ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 2, pp. 235–243. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © F.K. Schmidt, L.B. Belykh, Myagmarsuren Gomboogiin, Yu.Yu. Titova, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 2, pp. 250–258.

Formation and Nature of Catalysts Based on Nickel(0) Phosphine Complexes Active in Lower Alkene Dimerization and Oligomerization

F. K. Schmidt[a], **L. B. Belykh**[a], **Myagmarsuren Gomboogiin**[b]†, and **Yu. Yu. Titova**[a]
[a] *Irkutsk State University, Irkutsk, 664033 Russia*
[b] *National University of Mongolia, Ulan Bator, Mongolia*
e-mail: fkschmidt@chem.isu.ru

Received October 15, 2008

Abstract—The catalytic properties and formation mechanism of alkene dimerization–active complexes in systems based on $Ni(PPh_3)_4$ and boron trifluoride etherate are considered. The nature of the modifying action of Brønsted acids on the properties of metal complex catalysts for propylene dimerization is reported. The interaction between $Ni(PPh_3)_4$ and $BF_3 \cdot OEt_2$ is influenced by water. Depending on the water concentration, the reaction can proceed via formally one-electron oxidation to yield cationic Ni(I) complexes or via two-electron oxidation to yield Ni(II) hydrides. The catalytically active species in alkene dimerization and oligomerization in these systems are Ni(II) hydrido complexes.

DOI: 10.1134/S0023158410020114

The catalytic acceleration of lower alkene (C_2–C_4) dimerization and oligomerization by nickel complexes has been the subject of numerous studies [1–3]. In recent years, greatest attention has been focused on systems based on nickel α-diimine and bis(imino)pyridine complexes in combination with organoaluminum compounds, such as methylaluminoxanes [2, 3]. These systems show high productivity on the order of 1×10^6 mol (g-at Ni)$^{-1}$ h^{-1}. However, their productivity per Al g-atom is 2–3 orders of magnitude lower and does not exceed the productivity of conventional Ziegler systems of the $AlEt_2Cl$–$Ni(acac)_2$ type [4, 5].

In our earlier studies of the interaction of $AlR_{3-n}Cl_n$ organoaluminum compounds ($n = 0, 1, 2$) with $Ni(acac)_2$ and with $NiX_2(PR_3)_2$ (X = Cl, Br; R = alkyl, Ph), we established the formation of complexes of nickel in various oxidation states (Ni(II), Ni(I), Ni(0)) with phosphine, alkyl, and hydrido ligands as intermediates or final products [1, 6, 7]. These complexes play the key role in the formation and regeneration of complexes catalytically active in oligomerization. The alkylation of Ni(II) by organoaluminum compounds yields Nu(II) alkyl complexes. It is such complexes with one phosphine ligand in the coordination sphere of nickel that initiate alkene oligomerization and the regeneration of Ni(II) hydrido complexes, which are the true catalytic species. In our earlier work [7], we demonstrated for the first time that aluminum alkyl halides oxidize Ni(0) complexes to Ni(I). Under conditions of the catalytic oligomerization of lower alkenes (ethylene, propylene), the Ni(I) complexes undergo disproportionation to Ni(II) and Ni(0) [7]. Thus, the intermediate Ni(I) complexes are involved in the formation and regeneration of catalytically active species. We discovered the formation of the cationic complexes Ni(I)–$[Ni(PPh_3)_nL_{3-n}]BF_4$ ($n = 1, 2, 3$; $L = OEt_2$) in the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system [8] and demonstrated that the $[Ni(PPh_3)L_2]BF_4$ complexes are the precursors of the catalytic species in dimerization and oligomerization [8, 9]. It was established by chemical modeling that the Ni(II) hydrido complexes resulting from the interaction of Ni(0) with Brønsted acids are also catalytically active in alkene oligomerization [10, 11]. These results were later confirmed by other authors [12, 13].

However, Saraev et al. [14, 15], who investigated the same catalytic system $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ and the $[Ni(PPh_3)_3]BF_4$ complex, claim, without presenting any direct experimental evidence, that the main contribution to the acceleration of oligomerization is from cationic Ni(I) complexes and that the catalytic cycle involves σ-carbocations resulting from the interaction of these cationic Ni(I) complexes with alkenes in toluene.

The purpose of this work was to further investigate the catalytic properties of the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system in propylene dimerization and to elucidate the mechanism and nature of the catalytic nickel complexes.

---

† Deceased.

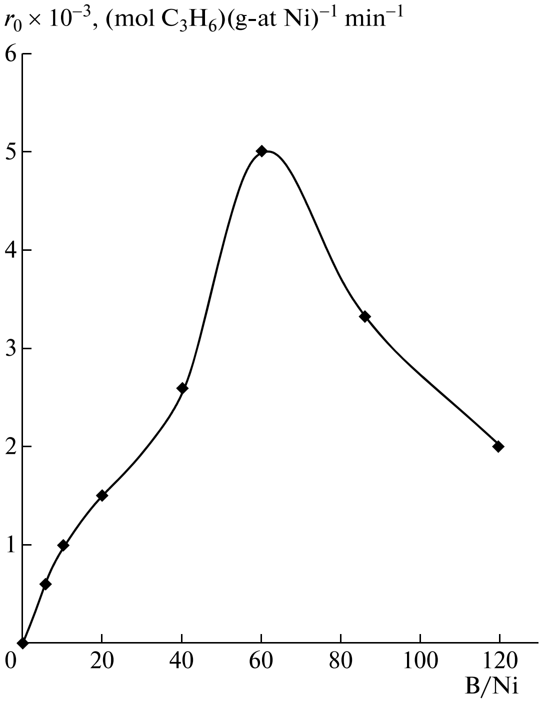


Fig. 1. Initial propylene dimerization rate (r_0) as a function of the B/Ni molar ratio in the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system. Reaction conditions: $C_{Ni} = 5 \times 10^{-3}$ mol/l, toluene as the solvent, $T = 15°C$.

EXPERIMENTAL

Chemicals and Solvents

Toluene was purified via a standard procedure used in organometallic chemistry [16]. The water concentration, measured by the Fischer method, was 2×10^{-3} mol/l in toluene and 3×10^{-2} mol/l in toluene-d_8.

