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Palladium and nickel complexes of (P,N)-ligands based on quinolines: Catalytic activity for polymerization and oligomerization

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Abstract

Four (P,N)-ligands (**1**–**4**) with different steric and electronic properties were synthesized. They were used to prepare the monocationic palladium complexes $[Pd(P,N)(CH_3)(NCCH_3)](PF_6)$ (**9**–**12**). The structures of the newly prepared ligand **3** and the neutral palladium complex $[Pd(P,N)(CH_3)Cl]$ (**10**) were analysed by X-ray. The catalytic activity of the palladium complexes toward the copolymerization of styrene and ethylene with CO was low or non-existent. The nickel complexes [Ni(P,N)(1-naphthyl)Cl] (**13**–**16**), modified with the ligands **1**–**4**, were prepared and their catalytic activity toward ethylene oligomerization was studied. They showed high activity at ambient temperature and low ethylene pressure (1–12 bar) in the presence of MAO.

Keywords: Quinoline; (P,N)-ligands; Palladium; Nickel; Oligomerization; Ethylene

1. Introduction

Unsymmetrical bidentate ligands with a nitrogen and phosphorous donor atom, referred to as (P,N)-ligands, can chelate a metal center or bridge two identical or two different metal centers. Owing to their bonding versatility and the relative ease with which the electronic and steric properties of the donor atoms can be modified, (P,N)-ligands play an important role in the coordination chemistry of transition metals as well as in homogeneous catalysis [1–9]. Despite their widespread applications in asymmetric catalysis, the (P,N)-ligands, and especially those based on quinoline, have only recently begun to attract attention with respect to the late-transition-metal-catalyzed oligomerization, polymerization and copolymerization reactions of olefins [10–16]. These studies have demonstrated that the architecture of the ligand plays an important role in adapting the activity of the coordinated metal center. Therefore, we focused on the design of efficient chelating (P,N)-ligands to modify the environment around the palladium or nickel center, based on their electronic and steric effects as mixed-donor ligands. We report the preparation of four (P,N)-ligands, **1**–**4**, based on quinoline, each having a unique set of steric and electronic properties. Our aim was to determine how these properties are reflected in the activity of their palladium $[Pd(P,N)(CH_3)(NCCH_3)](PF_6)$ (**9**–**12**) complexes toward copolymerization of styrene and ethylene with CO. The nickel complexes [Ni(P,N)(1-naphthyl)Cl] (**13**–**16**), modified with the ligands **1**–**4**, were also synthesized and their activity toward the oligomerization of ethylene was studied.

2. Results and discussion

2.1. Synthesis of the (P,N)-ligands

One way of changing the properties of the (P,N)-ligands is to change the substituents on the phosphorus atom. Therefore, we synthesized four ligands with the

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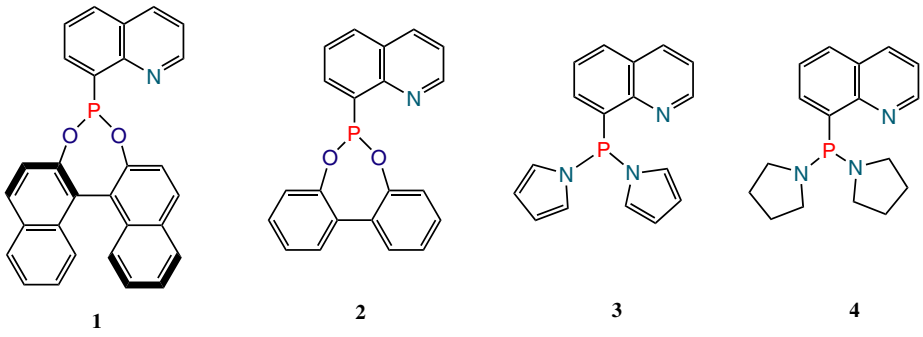


Chart 1.

8-substituted quinoline as a backbone, each having a different set of steric and electronic properties (Chart 1).

The phosphonito,N-ligands, 8-(3,5-dioxa-4-phospha-cyclohepta[2,1-a; 3,4-a′] dinaphtalen-4-yl)-quinoline (**1**) and 8-(1,3-dioxa-2-phospha-dibenzo[*a*,*c*]cyclohepten-2-yl)-quinoline (**2**), were prepared by means of one-pot two-step synthesis [11]. The first step is the *trans*-metallation at 183 K of 8-bromo-quinoline with *n*-BuLi and subsequent reaction with $PCl(NEt_2)_2$, leading to the key intermediate 8-(bis-diethylamino-phosphine)-quinoline. The second step is the addition of either (*R*)-binaphtol or 2,2′-dihydroxybiphenyl, leading to the ligands **1** and **2**, with 76% and 57% yield, respectively (Scheme 1).

