Paramagnetic Nickel(I) Complexes and Their Role in the Catalytic Dimerization of Norbornadiene

Ya. Ya. Otman, O. S. Manulik, and V. R. Flid

Moscow State Academy of Fine Chemical Technology, Moscow, 119571 Russia
e-mail: vitaly-flid@yandex.ru
Received November 9, 2007

Abstract—The kinetics of the formation of a paramagnetic nickel(I) complex from bis(η^3-allyl)nickel under conditions of catalytic norbornadiene dimerization is reported. It is demonstrated by ESR and GLC that the concentrations of Ni(I), norbornadiene and its pentacyclic dimers change in the same way. It might be inferred from this finding that Ni(I) is involved in the catalytic process as an intermediate. However, experiments on model systems have not confirmed this assumption. At the same time, they have not ruled out the participation of the paramagnetic complex in side catalytic reactions. The presence of Ni(I) in the reaction system is connected with the presence of free norbornadiene there. Hypotheses as to the probable structure and formation mechanism of the paramagnetic Ni(I) are suggested.

DOI: 10.1134/S0023158408040046

Due to the steady progress in physical methods of analysis, it is increasingly becoming possible to detect and control the conversion of intermediates directly during the catalytic reaction. However, elucidating the role of intermediate complexes in catalysis often poses serious difficulties. For example, in a number of processes catalyzed by nickel compounds, such as the dimerization, oligomerization, and polymerization of alkenes, dienes, and alkynes, paramagnetic Ni(I) complex species were detected by ESR [1–8]. It was suggested that these compounds are typical of nickel-complex catalysts and that both paramagnetic and diamagnetic alkyl or hydride nickel complexes stabilized by the substrate can be the reactive species in the above reactions [9, 10]. Nevertheless, the available data do not suggest any unambiguous conclusion regarding the participation of the paramagnetic species in the catalytic reaction.

The starting nickel compounds—bis(η^3-allyl)nickel and nickel tetracarbonyl—were synthesized by standard procedures [11, 12].

Bis(η^3-allyl)nickel was obtained by reacting anhydrous $NiBr_2$ with C_3H_5MgCl in diethyl ether ($NiBr_2/C_3H_5MgCl = 1 : 2$ mol/mol) at –5 to –10°C in vacuo (0.1 Pa) or in dry, thoroughly purified argon. All chemicals were purified before experiments. The yellowish orange reaction solution was concentrated using a low-temperature Vigreaux column, and the product was cooled to –80°C. Bis(η^3-allyl)nickel crystallized as yellow needles. The complex was sublimed in vacuo and was recrystallized from *n*-pentane at –80°C. Yield: 63%.

Nickel tetracarbonyl was obtained from a nickel chloride solution in methanol at the atmospheric pressure of CO. The reducing agent was an iron metal powder. The reaction was performed for 12 h at 20°C in the presence of small amounts of Na_2S. $Ni(CO)_4$ yield: 72%.

Nickel metal was evaporated onto a frozen norbornadiene (NBD) matrix (77 K) using a rotary vacuum setup with electrodes mounted inside. Nickel evaporation was carried out at 0.001 Pa. After the completion of the process, the temperature was raised to –5°C and the dark red solution was poured out into the reactor to be used in kinetic studies.

All manipulations involved in the synthesis and storage of the complexes and the transfer of the complexes into the reactor were carried out in vacuo (0.1 Pa) or in dry, thoroughly purified argon. The complexes were stored in vacuumized tubes at 77 K or were synthesized immediately before the experiment.

Norbornadiene (Aldrich, 99%) was distilled from sodium metal before use.

Toluene, benzene, and *meta*-xylene (special purity grade) were distilled from sodium metal in the presence of benzophenone before use.