Boron trifluoride etherate was vacuum-distilled from calcium hydride (53°C, 46 Torr) and was stored in a Schlenk flask as a 0.5 M solution in degassed toluene in an argon atmosphere. Hydrogen fluoride was removed from boron trifluoride by passing the latter through a column filled with boric anhydride and sodium fluoride. Brønsted acids were introduced into the catalytic system as toluene solutions.

$Ni(PPh_3)_4$ was synthesized as described in [17]; $[Ni(PPh_3)_3]BF_4$, as described in [8].

Catalyst Preparation

The catalyst was prepared in an argon or propylene atmosphere.

Catalyst preparation in an argon atmosphere. The reactor was vacuumized and was charged with $Ni(PPh_3)_4$ and degassed toluene under flowing argon. A toluene solution of boron trifluoride etherate was added to the $Ni(PPh_3)_4$ solution. The resulting solution was transferred into a temperature-controlled shaker, which was prevacuumized and then prefilled with propylene. The total volume of the catalyst solution was $V = 20$ ml, and the nickel concentration was $C_{Ni} = 5 \times 10^{-3}$ mol/l. The B/Ni molar ratio was varied between 0 and 120. The reactor was mounted on the shaker platform, and propylene was passed through the solution under vigorous agitation. When gaseous boron trifluoride was used, the reaction mixture was saturated with BF_3.

Catalyst preparation in the presence of propylene. The shaker reactor was vacuumized and was then charged with the nickel complex and degassed toluene under flowing argon. The reaction mixture was saturated with propylene, and a toluene solution of boron trifluoride etherate was added. The reactor was mounted on the shaker platform, and propylene was passed through the solution under vigorous agitation.

Carrying out the Reaction

Propylene was dimerized in a temperature-controlled 150-ml vessel at 1 atm while continuously feeding propylene into the reactor. The reaction products were identified by GLC using two 100-m-long copper capillary columns with dinonyl phthalate and vacuum oil as stationary phases. The carrier gas was nitrogen at a pressure of 0.6 atm, and the oven temperature was 50°C.

NMR spectra were recorded on a WP200SV (Bruker) pulsed spectrometer.

RESULTS AND DISCUSSION

Initially, it was established that the catalytic activity of the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system in propylene dimerization depends not only on the B/Ni molar ratio, but also on the catalyst preparation conditions. In particular, it depends on whether the components of the system interacted in an argon or propylene atmosphere. The initial propylene dimerization rate (r_0) on the catalyst formed in argon as a function of B/Ni passes through a maximum at B/Ni = 60 (Fig. 1).

The service life of the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ catalytic system prepared in argon does not exceed 10 min. A different situation is observed for the catalyst prepared in a toluene solution saturated with propylene ($C_{C_3H_6} \approx 1$ mol/l). In this case, the highest catalytic activity averaged over the reaction time (r_{av}) is attained at much smaller B/Ni ratios. Furthermore, the maximum activity can be increased by keeping $BF_3 \cdot OEt_2$ in a toluene solution before use.

The change in the catalytic activity of the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system caused by prolonged storage of the $BF_3 \cdot OEt_2$ solution in toluene in the light in an open tube can be due to the formation of the Brønsted acid HF in the reaction mixture via $BF_3 \cdot OEt_2$ decomposition yielding an alkyl halide followed by catalytic toluene alkylation [5]. Indeed, modifying

Effect of Brönsted acids on the propylene dimer yield ($C_{Ni} = 5 \times 10^{-3}$ mol/l, $T = 15°C$)

Catalytic system	Ni : B : HX	Dimer yield, mol (g-at Ni)$^{-1}$ h^{-1}	Composition of the dimer mixture, wt %		
			methylpentenes	*n*-hexenes	dimethylbutenes
$Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$	1 : 5 : 0	50	74.0	22.1	3.9
$Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$–H_2SO_4	1 : 5 : 0.7	540	72.2	20.9	6.9
$Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$–C_2H_5OH	1 : 5 : 0.5	560	69.1	29.9	1.0
$Ni(PPh_3)_4$–BF_3–HF	1 : 5 : 0.6	1050	62.6	31.7	5.7
$Ni(PPh_3)_4$–BF_3–HF	1 : 5 : 1	1550	66.9	31.4	1.7
$Ni(PPh_3)_4$–BF_3–H_2SO_4	1 : 5 : 0.25	1580	67.2	30.3	2.4
$Ni(PPh_3)_4$–BF_3–C_2H_5OH	1 : 5 : 0.35	1750	63.3	34.2	2.5
$Ni(PPh_3)_4$–BF_3–$BF_3 \cdot H_2O$	1 : 5 : 1	1600	67.6	26.4	6.0

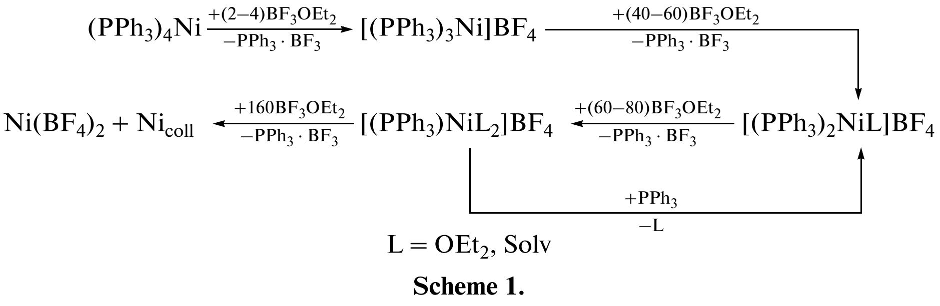
the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ catalytic system with Brønsted acids (H_2SO_4, C_2H_5OH, HF, H_2O) affords a sharp increase in the propylene dimerization rate (Fig. 3, table). The promoting effect of Brønsted acids on nickel catalysts was also observed with gaseous boron trifluoride in place of $BF_3 \cdot OEt_2$ (Fig. 3, table).

Note that the highest stability is shown by the catalytic system activated with ethanol, and the lowest activity is observed for the water-containing system (Fig. 3).

