Counterdisproportionation between Cationic Ni(II) and Phosphine Ni(0) Complexes

V. V. Saraev, P. B. Kraikivskii, D. A. Matveev, A. S. Kuzakov, A. I. Vil'ms, and A. A. Fedonina

Irkutsk State University, ul. Lermontova 126, Irkutsk, 664033 Russia E-mail: saraev@admin.isu.ru

Received May 18, 2007

Abstract—The interaction of Ni(II) bis-tetrafluoroborate complexes $[Ni(Dppe)_2](BF_4)_2$ and $[Ni(CH_3CN)_6](BF_4)_2$ (where Dppe = 1,2-bis(diphenylphosphino)ethane)) with Ni(0) phosphine complexes Ni(Dppe)_2 and Ni(PPh_3)_4 in 1 : 1 mixture of toluene–acetonitrile was studied by the EPR method. The counter-disproportionation was shown to occur in a solution between the cationic Ni(II) complexes and the Ni(0) complexes to give Ni(I) complexes almost in quantitative amounts. The structures of the cationic Ni(I) complexes obtained were found to depend on both the solvent nature and the presence of a free phosphine in a solution.

DOI: 10.1134/S1070328408060080

The catalytic systems based on Ni compounds and known as catalysts of a low-molecular oligomerization of unsaturated hydrocarbons [1, 2] cause an increased interest recently due to the high activity of some Ni complexes in polymerization of the lower olefins [3] and in polymerization and cyclotrimerization of alkynes [4].

Despite a great number of publications devoted to the nickel complex catalysts, the question of the structure of the active complexes remains open. The majority of the researchers traditionally assume that the oligomerization of olefins is directly associated with Ni(II) hydride complexes. These assumptions are based on the classic works of Tolman and his adherents concerned with the NMR identification of the Ni(II) hydride complexes and, first of all, in the model systems [5–7].

On the other hand, according to the EPR data, the process of formation of the nickel complex catalysts includes the formation and stabilization of the Ni(I) complexes, independent of the valence state of a transition metal in the initial compound [8, 9]. It has been found recently using a number of the most active catalytic systems (Ni(PPh₃)₄/BF₃ · OEt₂/ROH) that their activity in oligomerization of unsaturated hydrocarbons (ethylene, styrene) depends linearly on the concentration of the cationic Ni(I) complexes in these systems [10, 11], which allows one consider the Ni(I) cationic complexes as catalytically active species of the coordination-ionic transformation of unsaturated hydrocarbons.

However, the discovered regularities do not exclude the possible disproportionation of the cationic Ni(I) complexes to the Ni(II) and Ni(0) complexes at the initial moment and further reaction on the Ni complexes in the common oxidation states according to a traditional hydride or metallocyclic mechanism, respectively. At the same time, the available data on the stability of electroneutral Ni(II) phosphine complexes in aprotic solvents indicate the opposite situation, i.e., the predominant counterdisproportionation process Ni(II) + Ni(0) \longrightarrow 2Ni(I). For example, in the reactions occurring in aprotic solvents

$$(Ph_3P)_2NiX_2 + Ni(PPh_3)_4 \longrightarrow 2(Ph_3P)_3NiX, \quad (1)$$

$$(Ph_3P)_2NiX_2 + (\eta^2 - C_2H_4)Ni(PPh_3)_2$$

$$\longrightarrow 2(Ph_3P)_2NiX + C_2H_4,$$
(2)

where X = Cl, Br, the equilibrium is fully shifted to the right [12], which is widely used in the synthesis of the Ni(I) halide complexes with various phosphine ligands [13, 14].

The analogous processes are observed also in the case of the neutral nickel cyclopentadienyl complexes in toluene [15]:

$$NiCp_2 + Ni(PPh_3)_4 \longrightarrow 2CpNi(PPh_3)_2.$$
 (3)

To establish the participation in the counterdisproportionation reaction of the cationic Ni(II) complexes in addition to the neutral complexes, we studied in this work the interaction of Ni(II) bis-tetrafluoroborate complexes ([Ni(Dppe)_2](BF_4)_2 and [Ni(CH_3CN)_6](BF_4)_2, where Dppe = 1,2-bis(diphenylphophino)ethane) with Ni(0) phosphine complexes in the 1 : 1 mixture of toluene–acetonitrile.