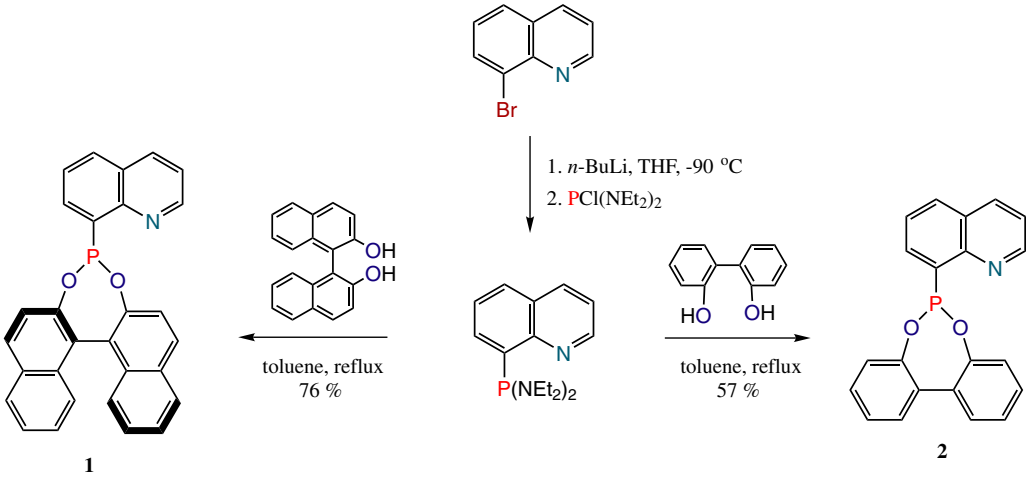
The same procedure was followed for the preparation of the ligand **3**. In this case, the chlorobis(1-pyrrolyl)phosphane had to be synthesized, according to a published procedure [17] (Scheme 2). The 8-(di(1*H*-pyrrol-1-yl) phosphino)quinoline (**3**) is a crystalline, air-stable compound, which was purified by flash chromatography; its structure was analysed by X-ray (Fig. 1). Table 1 gives a selection of characteristic bond lengths and bond angles of this structure.

The first step in the synthesis of 8-(dipyrrolidin-1-ylphosphino) quinoline (**4**) was the preparation of the bis(*N*,*N*-pyrrolidino)chlorophosphine [18]. The next steps were the lithiation of the 8-bromo-quinoline at 183 K and the addition of the chlorophosphine derivative. The evolution of the reaction was monitorized by in situ ^{31}P NMR spectroscopy. After 3 h, the signal of the initial phosphine at 163 ppm was replaced by the single resonance of the product, observed at 77.5 ppm. The work-up procedures, carried out in an inert atmosphere, led to a toluene solution, which contained almost exclusively compound **4** (Scheme 3). This solution was used to prepare palladium and nickel complexes without further purification. Ligand **4** is an air- and moisture-sensitive compound and cannot be isolated in its pure form.

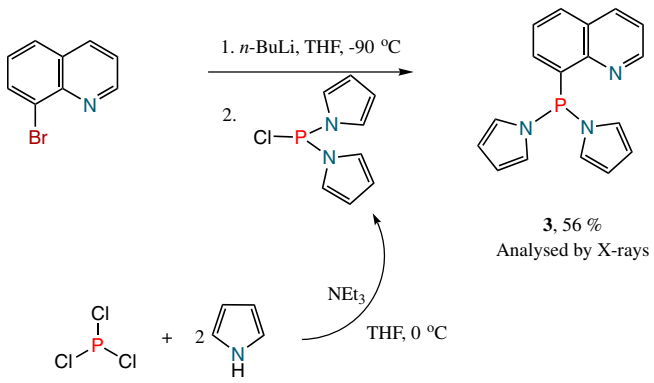
2.2. Synthesis of palladium complexes modified with the ligands 1–4 and their activity toward copolymerization of styrene and ethylene with CO

The (P,N)-ligands **1**–**4** were used to prepare the monocationic palladium complexes $[Pd(P,N)(CH_3)(NCCH_3)][PF_6]$ (**9**–**12**) according to a two-step procedure [19] involving the synthesis of the neutral complexes **5**–**8** as intermediates (Scheme 4).

The complex **6**, prepared with the ligand **2**, was obtained as crystals and was analysed by X-ray (Fig. 2). Table 2 gives a selection of characteristic bond lengths and bond



Scheme 1. Synthesis of phosphonito,N-ligands **1** and **2**.



Scheme 2. Synthesis of 8-(di(1*H*-pyrrol-1-yl)phosphino)quinoline (**3**).

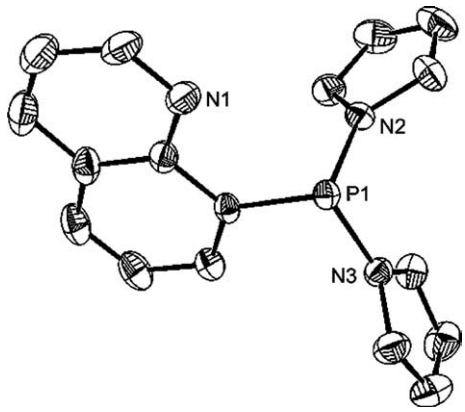
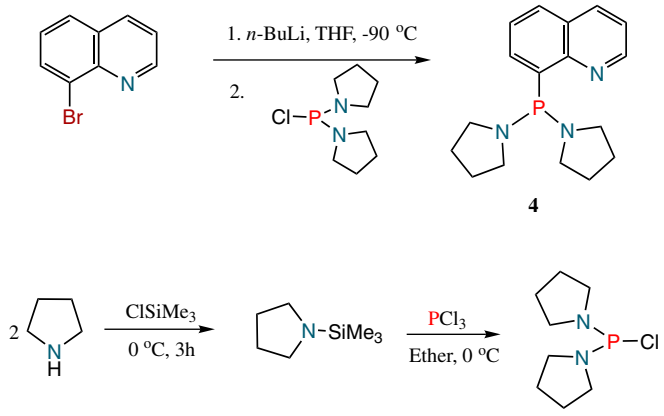