Compounds between hydrogen fluoride and a Lewis acid themselves catalyze alkene oligomerization proceeding via the cationic mechanism. However, the catalytic activity of the BF_3—water complex under the same conditions is at least 200 times lower than the activity of the catalytic system based on Ni(0) complexes, and the main propylene dimerization products in this case are 4- and 2-methylpent-2-ene. The formation of other products in the presence of the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ (or BF_3) catalytic systems promoted with proton-containing compounds (table), specifically, the formation of *n*-hexenes along with isohexenes is direct evidence that the process does not take place via the classical carbocation mechanism.

In order to elucidate the causes of the observed effects, we studied the interaction between the components in the initial system $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ and in the same system promoted with different Brønsted acids.

In an earlier work [8], it was demonstrated that, in the interaction between $BF_3 \cdot OEt_2$ and a $Ni(PPh_3)_4$ solution in toluene, the initial Ni(0) complex oxidizes into $[(PPh_3)_nNi(L)_{3-n}]BF_4$ ($n = 1$–3; L = OEt_2, Solv) complexes, in which nickel is in the oxidation state 1+ and is paramagnetic. The number of phosphine ligands in the coordination sphere of nickel depends on the B/Ni ratio and is $n = 3$ at B/Ni = 2–4, $n = 2$ at B/Ni = 40, and $n = 1$ at B/Ni = 60 (Scheme 1).



Scheme 1.

The coincidence between the B/Ni value at which the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system prepared in an argon atmosphere shows the highest activity (Fig. 1) and the B/Ni value maximizing the concentration of the Ni(I) complex with one phosphine ligand indicates that the $[(PPh_3)Ni(L)_2]BF_4$ complex either is catalytically active itself or is the precursor of active nickel complexes.

The ^1H NMR spectrum of the $Ni(PPh_3)_4$–$4C_2H_5OH$–$20BF_3 \cdot OEt_2$ reaction system at –50°C shows a well-resolved multiplet in a strong field ($\delta = -12.80$ ppm), which is a doublet of triplets with spin–

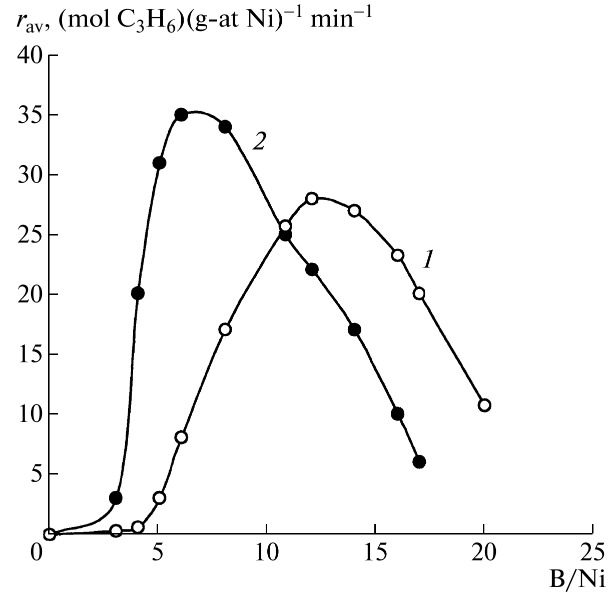


Fig. 2. Average activity of the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system (r_{av}) in propylene dimerization as a function of the B/Ni molar ratio: (*1*) fresh $BF_3 \cdot OEt_2$ solution prepared in the presence of propylene; (*2*) $BF_3 \cdot OEt_2$ solution held in toluene for 20 days. Reaction conditions: $C_{Ni} = 5 \times 10^{-3}$ mol/l, toluene as the solvent, $V = 20$ ml, $T = 15°C$, reaction time of 1 h.

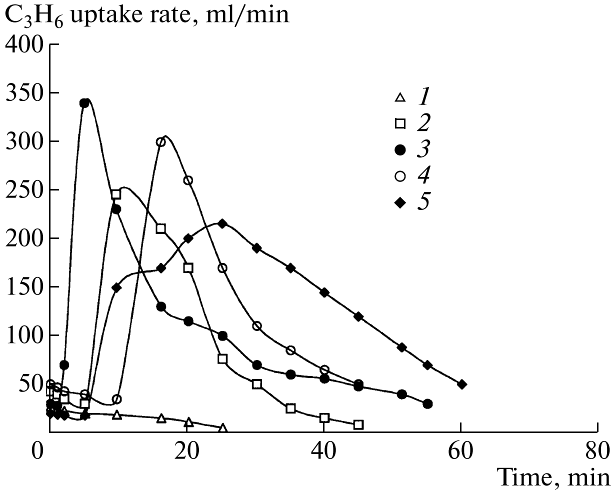
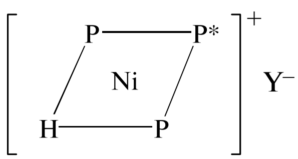


Fig. 3. Effect of Brønsted acids on the propylene uptake rate in the presence of the catalytic system $Ni(PPh_3)_4$–BF_3: (*1*) B : Ni = 5 : 1, (*2*) B : Ni : HF = 5 : 1 : 1, (*3*) B : Ni : H_2SO_4 = 5 : 1 : 0.25, (*4*) B : Ni : $BF_3 \cdot H_2O$ = 5 : 1 : 1, and (*5*) B : Ni : C_2H_5OH = 5 : 1 : 0.25. Reaction conditions: $C_{Ni} = 5 \times 10^{-3}$ mol/l, toluene as the solvent, $V =$ 20 ml, $T = 15°C$.

spin coupling constants of $^2J_{P-H} = 61.0$ Hz and $^2J_{P-H} =$ 92.8 Hz (Fig. 4).

This multiplet structure is due to the interaction of the proton in the coordination sphere of Ni with two equivalent phosphorus atoms ($^2J_{P-H} = 61.0$ Hz) and with one more distant phosphorus atom ($^2J_{P-H} =$ 92.8 Hz). Raising the temperature to –10°C gives rise to a poorly resolved multiplet feature, which turns into a doublet at +20°C. This is due to the stereochemical nonrigidity of the complex nickel hydride $[(PPh_3)_3NiH]BF_3OEt$. This is a well-known property of nickel hydrides with three phosphine ligands [18]. At –50°C and below, the chemical shifts of the two kinds of phosphorus nuclei differ significantly, and this leads to an A_2X-type spectrum.

