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Note

EPR study of the oxidation reaction of nickel(0) phosphine complexes with Lewis and Brønsted acids

V.V. Saraev [a,*], P.B. Kraikivskii [a,b], D.A. Matveev [a], S.N. Zelinskii [a,b], K. Lammertsma [b]

[a] *Department of Chemistry, Irkutsk State University, Str. K. Marksa, 1, Irkutsk 664033, Russian Federation*
[b] *Faculty of Sciences, Department of Chemistry, Vrije University, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands*

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Abstract

The oxidation of $Ni(PPh_3)_4$ with $BF_3 \cdot OEt_2$, H_3CCOOH, and F_3CCOOH, and that of $(PPh_3)_2Ni(C_2H_4)$ with $BF_3 \cdot OEt_2$ is studied by EPR spectroscopy. The reaction of the Ni(0) complexes with $BF_3 \cdot OEt_2$ gives Ni(II) complexes with which they react to form Ni(I) compounds with covalent Ni–F and Ni–B bonds that transform with excess $BF_3 \cdot OEt_2$ into cationic paramagnetic Ni(I) complexes. Acetic acid also adds oxidatively to $Ni(PPh_3)_4$ to form a Ni(II) complex that reacts further to give Ni(I) hydride and carboxylate complexes. The Ni(I) hydride is transformed by the acid into the Ni(I) carboxylate with release of hydrogen, the amount of which depends on the rate of acid addition. The following Ni(I) complexes are identified in the reaction medium: $[Ni(PPh_3)_3]BF_4$, $[(PPh_3)_2Ni(OEt_2)]BF_4$, $[(PPh_3)Ni(OEt_2)_n]BF_4$, $(PPh_3)_2NiBF_2$, $(PPh_3)_3NiOOCCH_3$, and $[(PPh_3)_2Ni(OEt_2)P(OEt)_3]BF_4$. Oxidation schemes of Ni(0) complexes by Lewis and Brønsted acids are given.

Keywords: Oxidation; Ni(0) complexes; Lewis and Brønsted acids; Ni(I) complexes; EPR

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1. Introduction

Ni(0) phosphine complexes in combination with Lewis (AX_n) and Brønsted (HX) acids exhibit high activity in the oligomerization of unsaturated hydrocarbons [1–3]. Lewis acids quantitatively oxidize Ni(0) to Ni(I) [4], so that the coordinatively unsaturated cationic Ni(I) complexes are, in fact, the active catalysts for the low molecular olefin oligomerization [5]. According to the literature [6], this oxidation can proceed by different directions that are summarized in Eqs. (1) and (2); for simplicity the phosphine ligands are not shown:

$$\mathrm{Ni(0)} + \mathrm{AX}_n \rightarrow \mathrm{Ni}{<}^{\mathrm{X}}_{\mathrm{AX}_{n-1}} \xrightarrow{\mathrm{Ni(0)}} \mathrm{NiX} + \mathrm{NiAX}_{n-1} \qquad (1)$$

$$\mathrm{Ni(0)} + \mathrm{AX}_n \rightarrow \left[\mathrm{Ni}^{+}\mathrm{AX}_n^{-}\right] \rightarrow \mathrm{Ni}^{+} + \dot{\mathrm{A}}\,\mathrm{X}_{n-1} + \mathrm{X}^{-} \qquad (2)$$

In Eq. (1), the Ni(I) complex results directly from a two-electron oxidative addition of the Lewis acid, giving a Ni(II) complex as byproduct. In Eq. (2), the Ni(I) complex is formed by two sequential one-electron transfers. Attempts have been made to establish which oxidation process is applicable with the Lewis acids $Al(Et)Cl_2$ [7], $AlBr_3$ [8] BBr_3, and $B(Ph)_2Br$ [9], but so far to no avail. Also the mechanism and products resulting from the oligomerization with Ni(0) complexes and Brønsted acids remain elusive although it is believed that intermediate Ni(II) hydride complexes are involved (Eq. (3)), based on their NMR identification in model systems [10,11]. Assuming a two-electron oxidative addition, the Ni(I) complexes are then formed by comproportionation

$$\mathrm{Ni(0)} + \mathrm{HX} \rightarrow \mathrm{Ni}{<}^{\mathrm{H}}_{\mathrm{X}} \qquad (3)$$

In the present study, we report EPR data on (1) the oxidation of tetrakis(triphenylphosphine)nickel(0) with boron trifluoride etherate, and acetic and trifluoroacetic acids,

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[*] Corresponding author. Fax: +7 3952 42 59 35.
E-mail address: saraev@chem.isu.ru (V.V. Saraev).

