Influence of alcohols on the formation of the nickel complexes active in ethene oligomerization in the catalytic system $Ni(PPh_3)_4/BF_3 \cdot OEt_2$

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Abstract

The influence of ethanol and selected other alcohols on the formation of active nickel complexes for ethylene oligomerization was studied for the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ system by EPR and ^1H NMR spectroscopy. Both the presence of Ni(I) complexes and Ni(II) hydrides could be established. Coordinatively unsaturated Ni(I) complexes were shown to be the active catalysts for ethylene oligomerization, whereas the Ni(II) hydrides were shown to be inactive. The alcohol act as a promoter for the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ by facilitating the formation of the active Ni(I) complexes.
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1. Introduction

In recent years nickel compounds, primarily known as low molecular oligomerization catalysts for unsaturated hydrocarbons [1–9], have attracted increasing interest as effective catalysts for low olefin polymerization [10–21]. Despite the mechanistic progress that is being made the catalytic role of the nickel complex and particularly the nature of its valence state remains unresolved. The conventional view is that Ni(II) hydride complexes catalyze the low molecular olefin oligomerization, which is based on their identification by NMR in model systems [22–29] and on the enhancement by proton donors [30–33]. On the other hand, Ni(I) intermediates have been detected by EPR spectroscopy in Ziegler-type catalytic systems [34], and consequently the question arises whether Ni(I) ions actively participate in the catalytic process. Indirect data [35–38] has been reported on the involvement of Ni(I) complexes in the catalytic oligomerization, but it is unclear whether Ni(I) converts to Ni(II) as the catalytically active species.

In this paper we explore how proton donors, such as alcohols and acids, influence the formation of active complexes from the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system for the ethylene oligomerization.

2. Experimental

All operations were carried out under argon. Precipitates were separated with glass filters using Schlenk techniques. All reagents were kept under argon in sealed ampoules.

Toluene and benzene (Merck) were distilled prior to use over sodium in the presence of benzophenone. Boron trifluoride etherate (Merck) was distilled over LiH before use. Ethanol (99%, Merck) was reacted with sodium (10 g/L) and diethylphtalate and subsequently distilled prior to use. All other alcohols were fractionally distilled using a rectification column.

HBF$_3$OEt was prepared by reaction of BF$_3$·OEt$_2$ with ethanol in a ratio of 2:1 using toluene as solvent. Of the two resulting phases the lower yellow one containing the product was collected by syringe and used immediately [39]. HBF$_4$ was used as a toluene solution (>48% by chromatography) in which it forms a complex. The HBF$_4$-toluene complex (>98%, NMR) was obtained by dropwise addition of acetylacetone (0.352 g, 3.52 mmol) within 2 min to a solution of BF$_3$·OEt$_2$ (1 g, 7.05 mmol) in 10 ml of toluene, followed by transfer of the lower phase under an Ar atmosphere into a polyethylene vessel, and used within 2 h [40]. Ni(PPh$_3$)$_4$ [41] (PPh$_3$)$_3$NiCl [42], and (PPh$_3$)$_2$NiCl [42] were prepared according to literature procedures.

[Ni(PPh$_3$)$_3$]BF$_4$: 0.23 ml of BF$_3$·OEt$_2$ was added with a syringe under Ar to a stirred solution of 0.5 g of Ni(PPh$_3$)$_4$ in 10 ml of toluene (B:Ni molar ratio of 4:1). After 10 min at room temperature the mixture was cooled to −10 °C and filtered 20 min later. [Ni(PPh$_3$)$_3$]BF$_4$ was precipitated from the solution by adding 5 ml of heptane, filtered, and washed (hexane–toluene) to give a brown solid. Calc. for C$_{54}$H$_{45}$P$_3$NiBF$_4$: Ni, 6.3; C, 69.5; H, 4.80; P, 9.99. Found: Ni, 6.6; C, 69.3; H, 4.86; P, 9.78.