Thus, the $[(PPh_3)_3NiH]BF_3OEt$ complex at low temperatures has a static structure in which the metal atom has a square-planar coordination sphere with two phosphine ligands *cis* to the proton and one phosphine ligand in the *trans* position:



Y^- $Y = BF_3OEt^-$; $P = PPh_3$.

The formation of Ni(II) hydrido complexes in the $Ni(PPh_3)_4$–4EtOH–$20BF_3OEt_2$ system can be attributed to the following reactions:

$$C_2H_5OH + BF_3OEt_2 \rightleftharpoons H^+BF_3OEt^- + Et_2O,$$

$$Ni(PPh_3)_4 + H^+BF_3OEt^-$$

$$\xrightarrow{-PPh_3} [HNi(PPh_3)_3]^+BF_3OEt^-.$$

Nickel hydrido complexes of the $[(PPh_3)_3NiH]BF_4$ type are coordinatively saturated, so it is natural that they are inactive in dimerization. The $[(PPh_3)_3NiH]BF_4$ complex still shows a low alkene dimerization activity at small B/Ni ratios owing to its slight dissociation and the formation of a complex nickel hydride with a vacant site in the coordination sphere of nickel.

An NMR study of the $Ni(PPh_3)_4$–BF_3OEt_2 (B/Ni = 60) system demonstrated that Ni(II) hydrido complexes can be formed by the direct interaction between the components of the catalytic system without introducing any proton donor. The ^1H NMR spectrum recorded at –20°C shows resonances characteristic of hydride ions in a strong field (Fig. 5): doublet of triplets at $\delta = -12.60$ ppm with $^2J_{P-H} = 61.0$ Hz (triplet) and $^2J_{P-H} = 92.8$ Hz (doublet) (**1**); doublet of doublets at $\delta = -10.10$ ppm with $^2J_{P-H} = 61.0$ Hz (doublet) and $^2J_{P-H} = 92.8$ Hz (doublet) (**2**); triplet at $\delta = -7.15$ ppm with $^2J_{P-H} = 55.0$ Hz (**3**); doublet at $\delta = -4.00$ ppm with $^2J_{P-H} = 55.0$ Hz (**4**); doublet at $\delta = -4.20$ ppm with $^2J_{P-H} = 91.0$ Hz (**5**).

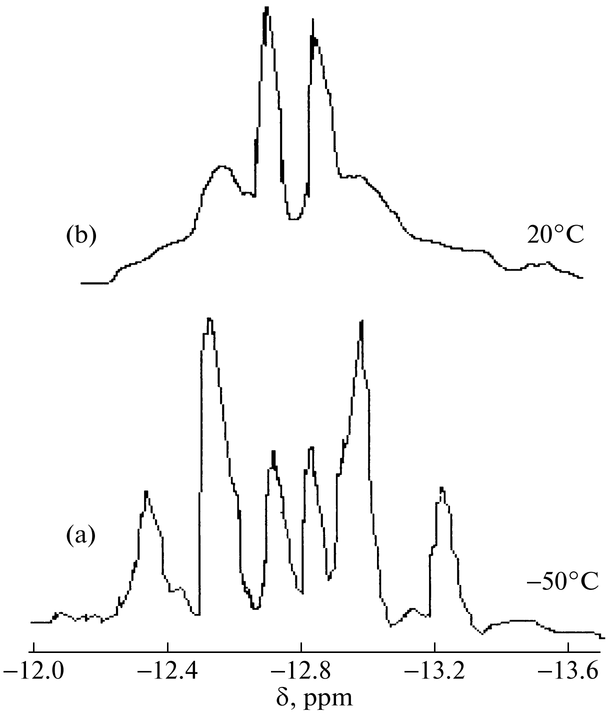


Fig. 4. ^1H NMR spectra of the reaction system $Ni(PPh_3)_4$–4EtOH–$20BF_3OEt_2$ in toluene-d_8 at (a) −50 and (b) 20°C ($C_{Ni} = 1 \times 10^{-2}$ mol/l).

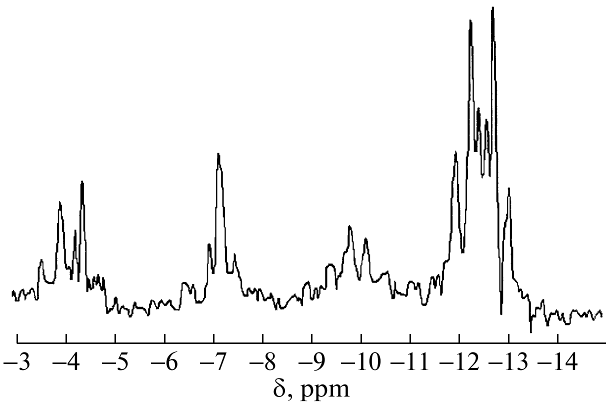
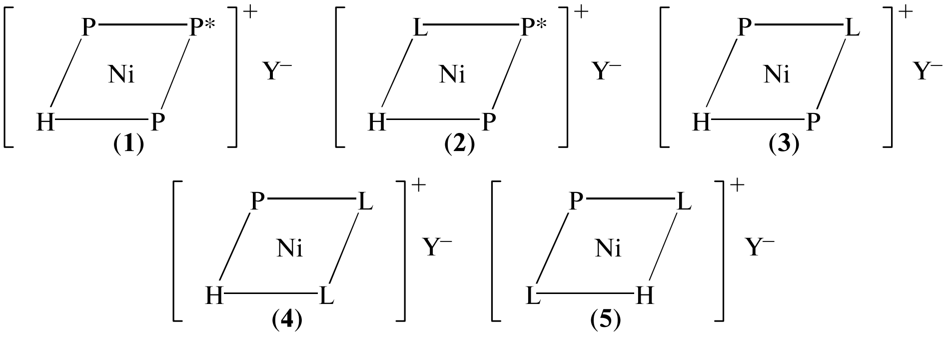


Fig. 5. ^1H NMR spectrum of the reaction system $Ni(PPh_3)_4$–$60BF_3OEt_2$ in toluene-d_8 at −20°C ($C_{Ni} = 1 \times 10^{-2}$ mol/l, $C_{H_2O} = 3 \times 10^{-2}$ mol/l).