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and (2) the oxidation of bis(triphenylphosphine)(π-ethylene)nickel(0) with boron trifluoride etherate to provide further mechanistic insights.

2. Experimental

All operations were performed under moisture and oxygen free argon using standard Schlenk-line technique at $t = 23$ °C under atmospheric pressure. Gas chromatography grade argon was purified [12] and checked by the $AlEt_3$ test. Vacuum-calcined tubes were used as reaction vessels.

Toluene, benzene, and hexane (Merck) were refluxed over sodium for 10 h, distilled to glass vessels that were coated with a sodium mirror, and stored at 20 kPa gauge argon pressure. Acetylacetone and trifluoroacetic acid (Merck) were distilled under argon before use. Acetic acid (Merck) was additionally dried by the usual freezing technique. Boron trifluoride etherate (Merck) was distilled over lithium hydride under argon less than 3 h before use and contained less than 0.05% of acidic protons according to NMR. Tetramethylpiperidinyloxy (TEMPO, Aldrich) has a 37–38 °C melting range.

$Ni(PPh_3)_4$ [13], $(PPh_3)_2Ni(C_2H_4)$ [14], and $[Ni(PPh_3)_3]BF_4$ [15] were synthesized by known methods. The initial concentration of the Ni(0) complex in a toluene solution was 10^{-2} mol/l. Reactions between the Ni(0) complex and the Lewis and Brønsted acids were carried out at 23 °C. Boron trifluoride etherate was introduced into the reaction mixture in 0.2 mol aliquots with respect to nickel.

3. Method

The reaction between the $Ni(PPh_3)_4$ complex and acetic acid was conducted in a thermostated reaction vessel (23 °C), plugged by a rubber stopper pierced with a syringe needle and thermally connected to a U-shaped gas measuring burette. A toluene solution of acetic acid was injected by a syringe (of 1 ml) into a vigorously stirred toluene solution of $Ni(PPh_3)_4$ in 0.01 ml portions (1 s) at intervals of 19 s, i.e., at an average volume rate of 5×10^{-4} ml/s. The syringe was filled with acetic acid in a 1-, 2-, 6-, 20-, 200-fold molar excess relative to Ni(0) and diluted with toluene to the desired 1 ml of volume. Hence, the average relative rates of acetic acid addition were 0.5, 1, 3, 10, and $100 \frac{[CH_3COOH]}{[Ni]} \times 10^{-3}\ s^{-1}$, respectively.

For the acid HBF_4, we used its toluene complex that contained >48% of HBF_4 (by chromatography) and was prepared by the method reported in Ref. [16]. Acetylacetone (0.352 g, 3.52 mmol) was added dropwise (2 min) to a vigorously stirred solution of 10 ml boron trifluoride etherate (1 g, 7.05 mmol, toluene), after which the reaction mixture was separated into two layers. The lower one, consisting of the HBF_4-toluene complex (⩾98% by NMR spectroscopy), was stored under argon in a polyethylene vessel and used within 2 h. HBF_3OH was prepared from equimolar amounts of boron trifluoride etherate and distilled water [17], and also stored under argon in a polyethylene vessel and used within 2 h.

EPR studies were carried out using a PS-100X spectrometer with an operating frequency of 9.6 GHz. Mn(II) in MgO and diphenylpicrylhydrazyl were used as standards. EPR spectra were recorded for samples frozen in a glass ampoule at −170 °C (liquid nitrogen vapors). These samples were collected with a syringe from the reaction vessel (23 °C) under argon and frozen in about 15 s. To estimate the concentrations of paramagnetic Ni(I) complexes in the samples, double integrated intensities of the EPR signals of the samples were taken and compared to those of the individual $[Ni(PPh_3)_3]BF_4$ complex in diethyl ether. The EPR spectra were simulated with our published program [18], in which the hyperfine interaction (HFI) is limited to the second-order term and where the main axes of the g-tensor and the HFI tensors coincide. The EPR parameters of all experimental signals shown in Fig. 1 were examined by computer modeling and are summarized in Table 1.

^{19}F NMR spectra were recorded at 25 °C on a Varian VXR-500S spectrometer using sealed ampoules and F_3CCOOH as standard.

