Research Note

Ethylene dimerization into 1-butene using 2-pyridylphosphole nickel catalysts

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Abstract

2-(2-Pyridyl)phospholes have been evaluated as ligands for the nickel-catalyzed oligomerization of ethylene. Under mild homogeneous reaction conditions, high catalytic activities (> 15 cycles per second) were recorded. The selectivity depends on the ethylene pressure. At 41 bar, high C_4 fraction contents (until 97%) and high 1-butene selectivities (80% of the C_4 fraction) were reached. This behavior is interpreted as a consequence of the steric hindrance of the intermediate cationic 2-pyridylphosphole nickel hydrides.
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1. Introduction

α-Olefins are key intermediates in the chemical industry [1]. The industrial synthesis[1] of 1-butene is nowadays achieved using nickel or titanium catalysts in large industrial processes like Alfabutol from IFP [3]. Alternatively α-olefins are obtained in the SHOP process developed by Shell [4]. The selectivity of the oligomerization process is determined by the control of the carbon–carbon bond formation and of the extension of the parallel double-bond migration isomerization. The control of these reactions is extremely attractive from both academic and technological viewpoints. High-performance Ni catalysts that selectively produce oligomers have been obtained via tailoring of the surrounding ligands [5]. However, despite the intense research efforts devoted to this area, there are still considerable limitations. For example, very few catalytic systems are able to produce selectively 1-butene from ethylene in both ho-

mogeneous [6] and heterogeneous phases [7]. Hence, the development of new ligands in order to obtain selective Ni catalysts is of great interest.

2-Pyridylphospholes **1** (Scheme 1) form tightly bonded P,N chelates with transition-metal centers such as Pd(II) or Ru(II) [8]. These donors are versatile ligands for performing fundamental studies on the control of catalyst behavior since their electronic and steric properties can be easily tuned by varying the substitution patterns (Scheme 1). Furthermore, the presence of two donors with different stereo- and electronic properties can induce selective processes in the metal coordination sphere [8]. Therefore, we have systematically investigated these P,N donors for the Ni-catalyzed oligomerization of ethylene.

2. Experimental

All experiments have been performed under argon, previously dried on 3 Å molecular sieves and purified on BASF R3-11 catalyst, using standard Schlenk tube techniques. The solvents were distilled under argon on sodium/benzophenone (cyclohexane, ethylic ether, tetrahydrofurane), on P_2O_5 (dichloromethane, pentane, acetonitrile) or on 3 Å molecular sieves (chlorobenzene), immediately before use. Solids were dried under reduced pressure. Phospholes **1a**–**b'**

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[1] 1-Butene can be obtained from refinery operations (C_4 fraction distillation, steam cracking or dehydrogenation of butane) or by synthesis using oligomerization processes. For details, see [2].
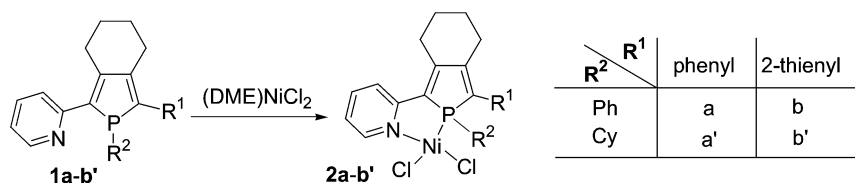
Scheme 1. Synthesis of Ni(II)-complexes bearing 2-pyridylphosphole ligands.

[8d,9] and NiCl$_2$(DME) (DME = 1,2-dimetoxyethane) [10] were prepared as described in the literature. Diethylaluminum chloride (AlEt$_2$Cl) was purchased from Aldrich and used as received. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass at CRMPO, University of Rennes, France. Elemental analyses were performed by the CRMPO, University of Rennes, France. The reaction products were quantitatively determined by gas chromatography using a 100-m-long capillary Petrocol (polimethylsilicon) column, working between 36 and 250 °C (5 °C/min) in a Varian 3400CX equipment.