The resonance at δ = −12.60 ppm was assigned to the above square-planar nickel hydrido complex with two equivalent and one inequivalent phosphine ligand (**1**), the signal at δ = −10.10 ppm is assignable to the square-planar nickel hydrido complex with two inequivalent phosphine ligands in the *cis* position (**2**), and the signal at δ = −7.15 ppm is assignable to the nickel hydrido complex with two equivalent phosphine ligands in the *trans* position (**3**). The doublets at δ = −4.20 ppm ($^2J_{P–H}$ = 91.0 Hz) and δ = −4.00 ppm ($^2J_{P–H}$ = 55.0 Hz) are likely due to the different nickel hydrido complexes **4** and **5**, each containing one phosphine ligand (Scheme 2).



Y = BF_3OH, P = PPh_3, L = OEt_2, solvent

Scheme 2.

The formation of Ni(II) complexes in this case is not unexpected considering that deuterotoluene contains water. The water concentration in toluene-d_8 measured by the Fischer method is 3×10^{-2} mol/l; therefore, the Ni/H_2O ratio under the NMR conditions was 1 : 3 ($C_{Ni} = 1 \times 10^{-2}$ mol/l). This water content of deuterotoluene is sufficient for the oxidation of the Ni(0) complex into Ni(II) hydrido complexes:

$$BF_3OEt_2 + H_2O \rightleftharpoons H^+BF_3OH^- + Et_2O,$$

$$Ni(PPh_3)_4 \rightleftharpoons Ni(PPh_3)_3 + PPh_3,$$

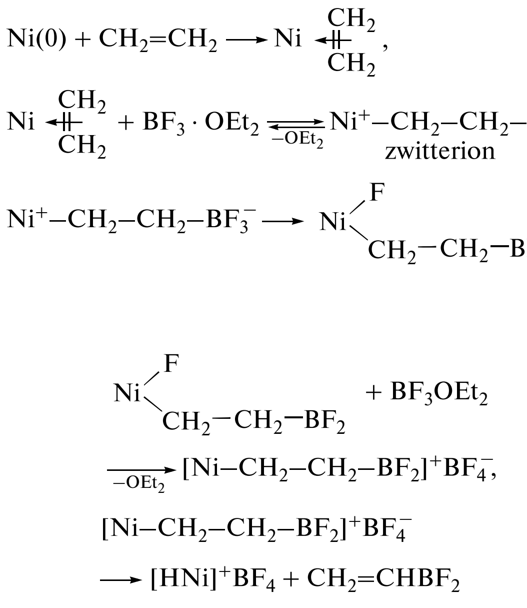
$$Ni(PPh_3)_3 + H^+BF_3OH^-$$

$$\rightleftharpoons [HNi(PPh_3)_3]^+BF_3OH^-.$$

The water concentration in the dehydrated toluene that was used in catalytic experiments and EPR studies was one order of magnitude lower ($C_{H_2O} = 3 \times 10^{-3}$ mol/l); that is, the Ni/H_2O molar ratio in the EPR studies of the $Ni(PPh_3)_4$–nBF_3OEt_2 system was 3 : 1 ($C_{Ni} = 1 \times 10^{-2}$ mol/l).

Thus, depending on the Ni/H_2O ratio, the interaction between $Ni(PPh_3)_4$ and $BF_3 \cdot OEt_2$ can proceed either via the formally one-electron oxidation of the Ni(0) complex to yield Ni(I) phosphine complexes or via the Ni(II) hydrido complex formation route. Because of the low concentrations of complexes typically used in catalysis and the high degree of dehydration of the solvents, the formation of nickel hydrido complexes in real catalytic systems is practically inevitable. Further investigation is required to elucidate the structural details of these complexes, but the formation of the hydrides should be considered an experimentally established fact.

As was noted above, the behavior of the $Ni(PPh_3)_4$–$BF_3 \cdot OEt_2$ system in propylene dimerization depended on the conditions under which this system was formed, and a substrate effect on the properties of the catalyst was observed. This is manifested in the fact that the B/Ni ratio maximizing the catalytic activity decreases from 60 for the catalyst prepared in an argon atmosphere to 13 for the catalyst prepared in the presence of propylene, and this accompanied by extension of the service life of the system (Figs. 1, 2). It can be assumed that, in the presence of propylene, there is an extra catalytic species formation route, which possibly involves zwitterions, whose formation takes place via the oxidative addition of the electrophile BF_3 to Ni(0) involving the alkene:



$$Ni(0) + CH_2{=}CH_2 \longrightarrow Ni \leftarrow\!\!\Vert\begin{matrix}CH_2\\ CH_2\end{matrix},$$

$$Ni \leftarrow\!\!\Vert\begin{matrix}CH_2\\ CH_2\end{matrix} + BF_3 \cdot OEt_2 \underset{-OEt_2}{\rightleftarrows} \underset{\text{zwitterion}}{Ni^+{-}CH_2{-}CH_2{-}BF_3^-},$$

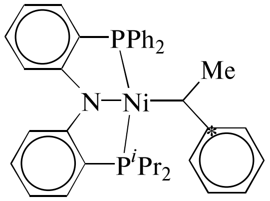
$$Ni^+{-}CH_2{-}CH_2{-}BF_3^- \longrightarrow Ni\begin{matrix}\diagup F\\ \diagdown CH_2{-}CH_2{-}BF_2\end{matrix},$$

$$Ni\begin{matrix}\diagup F\\ \diagdown CH_2{-}CH_2{-}BF_2\end{matrix} + BF_3OEt_2 \xrightarrow[-OEt_2]{} [Ni{-}CH_2{-}CH_2{-}BF_2]^+BF_4^-,$$

$$[Ni{-}CH_2{-}CH_2{-}BF_2]^+BF_4^- \longrightarrow [HNi]^+BF_4 + CH_2{=}CHBF_2$$

(for simplicity, the phosphine ligands are omitted here and the substrate is taken to be ethylene).