Fig. 1. ORTEP drawing of the compound **3**.

Table 1
Relevant bond lengths (Å) and angles (°) of ligand **3**

P(1)–N(2)	1.720(3)	N(2)–C(13)	1.378(4)
P(1)–N(3)	1.745(3)	N(2)–C(10)	1.383(4)
P(1)–C(1)	1.825(3)	N(3)–C(17)	1.370(4)
		N(3)–C(14)	1.380(4)
N(2)–P(1)–N(3)	99.55(13)	C(10)–N(2)–P(1)	128.9(2)
N(2)–P(1)–C(1)	99.72(13)	C(17)–N(3)–C(14)	107.4(3)
N(3)–P(1)–C(1)	100.23(14)	C(17)–N(3)–P(1)	122.3(2)
C(13)–N(2)–C(10)	108.2(3)	C(14)–N(3)–P(1)	130.3(2)
C(13)–N(2)–P(1)	122.7(2)		



Scheme 3. Synthesis of 8-(dipyrrolidin-1-ylphosphino)quinoline (**4**).

angles of this structure. As expected based on electronic grounds, chloride is *trans* to the better donor, phosphorus, while methyl is *trans* to the poorer donor, nitrogen.

The monocationic palladium complexes **9**–**12** were tested as catalyst precursors for the copolymerization of styrene with CO, under various reaction conditions but they were inactive, despite the fact that with **9** and **10** there is no formation of metallic palladium, at least until 200 bar carbon monoxide. Compounds **11** and **12** were more sensitive.

The copolymerizations of ethylene with CO proved successful only for complex **10**, at 35 bar ethylene, 35 bar CO and 80 °C. The complexes were used also for the oligomerization of ethylene using triisobutylaluminium ($^{i}Bu_3Al$) at 8–60 bar and up to 80 °C; they were inactive.

2.3. Synthesis of the nickel complexes modified with the ligands 1–4 and their activity toward oligomerization of ethylene

The complexes **13** and **14**, prepared with the ligands **1** and **2**, proved to be paramagnetic. Therefore, their characterization by NMR was impossible. The coordination of the nitrogen heterocycle to the metal center can be verified by infrared spectroscopy with the characteristic shift of the $\nu_{C=C}$, $\nu_{\beta(C-H)}$ and ν_{cycle}.

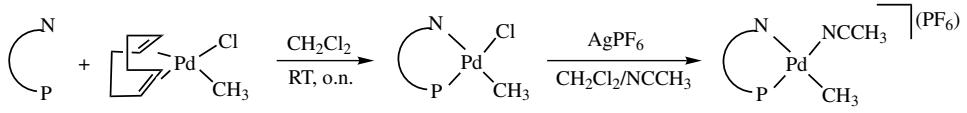
The complexes **15** and **16**, prepared with the ligands **3** and **4**, are diamagnetic and a full set of their NMR data were collected. The preparation of these two complexes was followed by in situ ^{31}P NMR. Both reactions were very fast and the characteristic signals of the products, appeared almost immediately (92.1 ppm for complex **15** and 95.8 ppm for complex **16**).

Very high yields of the nickel-complexes [Ni(P,N)(1-naphthyl)Cl] (**13**–**16**) were produced following a published procedure [20] using *trans*-chloro(1-naphthyl)bis (triphenylphosphine) nickel (II) (Scheme 5).

The nickel complexes **13**–**16** were tested for the oligomerization of ethylene using methylaluminoxane (MAO) as cocatalyst.

All catalysts were highly active at ambient temperature, reaching values of 1.3×10^5 g C_2H_4/mol Ni · h. The catalytic activity increased with increasing of the ethylene pressure in all cases. The oligomerizations required low ethylene pressure (1–12 bar) as it is shown in Table 3. The reaction temperature rose in all the experiments and at higher pressures, namely 10 bar for catalysts **13** and **14** and 20 bar for the other two complexes, the reactions were too fast to be controlled. This is why the data for the oligomerization reactions using the complexes **13** and **14** at 8 and 12 bar could not be collected. The optimum pressure for the catalysts **13** and **14** was 4 bar, while for the complexes **15** and **16** it was 12 bar.

When complexes **13** and **14** were used, the main oligomeric products were butenes and hexenes (C_4, C_6). In the case of complex **13**, hexenes usually formed, while with complex **14** the butenes are predominant. The amount of hexenes obtained increased with increasing ethylene pressure.