4. Results and discussion

4.1. Boron trifluoride etherate

$[Ni(PPh_3)_3]BF_4$: Diamagnetic $Ni(PPh_3)_4$ is known to partly dissociate in toluene [6], enabling association with Lewis acids. Resonance absorption is not observed upon addition of the first aliquots of boron trifluoride etherate until the B:Ni molar ratio is over 2. The resulting EPR resonance (labeled 1 in Fig. 1) is due to the tricoordinate complex $[Ni(PPh_3)_3]BF_4$ [8,18], whose saturated toluene solution is greenish-brown in color. This signal 1 reaches a maximum at a B:Ni ratio of 4, whereupon its intensity decreases. We note that the variation in intensity of this signal is within the integration error and ⩾90% of that if all the nickel were to become paramagnetic. The EPR spectra are the same for all samples taken from the reaction mixture at intervals of 30 s. Hence, the Ni(0) oxidation with $BF_3 \cdot OEt_2$ must proceed rather fast (<30 s).

The ^{19}F NMR spectrum of the reaction mixture shows a resonance at 25.58 ppm, which is assigned to F_2BBF_2 [19]; line broadening due to the presence of paramagnetic species masked the fine structure and hence its coupling constants could not be determined. The δ (^{19}F) intensity peaked 1–2 min after the start of the reaction and then diminished, indicating the depletion of F_2BBF_2.

Because HF and H_2O are potential contaminants in boron trifluoride etherate that might participate in the oxidation of Ni(0) to Ni(I), we conducted independent test on the interaction of $Ni(PPh_3)_4$ with mixtures of $BF_3 \cdot OEt_2 + HBF_4$ and $BF_3 \cdot OEt_2 + HBF_3OH$ in which the contents of the Brønsted acid were varied from 0% to 100%. However, as the content of HBF_4 or HBF_3OH was increased the Ni(I) EPR signal intensity reduced.

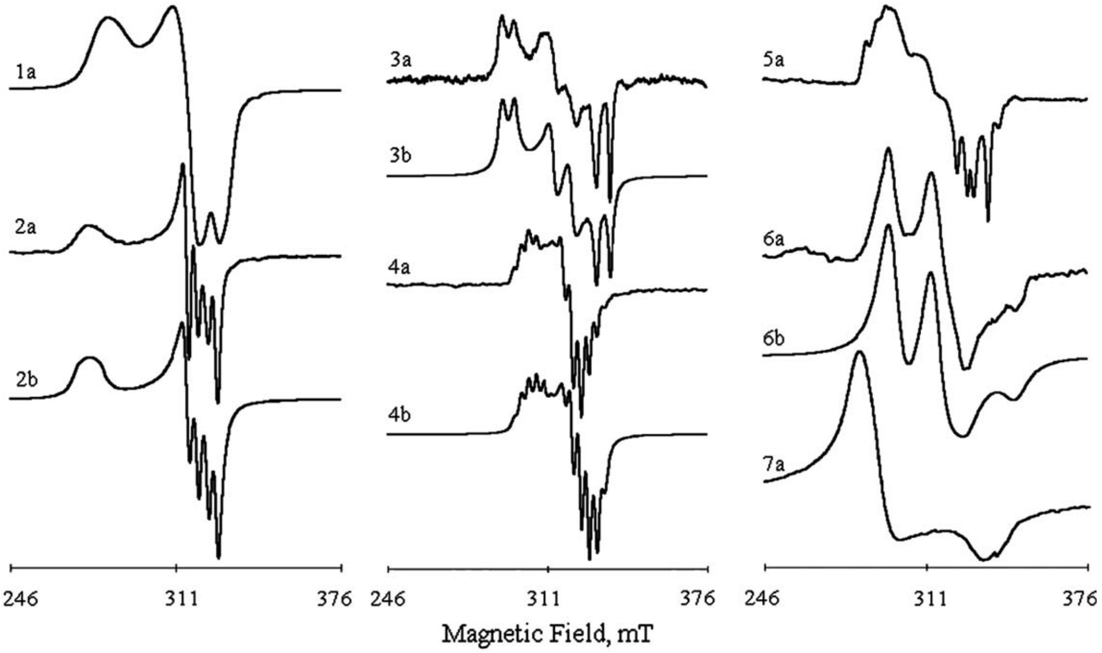


Fig. 1. Experimental (a) and model (b) EPR spectra of the Ni(I) complexes: (1) $[Ni(PPh_3)_3]BF_4$, (2) $[(PPh_3)_2Ni(OEt_2)]BF_4$, (3) $[(PPh_3)Ni(OEt_2)_n]BF_4$, (4) $(PPh_3)_2NiBF_2$, (5) mixture of complexes, (6) $[(PPh_3)_2Ni(OEt_2)P(OEt)_3]BF_4$, and (7) $(PPh_3)_3NiOOCCH_3$ in toluene at $T = 77$ K.