(PPh$_3$)$_3$NiOEt: 98.4 mg (2.14 mmol) of ethanol was added to 1 g (1.07 mmol) of [Ni(PPh$_3$)$_3$]BF$_4$ in 50 ml of toluene. The reaction mixture was stirred for 2 h and filtered. (PPh$_3$)$_3$NiOEt was precipitated from the solution by adding 10 ml of hexane, filtered, washed (hexane), and dried in vacuum to give yellow crystals. M.p. 15 °C. Calc. for C$_{56}$H$_{50}$P$_3$ONi: Ni, 6.6; C, 75.7; H, 5.6; P, 10.25. Found: Ni, 6.9; C, 73.4; H, 5.2; P, 9.77.

2.1. Method

Ethylene oligoimerization was carried out in a thermostated Schlenk vessel under argon at 23 °C. To a vigorously shaken solution of 0.2 g (0.181 mmol) of Ni(PPh$_3$)$_4$ in 10 ml of toluene (C_{Ni} = 18 mmol/L) was added 0.23 ml of BF$_3$·OEt$_2$ (molar ratio B:Ni = 10). After 3 min of stirring the required amount of the alcohol was added and the argon atmosphere was replaced for ethylene over a period of 10 s after which the ethylene consumption was monitored with a gas burette ($P_{ethylene}$ = 730 mm). Reaction products were analyzed with (GALS 311) GLC using a 50 m capillary column (KKL 50-08), a programmed temperature mode, and apiezon as liquid phase. ^{1}H NMR spectra were recorded at 25 °C in sealed ampoules with a Varian VXR-500S spectrometer using TMS as standard.

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 77 K (liquid nitrogen). 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 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 [43] 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 signals shown in Fig. 1 are summarized in Table 2.

3. Results and discussion

Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$ in toluene is amongst the most active catalytic systems in low olefin oligomerization [35,38]. The activity depends on the ratio of its components, reaching a maximum activity for ethylene oligomerization of ∼30,000 (C$_2$H$_4$ (mol))/(Ni (mol) × h) at a B:Ni ratio of ≈70, giving dimers (75%) and trimers (22%) as main products. At a B:Ni ratio of 10 the activity is reduced 100-fold, but when ethanol is added (ethanol:Ni = 5) the activity of the systems is nearly restored. Benzyl alcohol behaves similarly, but *iso*-propanol and *tert*-butanol are weaker promoters (see Table 1).

Proton donors added to Lewis acids are known to give strong Brønsted acids [39,44,45] that are capable of oxidative addition to Ni(0) to give Ni(II) hydrides. These hydrides are usually associated with the active species in Ni based catalytic systems. On the other hand, it has also been shown that during the formation of the Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$ catalytic system Ni(0) is oxidized quantitatively to give a number of Ni(I) cationic complexes of composition [(PPh$_3$)$_{3-n}$Ni(OEt$_2$)$_n$]BF$_4$ (n = 0, 1, 2) [38,46,47]. To investigate possible proton donor induced transformations of the Ni(0) to Ni(I) complexes, we studied by EPR and ^{1}H NMR spectroscopy their interaction with alcohols and acids.

3.1. [Ni(PPh$_3$)$_3$]BF$_4$/EtOH

The initial [Ni(PPh$_3$)$_3$]BF$_4$ cationic complex in toluene has an EPR signal characteristic for a tricoordinated structure (Fig. 1, signal 1) [48,49]. When absolute ethanol is added to the complex (EtOH:Ni = 5) this signal disappears and a composite EPR spectrum results as a superposition of two new resonances (Fig. 2, signals 2 and 3). With time signal 3 increases at the expenses of signal 2 and is the only one observed after 20–25 s. Throughout the entire process the integrated intensity of the EPR signals remains constant. The same EPR behavior is seen with

Table 1
Activity of the catalytic system Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$ promoted with alcohols in ethene oligomerization (B:Ni = 10; ROH:Ni = 5; T = 23 °C; P = 730 mmHg)

