

## 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 keto ylides 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  $2 \times 10^6$  (g<sub>PE</sub>/g<sub>Ni</sub>)/h and productivities higher than  $15 \times 10^6$  g<sub>PE</sub>/mol<sub>Ni</sub> are typically observed. These catalysts are also active for the polymerization of  $\alpha$ -olefins such as 1-hexene and 1-propene. 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.<sup>1–3</sup> 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,<sup>4–6</sup> 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 iodirhodium complex generated from Rh-(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(acac) and I<sub>2</sub> reported by Kealy<sup>7</sup> and a dihydride tetrakis(triphenylphosphine) ruthenium complex disclosed by Markham in 1972.<sup>8</sup> Since 1965, Yamamoto has developed a diethyl bis(2,2'-bipyridyl)iron complex for the polymerization of butadiene<sup>9</sup> and functionalized vinyl monomers,<sup>10</sup> but no activity was reported in ethylene. Considerable work has been achieved by Keim, eventually leading to the industrialization of the SHOP process.<sup>11</sup> Among the numerous catalysts prepared by Keim,<sup>12–15</sup> the nickel(II) complexes containing a phospho keto-ylide chelate proved to be the best candidates. In 1987, Klabunde<sup>16</sup> showed that, using the same kind of nickel complexes, it was possible to prepare high molecular weight polymers by removing a phosphine with a phosphine sponge, thus opening a vacant coordination site. In addition, the co-polymerization of ethylene with an olefin bearing a polar functionality was achievable if the polar substituent was separated by a spacer of two or more methylene units.<sup>17</sup> Although these catalytic complexes showed a unique tolerance to polar groups, water was still described as a poison of the catalytic systems.<sup>18</sup> By using a phosphorus ylide as ancillary ligand, Ostoja-Starzewski was able to polymerize ethylene without adding a phosphine sponge to

the reaction medium.<sup>19–21</sup> 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.<sup>22</sup> After these pioneering works were disclosed,<sup>23–25</sup> a major contribution was achieved by Brookhart and co-workers<sup>26,27</sup> with the use of bulky substituted  $\alpha$ -diimine 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.<sup>28</sup> Recently, neutral nickel(II) complexes based on salicylaldehyde ligands were developed by Grubbs.<sup>29,30</sup> These complexes allow the synthesis of high molecular weight polyolefins with excellent activity. Finally, Gibson<sup>31,32</sup> and Bennett<sup>33</sup> reported promising work in ethylene polymerization through 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.<sup>34</sup> To our knowledge, for the very first time, a latex of HDPE was prepared by direct catalytic polymerization in water.<sup>35,36</sup> 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 catalysts, we have also decided 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

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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  $\alpha$ -olefins will be presented.

## Experimental Section

Ligand **1a** and Ni(COD)<sub>2</sub> 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 effected on a 400 MHz Bruker instrument. Polymer analyses were made in a mixture of *d*<sub>3</sub>-trichloroethane and *d*<sub>6</sub>-benzene at 90 °C. GPC was determined in 1,3,4-trichlorobenzene at 145 °C, using a Waters AIC instrument. <sup>31</sup>P and <sup>19</sup>F NMR resonances, recorded on a 200 MHz AMX Bruker instrument, are reported relative to external standards (H<sub>3</sub>PO<sub>4</sub>, 85% in water, and CF<sub>3</sub>Cl).

