Very Active Neutral P,O-Chelated Nickel Catalysts for Ethylene Polymerization


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ABSTRACT: A series of highly active nickel-based neutral catalysts for ethylene polymerization is presented. These catalysts are obtained by direct complexation of simple fluorinated ketoylides onto bis-(1,5-cyclooctadiene)nickel. Catalyst formation readily occurs in the presence of an olefin, but due to the electron deficiency of the ligand, it hardly happens in the absence of an olefin or another Lewis base. Activities greater than \(2 \times 10^6 \text{gPE/gNi}/\text{h}\) and productivities higher than \(15 \times 10^6 \text{gPE/molNi}/\text{h}\) are typically observed. These catalysts are also active for the polymerization of \(\alpha\)-olefins such as 1-hexene and 1-propane. Polymer characterization indicates that highly linear, low molecular weight PEHD is formed by these complexes.

Introduction

For more than 40 years, early transition metal type catalysts have generated considerable scientific interest in industry and in academia. Despite all their advantages (high activity and regio- and stereospecificity), their strongly oxophilic nature limits them to the polymerization of nonpolar monomers, with Lewis bases being a poison. Consequently, less oxophilic (softer) catalytic systems based on late transition metals have emerged, so as to find new ways of preparing polymers or copolymers containing polar units or tolerating functionalities. To our knowledge, the very first late transition metal catalysts for ethylene polymerization are an iodorhodium complex generated from Rh[1,5-cyclooctadiene]nickel. Catalyst formation readily occurs in the presence of an olefin, but due to the electron deficiency of the ligand, it hardly happens in the absence of an olefin or another Lewis base. Activities greater than \(2 \times 10^6 \text{gPE/gNi}/\text{h}\) and productivities higher than \(15 \times 10^6 \text{gPE/molNi}/\text{h}\) are typically observed. These catalysts are also active for the polymerization of \(\alpha\)-olefins such as 1-hexene and 1-propane. Polymer characterization indicates that highly linear, low molecular weight PEHD is formed by these complexes.

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The reaction medium.

19–21 These bis(ylide)nickel and palladium catalysts are very active and lead to a wide range of polyethylene molecular weight through change in the ligand.\(^{22}\) After these pioneering works were disclosed, \(^{23–25}\) a major contribution was achieved by Brookhart and co-workers\(^{26,27}\) with the use of bulky substituted \(\alpha\)-diamine ligands for the preparation of nickel and palladium cationic complexes. These systems proved to be very active and able to copolymerize ethylene and \(\alpha\)-olefins with methyl acrylate.\(^{28}\) Recently, neutral nickel(II) complexes based on salicylaldimine ligands were developed by Grubbs.\(^{29,30}\) These complexes allow the synthesis of high molecular weight polyolefins with excellent activity. Finally, Gibson\(^{31,32}\) and Bennett\(^{33}\) reported promising work in ethylene polymerization via the use of very low cost and/or low toxicity metals, such as iron and cobalt stabilized with 2,6-bis(imino)pyridyl ligands. These catalysts display excellent activities when activated with MAO. Yet, the use of MAO precludes polymerization of polar olefins or olefins in the presence of water.

In a previous work, we have disclosed preliminary results about catalytic polymerization of ethylene in aqueous emulsion using binuclear phosphorus-oxygen chelating catalysts.\(^{34}\) To our knowledge, for the very first time, a latex of HDPE was prepared by direct catalytic polymerization in water.\(^{35,36}\) To continue our studies, we quickly realized that we needed to prepare extremely active catalysts, as we usually observed a loss of activity of 20–100 times when going from an organic medium to an aqueous dispersed medium. We chose to still work with neutral nickel catalysts as we expected MAO activation for cationic complexes to be close to impossible under such conditions. Moreover, we expected cationic complexes formed by borane activation, or an equivalent route, to react with hydroxide ions. Among the ligands that confer a very high activity to the catalytic systems, we have to admit to select those which are reasonably easy to synthesize. As it is usually accepted that activity is strongly related to the electrophilicity (acidity) of the metal, highly electrowithdrawing fluorinated groups were incorporated onto the ligand. Here, we present first results about the synthesis of these
ligands, their use in the preparation of the catalytic complexes, as well as the results obtained with these catalysts in organic phase. In a subsequent paper, results about emulsion polymerization of ethylene and α-olefins will be presented.