Kinetic experiments were carried out in temperature-controlled pumped 25-ml reactors fitted with a sampler. Kinetic data were processed using the DynaFit program (version 3.28.024). Analysis of the reaction mixture and reaction monitoring were carried out by gas chromatography (Kristall-2000 chromatograph with DB-35, SPB-20, and Supelco β-Dex capillary columns; an Al_2O_3-packed column; a flame ionization detector; and a thermal conductivity detector).
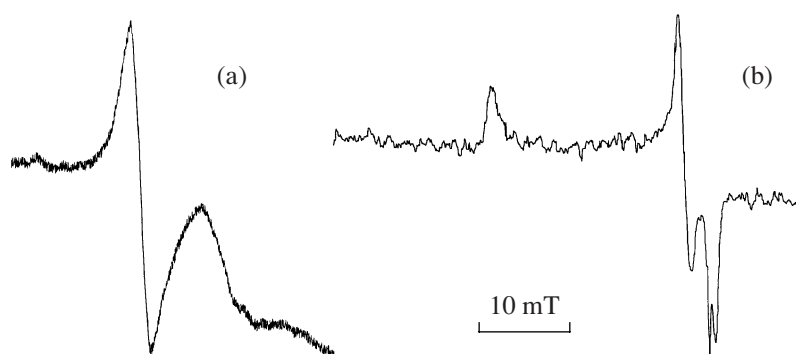
Fig. 1. ESR spectra of the Ni(I) complex resulting from the interaction between Ni(C₃H₅)₂ and norbornadiene: (a) T = 298 K (g = 2.066); (b) T = 77 K (g_1 = 2.002, g_2 = 2.021, g_3 = 2.166). The solvent is *meta*-xylene.

ESR studies of solutions were carried out in standard quartz tubes (Bruker) fitted with a vacuum valve. Norbornadiene and *meta*-xylene were place in a tube (total volume of 0.30 ml), and bis(η^3-allyl)nickel (0.005–0.05 g) was transferred into this tube by recondensation. ESR spectra were recorded on an ER-200 spectrometer (Bruker) operating at 9.7 Hz. A capillary with a crystalline standard (2,2-diphenyl-1-picrylhydrazyl, DPPH) was in the resonator of the spectrometer throughout the experiment. The signal from DPPH served as a *g*-factor reference and was used in the measurements of the relative concentration of paramagnetic centers in the samples.

Reaction products were identified by GC/MS and NMR spectroscopy. Mass spectra were recorded using an Agilent 6890 GC instrument with an MSD detector (5973 N) at an ionization energy of 50 eV. The ionization current was 100 mA, and the source temperature was 150°C. NMR spectra were recorded on a Bruker DPX-300 spectrometer (^{1}H, 300 MHz, CDCl₃ or C₆D₆; ^{13}C, 70 MHz, CDCl₃). The norbornadiene dimer structure was identified with reference to the literature [13–15].

Elemental and quantitative analyses were carried out using a Hitachi S-800 electron microscope with an energy-dispersive LZ-5 detector (Oxford Instruments). The accuracy of weight fraction determination was at least 0.01%.

RESULTS AND DISCUSSION

In the catalytic homodimerization of norbornadiene (reaction (I)) using the η^3-allyl nickel complexes Ni(η^3-all)₂ (η^3-all = C₃H₅, 1-CH₃C₃H₄, 2-CH₃C₃H₄) as catalyst precursors, we detected the formation of a paramagnetic nickel(I) complex [16].

(I)
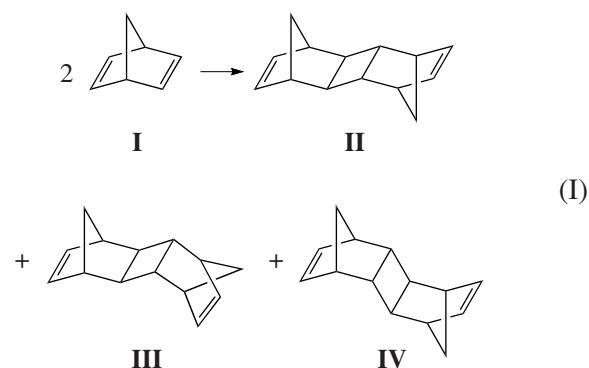
The shape and magnetic parameters of the ESR spectrum (Fig. 1) and a comparison of this spectrum with literature data [17–20] indicate that both the isotropic and anisotropic components are due to nickel(I) with the electronic configuration $3d^9$ and the spin moment 1/2. The formation of the paramagnetic nickel(I) complex was detected for the first time in a system free of common stabilizing ligands and Brønsted or Lewis acids [21, 22]. Moreover, upon the introduction of such compounds (phosphines, phosphites, and amines of various structures), the paramagnetic signals disappear. It is difficult to carry out a systematic study of the nickel(I) complex because of its extremely low concentration in the reaction solution (the fraction of Ni(I) is 10^{-4}–10^{-6} of the total nickel content of the system).