**Synthesis of 6,6,6,5,5,4,4-Heptafluoro-3-oxo-2-(triphenylphosphoranyliden)hexanoic Acid, Ethyl Ester (1b).** A slurry of carbethoxymethyltriphenylphosphonium 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 mL, 17.2 mmol). After 15 min stirring, the mixture is treated dropwise with heptafluorobutyl chloride (1.28 mL, 8.6 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 <sup>1</sup>H (ppm, in CDCl<sub>3</sub>): C<sub>6</sub>H<sub>5</sub> 7.4–7.8, 15H, m; OCH<sub>2</sub>, 3.78, 2H, q; CH<sub>3</sub>, 0.9, 2H, t (<sup>3</sup>J<sub>H-H</sub> = 7 Hz). <sup>13</sup>C (ppm, in CDCl<sub>3</sub>): 13.6, 60.3, 72.6 (<sup>1</sup>J<sub>C-P</sub> = 115 Hz), 124 (<sup>1</sup>J<sub>C-P</sub> = 100 Hz), 129.9 (<sup>2</sup>J<sub>C-P</sub> = 13 Hz), 132.6 (<sup>4</sup>J<sub>C-P</sub> = 3 Hz), 133.4 (<sup>3</sup>J<sub>C-P</sub> = 10 Hz), 165.7 (<sup>2</sup>J<sub>C-P</sub> = 13.5 Hz), 175.2 (<sup>2</sup>J<sub>C-F</sub> = 27 Hz, <sup>2</sup>J<sub>C-P</sub> = 6 Hz). <sup>19</sup>F (ppm, in CDCl<sub>3</sub>): COCF<sub>2</sub>–124.9, s; CF<sub>2</sub>–113.7, q (<sup>3</sup>J<sub>F-F</sub> = 1.5 Hz); CF<sub>3</sub>–80.7, t (<sup>3</sup>J<sub>F-F</sub> = 1.5 Hz). <sup>31</sup>P (ppm, in CDCl<sub>3</sub>), 20, s. IR (10% KBr pellet): 3062, 2981, 1709, 1682, 1579, 1571, 1486, 1437, 1330, 1251, 1234, 1200, 1157, 1105, 968, 935, 757, 692, 556, 516 cm<sup>-1</sup>. Anal. Calcd: C, 57.36; H, 3.70. Found: C, 57.61; H, 3.87.

**Synthesis of Pentafluorobenzyl-3-oxo-2-(triphenylphosphoranyliden)propanoic Acid, Ethyl Ester (1c).** Same experimental setup as for **1b**, with (ethoxycarbonylmethyl)-triphenyl phosphonium bromide (0.8 g, 2.0 mmol), triethylamine (0.6 mL, 4.2 mmol), and pentafluorobenzoyl chloride (0.3 mL, 2.1 mmol). Isolated yield: 52%. NMR <sup>1</sup>H (ppm, in CDCl<sub>3</sub>): C<sub>6</sub>H<sub>5</sub> 7.5–7.6 and 7.7–7.8, 15H, m; OCH<sub>2</sub>, 3.65, 2H, q; CH<sub>3</sub>, 0.58, 2H, t (<sup>3</sup>J<sub>H-H</sub> = 7 Hz). <sup>13</sup>C (ppm, in CDCl<sub>3</sub>): 13.5, 58.9, 74.2 (<sup>1</sup>J<sub>C-P</sub> = 110 Hz), 124.7 (<sup>1</sup>J<sub>C-P</sub> = 94 Hz), 128.8 (<sup>2</sup>J<sub>C-P</sub> = 13 Hz), 132.4 (<sup>4</sup>J<sub>C-P</sub> = 3 Hz), 133.5 (<sup>3</sup>J<sub>C-P</sub> = 10 Hz), 166.7 (<sup>2</sup>J<sub>C-P</sub> = 13 Hz), 178.7 (<sup>2</sup>J<sub>C-P</sub> = 7 Hz). <sup>19</sup>F (ppm, in CDCl<sub>3</sub>): C<sub>6</sub>F<sub>5</sub>–145.2, dd (<sup>3</sup>J<sub>F-F</sub> = 22 Hz, <sup>4</sup>J<sub>F-F</sub> = 6.7 Hz), –157.8, t (<sup>3</sup>J<sub>F-F</sub> = 22 Hz), –163.7, td (<sup>3</sup>J<sub>F-F</sub> = 22 Hz, <sup>4</sup>J<sub>F-F</sub> = 6.7 Hz). <sup>31</sup>P (ppm, in CDCl<sub>3</sub>), 18.3, s. IR: 1661, 1562, 1517, 1496, 1437, 1369, 1341, 1293, 1244, 1103, 1087, 983, 940, 692, 542 cm<sup>-1</sup>. Anal. Calcd: C, 64.21; H, 3.72. Found: C, 64.49; H, 3.84.