Experimental Section

Ligand 1a and Ni(COD)2 were purchased from a commercial supplier. All solvents and reagents were dried and degassed, according to standard Schlenk techniques. THF was distilled on sodium benzophenone prior to use. NMR analysis was carried out on a 400 MHz Bruker instrument. Polymer analyses were made in a mixture of d2-trichloroethane and d6-benzene at 90 °C. GPC was determined in 1,3,4-trichlorobenzene at 145 °C, using a Waters AIC instrument. 31P and 13C NMR resonances were recorded in CDCl3, 1H). B.N. results were reported relative to external standards (H3PO4, 85% in water, and CFCl3).

Synthesis of 6,6,6,5,5,4,4,4-Heptafluoro-3-oxo-2-(triphosphorylphosphonyle)hexanoic Acid, Ethyl Ester (1b).

A slurry of carboxethoxyethyltriphosphorylphosphonium bromide (3.4 g, 7.9 mmol) in 25 mL of anhydrous THF is cooled in an ice water bath and treated with triethylamine (2.4 mmol, 17.2 mmol). After 15 min stirring, the mixture is treated dropwise with pentafluorobenzoyl chloride (18.1 mL, 65.4 mmol). The mixture is allowed to reach room temperature and left for 1 h. The reaction medium is filtered, the precipitate is washed three times with cold THF, and the filtrate is dried in vacuo, resulting in a powder which is recrystallized in MeOH. Isolated yield: 63%. NMR (ppm, in CDCl3): δC 7.5–7.6, 7.8–7.9, 15H, m; δC 3.78, 2H; q; δC 1H, 0.2H, t (J H-H = 7 Hz). 13C (ppm, in CDCl3): 13C 13.6, 60.3, 72.6 (J C-P = 115 Hz), 124 (J C-C = 100 Hz), 129.5 (J C-P = 133 Hz), 132.4 (J C-C = 3 Hz), 133.5 (J C-C = 10 Hz), 166.7 (J C-P = 13 Hz). 10% Ni(COD)2, 2.07 ppm, s, 16H; 4.29 ppm, s, 8H (coordinated COD protons); ester protons of ligand 1a.

Typical Polymerization Procedure. In a Schlenk tube, 23.5 mg of Ni(COD)2 is dissolved in 8.5 mL of toluene. Then, 4 mL of this solution is added to the reactor, heated at 70 °C, and the polymerization is observed. The reaction medium (400 mL) is added to methanol (600 mL), and the polymer (70 g) is collected through filtration.

Results and Discussion

1. Synthesis of Fluorine-Containing Keto-Ylide Ligands. The rationale for our choice of ligand lies in

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the fact that their synthesis is particularly easy and well-known, since these molecules are also used in the field of organic chemistry, as precursors for vicinal tricarbonyl molecules, for example. In addition, it is well-known that the oxidative addition of such a ligand to zerovalent nickel compounds (most preferably Ni(COD)) leads to an alkylated metal due to transfer of a phenyl group from the phosphorus atom to the nickel atom (Scheme 1). Therefore, in the same step, ligand displacement and metal alkylation are effected, ruling out the use of an alkylating agent such as MAO. Finally, no additional Lewis base (such as triphenylphosphine or pyridine) is added to stabilize the metal center into a 16-electron conformation. Note that in our hands, ligand complexation occurs only after ethylene addition (vide infra). This route presents the additional advantage that no phosphine sponge is necessary to prepare high molecular weight polymers. The general method used to synthesize our ligands is outlined in Scheme 2. This reaction is described by Hamper as a one-pot synthesis when the phosphonium salt is bearing an ester group, because the acidity of the proton is high enough to be removed by a weak base such as triethylamine. The synthesis of ligand 1a is described by Hamper through the reaction of trifluoroacetic anhydride with the corresponding phosphonium salt 3. We have extended the reaction to the synthesis of ligands 1b–e using heptafluorobutanoyl chloride and pentfluorobenzyl chloride. The yield of the reaction ranges from 60% to 80%, and the final product is easily recrystallized from methanol. The ligands are characterized by 1H, 13C, 19F, and 31P NMR, IR, and microanalysis (see Experimental Section).