Saraev et al. [14, 15] express a different opinion, believing that the $[Ni(PPh_3)_3]BF_4$ complex is directly involved in the catalytic cycle. They hold that the catalytically active species are Ni(I) σ-carbocation complexes resulting from the interaction between the cationic complex $[Ni(PPh_3)_3]BF_4$ and an alkene, such as ethylene or styrene. The main argument they adduce in favor of carbocation formation is that the EPR signal from the paramagnetic Ni(I) complex disappears as styrene is introduced and a very weak, broad, unresolved resonance at 156 ppm appears in the ^{13}C NMR spectrum of the $[(PPh_3)_3Ni]BF_4$–$2PhCH{=}CH_2$ system. Assigning this signal to the Ni(I) σ-carbocation complex, Saraev et al. refer without any reason to a monograph by Koptyug [19], in which arenonium, not carbonium, ions are considered in fact. The carbocation $[PhC^+HCH_3]SbF_6^-$, which forms in superacid media at −90°C, was obtained by Olah et al. [20]. The signal from carbocation carbon occurs in a weaker field, at $\delta = 229.8$ ppm ($J_{C-H} = 159.7$ Hz) [20], while the ^{13}C NMR signal at $\delta = 156$ ppm, assigned by Saraev et al. [14] to the Ni(I) σ-carbocation complex, coincides, e.g., with the signal from the C(1) atom (starred below) in the phenyl moiety ($\delta = 155.9$ ppm) of the Ni(II) complex

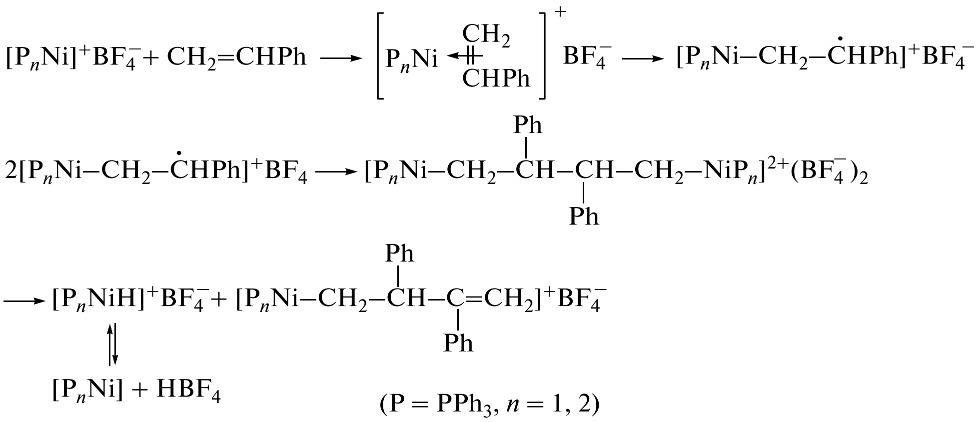


This complex [21] was synthesized by reacting the nickel hydrido complex LNiH (L = Ph–PNP–^iPr) with styrene and was characterized by X-ray structure determination. Therefore, the resonance at $\delta =$ 156 ppm [14] is certainly not due to the carbocation.

Our NMR monitoring of the $Ni(PPh_3)_4$–BF_3OEt_2–$2PhCH{=}CH_2$ reaction system in toluene indicated that styrene undergoes catalytic conversion: the ^{13}C NMR spectrum showed no resonance signals from the vinyl group of styrene ($\delta(CH_2) = 114.3$ ppm, $\delta(CH) = 127.3$ ppm) and exhibited signals at $\delta = 146.5$ and 41.8 ppm, which, according to Ascenso et al. [22], are due to the C(1) atom of the phenyl moiety of styrene and the CH groups of styrene oligomers (Fig. 6). The resonances from the CH_2 groups appear as poorly resolved signals at $\delta = 43$–45 ppm. Our spectra differ from the ^{13}C NMR spectra reported in [14, 15, 23], which show no resonance signals at 146–147 ppm characteristic of the C(1) atom of the phenyl rings in styrene oligomers. The radical difference between our experiments and the experiments reported in [14, 15, 23] is in the nature of the solvent. Note that the cationic complex $[(PPh_3)_3Ni]BF_4$ is poorly soluble in toluene ($C_{Ni} < 2 \times 10^{-5}$ mol/l). In order to increase its solubility, a toluene–ether solution was used in [14, 15, 23]. However, it is difficult to dehydrate ether by the methods used in those works. Note that the ^1H NMR spectrum of the reaction system $[(PPh_3)_3Ni]BF_4$–$2PhCH{=}CH_2$ [23] showed a signal at $\delta = 9.96$ ppm. Our NMR monitoring demonstrated that this signal is due to the proton of HBF_4 or HBF_3OH rather than a carbocation, contrary to what is stated in [23]. In our opinion, this is evidence that the solvents were dehydrated to an insufficient extent and that the initial complex underwent hydrolysis.

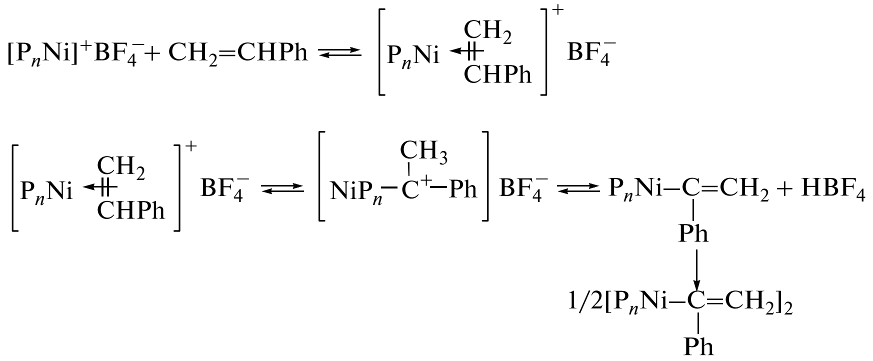
In addition, it was established that the thermal activation of $NiCl_2$ yields surface Ni(I) sites [24]. Investigation of the model reaction of Ni(I) with styrene and butadiene, which was also accompanied by the disappearance of the EPR signal from Ni(I), suggested a mechanism of the formation of polymerization sites. The key step of this mechanism is electron transfer from Ni(I) to a diene molecule, which results in the formation of a π-alkenyl complex between Ni(II) and a radical site in the CH_2 group [24]. However, the radical does not initiate polymerization and the reaction proceeds via a coordination mechanism involving the insertion of a monomer molecule into the Ni–C bond.

Based on the above data, the most likely reactions in the conversion of the Ni(I) styrene complexes can be represented as follows:



Scheme 3.

Since the $[P_nNiH]^+BF_4^-$ complex can irreversibly release HBF_4, there can be subsequent reactions between the Ni(0) complex and the Ni(II) complex:



Scheme 3a.

