Reactions of Aluminium Tribromide with Tetrakis(triphenylphosphine)nickel(0) and Tetrakis(triethylphosphite)nickel(0) Complexes

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Abstract—Reactions of aluminium tribromide with the Ni(0) phosphine and phosphite complexes are studied by EPR method. AlBr₃ was found to cause the oxidation of the transition metal in the $(PPh_3)_4Ni$ complex to the univalent state with the formation of the tetracoordinated $(PPh_3)_3NiBr$ complex. With an excess of AlBr₃, the phosphine ligands are eliminated from the coordination sphere of Ni(I), and the coordinatively unsaturated complexes are destroyed to give the colloidal nickel. In the reaction of $(P(OEt)_3)_4Ni$ with AlBr₃, Ni(0) is also oxidized to Ni(I), but the acido ligand is not eliminated even with a 15-fold excess of the Lewis acid. The activity of catalytic systems on the basis of the Ni(0) phosphine complexes and the Lewis acids in the low-molecular oligomerization reactions of olefines is determined by the cationic coordinatively unsaturated Ni(I) complexes formed in these systems.

The catalytic systems produced from the Ni(0) phosphine complexes and Lewis acids exhibit the high activity in the transformation reactions of the unsaturated hydrocarbons [1].

As we previously reported, the Lewis acids, such as AlCl₂Et [2] and BF₃ · OEt₂ [3], cause the quantitative oxidation of the transition metal in the phosphine (PPh₃)₄Ni complex to the univalent state and the formation of the Ni(I) halide complexes. In the excess of the Lewis acid, both the phosphine and acido ligands are eliminated from the Ni(I) coordination sphere, and the Ni(I) complex is converted to the cationic form. In the case of AlCl₂Et, the Ni(I) complex occurs as the ionic pair with the Lewis acid, while with BF₃ · OEt₂, it exists as the isolated cations.

With the aim to elucidate the role of the Lewis acids in the formation of the catalytically active Ni(I) complexes, we studied the reactions of aluminium tribromide with the tetrakis(triphenylphosphine)nickel(0) and tetrakis(triethylphosphite)nickel(0) complexes in toluene by the EPR method.

EXPERIMENTAL

The $(PPh_3)_4Ni$ and $(P(OEt)_3)_4Ni$ complexes used in the experiment were synthesized as described in [4] and [5], respectively. The $[(PPh_3)_3Ni]BF_4$ complex was produced by the oxidation of the $(PPh_3)_4Ni$ complex with boron trifluoride etherate [6]. The $(PBu_3)_2NiBr_2$ complex was synthesized by the known procedure [7]. The composite Ni(I) complex $(PBu_3)(PPh_3)_2NiBr$ was obtained by the contradisproportionation reaction between the $(PBu_3)_2NiBr_2$ and $(PPh_3)_4Ni$ complexes in toluene. The analytical grade AlBr₃ was purified by recondensation in vacuum. The organophosphorus compounds were prepared by standard procedures [8]. All reactions were performed in glass reactors under the atmosphere of argon free from oxygen and moisture traces. The solvents (toluene and hexane) were dehydrated, degassed in vacuum, and kept over the sodium surface under argon for a day. The EPR spectra were recorded on a SE/X-2542 spectrometer (9.6 GHz) at T = 77 K. The sweep range was calibrated using the DPPG free radical and Mn²⁺ in MgO. The EPR spectra were simulated with our own program [3], 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

After AlBr₃ is added to the toluene solution of the diamagnetic (PPh₃)₄Ni complex (with the molar ratio of Al : Ni = 1), an intense signal (*la* in figure) appears in the EPR spectrum with unresolved hyperfine structure (HFS). The signal *la* is typical of the tetrahedral Ni(I) complexes that have the trigonal distortion [9]. The lack of the resolved HFS lines suggests a short relaxation time of the electron spin in a complex with the pseudo-degenerate ground state. Further addition of AlBr₃ to the system results in a sharp reduction in the intensity of the *la* signal and its disappearance when Al : Ni = 2.

In order to interpret the EPR signal (1a), we obtained *in situ* the $(PPh_3)_3NiBr$ complex in toluene solution by oxidizing the $(PPh_3)_4Ni$ complex with molecular bromine. In this case, we recorded the same signal 1a, which disappeared on the addition of AlBr₃ to the system.



(a) Experimental and (b) model EPR spectra in toluene: (1) $(PPh_3)_4Ni-AlBr_3$; (2) $(PPh_3)_4Ni-(PBu_3)_2NiBr_2$; (3) $(PBu_3)(PPh_3)_2NiBr-AlBr_3$; (4) $(P(OEt)_3)_4Ni-AlBr_3$; and (5) $(PPh_3)_4Ni-BF_3 \cdot OEt_2$, T = 77 K.

Thus, in the reaction of AlBr₃ with $(PPh_3)_4Ni$, Ni(0) is oxidized to Ni(I) and the $(PPh_3)_3NiBr$ neutral complex is formed that is decomposed with the excess AlBr₃ in the system. One should note that in the EPR spectrum of the $(PPh_3)_3NiCl$ with similar composition and geometry, the HFS is not resolved at 77 K ether [10].

