ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2006, Vol. 32, No. 6, pp. 397–401. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.V. Saraev, P.B. Kraikivskii, S.N. Zelinskii, A.I. Vil'ms, D.A. Matveev, A.Yu. Yunda, A.A. Fedonina, K. Lammertsma, 2006, published in Koordinatsionnaya Khimiya, 2006, Vol. 32, No. 6, pp. 413–418.

EPR Study of (η^5-Cyclopentadienyl)nickel(I) Complexes with P- and N-Donor Ligands and 1,5-Cyclooctadiene

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Received March 9, 2005

Abstract—Mononuclear (η^5-cyclopentadienyl)nickel(I) complexes with triphenylphosphine, triethylphosphite, 2,2'-bipyridyl, and 1,5-cyclooctadiene formed in the course of reduction of nickelocene were studied by EPR method. Monocyclopentadienyl Ni(I) complexes of the composition $CpNiL_2$ were shown to form during nickelocene reduction irrespective of the method applied (the use of organometallic compound, alkali metal, thermal conditions) in the presence of stabilizing ligands L (L = PPh_3, $P(OEt)_3$, Bipy/2, COD/2) and in the course of contradisproportionation reaction between nickelocene and the corresponding NiL_4 complex. It was found that in the structure of these $CpNiL_2$ complexes (L = PPh_3, $P(OEt)_3$, Bipy/2), the main molecular axis is perpendicular to the L–Ni–L plane and these complexes should be considered as derivatives of trigonal structures of D_{3h} symmetry distorted by Cp ligand. In CpNi(COD) complex, the main axis passes through the Cp-ring center and this complex should be treated as a derivative of pentagonal structure of C_{5v} symmetry distorted by COD ligand. Nonequivalence of ^{31}P nuclei results from vibronic interaction effect in tricoordinate structures in pseudodegenerate electron state (Jahn–Teller effect).

DOI: 10.1134/S1070328406060029

Nickel(I) complexes stabilized with phosphine ligands are indispensable components of nickel complex catalysts of oligomerization of unsaturated hydrocarbons [1, 2] irrespective of the catalyst formation method: reaction of Ni(0) oxidation in the starting compound with the Lewis [3–5] or Brönsted [6] acid or reaction of Ni(II) reduction in the starting compound with organometallic compounds of nontransition elements [7, 8]. It was shown for catalytic system $Ni(PPh_3)_4–BF_3 \cdot OEt_2$ as an example that the phosphine cationic complexes of Ni(I) participate directly in the catalytic transformation of unsaturated hydrocarbons [9]. In connection with this, Ni(I) complexes stabilized with cyclopentadienyl ligands (Cp) are of great interest as potentially active forms that can be used in processes such as oligomerization of ethylene [10–16], polymerization of alkenes [17] and alkynes [18].

As was reported in [19, 20], the first stage of interaction of nickelocene $NiCp_2$ with organolithium and organomagnesium compounds MR (M = Li or MgX) is the exchange of one cyclopentadienyl group for the alkyl group with the formation of unstable 16-electron complex {CpNiR}. As a result of the coupling reaction of the alkyl groups [21, 22] or homolysis of these groups [23], this complex transforms to univalent nickel complex occurring as a dimer in a solution in the absence of stabilizing ligands:

$$NiCp_2 + MR \longrightarrow \{CpNiR\} + MCp,$$

$$2\{CpNiR\} \longrightarrow \{(NiCp)_2\} + (R–R),$$

$$\{CpNiR\} \longrightarrow \{(NiCp)_2\} + \dot{R}.$$

This paper reports the results of the EPR study of mononuclear (η^5-cyclopentadienyl)nickel(I) complexes with triphenylphosphine, triethylphosphite, 2,2'-bipyridyl, or 1,5-cyclooctadiene formed in the reaction of nickelocene reduction.

