensions about 0.6 mm was placed in a 0.7-mm-diameter capillary and sealed with picein.

X-ray diffraction analysis of compound **1** ($C_{30}H_{22}Cl_2Hf_1$) was carried out on a four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta < 54°$) at −120 °C. The crystals of **1** are triclinic, at −120 °C: $a = 13.499(5)$, $b = 14.572(6)$, $c = 15.315(6)$ Å, $\alpha = 65.81(2)°$, $\beta = 64.82(2)°$, $\gamma = 63.16(2)°$, $V = 2343(2)$ Å^3, space group $P\bar{1}$, $Z = 1$, $d_{calc} = 1.778$ g cm^{-3}, mol. weight 631.87, $F(000) = 1232$, $\mu = 4.664$ mm^{-1}. Of a total of 9549 measured reflections, 8492 independent reflections were used in the calculations and refinement.

The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F^2. The positions of hydrogen atoms were determined from geometric considerations and refined using the riding model with fixed thermal parameters. The final values of the R factors are as follows: $R = 0.0810$ based on 7458 reflections with $I > 2\sigma(I)$; and $wR1 = 0.2066$ and $GOF = 1.039$ based on 8492 independent reflections. All calculations were performed on an IBM-PC/AT computer using the SHELXTL PLUS program (Version 5).

Voltammetric measurements were carried out under a dry argon atmosphere in THF that had been prepurified and distilled directly into an electrochemical cell (evacuated and filled with argon), according to the procedure described previously.[15] THF (Aldrich) was purified by the ketyl method. A Bu_4NPF_6 (0.05 *M*) solution was used as the supporting electrolyte. Tetrabutylammonium hexafluorophosphate (Aldrich) was preliminarily dehydrated by melting *in vacuo*. Low-temperature electrochemical measurements were performed using a cell thermostatically controlled with isopropanol, which was cooled with liquid nitrogen in a Dewar vessel.

All measured potentials are given relative to an aqueous saturated calomel electrode by comparing the potential of the reference electrode (an Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the solution studied by a bridge filled with a solution of the supporting electrolyte, with the potentials of the redox transformations of ferrocene$^{0/+}$ or decamethylferrocene$^{0/+}$ (E^0 = 0.44 and 0.00 V, respectively; saturated calomel electrode).

A 1-mm disk platinum electrode sealed into glass and polished off with diamond paste (the grain size was ≤1 μm) was used as the working electrode. Voltammetric measurements were carried out using a PAR 175 generator of signals and a PAR 173 potentiostat with compensation of ohmic losses. Voltammograms were recorded on a two-coordinate RE0074 recorder.

We thank A. V. Kulikov for help in recording the ESR spectra and G. L. Soloveichik for helpful discussions and valuable advice.

This work was supported by the Russian Foundation for Basic Research (Project Nos. 96-03-33445a and 95-03-09836a).

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Received March 31, 1997;
in revised form May 19, 1997