EXPERIMENTAL

All the procedures were performed in the atmosphere of dry argon using the Schlenk technique. The precipitates were filtered on glass Schlenk filters. The

Complex*	g_{\parallel}	g_{\perp}	A _∥ , mT	A_{\perp}, mT
[Ni(Dppe) ₂]X				
$X = BF_4$	2.160	2.036	5.46(4P)	6.76(4P)
$X = AlCl_3Et$ [23]	2.160	2.031	5.3(4P)	6.7(4P)
$[(PPh_3)_3NiLNi(PPh_3)_3](BF_4)_2$				
Tricoordinate Ni(I)	2.454**	2.109**		
Tetracoordinate Ni(I)	1.980***	2.425***		
[Ni(PPh ₃) ₃]BF ₄ [24]	2.385 _z	2.12_{v}	6.1(1P) _z	$6.4(1P)_{y}$
		2.07 _r		8.1(1P) _r

 2.420_{v}

 2.476_{x}

1.973-

Parameters of EPR spectra of Ni(I) complexes

* $L = CH_3CN$.

 $[LNi(PPh_3)_3]BF_4$

** Signal 1'b (Fig. 2).

*** Signal *1"b* (Fig. 2).

prepared and synthesized reagents were kept in sealed tubes under argon.

Toluene, hexane (Merck) were distilled before use over metallic sodium in the atmosphere of argon. Acetonitrile (Merck) was additionally dried over molecular sieves (Aldrich 3A). All the solvents before use were degassed in vacuum and saturated with argon.

Commercial reagents triphenylphosphine, triethylphosphite, diphenylphosphinoethane (Merck) were used as received.

The Ni complexes $[Ni(PPh_3)_3]BF_4$, $Ni(PPh_3)_4$, Ni(Dppe)₂, $[Ni(Dppe)_2](BF_4)_2$, $[Ni(CH_3CN)_6](BF_4)_2$ were synthesized by the known procedures [10, 16-19], respectively, while the Co complexes $N_2Co(PPh_3)_3$ and $[Co(CH_3CN)_6](BF_4)_2$ were prepared as described in [19, 20].

The EPR spectra were recorded on a CMS-8499 spectrometer (working frequency 9.6 GHz) at a boiling point of liquid nitrogen. The sweep range was calibrated using the diphenylpicrylhydrazyl (DPPH) free radical and Mn²⁺ in MgO. The EPR spectra were simulated with our own program [21], where the hyperfine interaction (HFI) is limited to the second-order term and the main axes of the g-tensor and HFI tensors coincide.

RESULTS AND DISCUSSION

The starting Ni(II) and Ni(0) complexes $([Ni(Dppe)_2](BF_4)_2, [Ni(CH_3CN)_6](BF_4)_2, Ni(Dppe)_2, and Ni(PPh_3)_4)$ in 1 : 1 toluene–acetonitrile mixture (v/v) at 77 K do not produce EPR signals. The use of vitrifying toluene–acetonitrile mixture [22] provided satisfactory solubility of the starting cationic Ni(II) complexes. After the solutions of the Ni(II) and Ni(0) complexes were mixed, stirred for 30 s at room temperature (the molar ratio Ni(II) : Ni(0) = 1 : 1), and cooled

to 77 K, the EPR spectra were recorded. The EPR spectra were characteristic of the Ni(I) compounds, and the integrated intensity corresponded within the experimental error to the total concentration of nickel in a system. Hence, in a toluene-acetonitrile mixture, the process of couterdisproportionation occurs between the cationic Ni(II) complexes and the Ni(0) complexes with the formation of the Ni(I) complexes almost in the quantitative amount. Thus, not only neutral Ni(II) complexes [12–15], but also the cationic Ni(II) complexes in combination with phosphine Ni(0) complexes counterdisproportionate in a solution to the Ni(I) complexes.

Now let us consider the structures of the obtained cationic Ni(I) complexes using the EPR data (see in the table).