EXPERIMENTAL

All manipulations were carried out in the atmosphere of purified argon following Schlenk procedure. The precipitates were filtered on glass Schlenk filters. All reagents were stored in sealed tubes in the argon atmosphere.

Toluene, benzene, hexane, and cyclohexane (special purity grade) were distilled before use over metallic sodium in the presence of benzophenone.

Commercial reagents (Merck), i.e., 1,5-cyclooctadiene (COD), 2,2'-bipyridyl (Bipy), triphenylphosphine (PPh_3), triethylphosphite ($P(OEt)_3$) were used as received. Commercial Et_2AlOEt was distilled in vacuum.

The $NiCp_2$, $Ni(P(OEt)_3)_4$, $Ni(COD)_2$, and $Ni(PPh_3)_4$ complexes were synthesized by the known procedures [24–27], respectively.

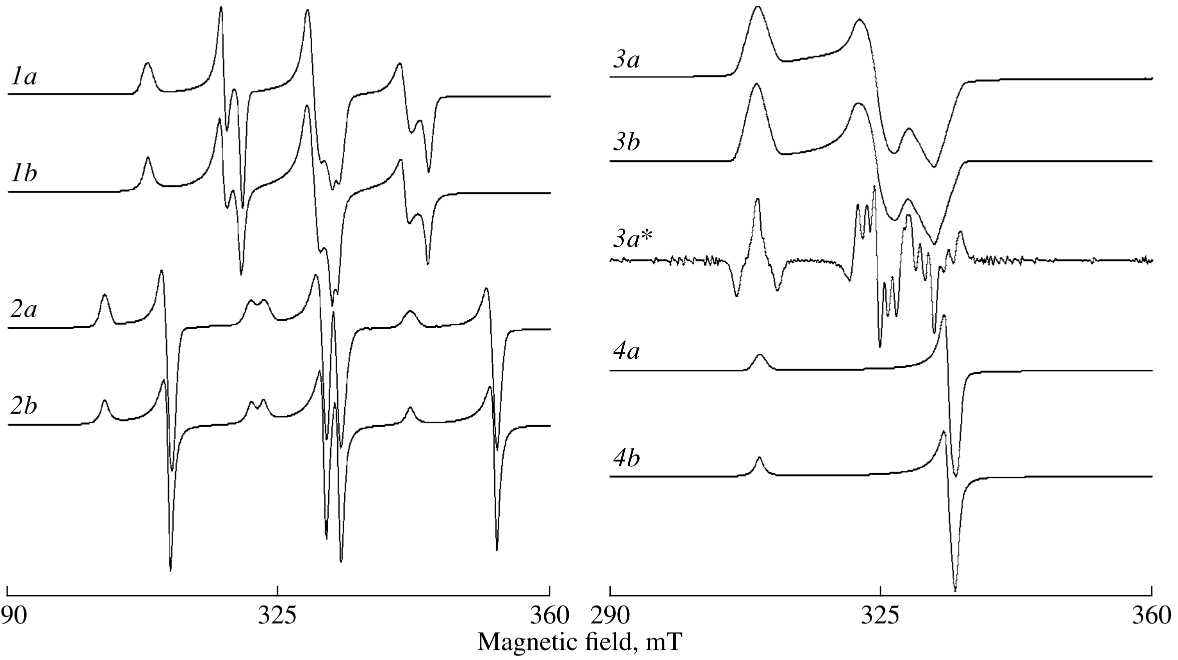


Fig. 1. (*a*) Experimental and (*b*) model EPR spectra of $CpNiL_2$ complexes in toluene solution at $T = 77$ K: L = (*1*) PPh_3, (*2*) $P(OEt)_3$, (*3*) Bipy/2, (*4*) COD/2; (*) is the second derivative of the EPR spectrum

Synthesis of $CpNi(PPh_3)_2$ (I). Sublimated crystalline $NiCp_2$ (1 mmol) was added to 10 ml of toluene solution of $Ni(PPh_3)_4$ (1 mmol); the reaction mixture was stirred at room temperature for 12 h. The solution obtained was cooled to –20°C and toluene was distilled off at this temperature in vacuum until a pasty mass was formed. The mass was washed with 20 ml of hexane cooled to –20°C with stirring. Then, a major part of the liquid was removed by siphon decantation. The solid was dried in vacuum (0.01 mmHg) at room temperature. The complex was formed as fine amorphous particles, which at a temperature above +15°C, fuse into tarry red-brown mass. The complex readily dissolves in toluene. The yield was 40%.

