

Catalysis of olefin oligomerization by Ni(I) complexes

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Abstract

Activity of nickel-complex catalysts is traditionally attributed with hydride Ni(II) complexes generated by oxidation of Ni(0) particles with Brønsted acids. In this work catalytic activity of Ni(I) complexes obtained in the system Ni(PPh₃)₄/BF₃·OEt₂ have been studied. On the basis of EPR and ¹H NMR data, the formation of dimeric catalytic complexes with ethylene and styrene has been found. Ethylene transformation on Ni(I) catalyst results in 1-butene, 2-butene and trimers mixture. In the case of styrene, the polymers with molecular mass 2500 were obtained. These polymers contain terminal double bonds which can be used in design of new graft copolymers.

Keywords: Catalysis, ethylene, styrene, oligomerization, nickel, complex

Introduction

Complexes of transition metals become more and more widespread as catalysts of hydrocarbon reactions^{1,2} and they successfully compete with more expensive systems based on noble metals. The activity of nickel-complex catalysts in oligo- and polymerization of unsaturated hydrocarbons opens routines to new polymers, valuable reagents and products of organic synthesis.³⁻¹⁰ Unfortunately, there is only limited data concerning with the nature of these catalysts, the structure of the active center and the reaction mechanism. Such a situation is connected with the complexity and multi-component composition of the usually used nickel catalysts. At the same time, relatively simple catalytic systems from triphenylphosphinic nickel complexes allow to carry out oligomerization and to obtain reliable information about mechanism of the reaction.¹¹

The activity of the nickel-complex catalysts is traditionally attributed to the hydride Ni(II) complexes generated by the oxidation of Ni(0) particles with Brønsted acids such as ROH,

CF_3COOH , HBF_3OR .¹¹⁻¹⁴ On the other hand, it was shown earlier¹⁵ that the phosphinic complex $\text{Ni}(\text{PPh}_3)_4$ can be oxidized by boron trifluoride giving rise to $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ which has been confirmed by a typical Ni(I) signal in EPR spectrum. Elimination of phosphorus-containing ligands is possible in the excess of $\text{BF}_3\cdot\text{OEt}_2$ and the resulting coordinating-unsaturated Ni(I) complexes are able to catalyze oligomerization of ethylene and propylene. This work is devoted to the study of triphenylphosphinic nickel(I) complexes as catalysts in ethylene and styrene oligomerization and to the clarification of the active center structure.

Results and Discussion

Quantitative oxidation of Ni(0) to Ni(I) in the catalytic system $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3\cdot\text{OEt}_2$ gives rise to three cationic Ni(I) complexes: $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$, $[(\text{PPh}_3)_2\text{Ni}(\text{OEt}_2)]\text{BF}_4$ and $[(\text{PPh}_3)\text{Ni}(\text{OEt}_2)_2]\text{BF}_4$ which ratio depends on concentration of the Lewis acid [16]. Maximum concentration of cationic complex $[(\text{PPh}_3)_3\text{Ni}]\text{BF}_4$ was found at molar ratio B: Ni = 4 and this complex exists in double degenerated basic state in toluene solution¹⁶ which is seen as spread asymmetric signal **1** in EPR spectrum at 77 K due to Jahn-Teller effect (Figure 1). This complex is inactive relative to ethylene at atmospheric pressure and room temperature. Elimination of one triphenylphosphinic ligand from coordinating sphere of cationic complex $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ by the action of $\text{BF}_3\cdot\text{OEt}_2$ results in $[\text{Ni}(\text{PPh}_3)_2(\text{OEt}_2)]\text{BF}_4$ complex (Figure 1, spectrum **2**). The obtained solution absorbs ethylene due to oligomerization. This is accompanied with disappearance of EPR signal **2** from $[\text{Ni}(\text{PPh}_3)_2(\text{OEt}_2)]\text{BF}_4$ and appearance of time-unstable signal **3** (Figure 1) with hyperfine structure from one phosphorus nucleus.