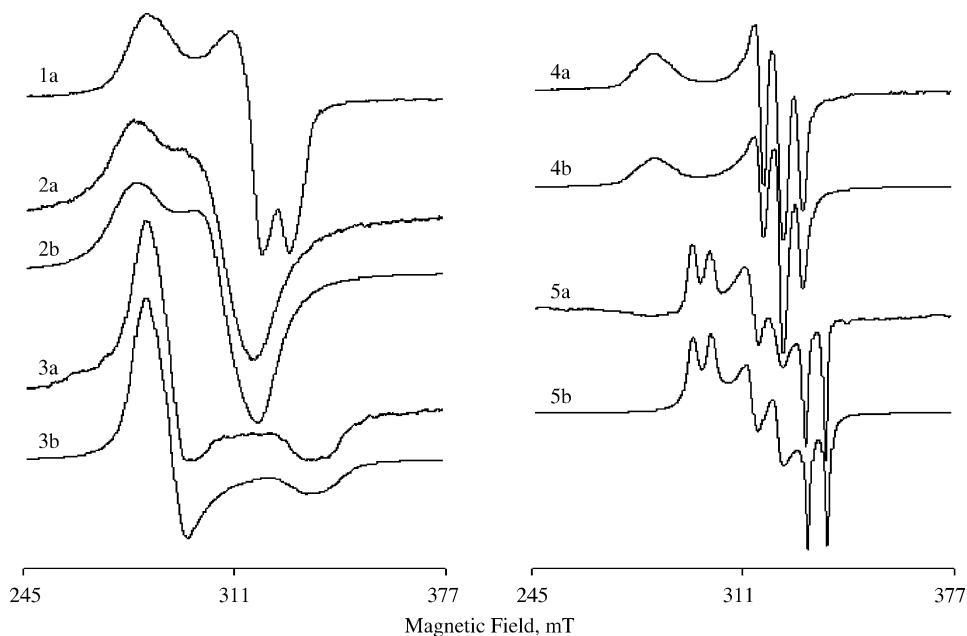| No.	Alcohol	Ethene oligomerization rate $\left(\frac{C_2H_4 \text{ (mol)}}{Ni \text{ (mol)} \times h}\right)$
1	C$_2$H$_5$OH	23000
2	C$_6$H$_5$CH$_2$OH	24000
3	*i*-C$_3$H$_7$OH	14600
4	*t*-C$_4$H$_9$OH	14500

Fig. 1. Experimental (a) and model (b) EPR spectra (in toluene at $T = 77\,K$) for (1) $[Ni(PPh_3)_3]BF_4$; (2) $(PPh_3)_2NiOEt$; (3) $(PPh_3)_3NiOEt$; (4) $(PPh_3)_2Ni(\mu\text{-}OEt)_2BF_2$; and (5) $(PPh_3)(OEt_2)Ni(\mu\text{-}OEt)_2BF_2$.

other alcohols, but the time for the full conversion of signal $2 \rightarrow 3$ differs amongst them as follows: ethanol (25 s) > propanol-1 > propanol-2 > butanol-1 > butanol-2 > 2-methylpropanol-1 > 2-methylpropanol-2 (40 min), reflecting a steric influence. It is noteworthy that the transformation period reduces as the HOR:Ni molar ratio increases. Resonances 2 and 3 were recorded independently for ethoxide complex $(PPh_3)_nNiOEt$ with n being 2 and 3, respectively; these complexes were prepared in situ from the reaction of $(PPh_3)_nNiCl$ with EtONa in toluene.

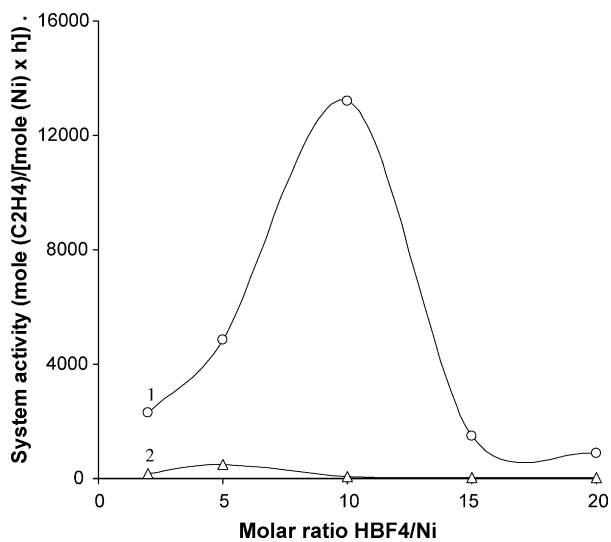Fig. 2. Dependence of the ethylene oligomerization of the $Ni(PPh_3)_4/HBF_4$ catalytic system on the activation (1) with and (2) without $BF_3 \cdot OEt_2$ using varying HBF_4:Ni ratios at $T = 296\,K$ ($C_{Ni} = 18\,mmol/L$, $P_{ethylene} = 730\,mm$).