The system $[Ni(Dppe)_2](BF_4)_2-Ni(Dppe)_2$. The EPR spectrum of a complex formed in this system (Fig. 1, *I*) contains hyperfine structure (HFS) from four practically equivalent ³¹P nuclei and corresponds to a tetragonal symmetry of the complex and quantitatively coincides with the spectrum of the $[Ni(Dppe)_2]AlCl_3Et$ complex identified previously in the $Ni(Dppe)_2$ -AlCl₂Et system formed in toluene [23]. Therefore, the cationic Ni(I) complex $[Ni(Dppe)_2]^+$ is also formed in the system $[Ni(Dppe)_2](BF_4)_2-Ni(Dppe)_2$ as a result of the counterdisproportionation reaction

$$[Ni(Dppe)_2](BF_4)_2 + Ni(Dppe)_2$$

$$\longrightarrow 2[Ni(Dppe)_2]BF_4.$$
(4)

The system $[Ni(CH_3CN)_6](BF_4)_2-Ni(Dppe)_2$. The EPR spectrum of a given system (Fig. 1, 2) appears as superposition of signals, one of them being due to the $[Ni(Dppe)_2]BF_4$ complex. If the counterdisproportionation reaction is performed in the presence of a free ligand Dppe (in equimolar amount with respect to the total content of nickel or in a higher amount), then only the spectrum of the $[Ni(Dppe)_2]BF_4$ complex is

Vol. 34 No. 6 2008



Fig. 1. The EPR spectra of the systems (*I*) $[Ni(Dppe)_2](BF_4)_2-Ni(Dppe)_2, (2) [Ni(CH_3CN)_6](BF_4)_2-Ni(Dppe)_2, (4) [Ni(CH_3CN)_6](BF_4)_2-Ni(PPh_3)_4 in a mixture toluene-acetonitrile at$ *T*= 77 K. Spectrum 3 is produced by subtraction of signal*I*from signal 2; (*) is a signal from DPPH.

recorded. Obviously, in the presence of a free Dppe, several Ni(I) complexes are formed in the system with different number of bidentate phosphine ligands. Signal 3 in the EPR spectrum (Fig. 1, 3) presents the result of the computer subtraction of individual signal 1 from signal 2. This signal $(g_{\parallel} > g_{\perp})$ contains HFS from the ³¹P nuclei, but it is not individual signal, which indicates that the system contains different in composition and (or) geometry Ni(I) complexes with one bidentate phosphine ligand. With account for the stoichiometry aspects, the system should also contain the Ni⁺ ions stabilized only by the acetonitrile molecules. The relatively high stability of the Ni(I) acetonitrile complexes is evidenced by the fact no colloidal ferromagnetic Ni(0) particles as the most probable products of decomposition of the Ni(I) acetonitrile complexes were discovered.

The system $[Ni(CH_3CN)_6](BF_4)_2-Ni(PPh_3)_4$. The EPR spectrum of Ni(I) complex in this system (Fig. 1, 4) corresponds to the ratio $g_{\parallel} > g_{\perp}$ and contains, like spectrum 3, the HFS from the ³¹P nuclei, but is not individual. This indicates the possibility of formation in



Fig. 2. (*a*) The experimental and (*b*) simulated EPR spectra of cationic Ni(I) complexes in vitrifying solutions at T = 77 K: (*l*) [(PPh₃)₃NiLNi(PPh₃)₃](BF₄)₂; (2) [Ni(PPh₃)₃]BF₄; (3) [LNi(PPh₃)₃]BF₄; L = CH₃CN. Curves *l* and *l*" are the components of signal *l*, (*) is a signal from DPPH.

the system of a number of Ni(I) complexes with the number of coordinated phosphine ligands less than 3.

When the reaction of couterdisproportionation is carried out in the presence of a free thiphenylphosphine in the equimolar amount with respect to the total amount of nickel, a novel EPR spectrum is recorded (Fig. 2, 1a), which can be considered as a superposition of two signals from axially-symmetric structures with the inverse ratio of g_{\parallel} and g_{\perp} . Given in the table are the parameters of the EPR modeled signals (1'b and 1''b), whose linear combination in equal ratio (Fig. 2, 1b) reproduces most adequately the experimental spectrum (Fig. 2, 1a). The variation of a free triphenylphosphine quantity in a wide range (1-10) and of the total nickel concentration (10⁻²-10⁻³ mol/l) did not almost influence the shape of the EPR signals. On the one hand, this indicates the coordination saturation of the Ni⁺ ion with the phosphine ligands in the complex, and, on the other hand, suggests steady relationship between the axiallysymmetric structures.