The structure of the allyl ligand (η^3-allyl, 2-methyl-η^3-allyl, or 1-methyl-η^3-allyl) has no effect on the ESR spectrum of the Ni(I) complex. This indicates that the unpaired electron is almost completely localized on the metal atom.

Since the Ni(I) complex is in a system in which a catalytic reaction takes place, we consider it necessary to study the formation kinetics of the paramagnetic species.

An analysis of the material balance and kinetic data indicates that a stoichiometric reaction between Ni(all)₂ and several norbornadiene molecules occurs initially, accompanied by the replacement of allyl ligands in the
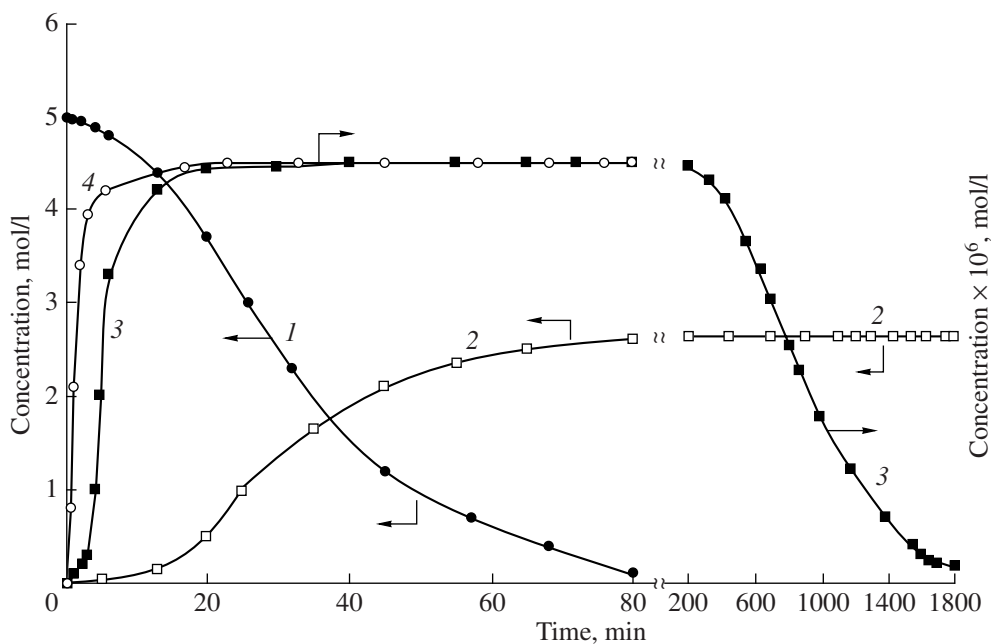
Fig. 2. Variation of the concentrations of norbornadiene, its dimers, and the paramagnetic nickel complex during the kinetic run at 333 K: (*1*) norbornadiene, (*2*) pentacyclic dimers of norbornadiene, (*3*) Ni(I) without addition of Ni(C$_7$H$_8$)$_2$ ([Ni(C$_3$H$_5$)$_2$] = 0.050 mol/l), and (*4*) Ni(I) upon addition of Ni(C$_7$H$_8$)$_2$ ([Ni(C$_3$H$_5$)$_2$] = [Ni(C$_7$H$_8$)$_2$] = 0.025 mol/l).

complex (stoichiometric norbornadiene allylation) [23, 24]. At 25°C, the reaction is almost complete in a few minutes.