We conclude that the $[Ni(PPh_3)_3]BF_4$ cationic complex is transformed by ethanol first to the electroneutral tricoordinate complex $(PPh_3)_2NiOEt$ and subsequently to the electroneutral tetracoordinate $(PPh_3)_3NiOEt$. The oxidation state of the transition metal does not change during this process; parameters of the EPR spectra are give in Table 2. Scheme 1 summarizes the possible sequence of events.
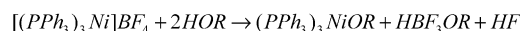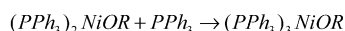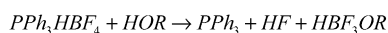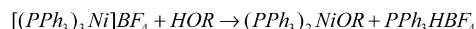
On addition of HOR to $[Ni(PPh_3)_3]BF_4$ the BF_4^- anion is exchanged for an alkoxy group to afford, under release of a PPh_3 ligand, a neutral tricoordinate Ni(I) complex, $(PPh_3)_2NiOEt$, which is responsible for EPR signal 2. The released PPh_3 is likely complexed to HBF_4, but liberated with additional alcohol, to subsequently coordinate to the newly formed $(PPh_3)_2NiOEt$ to give $(PPh_3)_3NiOEt$, which is responsible for EPR signal 3. We next explored the behavior of this complex toward $BF_3 \cdot OEt_2$.

3.2. $(PPh_3)_3NiOEt/BF_3 \cdot OEt_2$

On addition of an equimolar amount of boron trifluoride etherate to a toluene solution of $(PPh_3)_3NiOEt$ (B:Ni = 1), its EPR resonance is replaced for a new axially symmetric signal with a well resolved hyperfine structure (HFS) due to two equivalent ^{31}P nuclei (Fig. 1, signal 4). Its maximum intensity is half that of the initial complex $(PPh_3)_3NiOEt$. Its shape resembles that of bimetallic Ni(I)-bridged complexes, like $(PPh_3)_2Ni(\mu\text{-}X)_2AlR_2$ [34], and differs distinctly from $[(PPh_3)_2Ni(OEt_2)]BF_4$ [46]. Therefore, we assign the new EPR resonance to the di-ethoxy bridged structure $(PPh_3)_2Ni(\mu\text{-}OEt)_2BF_2$. Its intensity decreases on further addition of $BF_3 \cdot OEt_2$ while a new one emerges with a resolved HFS for a single ^{31}P nucleus (Fig. 1, signal 5,

Table 2
Parameters of EPR spectra for Ni(I) complexes

Signal	Complex	$g_{\|}$	$g_{\perp}$	$A_{\|}$ (mT)	$A_{\perp}$ (mT)	Ref.
1	$[Ni(PPh_3)_3]BF_4$	2.38_z	2.12_y	$6.1 (1P)_z$	$6.4 (1P)_y$	[49]
			2.07_x		$8.1 (1P)_x$	
2	$(PPh_3)_2NiOEt$	2.42	2.16	–	–	
3	$(PPh_3)_3NiOEt$	2.01	2.36	–	–	
4	$(PPh_3)_2Ni(\mu\text{-}OEt)_2BF_2$	2.42	2.10	4.6 (2P)	6.1 (2P)	
5	$(PPh_3)(OEt_2)Ni(\mu\text{-}OEt)_2BF_2$	2.29_z	2.14_y	$5.6 (1P)_z$	$8.0 (1P)_y$	
			2.03_x		$6.1 (1P)_x$	
6	$[(P(OEt)_3)_3NiL]BF_3X$	2.04_z	2.10_y	$17.5 (1P)_z$	$7.5 (1P)_y$	
			2.20_x	$7.4 (1P')_z$	$5.6 (1P')_y$	
				$7.4 (1P'')_z$	$3.3 (1P'')_y$	
					$18.5 (1P)_x$	