According to the data in [2], the decomposition process can be preceded by the formation of the coordinatively unsaturated structures, which in the case of the Ni(I) bromide complexes are likely to be unstable and quickly disproportionate to form the Ni(II) complexes and the colloidal nickel.

With the aim to identify the coordinatively unsaturated Ni(I) bromide complexes, we studied the reaction of AlBr₃ with the tetracoordinated mixed-ligand (PBu₃)(PPh₃)₂NiBr complex in toluene solution. The former complex contains the tributylphosphine ligand, which stabilizes nickel in univalent state more efficiently. In the EPR spectrum of the mixed-ligand complex (see 2*a* in the figure), the HFS is resolved in the parallel orientation from three ³¹P nuclei ($I_P = 1/2$), two of which are equivalent, and one ^{79,81}Br nucleus ($I_{Br} = 3/2$).

The EPR parameters corresponding to the best visual coincidence of the experimental and model EPR spectra are given in the table. Taking into account a small (~10%) difference in the magnetic moments for the ⁷⁹Br and ⁸¹Br isotopes, whose natural content is almost equal [11], the model spectra were calculated only for one isotope. Since the program for the EPR

spectrum calculation does not provide the variation in the angles between the axes of the *g*-tensor and the HFI tensors with the ligands, the found values of the HFI constants correspond not to the main values but to the values reduced to the *g*-tensor axes. In accordance with the theoretical developments [9], the experimental data (see table) satisfy the trigonal structure, where the main axis passes along the Ni–P bond with the tributylphosphine ligand.

After the addition of AlBr₃ in the equimolar amount to a solution of the mixed-ligand (PBu₃)(PPh₃)₂NiBr complex, the EPR spectrum exhibits a rapid transition of the 2a signal to the 3a signal (see figure), where the HFS from two equivalent ³¹P nuclei is resolved. The triaxial anisotropic signal 3a is typical of the tricoordinated Ni(I) complexes (PR₃)₂NiBr [12]. It is noteworthy that the EPR parameters of a new complex are close to the average values of similar parameters for two complexes (PPh₃)₂NiBr and (PBu₃)₂NiBr (given in table). The recorded spectrum is most likely produced by the Ni(I) complex with composition (PBu₃)(PPh₃)NiBr, which is formed due to the elimination of the triphenylphosphine ligand from the (PBu₃)(PPh₃)₂NiBr complex. Assuming that the ³¹P nuclei are magnetically equivalent in two different phosphine ligands, it should be noted that in the mixed ligand Ni(I) complexes $[(PBu_3)_{4-n} (PPh_3)_n Ni]BF_4$, the ³¹P nuclei are also magnetically equivalent [9].

Further introduction of $AlBr_3$ into the model system results in the intensity reduction of the 3a EPR signal,

Complex	<i>g</i>	g_{\perp}	$A_{\parallel}, \mathrm{mT}$	A_{\perp}, mT
(PPh ₃) ₃ NiBr	2.02	2.35		
(PBu ₃)(PPh ₃) ₂ NiBr	2.037	2.23	9.15(1P)	7.5(1P)
			7.63(2P)	5.0(2P)
			3.05(Br)	<5.0(Br)
(PBu ₃)(PPh ₃)NiBr	2.341 _z	2.108_{y}	$4.8(2P)_z$	$6.28(2P)_{y,x}$
		2.083_x	<2.0(Br) _z	$3.14(Br)_{y,x}$
(PPh ₃) ₂ NiBr	2.348 _z [12]	2.122 _y [12]	$4.3(2P)_{z}$ [12]	6.15(2P) _y [12]
		2.085_{x} [12]		$6.53(2P)_x$ [12]
				$3.04(Br)_{y,x}$ [12]
(PBu ₃) ₂ NiBr	2.291 _z [12]	2.100 _y [12]	$5.7(2P)_{z}$ [12]	6.69(2P) _y [12]
		2.083_{x} [12]		$6.78(2P)_x$ [12]
				$3.25(Br)_{y,x}$ [12]
(P(OEt) ₃) ₃ NiBr	1.989	2.207	17.0(1P)	14.5(1P)
			5.7(1P)	6.5(1P)
			4.5(1P)	5.5(1P)
			3.4(Br)	<3.0(Br)
[(PPh ₃) ₃ Ni]BF ₄	2.385 _z	2.12_{y}	$6.1(1P)_z$	6.4(1P) _y
	2.385 [3]	2.07 _x	<3.2(2P) _z	<3.2(2P) _y
		2.09 [3]	6.0(1P) [3]	$8.1(1P)_x$
				$<2.0(2P)_{x}$
				7.5(1P) [3]

Parameters of EPR spectra of Ni(I) complexes

which fully disappears when the molar ratio of Al : Ni = 3. An excess of $AlBr_3$ is likely to cause the further elimination of the phosphine ligands and decomposition of the Ni(I) complexes.