For $C_{41}H_{35}NiP_2$			
anal. calcd. (%):	C 75.96;	H 5.40;	Ni 9.06;
Found (%):	C 75.08;	H 5.01;	Ni 8.96.

Synthesis of CpNi(Bipy) (II). To a solution of $NiCp_2$ (1mmol) in 20 ml cyclohexane, a sublimated 2,2'-bipyridyl (1 mmol) was added and the mixture was stirred for 2 h at 75°C. The reaction was terminated in 20 min after the maximum intensity of EPR signal from CpNi(Bipy) complex was attained. The reaction mixture was cooled to –20°C and kept at the same temperature for 3 h. The precipitated violet crystals were filtered off at –20°C and dried in vacuum (0.01 mm Hg) at room temperature. At a temperature of +140°C, the product decomposed and slightly sublimated. The complex yield was 83% of the theoretical value.

For $C_{15}H_{13}N_2Ni$				
anal. calcd. (%):	C 64.35;	H 4.64;	N 10.01;	Ni 20.98
Found (%):	C 64.19;	H 4.60;	N 9.65;	Ni 20.96

The elemental analysis of the complexes was performed on a FLACH 1112 analyzer (EA series). The EPR spectra were recorded on a CMS-8400 spectrometer (working frequency 9.6 GHz) at the boiling point of liquid nitrogen. The sweep range was calibrated using the DDPG free radical and Mn^{2+} in MgO. The EPR spectra were simulated with our own program [28], where the hyperfine interaction (HFI) is limited to the second-order term and the main axes of the *g*-tensor and HFI tensors coincide. The NMR spectra were recorded at 25°C on a VXR-500S Varian spectrometer.

RESULTS AND DISCUSSION

Formation of Ni(I) complexes. Nickelocene is a high-spin compound ($S = 1$), but is EPR-undetectable even at $T = 4.2$ K due to strong splitting of the electron levels in a zero field [29]. After an equivalent amount of Et_2AlOEt is added to a toluene solution of nickelocene at room temperature with a twofold molar excess of PPh_3, the intense EPR signal appears with well resolved hyperfine structure (HFS) from two nonequivalent ^{31}P nuclei (Fig. 1). The same EPR spectrum is observed in the case of $NiCp_2$ interaction with a fourfold excess of PPh_3 in the absence of organoaluminium compound, if the reaction is performed at boiling point of toluene (110°C) or under the action of dispersed metallic

The EPR parameters of the $CpNiL_2$ complexes

Complex	g_x	g_y	g_z	A_x, mT	A_y, mT	A_z, mT
$CpNi(PPh_3)_2$ (**I**)	2.030	2.047	2.119	12.4 (P_1)	12.0 (P_1)	10.9 (P_1)
				11.6 (P_2)	11.4 (P_2)	9.35 (P_2)
CpNi(Bipy) (**II**)	2.032	2.079	2.183	1.2 (N)	1.1 (N)	0.8 (N)
	2.033 [30]	2.080 [30]	2.184 [30]	1.1 (N) [30]	0.9 (N) [30]	0.8 (N) [30]
$CpNi(P(OEt)_3)_2$ (**III**)	2.032	2.032	2.093	20.1 (P_1)	20.1 (P_1)	18.9 (P_1)
				22.0 (P_2)	22.0 (P_2)	20.5 (P_2)
CpNi(COD) (**IV**)	2.015	2.021	2.180			
	2.018 [31]	2.018 [31]	2.168 [31]			