Table 1
Parameters of EPR spectra for Ni(I) complexes

Signal	Complex	$g_\parallel$	$g_\perp$	$A_\parallel$ (mT)	$A_\perp$ (mT)	Ref.
1	$[Ni(PPh_3)_3]BF_4$	2.385_z	2.12_y 2.07_x	6.1 $(1P)_z$ <3.2 $(2P)_z$	6.4 $(1P)_y$ <3.2 $(2P)_y$ 8.1 $(1P)_x$ <2.0 $(2P)_x$	[8]
2	$[(PPh_3)_2Ni(OEt_2)]BF_4$	2.45	2.11	6.0 (1P) 3.7 (1P′)	7.6 (1P) 2.9 (1P′)	
3	$[(PPh_3)Ni(OEt_2)_n]BF_4$	2.03_z	2.14_y 2.30_x	5.7 $(1P)_z$	7.4 $(1P)_y$ 4.9 $(1P)_x$	
4	$(PPh_3)_2NiBF_2$	2.22	2.08	3.0 (2P) 3.0 (1B)	3.1 (2P) 3.1 (1B)	
5	Mixture of complexes	No EPR parameters determined				
6	$[(PPh_3)_2Ni(OEt_2)P(OEt)_3]BF_4$	2.01	2.21	19.5 (1P)	17.0 (1P)	
7	$(PPh_3)_3NiOOCCH_3$	2.04	2.35			

No Ni(I) EPR signals were even observed throughout the molar ratio range 1 < B:Ni <80 with a 100% content of HBF_4 or HBF_3OH. Consequently, the formation of Ni(I) complexes in the system $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ cannot be ascribed to the presence of HF and H_2O as contaminants.

$[(PPh_3)_2Ni(OEt_2)]BF_4$: With increasing the amount of boron trifluoride etherate in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ system, signal 1 decreases in intensity and another resonance emerges (labeled 2 in Fig. 1) that has its maximum at a B:Ni ratio of 50. The four equidistant components of the hyperfine structure (HFS) resolved in signal 2 are due either to two nonequivalent ^{31}P ($I_P = 1/2$) nuclei or to one ^{11}B ($I_B = 3/2$) nucleus. To distinguish between these two possibilities, EPR spectra were obtained for the complexes formed in the reaction of $BF_3 \cdot OEt_2$ with $[Ni(PPh_3)_3]BF_4$ in toluene to show the same signals. In this case, the formation of a Ni–B valence bond is highly improbable, so that the four-component HFS of signal 2 is attributed to two nonequivalent ^{31}P nuclei. The ratio between the g-factor components ($g_\parallel > g_\perp$) and the nonequivalence of the ^{31}P nuclei is typical for tricoordinate Ni(I) complexes; these have a ground pseudodegenerate electronic state [18]. Consequently, signal 2 can be assigned to $[(PPh_3)_2Ni(OEt_2)]BF_4$.

$[(PPh_3)Ni(OEt_2)_2]BF_4$: Increasing the amount of boron trifluoride etherate in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ system leads to the disappearance of signal 2 and to the emergence of yet another resonance (labeled 3 in Fig. 1), which has a maximum intensity at a B:Ni ratio of 80, while fur-

ther addition of boron trifluoride etherate leads to discoloration of the toluene solution, precipitation of finely divided metallic nickel, and the appearance of a broad EPR signal due to ferromagnetic nickel. Similar signal transformations are observed if $BF_3 \cdot OEt_2$ is added to a toluene solution of $Ni(PPh_3)_4$ in portions corresponding to B:Ni molar ratios of 3, 50, and 80. Signal 3 has a HFS with a well-resolved ^{31}P nucleus that indicates the presence of one phosphine ligand in the paramagnetic complex. Therefore, the successive change in EPR resonance absorptions from $1 \rightarrow 2 \rightarrow 3$ that is induced by excess $BF_3 \cdot OEt_2$ corresponds to the sequential elimination of organophosphorus ligands from the Ni(I) coordination sphere from $3 \rightarrow 2 \rightarrow 1$. We note that the activity of the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ system in low molecular ethylene oligomerization peaks within a B:Ni ratio of 60–70 [15].