**Synthesis of Pentafluorobenzyl-3-oxo-2-(triphenylphosphoranyliden)propanoic Acid, *tert*-Butyl Ester (1d).** Same experimental setup as for **1b**, with (*tert*-butoxycarbonylmethyl)triphenylphosphonium bromide (1.65 g, 4.0 mmol), triethylamine (1.3 mL, 8.2 mmol), and pentafluorobenzoyl chloride (0.6 mL, 4 mmol). Isolated yield: 62%. NMR <sup>1</sup>H (ppm, in CDCl<sub>3</sub>): C<sub>6</sub>H<sub>5</sub> 7.4–7.9, 15H, m; CH<sub>3</sub>, 0.96, 9H, s. <sup>13</sup>C (ppm, in CDCl<sub>3</sub>): 28.8, 76.3, 74.2 (<sup>1</sup>J<sub>C-P</sub> = 110 Hz), 124.7 (<sup>1</sup>J<sub>C-P</sub> = 94 Hz), 128.8 (<sup>2</sup>J<sub>C-P</sub> = 13 Hz), 132.4 (<sup>4</sup>J<sub>C-P</sub> = 3 Hz), 133.5 (<sup>3</sup>J<sub>C-P</sub> = 10 Hz), 166.7 (<sup>2</sup>J<sub>C-P</sub> = 13 Hz), 178.7 (<sup>2</sup>J<sub>C-P</sub> = 7 Hz). <sup>19</sup>F (ppm, in CDCl<sub>3</sub>): C<sub>6</sub>F<sub>5</sub>–145.2, dd (<sup>3</sup>J<sub>F-F</sub> = 22 Hz, <sup>4</sup>J<sub>F-F</sub> = 7.4 Hz), –158.0, t (<sup>3</sup>J<sub>F-F</sub> = 22 Hz), –163.8, td (<sup>3</sup>J<sub>F-F</sub> = 22 Hz, <sup>4</sup>J<sub>F-F</sub> = 7.4 Hz). <sup>31</sup>P (ppm, in CDCl<sub>3</sub>): 18.1, s. IR: 1666, 1552, 1516, 1495, 1437, 1359, 1303, 1247, 1167, 1108, 988, 941, 692, 543, 521 cm<sup>-1</sup>. Anal. Calcd: C, 65.27; H, 4.24. Found: C, 65.28; H, 4.31.

**Synthesis of pentafluorobenzyl-3-oxo-2-(triphenylphosphoranyliden)propanoic acid, benzyl ester (1e).** Same

experimental setup as for **1b**, with (benzyloxycarbonylmethyl)-triphenylphosphonium bromide (0.98 g, 2.0 mmol), triethylamine (0.58 mL, 4.2 mmol), and pentafluorobenzoyl chloride (0.3 mL, 2.1 mmol). Isolated yield: 32%. NMR <sup>1</sup>H (ppm, in CDCl<sub>3</sub>): C<sub>6</sub>H<sub>5</sub>, 7.2–7.4, 20H, m; CH<sub>2</sub>, 5.1, 2H, s. <sup>13</sup>C (ppm, in CDCl<sub>3</sub>): 65.7, 74.4 (<sup>1</sup>J<sub>C-P</sub> = 112 Hz), 124.5 (<sup>1</sup>J<sub>C-P</sub> = 94 Hz), 128.0, 128.2, 128.5, 128.8 (<sup>2</sup>J<sub>C-P</sub> = 13 Hz), 132.4 (<sup>4</sup>J<sub>C-P</sub> = 3 Hz), 133.5 (<sup>3</sup>J<sub>C-P</sub> = 10 Hz), 135.6, 166.3 (<sup>2</sup>J<sub>C-P</sub> = 13 Hz), 178.7 (<sup>2</sup>J<sub>C-P</sub> = 7 Hz). <sup>19</sup>F (ppm, in CDCl<sub>3</sub>): C<sub>6</sub>F<sub>5</sub>–145.7, dd (<sup>3</sup>J<sub>F-F</sub> = 23 Hz, <sup>4</sup>J<sub>F-F</sub> = 7 Hz), –157.4, t (<sup>3</sup>J<sub>F-F</sub> = 23 Hz), –163.8, td (<sup>3</sup>J<sub>F-F</sub> = 23 Hz, <sup>4</sup>J<sub>F-F</sub> = 7 Hz). <sup>31</sup>P (ppm, in CDCl<sub>3</sub>): 18.6, s. IR: 1648, 1554, 1519, 1487, 1440, 1341, 1288, 1274, 1066, 986, 754, 690, 545, 510, 501 cm<sup>-1</sup>. Anal. Calcd: C, 67.55; H, 3.67. Found: C, 67.32; H, 3.95.