2. Synthesis of the Catalytic System. Catalysts can be prepared by reacting the ylide with a suitable source of nickel(0) such as bis(1,5-cyclooctadiene)nickel (Ni(COD)). Isolated catalysts are most usually prepared by adding a strongly nucleophilic ligand such as phosphine or a less nucleophilic one (for example pyridine) to fill the vacancy. In our case, complex synthesis is readily followed by 1H NMR, since the resonances of the COD protons of the ligated and free forms are shifted from 4.29 to 5.56 ppm for the vinlylic protons and from 2.07 to 2.20 for the allylic ones. Similarly, free and bound ligands display notably different resonances for the ester group (see Experimental Section). When Ni(COD)2 is contacted with the ligand in a stoichiometric amount (or more) at room temperature (at a concentration of 0.1 mol/L or less), no observed reaction occurs within hours (Scheme 3). Upon heating at 60 °C, ligand insertion and rearrangement occurs, to form dimer 4 in 10% yield. The rest of Ni(COD)2 decomposes when exposed to heat. In the case of a ratio of Ni(COD)2 to ligand 1a smaller than 0.5, we observe the formation of complex 5, which has been crystallized and analyzed by X-ray (Figure 1). Water present in the reaction medium has been trapped in the crystal.

Complexes analogous to 4 and 5 have already been described by Klabunde. For example, starting from complex PhNi(PPh3)ClC6H4=CH2(O)PPh3, the addition of a phosphine sponge (Rh(acac)C2H4)2 leads to the complex 4. In our case, we believe that, due to the very low electron-donating character of our ligands, the displacement of COD by the ylide is difficult, and needs to be assisted by an additional Lewis base.

This Lewis base can be either an olefin, such as ethylene or 1-hexene, or a phosphine (Scheme 4). With ethylene, at a pressure of 1 atm and at room temperature, COD is partially displaced, and 22% of the nickel centers are transformed into nickel(II) enolato-phosphine. When 5 equiv (0.5 mol/L) of 1-hexene are reacted at room temperature with Ni(COD)2 (0.1 mol/L) and the ylide (0.1 mol/L), less than 20% of the complex is formed. However, after 15 min heating at 60 °C, not only is all the COD uncoordinated but also all the 1-hexene is polymerized. As shown below, our complexes are active not only for the polymerization of ethylene but also for the homo- and co-polymerization of other α-olefins.

When the solution of Ni(COD)2 and ylide is reacted with 20 equiv of PPh3, the solution turns from light yellow to deep purple at room temperature. NMR analysis indicates that 50% of the ylide is bound to the nickel, forming complex 6, and 50% is left unreacted because part of the nickel is engaged under the form of Ni(PPh3)4. Nevertheless, with less than 20 equiv of phosphine (10 equiv, e.g.), yields of complex 6 are lower, and some Ni(COD)2 remains unreacted. 6 is only active in polymerization (and not in oligomerization) if the phosphine is removed by contact with a phosphine sponge such as Ni(COD)2. Up to date, we have not been able to crystallize the phosphine bound complexes, so polymerization results with 6 will not be presented in this paper.

This set of observations prompted us to prepare in situ our complexes by reacting 1 equiv of ylide dissolved in toluene to 1 or 2 equiv of Ni(COD)2 in toluene at room
temperature for 30 min, in the presence of an olefin. We found the catalyst activity to be little dependent on the ratio of ylide: Ni(COD)$_2$, unless a large excess of Ni(COD)$_2$ is used (>4 equiv), where a slight deactivation is observed.