$$[(PPh_3)_3Ni]BF_4 + HOR \rightarrow (PPh_3)_2NiOR + PPh_3HBF_4$$

$$PPh_3HBF_4 + HOR \rightarrow PPh_3 + HF + HBF_3OR$$

$$(PPh_3)_2NiOR + PPh_3 \rightarrow (PPh_3)_3NiOR$$

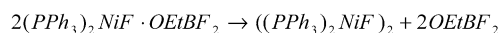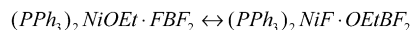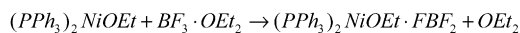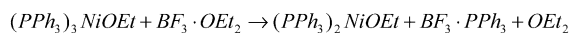$$[(PPh_3)_3Ni]BF_4 + 2HOR \rightarrow (PPh_3)_3NiOR + HBF_3OR + HF$$

Scheme 1.

Table 2) that has its maximum intensity at a B:Ni ratio of only 2 and fades after that. We speculate that additional $BF_3 \cdot OEt_2$ causes loss of another phosphine ligand followed by product degradation. Scheme 2 summarizes the proposed mechanism.

We believe that the phosphine-OEt_2 exchange with the Lewis acid BF_3 induces an equilibrium between $(PPh_3)_3$ NiOEt and the coordinatively unsaturated $(PPh_3)_2NiOEt$ complex even though the latter is not observed directly during the addition of $BF_3 \cdot OEt_2$. It seems fair to assume that 'free' BF_3 coordinates than immediately to $(PPh_3)_2NiOEt$, enabling fluoride-alkoxide exchange to give after complex break-up $(PPh_3)_2NiF$ as a diamagnetic dimer, which has been reported previously, and BF_2OEt. Coordination of this BF_2OEt with the BF_3-induced formation of $(PPh_3)_2NiOEt$ than results in the di-alkoxy bridged complex.

Removal of a phosphine ligand from the neutral complex to obtain the coordinatively unsaturated complex, the first step initiating the reaction sequence, should occur more easily than from cationic Ni(I) complexes on which we reported earlier.

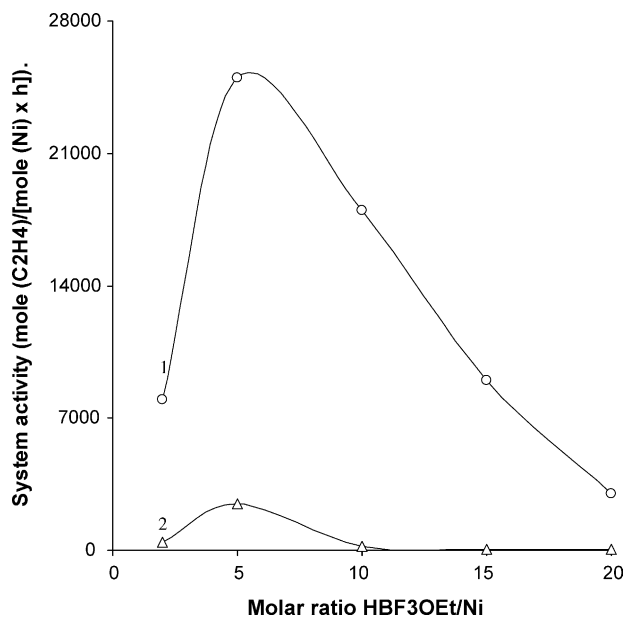$$(PPh_3)_3NiOEt + BF_3 \cdot OEt_2 \rightarrow (PPh_3)_2NiOEt + BF_3 \cdot PPh_3 + OEt_2$$

$$(PPh_3)_2NiOEt + BF_3 \cdot OEt_2 \rightarrow (PPh_3)_2NiOEt \cdot FBF_2 + OEt_2$$