As follows from Schemes 3 and 3a, the interaction between an alkene (here, styrene) and $[Ni(PPh_3)_3]BF_4$ can yield a mixture of Ni(II), Ni(0), and Ni(I) complexes. The Ni(I) styryl complex is dimeric and, accordingly, does not show itself in the EPR spectrum.

The introduction of triethyl phosphite into this system gives rise to an EPR signal from the cationic complex $[Ni(PPh_3)_2\{(P(OEt_3)_3\}_2]BF_4$ [23, 25], which can

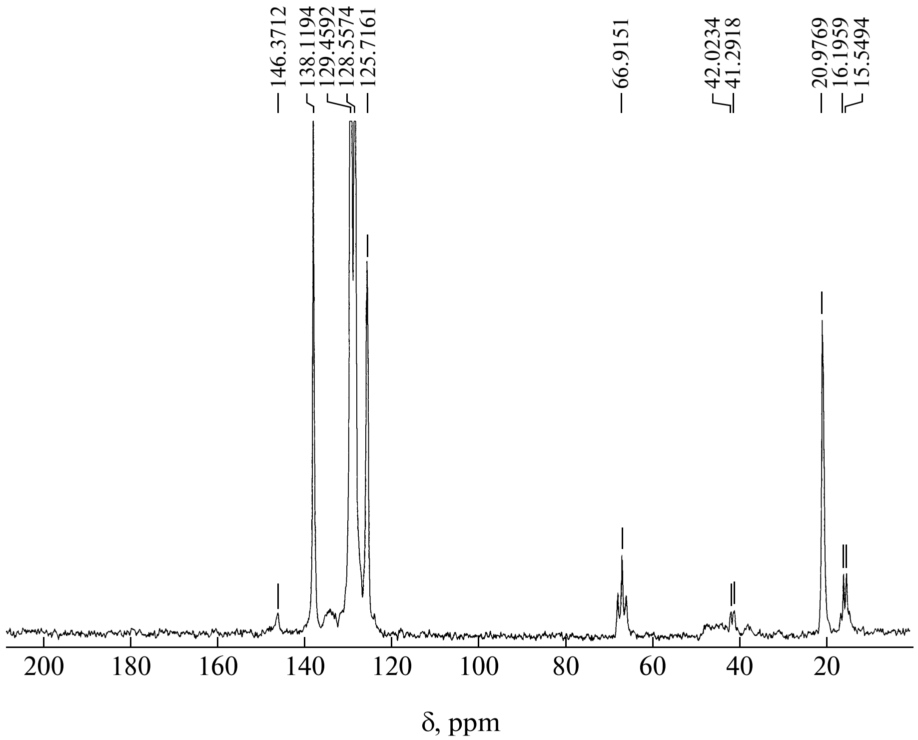
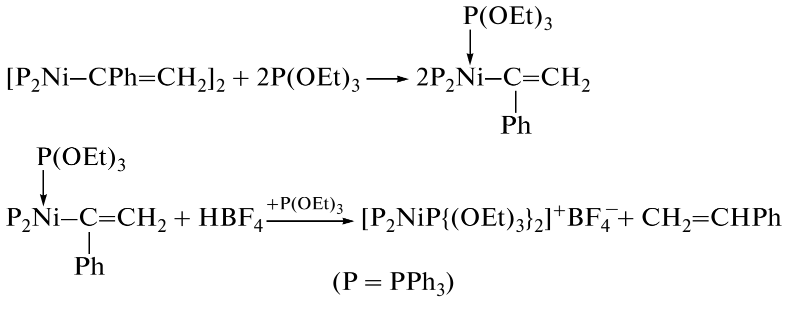


Fig. 6. ^{13}C NMR spectrum of the reaction system $Ni(PPh_3)_4{-}4BF_3OEt_2{-}2PhCH{=}CH_2$ in toluene-d_8 at 20°C ($C_{Ni} = 1 \times 10^{-2}$ mol/l).

form according to Scheme 4.



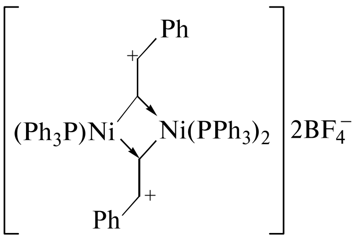
$$[P_2Ni{-}CPh{=}CH_2]_2 + 2P(OEt)_3 \longrightarrow 2P_2\overset{P(OEt)_3\downarrow}{Ni}{-}\underset{|\;Ph}{C}{=}CH_2$$

$$P_2\overset{P(OEt)_3\downarrow}{Ni}{-}\underset{|\;Ph}{C}{=}CH_2 + HBF_4 \xrightarrow{+P(OEt)_3} [P_2NiP\{(OEt)_3\}_2]^+BF_4^- + CH_2{=}CHPh$$

$$(P = PPh_3)$$

Scheme 4.

Some authors [14, 15, 23] explain the disappearance of the EPR signal upon the interaction between the cationic nickel complex $[Ni(PPh_3)_3]BF_4$ and styrene by the formation of the dimeric σ-carbocationic Ni(I) complex



(A).

The appearance of a signal from the complex $[Ni(PPh_3)_2\{(P(OEt_3)_3\}_2]BF_4$ upon the introduction of triethyl phosphite is explained in terms of the replacement of styrene by triethyl phosphite ligands and the decomposition of the diamagnetic dimeric carbocationic structures [14]. In our opinion, the formation of the dimeric σ-carbocationic Ni(I) complex (**A**) as the final product of the interaction between $[Ni(PPh_3)_3]BF_4$ and styrene in toluene or ether in the presence of phosphine is impossible.

According to Matveev [23], the signal from the complex $[Ni(PPh_3)_2\{P(OEt_3)_2\}]BF_4$ is at least one order of magnitude weaker than the signal from Ni(I) in the initial system. This is evidence that the conversions of Ni(I) are irreversible.