3. Results in Ethylene Homopolymerization. The different ligands used are represented in Scheme 1. The results of some representative ethylene polymerizations with catalysts 1a–g are presented in Table 1. We believe that these catalysts are more active nickel catalysts than those reported in open literature, when compared under similar conditions.$^{44,45}$ Very small amounts of catalyst are used in order to avoid important exotherms and complete loss of temperature control. The catalytic solution is added to the diluent of the reaction (toluene or heptane), and the combined solutions are injected into the reactor. As soon as the temperature reaches its set point, ethylene is added and an immediate ethylene uptake is observed. Two main points emerge from these results. First, the activities obtained are very high for late transition metal catalysts$^{31,46}$ and comparable to homogeneous metallocenes under the same conditions.$^{13}$ Second, the low molecular weight polyethylene thus produced is virtually devoid of branching (Table 1).

The influence of the ligand fluorine atoms on the activity is remarkable, as seen by comparison of entries 1 and 2 to entries 11 and 12 (nonfluorinated analogues). The CF$_3$ is the most active so that the polymerizations are hardly temperature controlled (exotherms of more than 40 °C are observed for catalyst amount of more than 12 μmol/L). The heptafluoropropyl ligand 1b (entry 3) gives almost the same activities as the trifluoro one (entry 1 for 1a and a measured activity of 1000 (kg/gNi)/h for the other ligand).$^{47}$ We also naively thought that, by increasing the bulk of the ester alkoxy group, it was possible to exert a control over the selectivity toward higher molecular weights. However, as this group is not directed to the metal center where the coordination, insertion, isomerization, and transfer steps take place, it is unable to impart such a property to the catalyst. Accordingly, no molecular weight difference can be observed by increasing bulk on the alkoxide substituent (entries 4, 6, and 8); yet a small increase in activity, which could be nonsignificant, is observed. As proposed by Brookhart,$^{28}$ control over molecular weight distribution can be obtained by blocking the axial faces of the metal, thus inhibiting the associative displacement of the coordinated growing chain through β-H elimination.

**Table 1. Polymerization Data for Catalysts 1a–g**

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<tr>
<th>entry no.</th>
<th>n (μmol/L)</th>
<th>catal no.</th>
<th>prod (kg/gNi)</th>
<th>act. (kg/gNi/h)</th>
<th>$M_w$</th>
<th>$M_n/M_w$</th>
<th>br/1000 C</th>
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<td>6</td>
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<tr>
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<tr>
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<tr>
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<td>1a</td>
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<td>1700</td>
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<td>1.1</td>
<td>na</td>
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</table>

$^a$ Polymerizations were carried out with the active catalyst in 400 mL of toluene at 3 bar of ethylene and 70 °C. $^b$ Determined by GPC at high temperature vs polyethylene standards uncorrected. $^c$ Reactions in 400 mL of heptane. $^d$ Solvent: toluene/water (300/100 mL). $^e$ Literature value. $^f$ Propylene polymerization. $^g$ Hexene polymerization. $^h$ Determined by SEC in THF vs polystyrene standards uncorrected.
Conclusion

In this paper, we have presented a family of electron deficient keto--ylide ligands which are particularly active for the polymerization of ethylene. Their synthesis and their use in the preparation of catalytic complexes have been reviewed. Finally, the results in ethylene homopolymerization have been discussed. Our actual work concentrates on the polymerization of ethylene in water and the co-polymerization of ethylene with other nonpolar and polar monomers.

Acknowledgment. We wish to thank Pr. P. Richard for the RX structure. R.S. wishes to thank CNRS for a BDI fellowship.

Supporting Information Available. Tables of crystal and intensity collection data, positional and thermal parameters, and all bond distances and angles and a figure showing the crystal structure for 5. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(7) Kealy, T. J. (du Pont de Nemours, E. I.) U. S. Patent 3,474,082, 10/1969. We believe that the rhodium complex is not a coordination catalyst for the polymerization because the extremely harsh conditions (125 °C, 3000 atm) and the use of radical sources (H2, ETOH, and KI) suggest that actually this patent deals with radical polymerization.
(40) The oligomerization is often due to the presence of a Lewis base. Indeed, the competition in the chelation between ethylene and the Lewis base leads to low molecular weight material.
(43) Oligomers can be synthesized if no phosphine sponge is used.
(46) Gibson reported catalytic activity of this order with 2,6-bisimidophenylidiron(I) chloride activated by MAO (100 equiv).

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