1-4 **5-8**, 69-95 % **9-12**, 89-97 %

Scheme 4. Synthesis of the palladium complexes [Pd(P,N)(CH_3)Cl] (**5**–**8**) and [Pd(P,N)(CH_3)($NCCH_3$)](PF_6) (**9**–**12**).

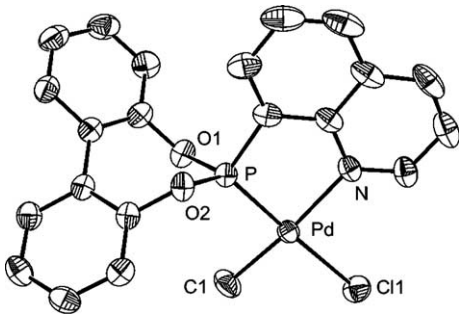
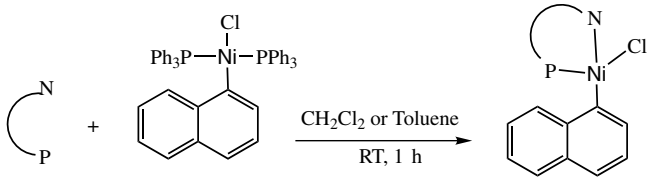


Fig. 2. ORTEP drawing of the complex (P,N)Pd(CH_3)Cl (**6**).

Table 2
Relevant bond lengths (Å) and angles (°) for complex **6**

Pd–C(1)	2.019(5)	P–O(2)	1.602(3)
Pd–P	2.1389(10)	P–O(1)	1.611(3)
Pd–N	2.159(3)	P–C(14)	1.801(4)
Pd–Cl(1)	2.3596(11)	O(1)–C(2)	1.399(4)
		O(2)–C(13)	1.403(5)
C(1)–Pd–P	90.98(17)	O(1)–P–C(14)	99.38(16)
C(1)–Pd–N	174.8(2)	O(2)–P–Pd	114.13(11)
P–Pd–N	83.98(10)	O(1)–P–Pd	125.33(11)
C(1)–Pd–Cl(1)	90.81(17)	C(14)–P–Pd	104.63(15)
P–Pd–Cl(1)	177.95(4)	C(2)–O(1)–P	122.4(2)
N–Pd–Cl(1)	94.21(10)	C(13)–O(2)–P	122.0(2)
O(2)–P–O(1)	102.20(14)	C(21)–N–C(22)	118.1(4)
O(2)–P–C(14)	109.77(18)	C(21)–N–Pd	124.6(3)
		C(22)–N–Pd	117.2(2)



1-4 **13-16**, 90-95 %

Scheme 5. Synthesis of [Ni(P,N)(1-naphtyl)Cl] (**13**–**16**) complexes.

When the catalysts **15** and **16** were tested, the oligomeric products contained 10–15% C_8–C_{12} fractions. With complex **15**, the activity increased with increasing ethylene pressure, but the oligomeric composition was hardly influenced. In the case of complex **16**, the amount of the higher fractions increased with increasing ethylene pressure.

At the same pressure, complexes **13** and **14** showed much higher activity in comparison with the complexes **15** and **16**. This is probably due to the greater steric bulkiness around the nickel atom.

Table 3
Results of the oligomerization of ethylene using nickel catalysts **13**–**16**

Nickel catalyst	P_{Et} (bar)	Activity (g C_2H_4/mol Ni · h)	Yield of oligomers (%)				
			C_4	C_6	C_8	C_{10}	C_{12}
13	1	0.28×10^5	49	51	–	–	–
	2	0.8×10^5	42	58	–	–	–
	4	1.29×10^5	36	64	–	–	–
14	1	0.17×10^5	82	18	–	–	–
	2	0.3×10^5	76	24	–	–	–
	4	1.3×10^5	66	34	–	–	–
15	2	0.14×10^5	44	43	10	3	<1
	8	0.48×10^5	43	45	11	1	<1
	12	0.96×10^5	43	46	10	1	<1
16	4	0.04×10^5	57	31	8	3	1
	8	0.50×10^5	42	42	11	4	1
	12	1.11×10^5	35	45	13	5	2

Oligomerization conditions: 15 μmol catalyst, 30 ml toluene, 5 ml sol. MAO (10% MAO solution in toluene) and ambient temperature.

3. Conclusions

The ligands **1**–**4** were synthesized in good yields and were characterized by NMR or X-ray analysis. They were used to prepare palladium complexes **9**–**12**, also in good yields, these compounds being fully characterized by NMR. The activity of the palladium complexes was investigated toward the copolymerization of styrene and ethylene with CO. They showed no activity in the case of styrene and only complex **10** proved useful for the copolymerization of ethylene with CO. Therefore, we concluded that even though the modifications introduced in the structure of (P,N)-ligands were significant, in terms of steric and electronic properties, they had little influence on the catalytic activity of the palladium complexes toward polymerizations.

The nickel complexes, modified with the ligands **1**–**4** were synthesized and characterized by IR, MS or NMR. They were highly active toward the oligomerization of ethylene at ambient temperature and in the presence of MAO as the cocatalyst.