**Typical Polymerization Procedure.** In a Schlenk tube, 23.5 mg of Ni(COD)<sub>2</sub> is dissolved in 8.5 mL of toluene. Then, 4 mL of this solution is added to 8.9 mg of ligand **1a**. The solution is left stirring for 15 min, and 0.6 mL of this solution is added to 400 mL of toluene in a thick glass reactor. The solution is then cannula transferred into a 1 L stainless steel reactor, equipped with a mechanical stirrer (magnetic induction), a thermocouple, a sampling valve, and an external jacket heated at 70 °C. Ethylene is immediately introduced at 3 bar. Ethylene is continuously fed into the reactor at 3 bar from a high-pressure 1 L reservoir. The pressure drop in the reservoir is recorded, to assess activity and productivity measurements. The reaction medium (400 mL) is added to methanol (600 mL), and the polymer (70 g) collected through filtration.

**Synthesis of *cis*-Bis{ethyl-1,1,1-trifluoro(3-diphenylphosphanyl)acetoenolato(*O,P*)}nickel(II) (5).** In a Schlenk tube, 113 mg (410 μmol) of Ni(COD)<sub>2</sub> and 178 mg (400 μmol) of ligand **1a** are solubilized in 4 mL of benzene. This solution is stirred during 2 h at room temperature and 0.4 mL are taken and introduced in a pressure NMR tube fitted with a Teflon adapter for vacuum lines.

NMR confirms that no COD has been displaced from the nickel center and that the resonances of the ligand are unchanged. NMR: Ni(COD)<sub>2</sub>, 2.07 ppm, s, 16H; 4.29 ppm, s, 8H (coordinated COD protons); ester protons of ligand **1a**, 0.83 ppm, t, 3H; 3.90 ppm, q, 2H.

A 1 mL aliquot of the starting reaction medium is transferred to another Schlenk tube which is heated 30 min at 60 °C. NMR: 60% Ni(COD)<sub>2</sub>, 2.07 ppm, s, 16H; 4.29 ppm, s, 8H; 40% free COD, 2.20 ppm, s, 5H; 5.57 ppm, s, 2.5H; 90% free ligand **1a**, 0.83 ppm, t, 3H; 3.90 ppm, q, 2H; 10% coordinated ligand **1a**, 0.65 ppm, t, 0.3H; 3.78 ppm, q, 0.2H.

To another 1 mL of the starting reaction medium is added 656 mg (250 μmol) of triphenylphosphine. The solution turns immediately to orange, and after 2 h stirring at room temperature, 0.4 mL of the brown solution is introduced in a NMR tube and the spectrum is run. NMR: 10% Ni(COD)<sub>2</sub>, 2.07 ppm, s, 1.6H; 4.29 ppm, s, 0.8H; 90% free COD, 2.20 ppm, s, 16H; 5.57 ppm, s, 8H; 50% free ligand **1a**, 0.83 ppm, t, 1.5H; 3.90 ppm, q, 1H; 50% coordinated ligand **1a**, 0.65 ppm, t, 1.5H; 3.78 ppm, q, 1H.