The curves plotted in Fig. 2 show how the concentrations of norbornadiene, its dimers, and the paramagnetic Ni(I) complex vary during the reaction. These data were obtained by GC and ESR. The reaction time was counted from the instant bis(η^3-allyl)nickel was added to the norbornadiene solution. The paramagnetic nickel complex concentration curve is S-shaped. The formation of the complex takes place during the induction period of norbornadiene cyclodimerization, the main catalytic process. After the induction period, the Ni(I) concentration reaches a steady-state level and almost does not change while there is free norbornadiene in the reaction system. At the end of the induction period, Ni(η^3-all)$_2$ in the system is almost completely absent (according to GC data, ~100% material balance is achieved for the products containing allyl groups). In spite of this, it is not impossible that the Ni(C$_3$H$_5$)$_2$ complex is present in large excess relative to Ni(I).

Our earlier detailed investigation of the formation of the true catalyst of norbornadiene cyclodimerization indicated the formation of the complex Ni(NBD)$_2$. The preparation and isolation of this complex is described in [25, 26]. The simultaneous presence of Ni(NBD)$_2$ and Ni(all)$_2$ in the system is a necessary condition for Ni(I) formation. This conclusion was drawn from the following experiment. Upon mixing of separately prepared solutions of these complexes in *meta*-xylene, the Ni(I) formation curve shows no induction period

(Fig. 2). In addition, the induction period of catalytic norbornadiene dimerization is considerably shorter.

Symbatic changes in the concentrations of paramagnetic nickel, norbornadiene, and its pentacyclic dimers (**II–IV**) are also typical of the subsequent stages of the reaction.

The steady-state portion of curve *3* in Fig. 2 corresponds to the catalytic process. The Ni(I) concentration decreases during this process. The Ni(I) disappearance rate is much higher when the reaction is conducted in the liquid phase (in the presence of a solvent) than when the reaction is conducted in the norbornadiene bulk (dimer **II**, which is the main product under these conditions, is a solid compound). When the solvent and the unreacted norbornadiene are removed during the reaction, the paramagnetic complex incorporated into structure **II** is stable in the solid state at room temperature in the absence of oxygen over several days.

The symbasis of the kinetic curves characterizing the changes of the concentrations of norbornadiene, its dimers, and the paramagnetic nickel complex during the reaction suggests that the complex can be an intermediate in the catalytic dimerization of norbornadiene.

Obviously, the nickel (I) complex includes one or several norbornadiene molecules, which act as stabilizers. The dependence of the relative amount of paramagnetic species on the allyl structure in the initial complex indicates that the formation of Ni(I) may involve the allyl ligand and its relative concentration increases as the positive charge on the Ni atom decreases [27]. For example, in the reactions of norbornadiene with homo-

ligand η^3-allyl nickel complexes, namely, $Ni(C_3H_5)_2$, $Ni(1\text{-}CH_3C_3H_4)_2$, and $Ni(2\text{-}CH_3C_3H_4)_2$, under identical conditions, the steady-state relative concentrations of paramagnetic nickel differ substantially. At 298 K, these concentrations are, respectively, 9×10^{-5}, 3×10^{-4}, and 1×10^{-6} of the total nickel concentration. As was shown above, when norbornadiene is in excess, each of the three bis-η^3-allyl nickel complexes is almost quantitatively converted into the same norbornadiene complex $Ni(C_7H_8)_2$. It is natural that the kinetics of the catalytic cyclodimerization of norbornadiene is absolutely identical for precursors with different allyl ligands.

The nickel(I) complex may have structure **V**, and a possible way of its formation is the counter disproportionation reaction between $Ni(all)_2$ and $Ni(NBD)_2$:

$$(II)$$

V
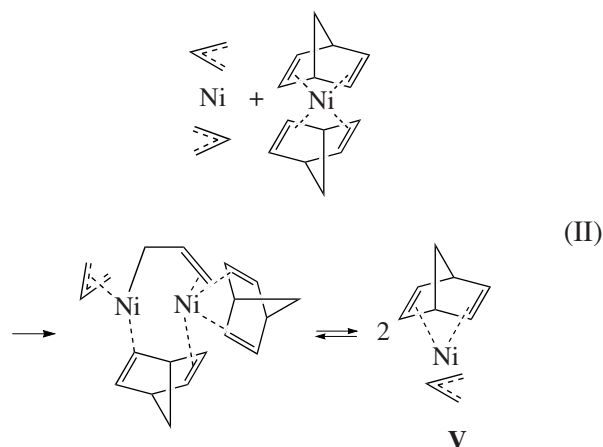
The formation of Ni(I) only via the reaction between $Ni(NBD)_2$ and $Ni(all)_2$ seems unlikely because of the high reactivity of the latter.