$$(PPh_3)_2NiOEt \cdot FBF_2 \leftrightarrow (PPh_3)_2NiF \cdot OEtBF_2$$

$$2(PPh_3)_2NiF \cdot OEtBF_2 \rightarrow ((PPh_3)_2NiF)_2 + 2OEtBF_2$$

$$(PPh_3)_2NiOEt + OEtBF_2 \rightarrow (PPh_3)_2Ni(\mu-OEt)_2BF_2$$

$$(PPh_3)_2Ni(\mu-OEt)_2BF_2 + BF_3 \cdot OEt_2 \rightarrow PPh_3(OEt_2)Ni(\mu-OEt)_2BF_2 + BF_3 \cdot PPh_3$$

$$4(PPh_3)_3NiOEt + 2(3+n)BF_3 \cdot OEt_2 \rightarrow$$

$$\rightarrow 2(PPh_3)_{2-n}(OEt_2)_nNi(\mu-OEt)_2BF_2 + ((PPh_3)_2NiF)_2 + 2(2+n)BF_3 \cdot PPh_3 + 2(3+n)OEt_2$$
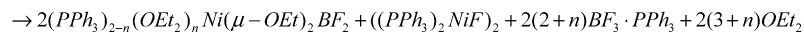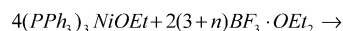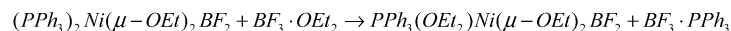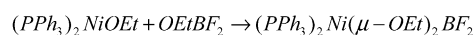
where $n = 0, 1$

Scheme 2.

Fig. 3. Dependence of the ethylene oligomerization of the Ni(PPh$_3$)$_4$/ HBF$_3$OEt catalytic system on the activation (1) with and (2) without BF$_3$·OEt$_2$ using varying HBF$_4$:Ni ratios at $T = 296$ K ($C_{Ni} = 18$ mmol/L, $P_{ethylene} = 730$ mm).

3.3. Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$/HBF$_4$

In the two component system Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$ (B:Ni = 4) nickel is monovalent and exists in the form of the tricoordinate complex [Ni(PPh$_3$)$_3$]BF$_4$ [48,49]. On adding proton acid HBF$_4$ to the reaction mixture as well as in the presence of excess of BF$_3$·OEt$_2$ phosphine ligands are eliminated from the Ni(I) cationic complex to give sequentially [(PPh$_3$)$_2$Ni(OEt$_2$)]BF$_4$ and [(PPh$_3$)Ni(OEt$_2$)$_2$]BF$_4$ for which the EPR spectra have been reported in reference [46]. The two approaches differ in that elimination of one (two) phosphine ligand(s) from cationic [Ni(PPh$_3$)$_3$]BF$_4$ requires a 3- (10-)fold excess of HBF$_4$ and a 50- (80-)fold excess of BF$_3$·OEt$_2$. The ease of forming the Ni(I) coordinately unsaturated complexes by the proton acid is due to capturing of the free phosphine as a poorly soluble phosphonium salt, HPPh$_3$BF$_4$. We note that varying the excess of the acid within the indicated range results in modest changes in the concentration of the Ni(I) complexes (~30%), but when the ratios surpass HBF$_4$:Ni > 10 or BF$_3$·OEt$_2$:Ni > 80 the Ni(I) complexes lose the last phosphine ligand and disintegrate to give colloidal nickel. Thus, both the weaker P—Ni bond of the Ni(I) alkoxide complexes and the insipiently formed Brønsted acids HBF$_3$OEt and HBF$_4$ enable the formation of coordinatively unsaturated Ni(I) complexes.

In the remainder of this paper, we explore the alternative mechanism for the alcohol promoted Ni-catalyzed ethylene oligomerization, namely the potential of forming Ni(II) complexes in the presence of Brønsted acids [22–25]. To this end the reaction of Ni(PPh$_3$)$_4$ with ethoxytrifluoroborate and tetrafluoroborate in deuterobenzene was studied by ^{1}H NMR.