To establish whether free radicals are involved in the formation of the cationic Ni(I) complexes, e.g., through one-electron oxidation, reactions between $Ni(PPh_3)_4$ and $BF_3 \cdot OEt_2$ were performed in the presence of the free radical spin trap TEMPO (mole ratio TEMPO:Ni = 0.01). However as virtually no effect was exerted on the signals of both the Ni(I) complexes and the TEMPO radical, we conclude that the oxidation of Ni(0) phosphine complexes does not involve free radicals and hence consider the one-electron mechanism for this oxidative system improbable under the conditions used.

To further explore the oxidative reaction, we carried out experiments with bis(triphenylphosphine)(π-ethylene)-nickel(0) in which two phosphine ligands of $Ni(PPh)_4$ have been replaced by a π-complexing ethylene group. This system behaves differently as the addition of even the first aliquots of boron trifluoride etherate (B:Ni ratio of 0.2) to the toluene solution of $(PPh_3)_2Ni(C_2H_4)$, which becomes yellow-brown, generates a new EPR resonance (labeled 4 in Fig. 1) whose intensity increases with an increasing concentration of $BF_3 \cdot OEt_2$ to reach a maximum at a B:Ni ratio of 1 (dark green; no precipitate). At this ratio, the intensity of the signal does not exceed 30% of the value calculated for the complete conversion of nickel to the paramagnetic state. At a B:Ni ratio of 2, signal 4 has disappeared fully and only at a B:Ni ratio of 8 does a strong new EPR resonance reappear (labeled 5 in Fig 1), which is a superposition of several signals with only that of signal 3 identifiable.

$(PPh_3)_2NiBF_2$: Signal 4 exhibits a comparatively complicated HFS, which is attributed to one ^{11}B and two equivalent ^{31}P nuclei as based on extensive comparisons with theoretical spectra calculated with the program described in Ref. [18]. By further taking into account the ratio between the g-factor components ($g_{\parallel} > g_{\perp}$), signal 4 is assigned to the tricoordinate $(PPh_3)_2NiBF_2$ structure with a Ni–B valence bond. This interpretation is supported by the reported synthesis of the Ni–B containing Ni(I) complex $\{(PPh_3)_2NiBPh_2 \cdot 1/2\,OEt_2\}_n$ ($n \geqslant 2$) that reportedly results from the $BBrPh_2$-mediated oxidation of $(PPh_3)_2Ni(C_2H_4)$ [9].

$[(PPh_3)_2Ni(OEt_2)P(OEt)_3]BF_4$: The disappearance of signal 4 at a B:Ni ratio of 2 and the appearance of signal 5 in the B:Ni ratio of 2–8 may be due to dimerization of the paramagnetic complexes and their subsequent dissociation caused by excess $BF_3 \cdot OEt_2$. To verify this assumption, triethylphosphite was introduced in a P:Ni molar ratio of 1 after signal 4 had disappeared, because this ligand is capable of destructing the Ni(I) dimers. Indeed, a new EPR resonance resulted (signal 6 in Fig. 1) that is characteristic for a tetrahedral Ni(I) complex containing one phosphite ligand [20] and hence, signal 6 is assigned to $[(PPh_3)_2Ni(OEt_2)P(OEt)_3]BF_4$. Unlike triethylphosphite, triphenylphosphine did not destroy the Ni(I) dimers under the same conditions, even when introduced in a 3-fold excess.

In contrast to the $Ni(PPh)_4$ system, $(PPh_3)_2Ni(C_2H_4)$ is highly sensitive to the manner in which $BF_3 \cdot OEt_2$ is introduced. For instance, addition in portions corresponding to a B:Ni ratio of 3, 6, and 9 gives subsequently a moderately strong signal 2 that transforms into signal 3, whose intensity remains virtually unchanged with the higher $BF_3 \cdot OEt_2$ content.