To establish the composition of a new complex, we studied the effect of the solvent nature on the EPR spec-

trum of individual complex [Ni(PPh₃)₃]BF₄ synthesized by the previously developed procedure [10]. The $[Ni(PPh_3)_3]BF_4$ complex in the ether-toluene mixture (1:1) given at T = 77 K the EPR spectrum characteristic for tricoordinate structures [21, 24] with $g_{\parallel} > g_{\perp}$ (Fig. 2, 2a), which does not change after the introduction of a free triphenylphosphine to the system. In a mixture toluene-acetonitrile, the spectrum of this complex fully coincides with that of the system $[Ni(CH_3CN)_6](BF_4)_2 - Ni(PPh_3)_4$, which is formed in the presence of a free triphenylphosphine. Hence, in the counterdisproportionation reaction in the presence of a free triphenylphosphine, the cationic Ni(I) complex is formed that contains three phosphine ligands and acetonitrile. This complex was isolated from a solution by vacuum evaporation at room temperature as a greenbrown powder. Attempts to obtain its crystals suitable for X-ray diffraction analysis were failure. The complex is likely to occur in the amorphous form only.

After the powder was dissolved in the toluene–acetonitrile mixture, the signal of the former intensity (Fig. 2, *1a*) was recorded again. If the above powder was dissolved in THF, the EPR spectrum became more simple and only the signal due to a complex with $g_{\parallel} < g_{\perp}$ was observed (Fig. 2, *3a*), which is characteristic of the trigonally distorted tetrahedral structures [25]. The absence of the HFS from the ³¹P nuclei indicates that the trigonal axis, along which the lone electron is delocalized, does not pass along the Ni-P bond. On the basis of the above data, the following structure was suggested for the paramagnetic complex



where $L = CH_3CN$.

Two signals observed in a mixture toluene–acetonitrile are likely to be due to both tri- and tetracoordinate Ni(I) complexes, which are bonded, for example, by acetonitrile bridges:



The elemental analysis data agree with the empirical formula of the complex

For C₁₁₀H₉₃B₂F₈NNi₂P₆

anal. calcd (%):	C, 69.33;	Н, 4.92;	N, 0.73
Found (%):	C, 70.24;	H, 5.1;	N, 0.82

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY V

The equatorial and azimuthal delocalization of the lone electrons in two bonded Ni(I) complexes is, probably, the main reason for their weak magnetic interaction in a binuclear structure.

The formation of a binuclear Ni(I) complex can be represented as follows:

$$[\operatorname{NiL}_6]X_2 + \operatorname{Ni}(\operatorname{PPh}_3)_4 + 2\operatorname{PPh}_3$$

$$\longrightarrow [(\operatorname{PPh}_3)_3\operatorname{NiLNi}(\operatorname{PPh}_3)_3]X_2 + 5L,$$
(5)

where $L = CH_3CN$, $X = BF_4$.

The existence of the cationic binuclear Ni(I) complex indirectly suggests that the binuclear structure is formed prior to the stage of the electron transfer between the Ni atoms. In the THF solution, the binuclear complex dissociates to monomers.

Note in conclusion that a single-electron transfer in a mixture toluene-acetonitrile occurs not only between Ni(II) and Ni(0), but also between Ni(II) and Co(0) and Co(II) and Ni(0), which results in the formation of the Ni(I) complexes. For instance, an intense EPR signals almost coinciding with a signal in Fig 2 (1a) is observed in the systems $[Ni(CH_3CN)_6](BF_4)_2 - N_2Co(PPh_3)_3$ $[Co(CH_3CN)_6](BF_4)_2$ -Ni(PPh₃)₄, which are formed in the presence of a free triphenylphosphine. Obviously, the complexes with the composition $[(PPh_2)_3NiLNi(PPh_2)_3]X_2$ and $[(PPh_3)_3NiLCo(PPh_3)_3]X_2$ are formed in the above systems in addition to the $[(PPh_3)_3CoLCo(PPh_3)_3]X_2$. In the former complexes, the Co⁺ ions in both tetra- and tricoordinate surrounding are likely to occur in a high-spin state and are not registered in the EPR spectrum at T = 77 K. The magnetic interaction between the Ni⁺ and Co⁺ ions in a heteronuclear complex is, obviously, responsible for the additional broadening of the EPT lines of the Ni⁺ ions, whose major width (25-30 mT) is determined by the orbital degeneracy of the Ni⁺ ground state in the tetra- and tricoordinate surrounding.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research—CRDF (grant no. 07-03-91123) and DAAD (grant no. A/05/56802).