sodium in a toluene–THF (3 : 1) mixture at room temperature. Under these conditions, the intensity of the spectrum reaches a maximum point and then decreases, which points to a subsequent change in the Ni oxidation state: Ni(II) ⟶ Ni(I) ⟶ Ni(0). Moreover, the analogous EPR spectrum was produced by a complex formed in contradisproportionation reaction between $NiCp_2$ and $Ni(PPh_3)_4$, which quickly proceeds in toluene at room temperature (the maximum intensity of the spectrum is attained in less than 2 h after the components were mixed together and then, the spectrum remains unchanged for indefinitely long time). Therefore, the recorded spectrum can be assigned to mononuclear complex (**I**). The EPR spectrum of this complex in liquid solution does not exhibit nonequivalence of the phosphine ligands [30].

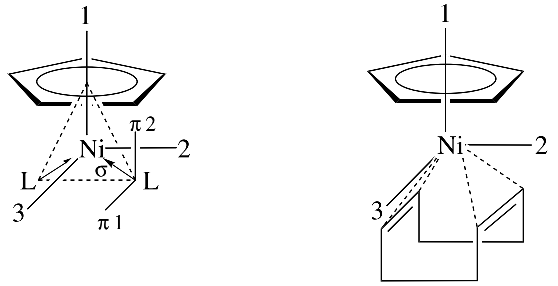
If 2,2'-bipyridyl, triethylphosphite, or 1,5-cyclooctadiene are used as stabilizing ligands under similar conditions described above (reduction or contradisproportionation), then complexes **II**, $CpNi(P(OEt)_3)_2$ (**III**), and CpNi(COD) (**IV**) are formed. The EPR spectra of these complexes are shown in Fig. 1. Unlike the spectrum of phosphine complex **I**, the spectrum of phosphite complex **III** shows more distinctly the nonequivalence of the ^{31}P nuclei due to an increase in HFS constants and a decrease in the widths of individual lines. Note that the EPR spectrum of analogous complex $CpNi(P(OMe)_3)_2$ in liquid solution also shows nonequivalence of the ^{31}P nuclei [30].

In the EPR spectrum of bipyridyl complex **II**, the HFS from the ^{14}N nuclei is poorly resolved and can be reliably resolved only by a doduble differentiation of the EPR signal (Fig. 1, curve 3*a**). Complexes **I** and **II** were isolated as individual compounds and characterized by elemental analysis. The EPR parameters of bipyridyl complex **II** and cyclooctadienyl complex **IV** coincide within the limits of measurement error with the literature data for these complexes obtained for the solid solutions (THF solution at –196°C) [30, 31].

Thus, monocyclopentadienyl complexes of Ni(I) of the composition $CpNiL_2$ are formed during nickelocene reduction irrespective of the method applied (the use of organometallic compound, alkali metal, thermal treatment) in the presence of stabilizing ligands L (L = PPh_3, $P(OEt)_3$, Bipy/2, COD/2), as well as in the reaction of contradisproportionation between nickelocene and the corresponding NiL_4 complex.

Structure of (η^5-Cp)NiL_2 complexes. The EPR spectral parameters of 19-electron $CpNiL_2$ complexes (table) calculated from characteristic points of the experimental spectra of solid toluene solutions and refined by computer simulation of these spectra indicate three-axis anisotropy of the EPR parameters. An exception is the $CpNi(P(OEt)_3)_2$ complex, which has two-axis anisotropic EPR parameters. It is necessary to establish the nearest and the highest symmetry to which the first coordination sphere of Ni(I) belongs, in order to assign the *g*-factor components to the corresponding molecular axes. Let us begin our consideration with complexes with P- and N-donor ligands.