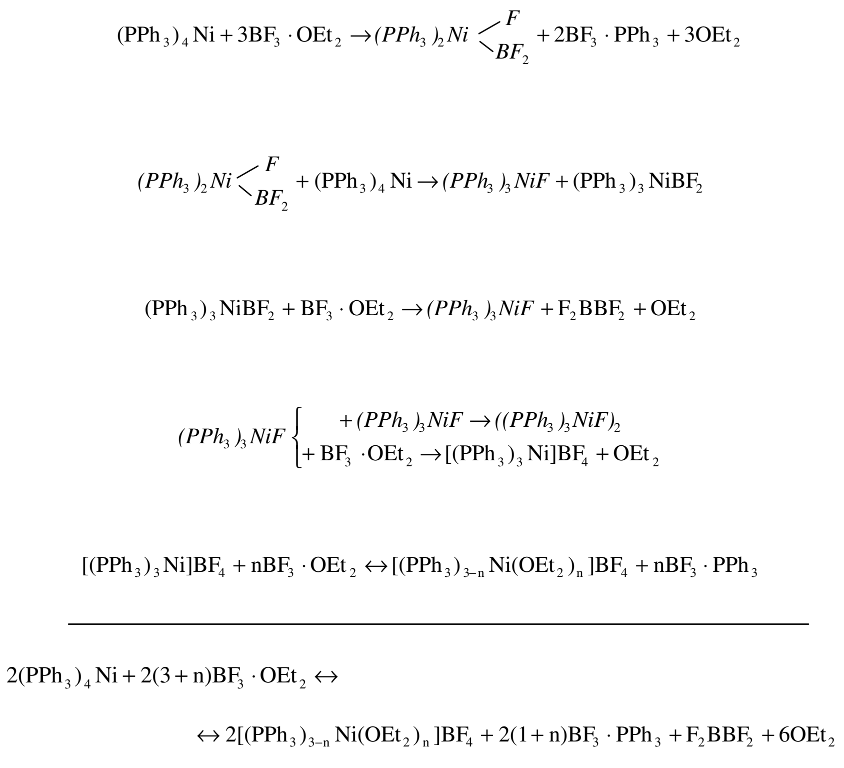
In summary, the experimental data provide evidence that the Ni(0) complexes, $Ni(PPh_3)_4$ and $(PPh_3)_2Ni(C_2H_4)$, can be oxidized by addition of Lewis acids with kinetic factors influencing the composition of the redox products. The sequential steps for the formation of Ni(I) complexes in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system are summarized in Scheme 1.

In Scheme 1 the prospective Ni(II) and Ni(I) complexes are shown in italics.

The first step consists of the oxidative addition to form the Ni(II) complex, which then reacts with the Ni(0) precursor to give Ni(I) complexes with covalent Ni–F and Ni–B bonds. Such processes are known to underlie the synthesis of, e.g., $(PR_3)_nNiX$ (X = Cl, Br, J) [21]. The Ni(I) borides in Scheme 1 enter the metathesis reaction as boron trifluoride etherate to be converted to Ni(I) fluorides. In the presence of excess $BF_3 \cdot OEt_2$, these are transformed into the monomeric paramagnetic cationic Ni(I) complexes that contain several phosphine ligands. The dimerization of the Ni(I) fluoro complexes is hampered, because the oxidation occurs only in the presence of an excess of $BF_3 \cdot OEt_2$ (B: Ni > 2). The substitution of phosphine ligands for diethyl ether molecules is an equilibrium process that is supported by the significant excess of $BF_3 \cdot OEt_2$ that is needed relative to Ni(I). The overall reaction of the phosphine complex $Ni(PPh_3)_4$ with $BF_3 \cdot OEt_2$ is given in Scheme 1. Equilibrium signs are used to take into account both the phosphine ligand substitution process and the potential oxidative addition of F_2BBF_2 to the Ni(0) complex [22].

4.2. Acetic acid

$(PPh_3)_3NiOOCCH_3$: The addition of acetic acid to a toluene solution of diamagnetic $Ni(PPh_3)_4$ results in the evolution of hydrogen, and an EPR signal (labeled 7 in Fig. 1) whose intensity maximizes at a CH_3COOH:Ni ratio of 3. Further addition of acetic acid up to a CH_3COOH:Ni ratio of 150 does not cause any visible change in the EPR



$$(PPh_3)_4Ni + 3BF_3 \cdot OEt_2 \rightarrow (PPh_3)_2Ni\begin{matrix}\diagup F\\ \diagdown BF_2\end{matrix} + 2BF_3 \cdot PPh_3 + 3OEt_2$$

$$(PPh_3)_2Ni\begin{matrix}\diagup F\\ \diagdown BF_2\end{matrix} + (PPh_3)_4Ni \rightarrow (PPh_3)_3NiF + (PPh_3)_3NiBF_2$$