Evidently, we have here substitution of phosphinic ligand and, probably, ether with ethylene giving rise in π -complex $[(\text{PPh}_3)\text{Ni}(\eta^2\text{-C}_2\text{H}_4)_2]\text{BF}_4$. This complex is unstable and exists in solution for several second, after that EPR signal **3** disappears and is not visible during the whole reaction. Maximum activity of the catalyst falls at the first 40-80 seconds reaching 30000 ethylene (mol consumed) / $[\text{Ni}(\text{mol}\cdot\text{h})]$ at B: Ni = 80, after that the reaction velocity slumps (Figure 2). The principal products of the reaction are butene-2 (60-65%), butene-1 (25-30%) and up to 10% of trimers (methylpentenes and *n*-hexenes).

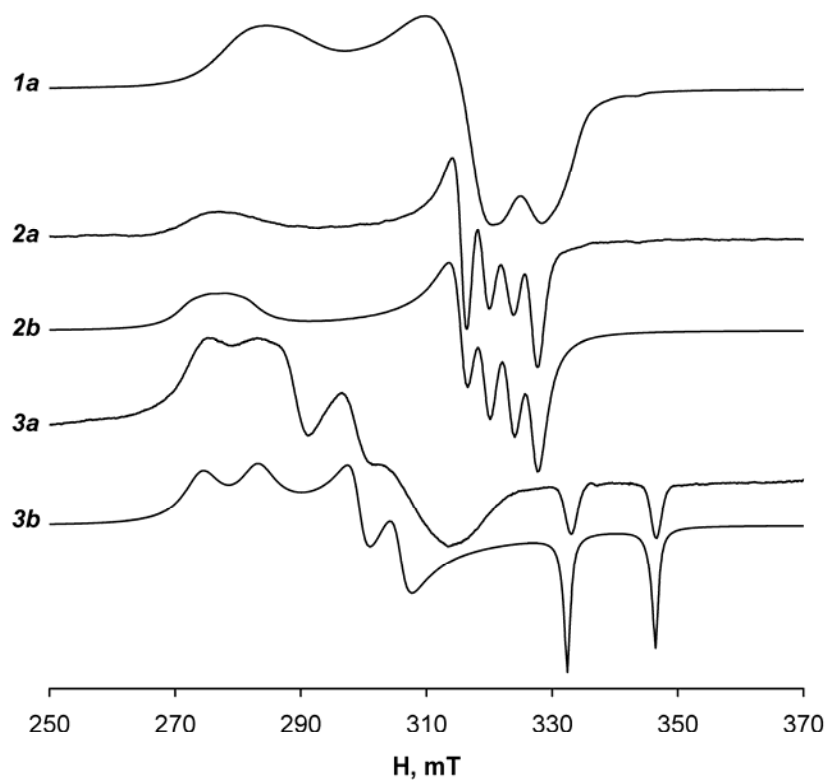


Figure 1. Experimental (*a*) and simulated (*b*) EPR spectra of the nickel(I) complexes: $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ (**1**), $[(\text{PPh}_3)_2\text{Ni}(\text{P}(\text{OEt})_3)_2]\text{BF}_4$ (**2**) and $[(\text{PPh}_3)\text{Ni}(\eta^2\text{-C}_2\text{H}_4)_2]\text{BF}_4$ (**3**) in toluene solution, $T = 77 \text{ K}$.