The X-ray diffraction data [30] for the CpNi(Bipy) complex show that the planes of cyclopentadienyl and bipyridyl ligands in this complex are mutually orthogonal, which makes it possible to select the following system of coordinates (1, 2, 3) for complexes with P- and N-donor ligands (Fig. 2a). Axis 2 lies in the L–Ni–L plane, axis 3 is perpendicular to this plane. The model suggested can be described as a structure with the initial pentagonal C_{5v} symmetry distorted by



(a) (b)

Fig. 2. The Ni coordination sphere in the CpNi complexes with (a) P- and N-donor ligands and (b) COD.

ligands L or as a structure with the initial trigonal D_{3h} symmetry distorted by ligand Cp. In both cases, the unpaired electron occupies pseudodegenerate orbital [29, 32], thus giving rise to the following relation between the g-factor components $g_z > g_y, g_x$ [28], which corresponds to the experimental data. However, in the former case, the principal axis of the complex is axis 1, while in the latter case, it is axis 3. The direction of the principal axis of the complex can be determined from the data on HFI with the nuclei of the ligands.

A great deal of experimental data on Ni(I) complexes with ternary phosphines and phosphites [33] indicate and the tensor of HFI with ^{31}P nuclei is almost axially symmetric; its principal axis is directed along the Ni–P bond. Of the three main components of this tensor (T_σ, $T_{\pi1}$, $T_{\pi2}$), the greatest is T_σ corresponding to the direction of the axis along the Ni–P bond such that $T_{\pi1} \approx T_{\pi2}$. Obviously, the principal axes of the g-tensor (axis 1 or 3) and the HFI tensor (axis σ) do not coincide. In order to determine the mutual orientation of these tensors, let us use the results of theoretical studies of the EPR of solid solutions of model species, where the principal axes of the axially symmetric g-tensors and of HFI tensor make an angle ψ [34]. According to the results obtained, the coordinates of extreme points in the spectral curve, in whose vicinity the resonance field changes insignificantly with changing direction of external magnetic field (characteristic points), are determined in the first approximation by the following expressions:

$$\begin{aligned} H^y &= (h\nu - |T_\perp| m)/g_\perp \beta_e, \\ H^x &= (h\nu - [T_\parallel^2 \sin^2\psi + T_\perp^2 \cos^2\psi]^{1/2} m)/g_\perp \beta_e, \qquad (1) \\ H^z &= (h\nu - [T_\parallel^2 \cos^2\psi + T_\perp^2 \sin^2\psi]^{1/2} m)/g_\parallel \beta_e, \end{aligned}$$

where $h\nu$ is the energy of a quantum of electromagnetic field, β_e is the Bohr magneton, m is the magnetic quantum number of a nucleus, $g_\perp$, $g_\parallel$ are components of the axially symmetric g-tensor, $T_\perp$ and $T_\parallel$ are components of axially symmetric HFI tensor. Indices x, y, z indicate the direction of magnetic field along the corresponding molecular axes.

The first of the three expressions (1) is an explicit solution, whereas the other two equations are approximate solutions to the extremum problem that are obtained on condition that HFI anisotropy is low [34].

In line with expressions (1), the apparent HFI constants (the distances between neighboring characteristic points) will be

$$\begin{aligned} A_y &= |T_\perp|/g_\perp \beta_e, \\ A_x &= [T_\parallel^2 \sin^2\psi + T_\perp^2 \cos^2\psi]^{1/2}/g_\perp \beta_e, \qquad (2) \\ A_z &= [T_\parallel^2 \cos^2\psi + T_\perp^2 \sin^2\psi]^{1/2}/g_\parallel \beta_e. \end{aligned}$$

At $\psi = 0$, formulas (2) acquire the form common for HFS constants expressed in terms of magnetic field units, when the principal axes of the g-tensor and HFI tensor coincide.