4. Experimental

4.1. General data

All the reactions were carried out in nitrogen atmosphere by means of Schlenk techniques. CP grade chemicals were used as received. Solvents were dried by standard methods

and freshly distilled under nitrogen. Carbon monoxide (CP grade, 99.5%) was supplied by AGA. One and two-dimensional NMR spectra were measured on Bruker instruments (AC 200, AVANCE 400 and AMX 500) at ambient temperature. The MS spectra were measured by MALDI-FT-ICR in the positive mode on an IonSpec Ultima instrument. Our microanalytical laboratory performed elemental analyses. The IR spectra were recorded on a Bio-Rad Excalibur Series FT-IR Spectrometer.

4.2. 8-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a; 3,4-a′]-dinaphthalen-4yl)-quinoline (*1*)

In a Schlenk flask, a precooled solution of *n*-BuLi (3.0 ml, 1.6 M in hexane) was added to a THF solution (40 ml) of 8-bromo-quinoline (1 g, 4.8 mmol) at −90 °C. The reaction temperature was increased to −78 °C, where it remained for 5 min (the color of the solution turned from light yellow to dark orange). Then, an equimolecular amount of $PCl(NEt_2)_2$ (1 g, 4.8 mmol) was added. The reaction mixture was allowed to warm up to room temperature and was stirred for 4–5 h (the solution turned yellow). The volatiles were removed in vacuo, toluene was added and the solution was filtered through a pad of Celite. 8-(Bis-diethylaminophosphine)-quinoline was obtained and its presence was confirmed by ^{31}P NMR of the crude product, the spectra showing a single resonance at δ 96.5 ppm. An equimolar amount of (*R*)-binaphtol (1.373 g, 4.8 mmol) was then added and the reaction mixture was heated under reflux in toluene for 24 h. After cooling to room temperature, the solvent was removed and the residue was washed twice with pentane and diethyl ether; the product was dried under high vacuum. A pale yellow solid (1.6 g) was obtained (76%). ^1H NMR (CD_2Cl_2) δ 9.09 (dd, ^3J 4.1, ^4J 1.9, 1H, CH=N); 8.21 (d, *J* 8.3, 1H); 8.04 (d, *J* 8.7, 1H); 7.95 (d, *J* 8.2, 1H); 7.84 (d, *J* 8.0, 1H); 7.73 (d, *J* 8.0, 1H); 7.64 (t, 2H); 7.50 (q, 1H); 7.51–7.26 (m, 9H), 6.29 (d, *J* 8.7, 1H). ^{31}P NMR: δ 183.1. Calc. for $C_{29}H_{18}NO_2P$ (443.43): C, 78.55; H, 4.09; N, 3.16. Found: C, 78.67; H, 4.12; N, 3.23%.

4.3. 8-(1,3-Dioxa-2-phospha-dibenzo[a,c]cyclohepten-2-yl)-quinoline (*2*)

Following the procedure used to prepare compound **1** but using the 2,2′-dihydroxydiphenyl (893 mg, 4.8 mmol) in the second step, the title compound was obtained as a white powder (940 mg, 57% yield). ^1H NMR (CD_2Cl_2) δ 9.09 (dd, ^3J 5.5, ^4J 1.5, 1H, CH=N); 8.29 (dd, ^3J 9.7, ^4J 1.5, 1H); 7.94 (d, *J* 8.0, 1H); 7.82 (d, *J* 7.0, 1H); 7.56 (q, 1H); 7.49–7.43 (m, 3H); 7.26 (t, *J* 7.3, 2H); 7.18 (t, *J* 7.5, 2H); 6.74 (d, *J* 7.9, 2H). ^{31}P NMR: δ 185.9. HRMS: Found, 344.0834; calc. for $C_{21}H_{14}NO_2P$, 344.0823.

4.4. 8-(Di(1H-pyrrol-1-yl)phosphino)-quinoline (*3*)

In a Schlenk flask, a precooled solution of *n*-BuLi (3.0 ml, 1.6 M in hexane) was added to a THF solution (40 ml) of 8-bromo-quinoline (1 g, 4.8 mmol) at −90 °C. The reaction temperature was increased to −78 °C where it remained for 5 min, when an equimolecular amount of chloro-bis(1-pyrrolyl) phosphane [2] (955 mg, 4.8 mmol) was added (the solution became colorless). The reaction mixture was allowed to warm up to room temperature and stirred for 4–5 h (pale yellow solution). The volatiles were removed in vacuo and the product purified by flash chromatography using 3% triethylamine in a mixture of hexane:ethylacetate, 4:1. A crystalline pale green product (700 mg) was obtained (50%). Single crystals of complex **3** were investigated by X-ray analysis. ^1H NMR ($CDCl_3$) δ 8.80 (dd, ^3J 5.8, ^4J 1.6, 1H, CH=N); 8.15 (dd, ^3J 9.7, ^4J 1.5, 1H); 7.91 (d, *J* 8.1, 1H); 7.51 (dt, ^3J 15.2, ^4J 1.1, 1H); 7.40 (q, *J* 4.2, 1H); 7.04–7.01 (m, 1 H); 6.85–6.78 (m, 4H, CH=); 6.31–6.30 (m, 4H, CH=). ^{13}C NMR δ 150.1, 148.5 (d), 136.08, 135.7 (d), 132.3 (d), 130.7, 127.6, 126.6, 121.8 (Ar); 124.4, 124.3 (NCH=); 111.77, 111.74 (CH=). ^{31}P NMR: δ 68.2. Calc. for $C_{17}H_{14}N_3P$: C, 70.10; H, 4.84; N, 14.43. Found: C 69.93; H, 4.93; N, 14.07%. HRMS: Found, 291.0918; calc. for $C_{17}H_{14}N_3P$, 291.0929.