The paramagnetic Ni(I) complex may also be of hydride nature (**VI**) and be formed, for example, from **V** according to the reaction

$$(C_3H_5)Ni(C_7H_8) + nC_7H_8$$
$$\longrightarrow H\text{--}Ni(C_7H_8)_n + C_{10}H_{12}. \qquad (III)$$
VI
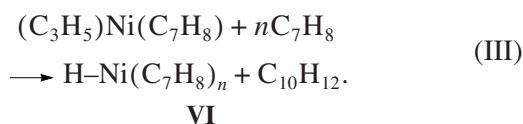
The $C_{10}H_{12}$ compounds are products of stoichiometric norbornadiene allylation [23, 24]. The coefficient n can vary between 1 and 3, depending on the norbornadiene coordination mode in complex **VI**.

In order to elucidate the role of the paramagnetic Ni(I) complex in catalysis, we simulated two systems not based on allyl fragments [25].

In the first case, atomic nickel was evaporated in vacuo onto a norbornadiene matrix frozen at 77 K. Defrosting this matrix yields a dark red reaction solution, indicating the presence of nickel π-complexes with the general formula $[Ni(C_7H_8)_2]_n$ in the system. It is likely that these complexes are polynuclear and differ in the number of nickel atoms. When norbornadiene is in excess, they catalyze its cyclodimerization, though at a smaller rate than in the case of a mononuclear precursor. No paramagnetic species in were detected in this reaction system.

In the second case, the initial complex was nickel tetracarbonyl, $Ni(CO)_4$. As the reaction solution consisting of norbornadiene, the solvent, and a catalytic amount of $Ni(CO)_4$ was heated to 353 K, the complete removal of CO from the coordination sphere of the metal and $Ni(NBD)_2$ formation took place. The solution was cooled to room temperature, and the catalytic reaction that occurred in the system was investigated by ESR. As in the first case, no paramagnetic species were detected in the system. The catalytic activity of the system was comparable with the activity of the $Ni(all)_2$-based system. Evidently, the catalytic reaction (I) does not involve the paramagnetic Ni(I) complex.

The results of this study do not allow us to make a substantiated conclusion as to the structure of this complex. It is possible to claim, however, that, if the paramagnetic Ni(I) complex contains an allyl fragment, its participation in the catalytic cycle of the main reaction is quite unlikely. If the Ni(I) complex has a hydride nature, it can participate in the catalytic process as an intermediate, but the contribution from the hydride component to the overall norbornadiene cyclodimerization mechanism will be insignificant. Apparently, Ni(0) and Ni(I) compounds catalyze different processes, and a detailed structural study of all products of norbornadiene homodimerization, including the products forming in minor amounts, is required to understand the role of the paramagnetic nickel complex in catalysis. At the same time, it is beyond question that the formation of the Ni(I) complexes under the conditions examined is due to the unique ability of norbornadiene to stabilize unstable compounds in valent states unnatural for them.

ACKNOWLEDGMENTS

REFERENCES

1. Saraev, V.V. and Shmidt, F.K., *Elektronnyi paramagnitnyi rezonans metallokompleksnykh katalizatorov* (Electron Paramagnetic Resonance of Metal Complex Catalysts), Irkutsk: Irkutsk. Gos. Univ., 1985.

2. Pasynkiewicz, S., Oledzka, E., and Pietrzikowski, A., *J. Mol. Catal. A: Chem.*, 2004, vol. 224, nos. 1–2, p. 117.

3. Pasynkiewicz, S., Oledzka, E., and Pietrzikowski, A., *Appl. Organomet. Chem.*, 2004, vol. 18, no. 11, p. 583.

4. Saraev, V.V., Kraikivskii, P.B., Annenkov, V.V., et al., *Kinet. Katal.*, 2005, vol. 46, no. 5, p. 757 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 5, p. 712].