At $0 < \psi < \pi/2$, the apparent constants A_x and A_z represent combinations of components of HFI tensors. According to experimental data (table), the apparent constant A_z is the smallest among the three constants for all Ni(I) complexes with P- and N-donor ligands. Since $|T_\parallel| > |T_\perp|$, then the relationship $A_z < A_y, A_x$ is likely to be fulfilled only at sufficiently large ψ angles. Unfortunately the system of equations (2) cannot be used directly in order to quantitatively estimate the value of ψ (as well as $|T_\parallel|$ and $|T_\perp|$) from the experimental data, since in the Ni(I) complexes under study, unlike the model, the g-tensor and the HFI tensor are triaxial-anisotropic and therefore, three rotation angles (Euler angles [34]) should be taken into consideration when describing their relative orientation.

Let us estimate the lower limit of the ψ value for triethylphosphite complex **III**, whose axial-symmetric tensors are the closest to the chosen model in terms of symmetry and consider the inequality

$$A_z^2 < A_y^2, \qquad (3)$$

which gives

$$\cos^2\psi < \frac{(g_\parallel/g_\perp)^2 - 1}{(T_\parallel/T_\perp)^2 - 1}. \qquad (4)$$

If the ratio of components of the HFI tensor with ^{31}P for the P(OEt)$_3$ ligand is considered to change insignificantly in the series of the Ni(I) complexes with thriethylphosphite, then one can use the value $|T_\parallel|/|T_\perp| = 1.2$ for the complex $[(P(OEt)_3)Ni(PPh_3)_3]BF_4$, where the principal axes of the axially-symmetric g-tensor and the HFI tensor for the P(OEt)$_3$ ligand coincide (triethylphosphite is located at a trigonal pyramid vertex) [35]. By substituting the experimental values of the g-tensor for complex **III** into formula (4), we obtain that $\psi > 68°$. Taking into account that the difference $(A_y - A_z)$ is noticeably greater than the difference $(A_x - A_y)$ for all CpNiL$_2$ complexes with P- and N-donor ligands, one can conclude that the angle ψ between the principal axis of the g-tensor and the HFI tensor is substantially greater than 68° and is obviously close to $\pi/2$. This is likely to occur when the principal axis of the g-tensor is the molecular axis 3 (Fig. 2a). Hence, the principal molecular in complexes **I**, **II**, and **III** is perpendicular to the L–Ni–L plane and these complexes should be considered as the derivatives of trigonal structures of the D_{3h} symmetry distorted by the Cp ligand.

Nonequivalence of the ^{31}P nuclei seems to be due to the vibronic interaction effect in tricoordinate structures in pseudodegenerate ground state (Jahn–Teller pseudoeffect) [28].

The cyclooctadiene ligand in complex **IV** supplied 4 carbon atoms to the Ni coordination sphere (Fig. 2b). If we assume that the C atoms of the COD ligand form a regular square in the first approximation, then the created tetragonal field will be superimposed on the axial field of cyclopentadienyl ligand, whose principal symmetry axes (C_4 and C_5) coincide and are directed along the molecular axis 1. Hence, unlike complexes **I**, **II**, and **III**, in complex **IV**, the principal axis corresponding to the largest component of the g-factor passes through the Cp ring center. Therefore, complex **IV** should be treated as a derivative of pentagonal structure with C_{5v} symmetry distorted by the COD ligand.

It is known that the tetragonal distortion of high-symmetry structure cannot be the reason for appearance of triaxial anisotropy of the g-factor. [36]. The EPR spectra of complex **IV** recorded as narrow lines (long relaxation times) at a high temperature (77 K) with triaxial anisotropy of the g-factor indicate the orthorhombic distortion of the complex, probably, as a result of Jahn–Teller effect, which has steady-state nature at a temperature of the complex recording. Further studies are required in order to establish the details of the influence of Jahn–Teller effect on the EPR spectra of Ni(I) cyclopentadienyl complexes.

ACKNOWLEDGMENTS

This work was supported by the NWO Foundation (the Netherlands) and the Russian Foundation for Basic Research (International grant no.047.015.014).

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