Thus, the detection in the model system of the coordinatively unsaturated Ni(I) bromide complex with tributylphosphine ligand indicates that the $(PPh_3)_2NiBr$ structures can form also in the starting system. These structures are not detected since they occur in a narrow interval of the A1 : Ni ratios that can be controlled with difficulty.

One should note that the EPR spectra did not exhibit the signals from the bridging structures typical of the systems based on AlCl₂Et [2].

The reaction of $AlBr_3$ with $(PPh_3)_4Ni$ can be written as follows:

(PPh₃)₄Ni ^{AlBr₃}→ (PPh₃)₃NiBr

 $\xrightarrow{AlBr_3} (PPh_3)_2 NiBr \xrightarrow{AlBr_3} Destruction of Ni(I).$

In order to study the possibility of using AlBr₃ for eliminating the acido ligand from the Ni(I) coordination sphere, its reaction with the Ni(0) complex (P(OEt)₃)₄Ni in toluene was investigated. This study was based on the data on the formation of the cationic Ni(I) complexes of the composition [(P(OEt)₃)₄Ni]AlCl₃Et in the catalytic (P(OEt)₃)₄Ni– AlCl₂Et system [13]. The addition of AlBr₃ to the toluene solution of the diamagnetic $(P(OEt)_3)_4Ni$ complex (with the molar ratio of Al : Ni = 2) produces an intense EPR signal (*4a* in figure) with the resolved complicated HFS from the ligands. Analogous spectra were obtained in the oxidation of the $(P(OEt)_3)_4Ni$ complex in toluene with the molecular bromine and by full replacement of the triphenylphosphine ligands by the triethylphosphite ligand technique [9]. Thus, aluminium tribromide also causes the oxidation of Ni(0) in the $(P(OEt)_3)_4Ni$ complex to give the tetrahedral neutral complex $(P(OEt)_3)_3NiBr$.

If an excess AlBr₃ is introduced into the system after the $(P(OEt)_3)_3$ NiBr complex formation, the 4*a* EPR signal remains unchanged even at the molar ratio of Al : Ni = 15. Hence, aluminium tribromide causes neither the elimination of the triethylphosphite ligands nor the conversion of the neutral bromide complex into the cationic form through the migration of the Br⁻ anion to the outer sphere. Therefore, the Ni(I) bromide phosphine complexes can only occur in the neutral form independent of the ligand environment.

As we previously showed in [14], the activity of the catalytic system $(PPh_3)_4Ni-BF_3 \cdot OEt_2$ in the processes of the low-molecular oligomerization of the olefine hydrocarbons is directly determined by the obtained cationic Ni(I) complexes. One of the shortcomings of

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this system is the need to use large amounts of the boron trifluoride etherate (up to 80 molar fractions) in order to ensure the required coordination unsaturation of the Ni(I) cationic complexes. Since AlBr₃ actively eliminates the triphenylphosphine ligands, it was interesting to estimate whether it can be used as the acceptor of phosphines in the catalytic system. For this purpose, we studied the AlBr₃ reaction with the individual cationic complex [Ni(PPh₃)₃]BF₄ isolated from the (PPh₃)₄Ni–BF₃ · OEt₂ catalytic system.

The $[Ni(PPh_3)_3]BF_4$ cationic complex in toluene produces the EPR signal (*5a* in figure) typical for the tricoordinated structures. The magnetic inequivalence of the ³¹P nuclei is caused by the distortion of the trigonal structure due to the Jahn–Teller effect [3]. The model signal *5b* made it possible to discover the triaxial anisotropy of the EPR parameters of this complex (see in table).

When the equimolar amount of AlBr₃ was added to the toluene solution of the $[Ni(PPh_3)_3]BF_4$ complex, the EPR spectrum exhibits a full replacement of the 5*a* signal by the 1*a* signal from the neutral $(PPh_3)_3NiBr$ complex. The further addition of AlBr₃ to the system results only in the intensity reduction of the 1*a* signal, which completely disappears at Al : Ni = 2. The starting stage of this interaction can be represented as follows:

 $[(PPh_3)_3Ni]BF_4 + AlBr_3$ $\longrightarrow (PPh_3)_3NiBr + AlBr_2F \cdot BF_3.$

Hence, the reaction of aluminium tribromide with the cationic Ni(I) complex results, first of all, in the ionic exchange of the acido ligands and in the conversion of the potentially active Ni(I) cationic complex into the inactive molecular form.

This conclusion was confirmed by the catalytic tests for the activity in the dimerization reactions of propylene and ethylene. The $(PPh_3)_4Ni-AlBr_3$ and $[Ni(PPh_3)_3]BF_4-AlBr_3$ systems in toluene were found to show zero activity in these processes. The results obtained support the previous conclusion that the high activity of the catalytic systems in the dimerization reactions of the olefine hydrocarbons produced from the Ni(0) phosphine complexes and the Lewis acids is determined by the formed Ni(I) cationic complexes.

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