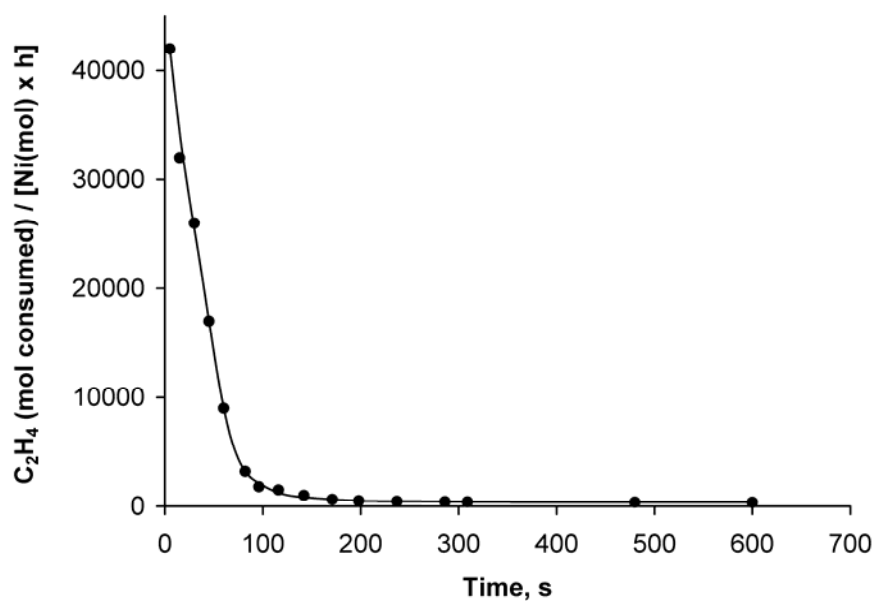


Figure 2. Time dependence of activity of $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2$ (B: Ni = 80) catalytic system in ethylene oligomerization.

The disappearance of EPR signals in the beginning of the catalytic reaction can be attributed with a change of Ni(I) oxidation degree or with dimerization of these ions. On the other hand, addition of triethylphosphite (catalytic poison), to the reaction mixture stops the oligomerization immediately and an intensive EPR signal from Ni(I) appears. This spectrum corresponds to $[(PPh_3)Ni(P(OEt)_3)_3]BF_4$ complex.