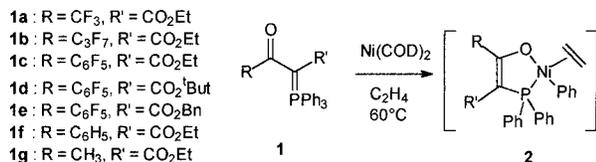
To another 2 mL of the starting reaction medium is added 126 μL (1 mmol) of hexene. The solution turns immediately to yellow. The solution is stirred for 2 h at 60 °C. The solution is dark brown. NMR: 100% free COD, 2.20 ppm, s, 16H; 5.57 ppm, s, 8H (free COD protons); hexene, no more peaks between 4.5 and 5.0 ppm (allylic protons) and also between 5.7 and 6.0 ppm (vinylic protons), but many broad peaks appeared in the region between 0.6 and 2.0 ppm (polyhexene).

To a solution of Ni(COD)<sub>2</sub> (206 mg) in toluene is added the ligand **1a** (667 mg). The solution is stirred 2 h at 60 °C and overnight at room temperature. The solution is filtered to remove the nickel metal and dried under vacuum. The yellow solid is recrystallized in a solution of toluene/heptane to yield 60% (485 mg) of complex **5**. RMN <sup>1</sup>H: 0.65 ppm, t, 3H; 3.65 ppm, q, 2H; 6.56 ppm, t, 4H; 6.80 ppm, t, 2H; 7.30 ppm, d, 4H. RMN <sup>19</sup>F: –68.1 ppm, s. RMN <sup>31</sup>P: 37.3 ppm, s.

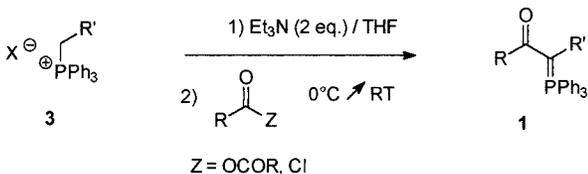
## Results and Discussion

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

### Scheme 1. Synthesis of the Polymerization Catalyst 2 Starting from the Ligand 1



### Scheme 2. One-Pot Synthesis of the Ligand 1 Starting from Commercially Available Phosphonium Salt 3



the fact that their synthesis is particularly easy and well-known,<sup>37</sup> since these molecules are also used in the field of organic chemistry, as precursors for vicinal tricarbonyl molecules, for example.<sup>38</sup> In addition, it is well-known that the oxidative addition of such a ligand to zerovalent nickel compounds (most preferably Ni(COD)<sub>2</sub>) leads to an alkylated metal due to transfer of a phenyl group from the phosphorus atom to the nickel atom (Scheme 1).<sup>39</sup> 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.<sup>40</sup> The general method used to synthesize our ligands is outlined in Scheme 2. This reaction is described by Hamper<sup>41</sup> 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 pentafluorobenzoyl 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 <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P 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)<sub>2</sub>). Isolated catalysts are most usually prepared by adding a strongly nucleophilic ligand such as phosphine<sup>42</sup> or a less nucleophilic one (for example pyridine),<sup>18</sup> to fill the vacancy. In our case, complex synthesis is readily followed by <sup>1</sup>H 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 vinylic 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)<sub>2</sub> 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

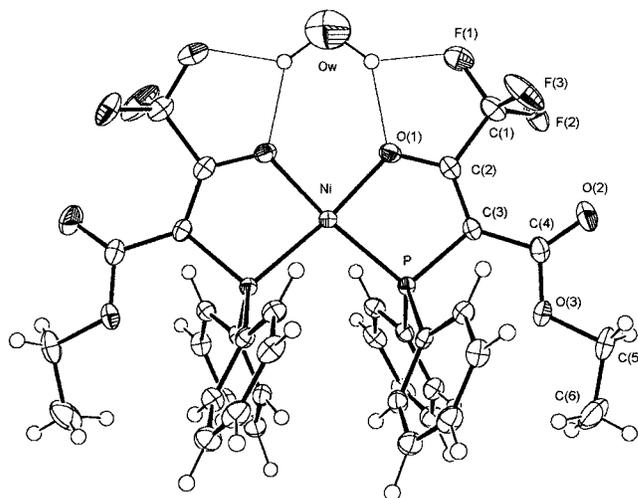


Figure 1. Crystal structure of **5** (ORTEP diagram).

heating at 60 °C, ligand insertion and rearrangement occurs, to form dimer **4** in 10% yield. The rest of Ni(COD)<sub>2</sub> decomposes when exposed to heat. In the case of a ratio of Ni(COD)<sub>2</sub> 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.