REFERENCES

- Keim, W., Behr, A., Poper, M., *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F.G.A., and Abel, E.W., Eds., Oxford: Pergamon, 1982, vol. 8, p. 371.
- Shmidt, F.K., Kataliz kompleksami perekhodnykh metallov pervogo perekhodnogo ryada reaktsii gidrirovaniya i dimerizatsii (Catalysis of Hydrogenation and Dimerization by First Transition Row Metal Complexes), Irkutsk: IGU, 1986.
- Zhang, L., Brookhart, M.A., and White, P.S., Organometallics, 2006, vol. 25, no. 8, p. 1868.
- Pasynkiewicz, S., Oledzka, E., and Pietrzykowski, A., J. Mol. Catal. A, 2004, vol. 224, nos. 1–2, p. 117.

Vol. 34 No. 6 2008

- 5. Tolman, C.A., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 14, p. 4217.
- Shmidt, F.K., Mironova, L.V., Kalabina, A.V., et al., Neftekhimiya, 1976, vol. 16, no. 4, p. 547.
- 7. Keim, W., Angew. Chem., 1990, vol. 102, no. 3, p. 251.
- Saraev, V.V. and Shmidt, F.K., *Koord. Khim.*, 1997, vol. 23, no. 1, p. 45 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 23, no. 1, p. 40].
- 9. Saraev, V.V. and Shmidt, F.K., J. Mol. Catal. A, 2000, vol. 158, no. 1, p. 149.
- Saraev, V.V., Kraikivskii, P.B., Zelinskiy, S.N., et al., J. Mol. Catal. A, 2005, vol. 236, nos. 1–2, p. 125.
- 11. Saraev, V.V., Kraikivskii, P.B., Annenkov, V.V., et al., *ARKIVOC*, 2005, no. XV, p. 44.
- 12. Heimbach, P., Angew. Chem., 1964, vol. 76, no. 13, p. 586.
- Saraev, V.V., Shmidt, F.K., Mironova, L.V., and Gruznykh, V.A., *Koord. Khim.*, 1976, vol. 2, no. 9, p. 1249.
- 14. Nilges, M.J., Barefield, E.K., Belford, R.L., and Davis, P.H., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 3, p. 755.
- Saraev, V.V., Kraikivskii, P.B., Zelinskii, S.N., et al., *Koord. Khim.*, 2006, vol. 32, no. 6, p. 413 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 6, p. 397].

- 16. Venanzi, L.M., J. Chem. Soc., 1958, vol. 63, no. 2, p. 719.
- 17. Hartung, H., Baumeister, U., Walter, B., and Maschmeier, M., Z. Anorg. Allg. Chem., 1989, vol. 578, no. 1, p. 177.
- Miedaner, A., Curtis Haltiwanger, R., and DuBois, D.L., Inorg. Chem., 1991, vol. 30, no. 3, p. 417.
- 19. De Souza, R.F., Monteriro, A.L., Seferin, M., et al., *J. Coord. Chem.*, 1996, vol. 40, no. 4, p. 311.
- 20. Speier, G. and Marko, L., *Inorg. Chim. Acta*, 1969, vol. 3, p. 126.
- 21. Saraev, V.V., Kraikivskii, P.B., Lazarev, P.G., et al., *Koord. Khim.*, 1996, vol. 22, no. 9, p. 648 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 22, no. 9, p. 608].
- 22. Meyer, B., *Low Temperature Spectroscopy*, New York: American Elsevier, 1971.
- 23. Saraev, V.V., Shmidt, F.K., Gruznykh, V.A., et al., *Koord. Khim.*, 1979, vol. 5, no. 6, p. 897.
- Kraikivskii, P.B., Saraev, V.V., Matveev, D.A., et al., *Koord. Khim.*, 2003, vol. 29, no. 6, p. 461 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 29, no. 6, p. 431].
- 25. Saraev, V.V., Kraikivskii, P.B., Lazarev, P.G., et al., *Koord. Khim.*, 1996, vol. 22, no. 9, p. 655 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 22, no. 9, p. 615].