¹⁷ There is a straight-line relationship between the oligomerization velocity at the moment of triethylphosphite introduction and intensity of new EPR signal (Figure 3). Therefore, activity of the system is connected with cationic Ni(I) complexes which are present in the form of diamagnetic dimers during ethylene oligomerization. Termination of the reaction by triethylphosphite is accompanied by destruction of the dimers and release of the paramagnetic Ni(I) particles.

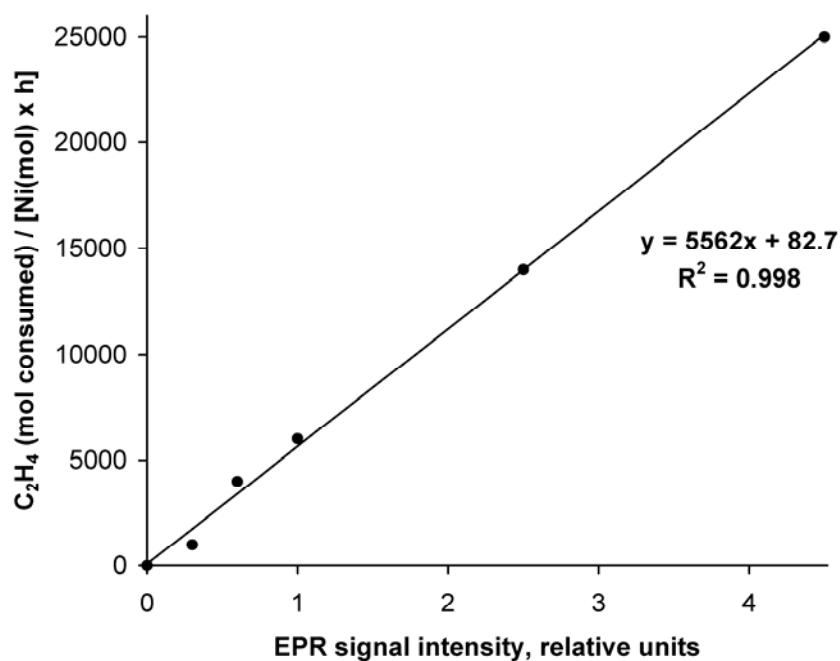
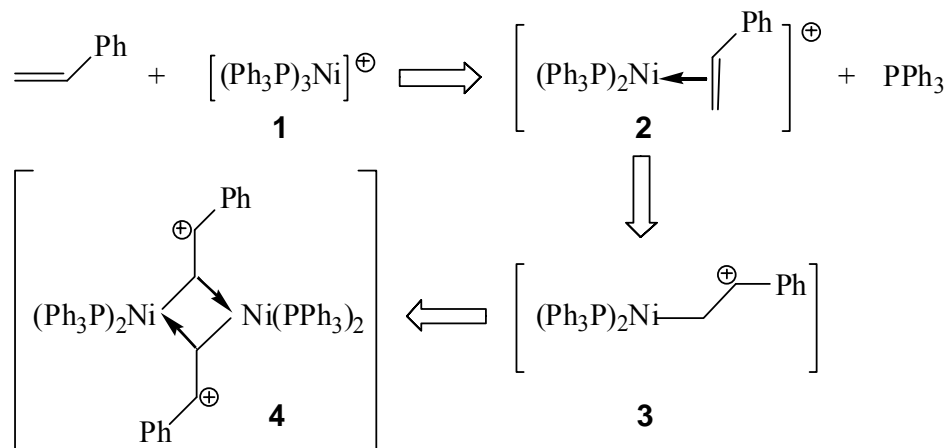