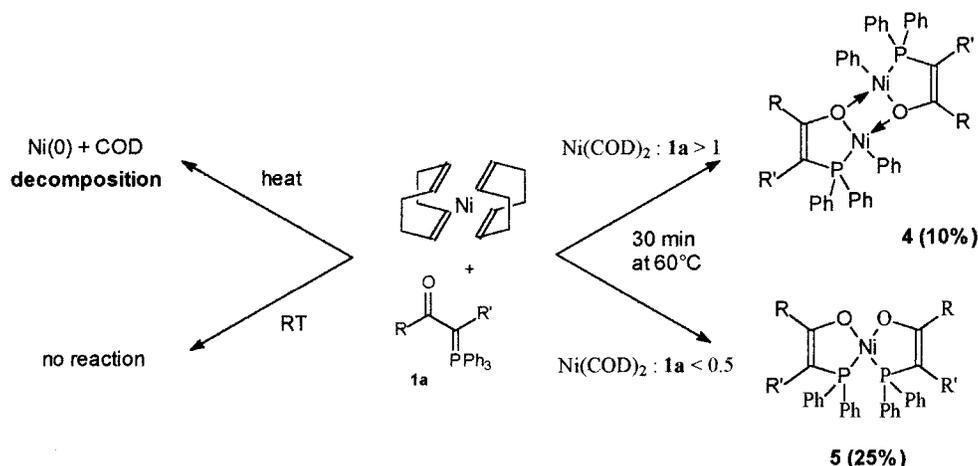
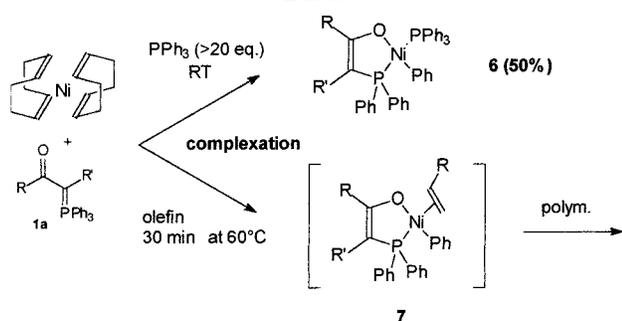
Complexes analogous to **4** and **5** have already been described by Klabunde.<sup>16</sup> For example, starting from complex PhNi(Ph<sub>2</sub>PCH=C(Ph)O)(PET<sub>3</sub>), the addition of a phosphine sponge (Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>) leads to the complex **4**. In our case, 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)<sub>2</sub> (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  $\alpha$ -olefins.

When the solution of Ni(COD)<sub>2</sub> and ylide is reacted with 20 equiv of PPh<sub>3</sub>, 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(PPh<sub>3</sub>)<sub>4</sub>. Nevertheless, with less than 20 equiv of phosphine (10 equiv, e.g.), yields of complex **6** are lower, and some Ni(COD)<sub>2</sub> 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)<sub>2</sub>.<sup>43</sup> 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)<sub>2</sub> in toluene at room

**Scheme 3. Possible Reactions of a Solution of Ni(COD)<sub>2</sub> and Ligand 1a under Different Conditions of Ratio and of Temperature****Scheme 4. Reactions of Complexation of a Solution of Ni(COD)<sub>2</sub> and Ligand 1a Exposed to Different Lewis Bases**

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)<sub>2</sub>, unless a large excess of Ni(COD)<sub>2</sub> 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.<sup>44,45</sup> 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 catalyst<sup>31,46</sup> and comparable to homogeneous metallocenes under the same conditions.<sup>1,3</sup> 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<sub>3</sub> 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