$$(PPh_3)_3NiBF_2 + BF_3 \cdot OEt_2 \rightarrow (PPh_3)_3NiF + F_2BBF_2 + OEt_2$$

$$(PPh_3)_3NiF\begin{cases} + (PPh_3)_3NiF \rightarrow ((PPh_3)_3NiF)_2 \\ + BF_3 \cdot OEt_2 \rightarrow [(PPh_3)_3Ni]BF_4 + OEt_2 \end{cases}$$

$$[(PPh_3)_3Ni]BF_4 + nBF_3 \cdot OEt_2 \leftrightarrow [(PPh_3)_{3-n}Ni(OEt_2)_n]BF_4 + nBF_3 \cdot PPh_3$$

$$2(PPh_3)_4Ni + 2(3+n)BF_3 \cdot OEt_2 \leftrightarrow$$
$$\leftrightarrow 2[(PPh_3)_{3-n}Ni(OEt_2)_n]BF_4 + 2(1+n)BF_3 \cdot PPh_3 + F_2BBF_2 + 6OEt_2$$

where n = 0, 1, 2

Scheme 1.

signal, indicating that the formed Ni(I) complex is stable in an acidic medium. The observed EPR signal is typical for a tetrahedral Ni(I) complex with trigonal symmetry [20] and is therefore assigned to $(PPh_3)_3NiOOCCH_3$. To verify this assumption, we synthesized this complex by reacting $(PPh_3)_3NiCl$ with sodium acetate (Eq. (4)) and obtained the same EPR signal 7, but could not determine the HFS constants for the phosphorus nuclei due to line broadening, which is likely the result of the dynamic character of the Jahn–Teller effect in the tetracoordinate Ni(I) complex [20]

$$(PPh_3)_3NiCl + NaOOCCH_3 \rightarrow (PPh_3)_3NiOOCCH_3 + NaCl \tag{4}$$

The integral intensity of the EPR signal and the amount of released hydrogen depend on the rate at which acetic acid is added to the toluene solution of $Ni(PPh_3)_4$. The slower the rate at which the acid is added, the greater the amount of hydrogen is formed until a CH_3COOH:Ni ratio of 3 is reached after which its formation ceases.

Fig. 2 shows the relationship between the amount of released hydrogen and the rate of acetic acid addition. On adding a toluene solution of acetic acid to $Ni(PPh_3)_4$ at a rate of $\frac{[CH_3COOH]}{[Ni]} \times 10^{-3}\ s^{-1}$, about 0.47 mol of molecular hydrogen is released with respect to 1 mol of the starting Ni(0) complex, whereas this is only 0.09 mol of H_2 when the rate is increased 100-fold. The amount of released hydrogen is proportional to the Ni(I) acetate concentration.

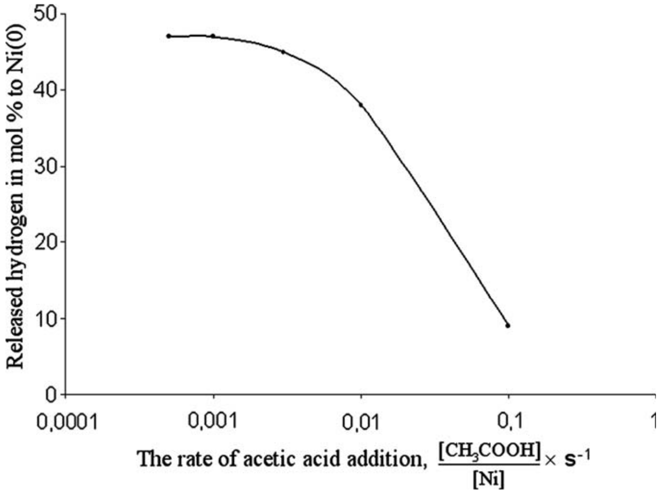
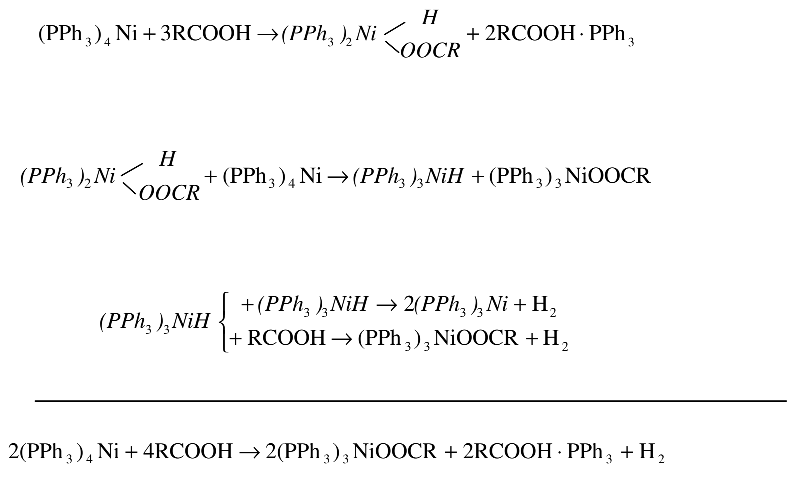