Figure 3. Catalytic activity of $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ (B: Ni = 80) system in ethylene oligomerization vs. Ni (I) concentration.

The detail study of the diamagnetic particles is experimentally complicated using gaseous substrate, so we have used styrene in this reaction. In contrast to ethylene, styrene reacts actively with the initial cationic complex $[Ni(PPh_3)_3]BF_4$. For example, the addition of styrene (molar ratio styrene: Ni = 2) to catalytic system $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ (B: Ni = 4) in which nickel is present as $[Ni(PPh_3)_3]BF_4$ results in immediate disappearance of EPR signal from initial Ni(I) complex. At the same time, a set of signals in NMR ^{13}C was noted in the weak field (156, 140, 136, 135 and 129 ppm, Figure 4) which is characteristic for benzene cycle conjugated with carbocation.¹⁸ These results suppose the earlier suggestion about formation of Ni(I) carbocationic complexes in the catalytic system which was done on the bases of UV spectroscopy data.¹⁹ So,

the following scheme of styrene activation on cationic complex $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ might be applied (Scheme 1.).

Unlike to the ethylene system, π -complex **2** was not found in the case of styrene which is connected with more rapid π - σ -rearrangement.



Scheme 1. Styrene activation on cationic complex.

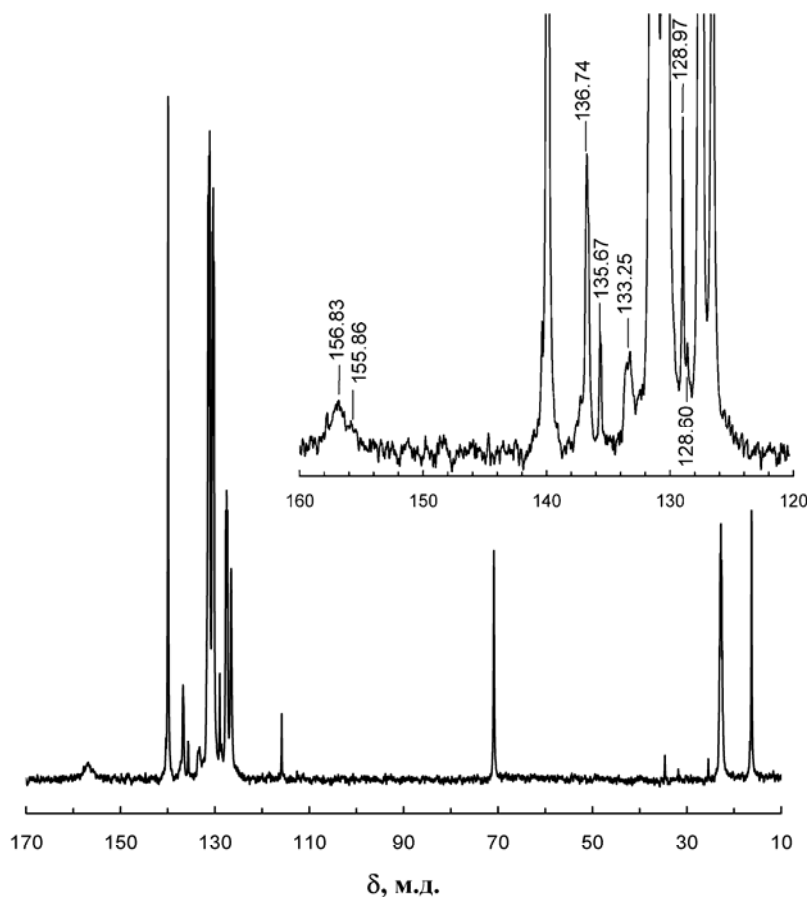


Figure 4. NMR ^{13}C spectrum of $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2/\text{C}_8\text{H}_8$ system (Ni: B: $\text{C}_8\text{H}_8 = 1: 4: 2$) in toluene- d_8 .

The addition of styrene (styrene: Ni = 200) to the catalytic system $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2$ (B: Ni = 4) in which nickel exists as cationic complex $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ results in styrene polymerization. The data from Figure 5 show an induction period before the active styrene conversion due to substitution of the phosphine ligand with styrene. The reaction proceeds up to full conversion of the monomer, but the polymer yield is 67% only, which points to the formation of low-molecular ethanol-soluble oligomers. The addition of new monomer portions to the reaction mixture after completion of the polymerization gives rise to resuming of the process, up to styrene : Ni = 800 at which ratio high viscosity of the system makes impossible the reaction. This points to relative stability of the carbocationic centers and correlates with the possibility to observe carbocations in NMR spectra. The obtained product is a paraffin-like material, it has band in FTIR spectrum at 1640 cm^{-1} which corresponds to the absorbance of double bonds. NMR ^{13}C spectra show signal at 137-138 ppm pointing to terminal unsaturated moieties $\text{CH}_2=\text{C}_{\text{Ph}}$, their contents is 1.5 mol. % from the total styrene units. Molecular mass of the polymer is 2500.