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

| entry no. <sup>a</sup> | <i>n</i> (μmol/L) | catal no. | prod (kg/g <sub>Ni</sub> ) | act. (kg/g <sub>Ni</sub> /h) | <i>M</i> <sub>w</sub> <sup>b</sup> (g/mol) | <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> | br/1000 C |
|------------------------|-------------------|-----------|----------------------------|------------------------------|--------------------------------------------|-----------------------------------------------|-----------|
| 1                      | 6                 | <b>1a</b> | 272                        | >2000                        | 3500                                       | 2.7                                           | 0.9       |
| 2 <sup>c</sup>         | 9                 | <b>1a</b> | 102                        | 970                          | 4800                                       | 3.1                                           | 0.8       |
| 3                      | 12                | <b>1b</b> | 154                        | 1400                         | 3700                                       | 3.2                                           | 1.0       |
| 4                      | 13.5              | <b>1c</b> | 58                         | 610                          | 3800                                       | 3.7                                           | 0.8       |
| 5 <sup>c</sup>         | 9                 | <b>1c</b> | 58                         | 420                          | 5000                                       | 3.2                                           | 0.6       |
| 6                      | 9                 | <b>1d</b> | 112                        | 1180                         | 3700                                       | 3.0                                           | 0.7       |
| 7 <sup>c</sup>         | 9                 | <b>1d</b> | 126                        | 500                          | 4700                                       | 3.7                                           | 0.8       |
| 8                      | 9                 | <b>1e</b> | 100                        | 1080                         | 3700                                       | 3.5                                           | 0.8       |
| 9 <sup>c</sup>         | 9                 | <b>1e</b> | 64                         | 560                          | 4600                                       | 3.4                                           | 0.7       |
| 10 <sup>d</sup>        | 15                | <b>1b</b> | 51                         | 140                          | 4400                                       | 3.6                                           | 0.9       |
| 11                     | 135               | <b>1f</b> | 8                          | 35                           | 8000                                       | 2.9                                           | 1.0       |
| 12 <sup>e</sup>        | 60                | <b>1g</b> | 0.5                        | 10                           | 10 000                                     | 3.1                                           | 1.1       |
| 13 <sup>f</sup>        | 30                | <b>1a</b> | 1                          | 15                           | 1500                                       | 2.0                                           | na        |
| 14 <sup>g</sup>        | 30                | <b>1a</b> | 0.5                        |                              | 1700 <sup>b</sup>                          | 1.4                                           | na        |

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

**1a** (entries 1 and 3). The pentafluoro catalysts **1c–e** are less active (entries 4–9), probably because of the decreased electrophilicity. The presence of the ester in α of the ketone was thought to be important as it stabilizes by resonance the enolate bond formed during the complexation step of the metal. Indeed, there is a slight difference in activity between ligands **1a** and the ligand in which R' is a proton under the same conditions (entry 1 for **1a** and a measured activity of 1000 (kg/g<sub>Ni</sub>)/h for the other ligand).<sup>47</sup> 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 alkoxy substituent (entries 4, 6, and 8); yet a small increase in activity, which could be nonsignificant, is observed. As proposed by Brookhart,<sup>28</sup> 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.

In our case, the square planar geometry of the catalyst implies that both axial faces of the nickel center are readily accessible, thus leading to low molecular weight distribution. Notably, the polydispersity indices are characteristic of single site homogeneous catalysts. Molecular weights determined by GPC and NMR tend to prove that low molecular weight polyethylene is synthesized. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR microstructure studies showed three general features of the polymers obtained: first, there is an equal number of unsaturated and saturated chain ends, second, there is a very low methyl branching content (less than 1 per 1000 C) and third, few internal double bonds due to  $\beta$ -H transfer followed by  $\beta$ -H addition on a more substituted carbon are observed (1 per 1000 C). This hints that the dominant mechanism for the production of this highly linear polymer is initiation by a nickel hydride, propagation, and termination by  $\beta$ -hydride elimination.

The influence of the solvent on the activity has also been studied. As the solubility of ethylene in toluene is 4 times greater than in heptane,<sup>48</sup> the observed activities are superior in toluene than in heptane (entries 6 and 7). However, there is no solvent effect on the molecular weight. Very low activities were observed in THF. Our current work deals with the polymerization of ethylene in very polar solvent such as water.<sup>35</sup>

## 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.

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**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>.

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