2.1. Synthesis of the nickel complexes 2a–b′

General procedure: A solution of 1-phenyl-2-(2-pyridyl)-5-(phenyl)phosphole **1a** (0.33 g, 0.90 mmol) in CH$_2$Cl$_2$ (5 mL) was added, at room temperature, to a solution of (DME)NiCl$_2$ (0.19 g, 0.90 mmol) in CH$_2$Cl$_2$ (5 mL). The solution was stirred 3 h at room temperature, and the volatile materials were removed under vacuum. The residue was washed with diethyl ether (3 × 10 mL) and dried under vacuum. Complex **2a** was obtained as yellow solid (0.39 g, 89%); HR-MS (FAB-mNBA): m/z: 460.0532 [M–Cl]$^+$; calcd for C$_{25}$H$_{22}$NPNiCl$_2$ (497.025): C 60.41, H 4.46, N 2.82; found: C 60.33, H 4.37, N 2.89.

All complexes have been synthesized using the same procedure and have been characterized by high-resolution mass spectrometry and elemental analyses.

2.2. Oligomerization reactions

Ethylene oligomerization reactions were performed using a 120-mL glass reactor (ambient pressure reactions) or a 250-mL Pressure autoclave, double walled and with magnetically driven mechanical stirring (for reaction performed until 41.0 bar). The reaction temperature was controlled by an external circulation bath set at the reaction run temperature. In a typical run, 33 μmol of the nickel complex and 50 mL of chlorobenzene were feed, the system was saturated with ethylene, and then 1.2 mL of a 1.8 mol/L solution of the alkylaluminum cocatalyst was added (Al/Ni molar ratio of 70). The ethylene pressure was then enhanced to the run value and kept constant during the reaction. After the desired reaction time the reactor was cooled to −10 °C, and the products were withdrawn and analyzed by gas chromatography.

3. Results and discussion

Complexes **2a**–**b′** were readily obtained by reacting 2(2-pyridyl)phospholes **1a**–**b′** with one equivalent of (DME) NiCl$_2$ in dichloromethane at room temperature (Scheme 1). The paramagnetic complexes **2a**–**b′** were characterized by high-resolution mass spectrometry and give satisfactory elemental analyses.

Complexes **2a**–**b′** were evaluated as catalyst precursors for ethylene oligomerization under homogeneous phase conditions in the presence of an alkylaluminum cocatalysts. Under mild reaction conditions (1.1 bar, 0 °C), all complexes exhibit good to high catalytic activities, with turnover frequencies (TOF) ranging from 1.9 to 3.4 s^{-1} (Table 1, entries 1–4). Surprisingly, the catalytic activity is not influenced by the nature of the P substituent (R^2) (entries 1 vs 3 and 2 vs 4) but varies with the nature of the R^1 substituents (entries 1 vs 2 and 3 vs 4). It is well known that thienyl and phenyl groups possess very different electron-donating properties [11], and we have established that the dienic moiety of the phosphole ring is highly polarizable [12]. Thus, it seems very likely that the substituent at the C^5 position of the phosphole ring influences the donor ability of the pyridyl donor, and thus the behavior of the catalyst. The highest catalytic activities are observed when R^1 is a thienyl group (entries 2 vs 1, 4 vs 3). In all cases, the major products are butenes (71–89%); however, under such reaction conditions, the selectivity in 1-butene is extremely low (1–2%) (Table 1).
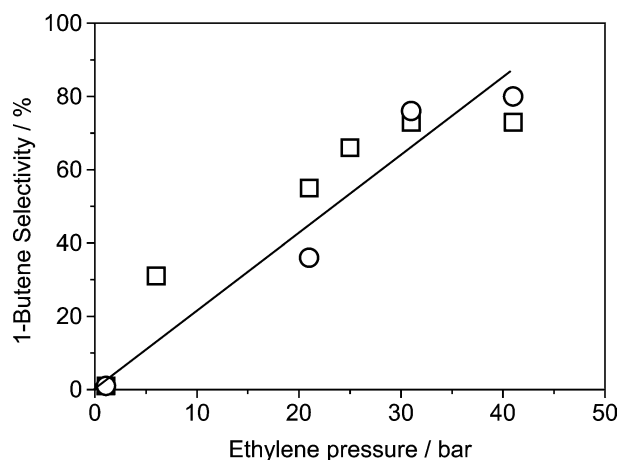
The influence of the ethylene pressure was studied with complex **2b**, a precursor leading to one of the most active catalyst. Increasing the pressure from 1.1 to 21.0 bar results in a continuous enhancement of the catalytic activity (Table 1, entries 2, 5, and 6) until 21 bar. Further augmentation of the pressure has a negative effect on the TOF (Table 1, entries 7–9). Such effects of the ethylene pressure on the activity have already been observed with other Ni-based catalytic systems [13].