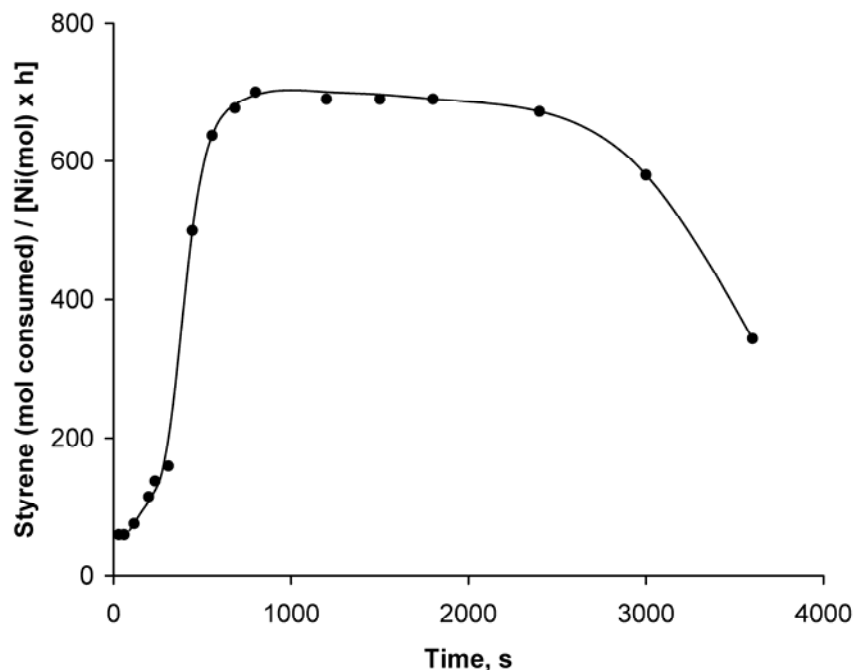


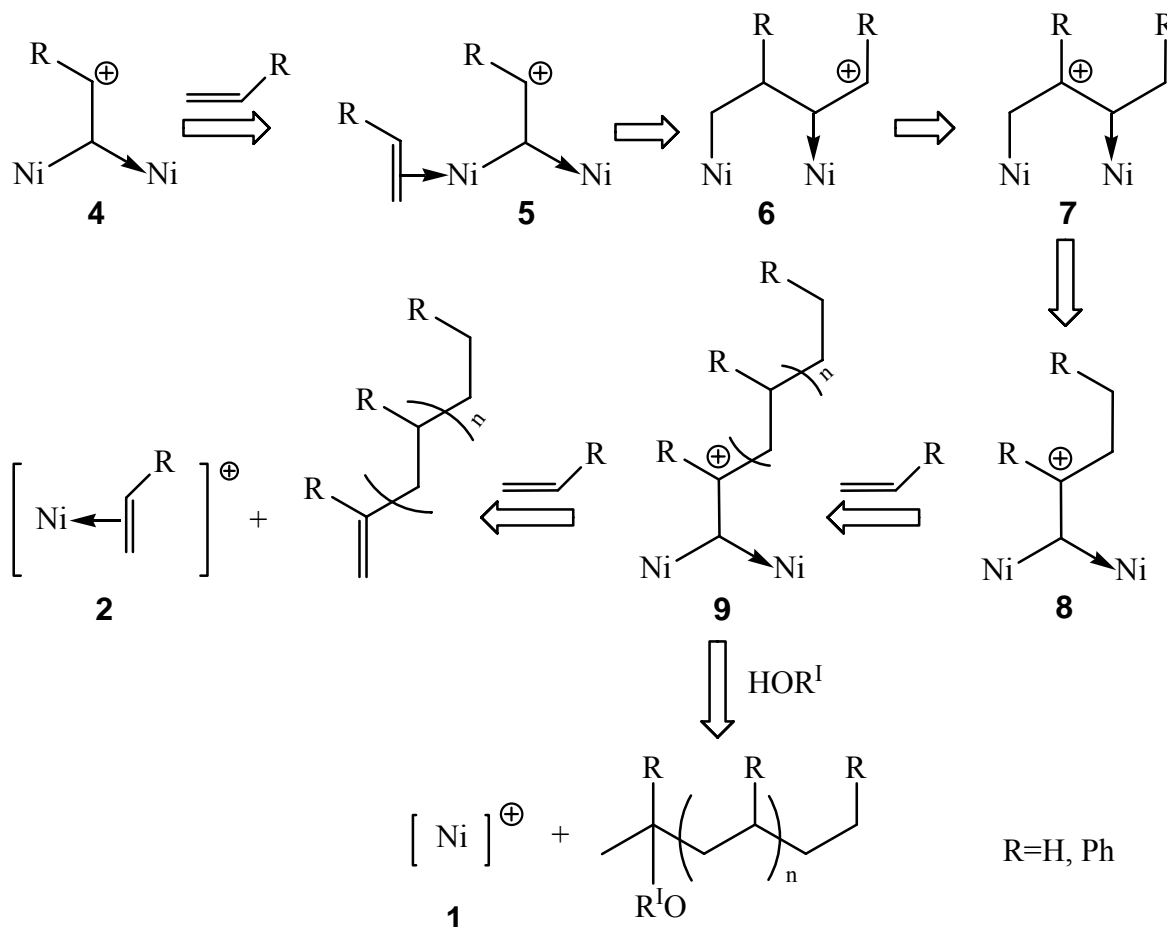
Figure 5. Time dependence of catalytic activity of $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2$ (B: Ni = 4) system in styrene polymerization, 20°C .