4.5. 8-(Dipyrrolidin-1-ylphosphino)-quinoline (*4*)

In a Schlenk flask, a precooled solution of *n*-BuLi (3.0 ml, 1.6 M in hexane) was added to a THF solution (40 ml) of 8-bromo-quinoline (1 g, 4.8 mmol) cooled at −90 °C. The reaction temperature was increased to −78 °C and remained at this temperature for 5 min, when an equimolecular amount of bis(*N*,*N*-pyrrolidino) chlorophosphine [3] (955 mg, 4.8 mmol) was added. The reaction mixture was stirred for 3 h, while it warmed up to ambient temperature. The process was followed by in situ ^{31}P NMR. After 3 h, the signal of the initial phosphine at 163 ppm was replaced by the single resonance of the product observed at 77.5 ppm. The volatiles were removed in vacuo, toluene was added and the resulting mixture was filtered under nitrogen. A clear yellow toluene solution was obtained, which contained almost exclusively the compound **4**. This solution was used to prepare palladium and nickel complexes without further purification.

4.6. General procedure for the preparation of the chloro-(methyl)palladium complexes *5*–*8*

The ligands (0.8 mmol) were dissolved in 3 ml dichloromethane and added by a syringe to a solution of (η^2,η^2-cycloocta-1,5-dien)chloro(methyl)palladium ((COD)Pd(Me)Cl) [21] (212 mg, 0.80 mmol) and 3 ml dichloromethane. The mixture was stirred for 1–3 d under argon at ambient temperature. The solution was then filtered through Celite and the solvent evaporated; yellow oil was obtained. This was washed with hexane (3×), redissolved in dichloromethane and cooled; the products were precipitated by the addition of hexane. Each complex was isolated by filtration and then dried under high vacuum.

*4.6.1. {8-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a; 3,4-a′] dinaphthalen-4yl)-quinoline}chloro(methyl)palladium (**5**)*

360 mg (75%) white solid were obtained. ^{1}H NMR ($CDCl_3$) δ 10.03 (d, J 3.5, 1H, CH=N); 8.41 (d, J 8.35, 1H); 8.11 (d, J 8.05, 1H); 8.06 (d, J 8.85, 1H); 8.01–7.95 (m, 3H); 7.70–7.68 (m, 1H); 7.65 (d, J 8.85, 1H); 7.55–7.51 (m, 2H); 7.45–7.42 (m, 2H); 7.38–7.32 (m, 3H); 7.18 (t, J 8.05, 1H); 7.12 (d, J 8.85, 1H); 0.69 (s, 3H, Pd–CH_3). ^{31}P NMR: δ 163.7. HRMS: Found, 564.8768 (M^+-Cl); calc. for $C_{30}H_{21}NO_2PPd$, 564.8773.

*4.6.2. {8-(1,3-Dioxa-2-phospha-benzo[a,c]cyclohepten-2-yl)-quinoline}chloro(methyl)palladium (**6**)*

Yellow crystals (276 mg, 69%) were obtained and were analyzed by X-ray. ^{1}H NMR ($CDCl_3$) δ 10.01 (d, J 4.05, 1H, CH=N); 8.42 (d, J 8.25, 1H); 8.15 (d, J 6.05, 1H); 7.67 (q, J 8.25, J 4.85, 1H); 7.60 (t, J 4.15, 2H, Ph); 7.54 (t, J 3.55, 2H, Ph); 7.44–7.40 (m, 4H, Ph); 7.15 (d, J 7.60, 2H); 0.82 (s, 3H, Pd–CH_3). ^{31}P NMR: δ 162.2. HRMS: Found, 464.0033 (M^+-Cl); calc. for $C_{22}H_{17}NO_2PPd$, 464.0026.

*4.6.3. {8-(Di(1H-pyrrol-1-l)phosphino)-quinoline}chloro-(methyl)palladium (**7**)*

A yellow solid (280 mg, 78%) was obtained. ^{1}H NMR ($CDCl_3$) δ 9.95 (dd, ^3J 4.83, ^4J 1.56, 1H, CH=N); 8.44 (dt, ^3J 8.34, ^4J 1.83, 1H); 8.19 (d, J 8.08, 1H); 8.13 (q, ^3J 9.74, ^4J 7.20, 1H); 7.77 (t, J 8.27, 1H); 7.68 (q, ^3J 6.57, ^4J 4.84, 1H); 6.98 (s, 4H, CH=); 6.40 (s, 4H, CH=); 1.13 (d, J 2.17, 3H, Pd–CH_3). ^{31}P NMR: δ 94.6. HRMS: Found, 412.7269 (M^+-Cl); calc. for $C_{18}H_{17}N_3PPd$, 412.7279.