Fig. 2. Plot of the amount of released hydrogen vs. the rate of acetic acid addition to a toluene solution of the $Ni(PPh_3)_4$ complex at $T = 298$ K.

4.3. Trifluoroacetic acid

$(PPh_3)_3NiOOCCF_3$: To establish whether a stronger Brønsted acid affects the formation of the Ni(I) complexes, we oxidized $Ni(PPh_3)_4$ with trifluoroacetic acid. The EPR



$$(PPh_3)_4Ni + 3RCOOH \rightarrow (PPh_3)_2Ni\begin{matrix} H \\ OOCR \end{matrix} + 2RCOOH\cdot PPh_3$$

$$(PPh_3)_2Ni\begin{matrix} H \\ OOCR \end{matrix} + (PPh_3)_4Ni \rightarrow (PPh_3)_3NiH + (PPh_3)_3NiOOCR$$

$$(PPh_3)_3NiH\begin{cases} +(PPh_3)_3NiH \rightarrow 2(PPh_3)_3Ni + H_2 \\ + RCOOH \rightarrow (PPh_3)_3NiOOCR + H_2 \end{cases}$$

$$2(PPh_3)_4Ni + 4RCOOH \rightarrow 2(PPh_3)_3NiOOCR + 2RCOOH\cdot PPh_3 + H_2$$

where R = CH_3, CF_3.

Scheme 2.

signal of the resulting Ni(I) complex does not differ significantly in shape from that of the Ni(I) acetate complex obtained with acetic acid. The parameters of the EPR signal of the trifluoroacetate complex ($g_{\parallel} = 2.04$, $g_{\perp} = 2.35$) correspond to the tetracoordinated Ni-structure $(PPh_3)_3NiOOCCF_3$. We note that oxidative addition with trifluoroacetic acid occurs 5–7 times more rapidly than for acetic acid. Scheme 2 summarizes the sequence of steps that likely govern the oxidative interaction of both acetic and trifluoroacetic acids with $Ni(PPh_3)_4$.

In Scheme 2, the prospective Ni(II) and Ni(I) complexes are shown in italics.

The first step is the well-established oxidative addition of the acid to form the Ni(II) carboxylate hydride [6], which subsequently comproportionates in the presence of $Ni(PPh_3)_4$ to give Ni(I) hydride and carboxylate complexes. The Ni(I) hydride, being unstable in an acidic medium, is transformed by the acid into the Ni(I) carboxylate or decomposes bimolecularly to reform the Ni(0) complex, which reenters the oxidative addition cycle. Any decomposition of Ni(I) hydride is accompanied by evolution of hydrogen. The overall reaction summarizing the process of the slow addition of an organic acid to phosphine complex $Ni(PPh_3)_4$ is given in Scheme 2.

We assume that the formation of Ni(I) complexes is influenced by the rate of acid addition, which, when slow, enables the intermittently formed Ni(II) carboxylate hydride to comproportionate in the presence of unreacted $Ni(PPh_3)_4$.

5. Conclusions

Our study of the oxidation of Ni(0) phosphine complexes with Lewis and Brønsted acids (boron trifluoride etherate, acetic and trifluoroacetic acids) shows that (1) the reaction proceeds through a two-electron oxidative addition (Eqs. (1) and (3)), (2) the Ni(I) complexes result from comproportionation of Ni(0) and Ni(II) complexes, and (3) the relative concentration of the Ni(I) complexes depends on kinetic factors and increases as the rate of comproportionation increases relative to that of the oxidative addition.

This process of oxidative addition of boron trifluoride etherate to Ni(0) complexes may similarly govern the corresponding addition using organoaluminum compounds [23].

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