Of particular interest, the ethylene pressure has a dramatic effect on the selectivity of the catalytic system. The total amount of butenes (C$_4$ fraction, column 8) does not vary with the ethylene pressure and is always higher than 90%. However, the selectivity in 1-butene increases from 1% at 1.1 bar (entry 2) to 73% at 31 bar (entry 8). This trend is also observed with precursor **2a** as illustrated in Fig. 1. Increasing the pressure from 1.1 to 41 bar at 10 °C with **2a** results in an increase of the 1-butene selectivity from 1 to 80% (Table 1, entries 11–14). The last result is particularly noteworthy since the catalytic system yields almost

Table 1
Catalytic performance of complexes **2a**–**b′** in ethylene oligomerization: Effect of the reaction conditions and of the nature of the 2(2-pyridyl)phosphole ligand

Entry	Cat[a]	Pressure	Temperature	Time	Weight	TOF	Selectivity (%)				
		(bar)	(°C)	(h)	(g)	(s^{-1})	C_4[b]	1-Butene	C_6[c]	Linear[d]	C_8[e]
1	**2a**	1.1	0	1	7.6	2.3	79	2	11	39	10
2	**2b**	1.1	0	1	10.6	3.2	89	1	11	40	0
3	**2a′**	1.1	0	1	6.2	1.9	71	1	24	40	5
4	**2b′**	1.1	0	1	11.4	3.4	82	2	17	32	1
5	**2b**	6.0	0	1	24.7	7.4	94	31	6	58	0
6	**2b**	21.0	0	1	52.0	15.6	90	55	8	75	2
7	**2b**	25.0	0	1	50.6	15.2	92	66	8	60	0
8	**2b**	31.0	0	1	26.0	7.8	97	73	3	70	0
9	**2b**	41.0	0	1	5.5	1.6	91	73	8	75	1
10	**2a**	21.0	0	1	12.8	3.8	95	66	5	71	0
11	**2a**	1.1	10	2	14.4	2.2	90	1	9	43	1
12	**2a**	21.0	10	2	81.7	12.3	89	36	10	69	1
13	**2a**	31.0	10	2	17.7	2.7	94	76	6	87	0
14	**2a**	41.0	10	2	9.7	1.5	97	80	3	69	0
15	**2b′**	21.0	0	1	20.0	6.0	96	65	4	63	0

[a] Catalytic precursor as defined in Scheme 1.
[b] C_4 fraction, defined as the amount of C_4 olefins (1-butene + 2-butene) divided by the total amount of olefins $\times 100$.
[c] C_6 fraction, defined as the amount of C_6 olefins (hexenes + methylpentenes) divided by the total amount of olefins $\times 100$.
[d] Linearity of the C_6 fraction, defined as the amount of hexenes divided by the total amount of C_6 olefins (hexenes + methylpentenes) $\times 100$.
[e] C_8 and plus fraction, defined as the amount of C_8 plus C_{10}, C_{12} and C_{14} olefins divided by the total amount of olefins $\times 100$.

Fig. 1. Dependence of the selectivity in 1-butene with the ethylene pressure for **2a** (○) and **2b** (□).

only butenes (97%) and the selectivity in 1-butene is remarkably high (80%). The positive influence of the ethylene pressure on the 1-butene selectivity is also recorded with **2b′** (see entries 4 and 15, Table 1), indicating that this behavior is characteristic of these novel nickel–pyridylphosphole catalysts. These results shows that nickel catalysts containing heteroditopic P,N ligands give unusually high selectivity in 1-butene and constitute a demonstration of the potential of 2-pyridylphospholes as ligands in homogeneous catalysis.

A second important point to note is that the C_6 fraction is mainly constituted by linear hexenes at high pressure (column 11, Table 1). It can be seen that at 1.1 bar the C_6 fraction contains 32 to 40% (entries 1–4, Table 1) of linear hexenes and that this amount increases with the ethylene pressure up to 87% (entry 14, Table 1). The total amount of the C_6 fraction has very low variations. Complexes **2a** and

2b gives low amounts of C_6 (3 to 11%) but complexes **2a′** and **2b′**, at low ethylene pressure, give 24 and 17%, respectively. This results suggests that the higher steric hindrance of the complex containing the cyclohexyl fragment compared with the phenyl one, combined with the high steric hindrance of the pyridyl ligand, is responsible for a decrease in the amount of β-elimination process. This explanation is nowadays well accepted as the reason why sterically hindered nickel–diimine complexes are able to polymerize ethylene [14].