*4.6.4. {8-(Dipyrrolidin-1-ylphosphino)quinoline}chloro-(methyl)palladium (**8**)*

A yellow solid 346 mg was obtained (95%). ^{1}H NMR ($CDCl_3$) δ 9.93 (s, 1H, CH=N); 8.34 (dt, ^3J 8.29, ^4J 1.72, 1H); 8.04–8.00 (m, 2H); 7.69 (t, J 8.01, 1H); 7.57 (q, ^3J 6.55, ^4J 4.84, 1H); 3.25–3.17 (m, 8H, CH_2); 1.89–1.79 (m, 8H, CH_2); 0.85 (s, 3H, $PdCH_3$). ^{31}P NMR: δ 95.5. ^{13}C NMR δ 153.0, 149.1 (d), 138.0, 136.9 (d), 132.8, 131.3, 129.3 (d), 128.2, 127.0 (d), 122.6 (Ar); 48.2 (d, CH_2); 26.1(d, CH_2); 0.002 ($PdCH_3$). HRMS: Found, 420.7912 (M^+-Cl); calc. for $C_{18}H_{25}N_3PPd$, 420.7919.

*4.7. General procedure for the preparation of the methyl-(acetonitrile)palladium complexes **9–12***

In a two-neck, 50-ml flask covered with aluminum foil, chloro(methyl)palladium complexes **5–8** (0.44 mmol) were dissolved in 5 ml of a mixture of dichloromethane/acetonitrile (5:1, v/v) under argon and cooled to 0 °C. The $AgPF_6$ (0.44 mmol), dissolved in a 3-ml solution of dichloromethane/acetonitrile (5:1, v/v), was added to the mixture through a dropping funnel. The reaction mixture was stirred for 1 h at 0 °C and was warmed to ambient temperature, at which it was maintained for another hour. Filtration through Celite removed the precipitated silver chloride. The pale yellow filtrate was evaporated under vacuum and yellow oil was obtained; upon treatment with hexane (3 × 3 ml) and drying under vacuum, the complexes **9–12** were obtained as powders (89–97% yield).

*4.7.1. (Acetonitril-κN){8-(3,5-dioxa-4-phospha-cyclohepta[2,1-a; 3,4-a′]dinaphthalen-4yl)-quinoline}methyl palladium(+) hexafluoro phosphate (**9**)*

A beige powder (316 mg) was obtained (96%). ^{1}H NMR (CD_2Cl_2) δ 9.24 (s, 1H, CH=N); 8.61 (d, J 7.73, 1H); 8.26 (d, J 8.02, 1H); 8.15 (d, J 8.80, 1H); 8.09–8.05 (m, 3H); 7.66 (d, J 8.82, 1H); 7.61–7.57 (m, 2H); 7.52 (t, J 7.1, 1H); 7.42–7.37 (m, 5H); 7.22 (t, J 10.0, 1H); 7.16 (d, J 8.82, 1H); 2.22 (s, 3H, $NCCH_3$); 0.46 (s, 3H, $PdCH_3$). ^{31}P NMR: δ 164.3, −143.1 (PF_6). ^{19}F NMR: δ −73 (d). HRMS: Found, 564.8765 ($M^+-NCCH_3-PF_6$); calc. for $C_{30}H_{21}NO_2PPd$, 564.8773.

*4.7.2. (Acetonitril-κN){8-(1,3-dioxa-2-phospha-dibenzo-[a,c]cyclohepten-2-yl)-quinoline}methylpalladium(+) hexafluoro phosphate (**10**)*

A beige powder (277 mg) was obtained (97%). ^{1}H NMR (CD_2Cl_2) δ 9.24 (s, 1H, CH=N); 8.62 (d, J 7.97, 1H); 8.31 (d, J 7.97, 1H); 7.92 (s, 1H); 7.74–7.64 (m, 3H, Ph); 7.57–7.45 (m, 5H, Ph); 7.19 (d, J 7.08, 2H); 2.47 (s, 3H, $NCCH_3$); 0.63 (s, 3H, $PdCH_3$). ^{31}P NMR: δ 162.9, −143.1 (PF_6). HRMS: Found, 464.0033 ($M^+-NCCH_3-PF_6$); calc. for $C_{22}H_{17}NO_2PPd$, 464.0026.