5. Saraev, V.V., Kraikivskii, P.B., Vil'ms, A.I., et al., *Kinet. Katal.*, 2007, vol. 48, no. 6, p. 834 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 6, p. 778].

6. Raspolli, G.A.M., Geri, G., Sbrana, G., et al., *J. Mol. Catal. A: Chem.*, 1996, vol. 111, no. 3, p. 273.

7. Kaminsky, W. and Laban, A., *Appl. Catal., A*, 2001, vol. 222, no. 1, p. 47.

8. Otman, Ya.Ya., Mel'nikov, P.V., Polenov, E.A., and Flid, V.R., *Vestn. MITKhT*, 2007, vol. 2, no. 5, p. 17.

9. 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].

10. Saraev, V.V. and Shmidt, F.K., *J. Mol. Catal. A: Chem.*, 2000, vol. 158, no. 1, p. 127.

11. Flid, V.R., Kuznetsov, V.R., and Dmitriev, D.V., *Kinet. Katal.*, 1999, vol. 40, no. 3, p. 334 [*Kinet. Catal.* (Engl. Transl.), vol. 40, no. 3, p. 301].

12. Dzhemilev, U.M., Popod'ko, N.R., and Kozlova, E.V., *Metallokompleksnyi kataliz v organicheskom sinteze* (Catalysis by Metal Complexes in Organic Synthesis), Moscow: Khimiya, 1999.

13. Arnold, D.A., Trecker, D.J., and Whipple, E.B., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 12, p. 2596.

14. Khalilov, L.M., Shitikova, O.V., Spirikhin, L.V., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2000, no. 1, p. 63.

15. Khusnutdinov, R.I., Dokichev, V.A., Panasenko, A.A., et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, no. 11, p. 2492.

16. Flid, V.R., Manulik, O.S., Grundel, L.M., and Belov, A.P., *Teor. Eksp. Khim.*, 1990, no. 4, p. 490.

17. Nobile, C.F., Vasapollo, G., Giannoccaro, P., and Sacco, A., *Inorg. Chim. Acta*, 1981, vol. 48, no. 2, p. 261.

18. Barefield, E.K., Krost, D.A., and Edvards, D.S., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 20, p. 6219.

19. 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].

20. Saraev, V.V., Tkach, V.S., and Kraikivskiii, P.B., *Koord. Khim.*, 1998, vol. 24, no. 8, p. 602 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 24, no. 8, p. 397].

21. 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].

22. Saraev, V.V., Kraikivskii, P.B., Zelinskii, S.N., et al., *Koord. Khim.*, 2001, vol. 27, no. 2, p. 136 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 27, no. 2, p. 123].

23. Flid, V.R., Manulik, O.S., Dmitriev, D.V., et al., *Eurasian Chem. Tech. J.*, 2001, vol. 3, no. 11, p. 73.

24. Flid, V.R., Manulik, O.S., Belov, A.P., and Grigor'ev, A.A., *Metalloorg. Khim.*, 1991, vol. 4, no. 4, p. 864.

25. Flid, V.R., Manulik, O.S., Grigor'ev, A.A., and Belov, A.P., *Kinet. Katal.*, 1998, vol. 39, no. 1, p. 56 [*Kinet. Catal.* (Engl. Transl.), vol. 39, no. 1, p. 51].

26. Flid, V.R., Manulik, O.S., Grigor'ev, A.A., and Belov, A.P., *Kinet. Katal.*, 2000, vol. 41, no. 5, p. 658 [*Kinet. Catal.* (Engl. Transl.), vol. 41, no. 5, p. 597].

27. Nesmeyanov, A.N. and Kocheshkov, K.A., *Metody elementoorganicheskoi khimii. Kobal't, nikel', platinovye metally* (Methods of Organometallic Chemistry: Cobalt, Nickel, and the Platinum Metals), Moscow: Nauka, 1978.