The coordination ionic mechanism suggested in [14, 15] for alkene dimerization on σ-carbocationic Ni(I) complexes, according to which an unreactive carbocation exists in the system, seems to be in conflict with the fundamentals of carbocation chemistry. The chain propagation rate in styrene polymerization via the cationic mechanism is on the order of 10^5 mol l^{-1} s^{-1}, four orders of magnitude higher than the styrene polymerization rate reported in [14, 15]. Moreover, the results of those studies are at variance with the mechanism suggested by the authors. According to their data, amines completely inhibit polymerization on carbocation sites. At the same time, as was reported in the same works, the polymerization rate deceases, but remains measurable. The catalytic cycle suggested in [14, 15] includes proton transfer along the carbon backbone. If this were the case, the introduction of NR_3 would cause the formation of $[NR_3R']^+$ cations and would completely inhibit the oligomerization process. In fact, this was not observed n experiments. This result provides unambiguous evidence that the carbocation sites in the systems examined cannot make a significant contribution into the catalytic process, which actually takes place on Ni(II) hydrido complexes, as was proved by numerous works more than 30 years ago [1] and confirmed by recent studies [2, 3]. As for the electrophilic addition of alcohols to the double bond [23], there is no surprise because real systems contain free BF_3, HBF_4, and other species capable of catalyzing this reaction.

Thus, our results demonstrate that the most likely catalytic species in systems of the $Ni(PPh_3)_4$–BF_3OEt_2 type are Ni(II) hydrido complexes. The detailed mechanism of the interaction of alkenes with cationic Ni(I) complexes, which is of interest for the chemistry of univalent nickel complexes, needs special investigation.

ACKNOWLEDGMENTS

The authors are grateful to Doctor of Chemistry V.S. Tkach for active discussion of the results and Doctor of Chemistry A.V. Rokhin and Candidate of Chemistry A.G. Proidakov for assistance in NMR experiments.

REFERENCES

1. Shmidt, F.K., *Kataliz kompleksami metallov pervogo perekhodnogo ryada reaktsii gidrirovaniya i dimerizatsii* (Hydrogenation and Dimerization Catalyzed by Complexes of First-Row Transition Metals), Irkutsk: Irkutsk. Gos. Univ., 1986.
2. Gibson, V. and Spitzmesser, S., *Chem. Rev.*, 2007, vol. 103, p. 283.
3. Ivanichev, S.S., *Usp. Khim.*, 2007, vol. 76, p. 669.
4. Shmidt, F.K., Mironova, L.V., Saraev, V.V., Gruznykh, V.A., Dmitrieva, T.V., and Ratovskii, G.V., *Kinet. Katal.*, 1974, vol. 20, p. 622.
5. Mironova, L.V., Shmidt, F.K., Tkach, V.S., and Dmitrieva, T.V., *Neftekhimiya*, 1978, vol. 18, p. 205.
6. Tkach, V.S., Shmidt, F.K., Saraev, V.V., and Kalabina, A.V., *Kinet. Katal.*, 1974, vol. 15, p. 617.
7. Shmidt, F.K., Mironova, L.V., Saraev, V.V., Gruznykh, V.A., Dmitrieva, T.V., and Ratovskii, G.V., *Kinet. Katal.*, 1979, vol. 20, p. 622.
8. Tkach, V.S., Grusnykh, V.A., and Shmidt, F.K., *React. Kinet. Catal. Lett.*, 1991, vol. 43, p. 431.
9. Shmidt, F.K., Tkach, V.S., Belykh, L.B., and Myagmarsuren Gomboogiin, *Vestn. IrGTU*, 2008, vol. 33, p. 112.
10. Shmidt, F.K., Mironova, L.V., Proidakov, A.G., Kalabin, G.A., Ratovskii, G.V., and Dmitrieva, T.V., *Kinet. Katal.*, 1978, vol. 19, p. 150.
11. Nesmeyanov, A.N., Shmidt, F.K., Mironova, L.V., Isaeva, L.S., Lorens, L.N., and Proidakov, A.G., *Dokl. Akad. Nauk SSSR*, 1977, vol. 233, p. 379.
12. Pomogailo, A.D., *Polimernye immobilizovannye metallokompleksnye katalizatory* (Polymer Immobilized Metal Complex Catalysts), Moscow: Nauka, 1988.
13. Meihard, D., Reuter, P., and Rieger, B., *Organometallics*, 2007, vol. 26, p. 751.
14. Saraev, V.V., Kraikivskii, P.B., Annenkov, V.V., Vil'ms, A.I., Matveev, D.A., Danilovtseva, E.N., Ermakova, T.G., Kuznetsova, N.P., and Lammertsma, K., *Kinet. Katal.*, 2005, vol. 46, p. 757 [*Kinet. Catal.* (Engl. Transl.), vol. 46, p. 712].
15. Saraev, V.V., Kraikivskii, P.B., Zelinsky, S.N., Matveev, D.A., Vilms, A.J., Rohin, A.V., and Lammertsma, K., *J. Mol. Catal.*, 2005, vol. 236, p. 125.
16. Gordon, A.J. and Ford, R.A., *A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
17. Wilke, J. and Herrmann, S., *Angew. Chem.*, 1962, vol. 74, p. 693.
18. Siedle, A.R., Newmark, R.A., and Cleason, W.B., *Inorg. Chem.*, 1991, vol. 30, p. 2005.
19. Koptyug, V.A., *Arenonievye iony: Stroenie i reaktsionnaya sposobnost'* (Arenonium Ions: Structure and Reactivity), Novosibirsk: Nauka, 1983.
20. Olah, G.A., Spear, R.J., and Forsyth, D.A., *J. Am. Chem. Soc.*, 1976, vol. 98, p. 6284.
21. Liang, L.C., Chien, P.S., and Lee, P.Y., *Organometallics*, 2008, vol. 27, p. 3082.
22. Ascenso, J., Dias, A.R., Gomes, P.T., Romao, C.C., Neibecker, D., Tkachenko, J., and Revillion, A., *Makromol. Chem.*, 1989, vol. 190, p. 2773.
23. Matveev, D.A., *Cand. Sci. (Chem.) Dissertation*, Irkutsk: Irkutsk State Univ., 2005.
24. Makovetskii, K.L., *Doctoral (Chem.) Dissertation*, Moscow: Topchiev Inst. of Petrochemical Synthesis, 1978.
25. Saraev, V.V., Tkach, V.S., Kraikivskii, P.B., Alsarsur, I.A., Myagmarsuren, G., and Shmidt, F.K., *Koordin. Khimiya*, 1998, vol. 24, p. 602 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 24, p. 563].