The comparison of the catalytic behavior of the nickel–2-pyridylphosphole catalysts herein described with other nickel catalysts is somehow difficult due to the large amount of systems that have been described in the open and patent literature [15–17]. Despite this difficulty, some general features can be drawn:

(1) A large group of catalytic systems including Ni(acac)$_2$/AlEt$_2$Cl [18], Ni(π-allyl)$_2$ or Ni(π-allyl)Cl/AlEt$_2$Cl [19], Ni(acac)$_2$/EtAlCl$_2$ [20,21], or PhNi(PPh$_3$)$_2$Br/AgClO$_4$ [22] give a majority of dimmers (90–98%) which are mainly internal olefins (1-butene < 5%). These examples were the first reports of nickel-catalyzed oligomerization of ethylene and have been shown to involve nickel hydrides as active species.

(2) A second group comprises nickel complexes bearing chelating P,O ligands like Ni(Ph)PPh$_3$(Ph$_2$PC$_6$H$_4$COO) [23–25], which conduct to terminal (α) linear olefins with a large molecular weight distribution. It seems that the chelate ligand minimizes the double-bond migration isomerization, but with the corresponding enlargement of the product distribution.
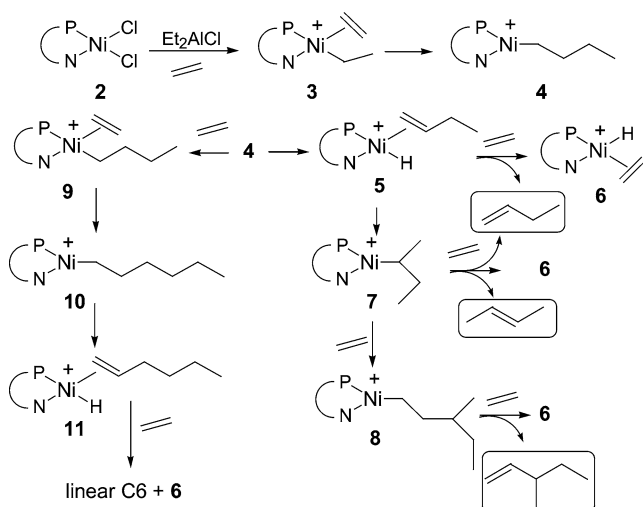
Scheme 2. Mechanism of ethylene oligomerization catalyzed by Nickel hydride species.

The catalytic behavior of the nickel–2-pyridylphosphole systems is intermediate between these groups and can be rationalized as a classical mechanism involving a hydrido or an alkyl-nickel species **3** and **4**, respectively, formed from the precatalysts **2a**–**b′** and the alkylaluminum cocatalyst under ethylene pressure (Scheme 2).

The key intermediate **4** is formed by insertion of ethylene on the nickel–carbon bond at **3**. This intermediate can give **5** by β-elimination or **9** by an insertion reaction followed by coordination of ethylene. The intermediate **6** can produce 1-butene and complex **3** or reinsert the olefin giving the secondary alkyl-nickel species **7**. Compound **7** can product 1-butene or 2-butene through β-elimination, or can coordinate another ethylene molecule giving **8**, which will afford methylpentenes. By the same reaction path, **9** can give **10** and **11**, which led to linear hexenes. The key point for the production of 1-butene is the selective formation of **6** over **7** from intermediate **5** (Scheme 2), a process clearly favored by increasing ethylene pressure (Scheme 2).

Scheme 2 shows that the selectivity toward 1-butene is determined by the steric hindrance of the cationic nickel–phosphole intermediate which disfavors species containing more hindered hydrocarbon fragments bonded to the nickel center, as the case of intermediate **7** that would conduct to the formation of 2-butenes.

In conclusion, we have described new nickel catalytic systems using 2-pyridylphosphole ligands for the dimerization of ethylene. These catalytic systems are highly efficient and associate high catalytic activities under mild reaction conditions with unusually high selectivities in 1-butene. Ni–(2-pyridyl)phosphole complexes are among the very rare catalytic systems affording efficiency for 1-butene from ethylene. These results hold very promising future prospects since further variations of the ligand structures are possible. The specific role played by the heteroditopic P,N ligand and the use of these versatile catalytic systems in biphasic conditions are under active investigation.

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