In the case of methylacrylate and methacrylate the polymerization was not observed. The inactivity of monomers with an acceptor substituent at the double bond indicates mainly cationic nature of the active Ni complexes. On the other hand, addition of triethylamine as typical inhibitor of cationic polymerization results in 30% deceleration of the reaction only at the ration NEt_3 : Ni = 5. Similarly to ethylene, triethylphosphite completely suppresses the reaction

giving rise to paramagnetic complex $[(PPh_3)Ni(P(OEt)_3)_3]BF_4$. Introduction of large amounts of ethanol into the system also terminates polymerization, and the signals of the ethoxy groups were found in ^{13}C NMR spectrum (74-83 and 64-68 ppm).

Results of this work and previous data¹⁹ allow us to propose the following scheme of the reactions of unsaturated hydrocarbons on Ni(I) cationic complexes (Scheme 2.).

Products of these reactions are unsaturated compounds useful as starting compounds for organic synthesis and polymer chemistry.



Scheme 2. Transformations of unsaturated hydrocarbons on Ni(I) cationic complexes.

Experimental Section

General Procedures. All operations with nickel catalysts were carried out in purified argon by the Shlenk-technology. Glass Shlenk filters were used for filtration. All reagents were stored in argon-filled ampoules. Toluene, benzene and heptan (Merck) were distilled under sodium in the presence of benzophenone before use. Boron trifluoride etherate (Merck) was distilled under LiH

in argon. Ethanol was dehydrated by distilling with sodium (10 g/L). Diethyl ether was distilled under sodium and stored under sodium mirror. Styrene was distilled in vacuum (32 °C/10 mm Hg). The EPR spectra were run on a PS-100X instrument at 25°C. Diphenylpicrylhydrazile and Mn^{2+} in MgO were used as the field standards. NMR spectra were recorded at 20 °C on a VXR-500S "Varian" spectrometer. FTIR spectra were obtained on a Bruker IFS25 spectrometer (KBr pellets). Molecular mass of the polystyrene sample was determined by isopiestic method using azobenzene as standard.²⁰

Synthesis of $[Ni(PPh_3)_3]BF_4$ complex¹⁵. $BF_3 \cdot OEt_2$ (0.23 mL) was added with a syringe upon stirring to a solution of $Ni(PPh_3)_4$ (0.5 g, B:Ni = 4:1) in toluene (10 ml) during 10 min at room temperature under argon. The mixture was cooled down to -10 °C and precipitate was filtered off. $[(PPh_3)_3Ni]BF_4$ complex was isolated from filtrate by precipitation with heptane as brown solid with 75% yield (0.3 g). Found, %: Ni 6.6, C 69.3; H 4.86; P 9.78. $C_{54}H_{45}P_3NiBF_4$. Calcd, %: Ni 6.3; C 69.5; H 4.80; P 9.99.

Ethylene oligomerization. Toluene (10 ml) and nickel complex (10^{-4} mol) were placed into temperature-controlled reactor placed on a shaker at 20 °C and ethylene was bubbled through the solution of catalyst. Amount of the unreacted ethylene was measured volumetrically. The catalyst was destroyed by the addition of water after the reaction end, and the organic fraction was dried under calcium chloride; the oligomerization products were distilled off and analyzed by GLC on a "GALS" chromatograph equipped with flame-ionization detector and capillar column (15 m, HP-5).

Styrene polymerization. Toluene (10 ml) and nickel complex (10^{-4} mol) were placed into a temperature-controlled reactor at 20 °C and styrene was added under vigorous stirring. Unreacted styrene was monitored using GLC data obtained on a "GALS" chromatograph equipped with flame-ionization detector, phase: apieson, column length: 1500 mm, diameter: 5 mm. The resulting polymer was precipitated into ethanol and dried in vacuum.

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