3.4. Ni(PPh$_3$)$_4$/HBF$_3$X

The acidic protons of HBF$_3$OEt and HBF$_4$ in C$_6$D$_6$ have low field ^{1}H NMR chemical shifts at +9.7 and +12.5 ppm, respectively. When Ni(PPh$_3$)$_4$ is added in a B:Ni ratio of 3, these resonances decreases and new ones emerge at −8.0 and −5.0 ppm, respectively, that are indicative of hydrides. For comparison, the hydride ion of low spin pentacoordinated complex {[P(OEt)$_3$]$_4$NiH}BF$_3$OEt is observed at −15.1 ppm [25]. However, the high field resonances are rather broad ($\Delta \nu = 95$ Hz) and extremely sensitive to oxygen, disappearing with even the slightest contact with air. Therefore, they must be attributed to result from either Ni(I) or high spin Ni(II) complexes. The EPR spectrum of the HBF$_3$OEt system does suggest the presence of a various Ni(I) complexes, but only in low concentration; the spectrum displays a superposition of non-interpretable signals. On the other hand, the EPR spectrum of the HBF$_4$ system indicates the absence of such Ni(I) complexes. Consequently, the broad NMR resonances must be attributed to the high spin tetrahedral Ni(II) complex [(PPh$_3$)$_3$NiH]BF$_3$X.

In the next experiments we distinguish between the relative activities of the Ni(I) cationic and Ni(II) hydride complexes for the Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$ catalyzed ethylene oligomerization by adding, respectively, the Brönsted acid HBF$_4$ to the catalytic system or the Lewis acid to the mixture of Ni(PPh$_3$)$_4$/HBF$_4$.

3.5. Ni(I) catalysis—the tricomponent Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$/HBF$_4$ system

When the addition of BF$_3$·OEt$_2$ to the Ni(0) complex Ni(PPh$_3$)$_4$ in toluene (B:Ni ratio of 4) is followed by
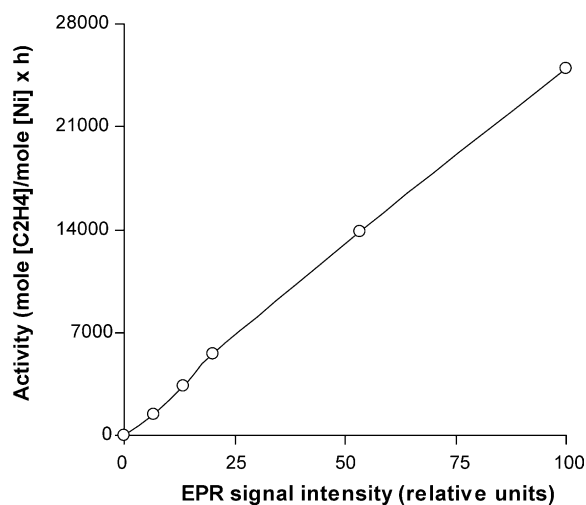
Fig. 4. Relationship between the activity of the system Ni(PPh$_3$)$_4$/ BF$_3$·OEt$_2$/HBF$_3$OEt and the EPR signal intensity.
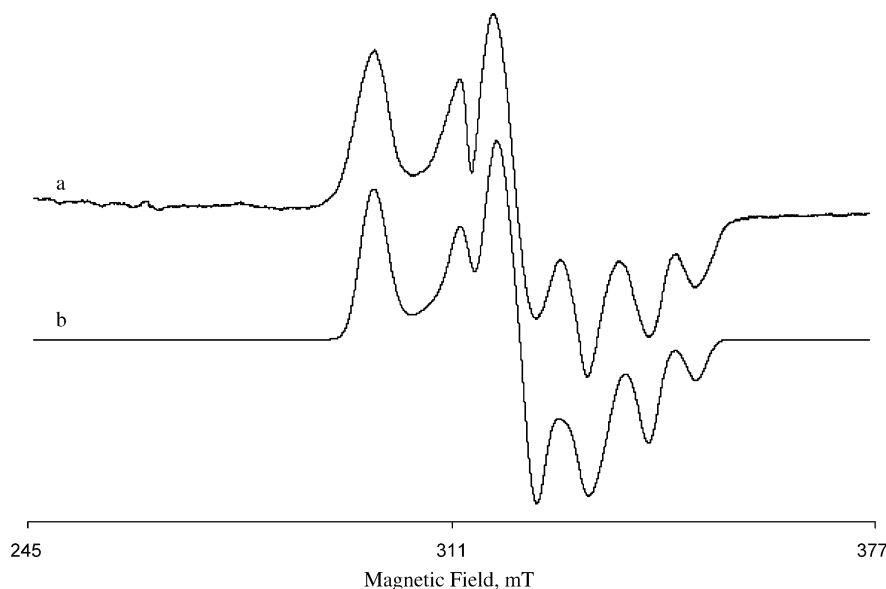
Fig. 5. Experimental (a) and model (b) EPR spectra (in toluene at $T = 77$ K) for [(P(OEt)$_3$)$_3$NiL]BF$_3$X.

addition of HBF$_4$ ($2 < $B:Ni ratio$ < 20$) a catalytic system results with a Ni(I) active catalysts (see above) that has a high activity in ethylene oligomerization. The dependence of the system activity ((mol (C$_2$H$_4$)/(mol(Ni) × h)) peaks at a HBF$_4$:Ni molar ratio of 10 (Fig. 2). We note that the activity maximum for this tricomponent system requires about 1/6 of the amount of boride that is needed for the two-component system Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$.

3.6. Ni(II) catalysis—the tricomponent Ni(PPh$_3$)$_4$/HBF$_4$/BF$_3$·OEt$_2$ system

Instead, when BF$_3$·OEt$_2$ is added to a premixed solution of Ni(PPh$_3$)$_4$ and HBF$_4$ (B:Ni ratio of 3) in toluene in a ratio of $2 < $B:Ni$ < 80$, the resulting system, containing Ni(II) hydride complexes, shows very low ethylene oligomerization activity, less than 2% of the Ni(I) catalyzed system (Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$/HBF$_4$), irrespective of the B:Ni ratio. The Ni(PPh$_3$)$_4$/HBF$_4$ system itself shows a similar low activity (Fig. 2), just like the Ni(PPh$_3$)$_4$/HBF$_3$OEt system, sharply contrasting that of the three component Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$/HBF$_3$OEt (B:Ni = 4) that is driven by the Ni(I) catalyst (Fig. 3).

Catalytic systems based on Ni(I) cationic complexes have a distinguishing feature. After the oligomerization of ethylene has started, the EPR signals of Ni(I) disappear. This may be associated with either a change in the oxidation state of Ni(I) or formation of Ni(I) dimers. However, if triethylphosphite P(OEt)$_3$, a catalytic poison, is added to the system (P:Ni > 3) when it is shows its highest activity, the oligomerization ceases instantly and new intensive EPR signals of mononuclear Ni(I) complexes emerge with an intensity that is proportional to the rate of ethylene oligomerization at the time of poisoning (Fig. 4). The EPR signal (Fig. 5) is typical

for a Ni(I) tetragonal complex, such as [(P(OEt)$_3$)$_3$NiL]BF$_3$X with L and X likely being PPh$_3$ and OEt, respectively (see Table 2), as it shows three nonequivalent phosphorus ligands in a trigonal arrangement with a pseudo-degenerate ground state [43]. The individual line is wide ($\Delta B > 3$ mT), so that the hyperfine structure from the PPh$_3$ ligand cannot be defined, which is in line with the spectrum reported for [(P(OBu)$_3$)$_2$Ni(PPh$_3$)$_2$]BF$_4$ [43].

These data indicate that the catalytic nickel system is monovalent during the ethylene oligomerization and exists in the form of diamagnetic dimers, which dissociate and coordinate phosphite ligands to form mononuclear complexes. The extreme dependence of the catalytic activity on the amount of Brønsted acid indicates the sensitivity of the active catalyst. On the one hand, the acid eliminates phosphine ligands to form the active catalytic species, i.e., the coordinately unsaturated Ni(I) cationic complexes with one phosphine ligand, while on the other hand they are destroyed with excess acid.

4. Conclusions

The following mechanistic conclusions can be drawn from this study:

1. Coordinatively unsaturated Ni(I) complexes are the active ethylene oligomerization catalysts of the Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$ system.
2. Proton donors, such as alcohols, promote the Ni(PPh$_3$)$_4$/BF$_3$·OEt$_2$ catalytic system by facilitating the formation of the coordinatively unsaturated Ni(I) complexes.
3. Proton donors, such as alcohols, enable the formation of Ni(II) hydrides, but these are not the active ethylene

oligomerization catalysts at room temperature and under atmospheric pressure.

Acknowledgements

References

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