*4.7.3. (Acetonitril-κN){8-(di(1H-pyrrol-1-yl)phosphino)-quinoline}methylpalladium(+) hexafluoro phosphate (**11**)*

A light brown powder (242 mg) was obtained (92%). ^{1}H NMR (CD_2Cl_2) δ 9.25 (dd, ^3J 4.74, ^4J 1.45, 1H, CH=N); 8.62 (d, J 8.38, 1H); 8.33 (d, J 8.10, 1H); 8.23 (q, ^3J 9.44, ^4J 6.71, 1H); 7.96 (q, ^3J 6.62, ^4J 4.80, 1H); 7.87 (dt, ^3J 8.35, ^4J 1.34, 1H); 7.01 (m, 4H, CH=); 6.52 (m, 4H, CH=); 2.43 (s, 3H, $NCCH_3$); 0.94 (s, 3H, Pd–CH_3). ^{31}P NMR: δ 97.76, −143.1 (PF_6). HRMS: Found, 598.7443; calc. for $C_{20}H_{20}F_6N_4P_2Pd$, 598.7448.

*4.7.4. (Acetonitril-κN){8-(dipyrrolidin-1-ylphosphino)-quinoline}methylpalladium (+) hexafluoro phosphate (**12**)*

A pale yellow powder (237 mg) was obtained (89%). ^{1}H NMR (CD_2Cl_2) δ 9.25 (s, 1H, CH=N); 8.45 (dt, ^3J 8.36, ^4J 1.60, 1H); 8.10 (d, J 8.0, 1H); 8.05 (q, ^3J 13.1, ^4J 9.0, 1H); 7.88–7.85 (m, 1H); 7.76 (t, J 8.15, 1H); 3.23–3.14 (m, 8H, CH_2); 2.5 (s, 3H, $CNCH_3$), 1.91–1.81 (m, 8H, CH_2); 0.57 (s, 3H, Pd–CH_3). ^{31}P NMR: δ 94.67, −143.1 (PF_6). ^{13}C NMR δ 153.5, 148.3 (d), 139.0, 135.8 (d), 133.3, 132.2 (d), 129.5 (d), 127.5 (d), 123.9 (Ar), 120.5 ($CNCH_3$), 48.3 (d, CH_2), 26.1 (d, CH_2), 2.64 ($CNCH_3$), −1.4 ($PdCH_3$). HRMS: Found, 420.7915 ($M^+-NCCH_3-PF_6$); calc. for $C_{18}H_{25}N_3PPd$, 420.7919. Calc. for $C_{20}H_{28}N_4F_6P_2Pd$ (606.83): C, 39.59; H, 4.65; N, 9.23. Found: C, 40.00; H, 4.99; N, 8.90%.

4.8. General procedure for the preparation of the nickel complexes 13–16

A solution of each of the ligands **1**–**4** (0.5 mmol) in CH_2Cl_2 (3 ml) was added to a solution of *trans*-chloro(1-naphthyl)bis(triphenylphosphyne)nickel (II) (372 mg, 0.5 mmol) in CH_2Cl_2 (10 ml) and the reaction mixture was stirred for 1 h. The resultant solution was concentrated to about 5 ml and hexane (5 ml) was added to completely precipitate the nickel complexes **13**–**16**, which were isolated by filtration and dried under high vacuum.

4.8.1. Chloro(1-naphthyl){8-(3,5-dioxa-4-phosphacyclohepta[2,1-a; 3,4-a′]dinaphthalen-4yl)-quinoline}nickel (II) (13)

A beige powder (312 mg) was obtained (94%). Paramagnetic compound. HRMS: Found, 628.0973 (M^+-Cl); calc. for $C_{39}H_{25}NO_2PNi$, 628.09709. IR (KBr) cm^{-1}: 1622m ($\nu_{C=C}$); 1157m ($\nu_{\beta(C-H)}$); 1030, 1000s (ν_{cycle}).

4.8.2. Chloro(1-naphthyl){8-(1,3-dioxa-2-phosphadibenzo-[a,c]cyclohepten-2-yl)quinoline}nickel (II) (14)

A beige powder (268 mg) was obtained (95%). Paramagnetic compound. HRMS: Found, 470.1307 ($M^+-Ni-Cl$); calc. for $C_{31}H_{21}NO_2P$, 470.13044. IR (KBr) cm^{-1}: 1601m ($\nu_{C=C}$); 1158m ($\nu_{\beta(C-H)}$); 1051, 1000m (ν_{cycle}).

4.8.3. Chloro(1-naphthyl){8-(di(1H-pyrrol-1-yl)-phosphino)quinoline}nickel (II) (15)

A yellow powder (238 mg) was obtained (93%). ^1H NMR (500 MHz, $CDCl_3$): δ 10.1 (s, 1H, CH=N); 9.02 (d, 1H, NiCCH); 8.52 (d, 1H); 8.22 (d, 1H); 8.07 (s, 1H); 7.76 (s, 2H), 7.53 (d, 1H); 7.35 (m, 3H); 7.25 (s, 2H); 7.12 (s, 1H); 7.00 (s, 1H); 6.41 (s, 2H); 6.14 (s, 2H); 5.79 (s, 2H). ^{31}P NMR: δ 92.1. HRMS: Found, 477.1673 (M^+-Cl); calc. for $C_{27}H_{21}N_3NiP$, 477.1689. IR (KBr) cm^{-1}: 1606m ($\nu_{C=C}$); 1151w ($\nu_{\beta(C-H)}$); 1039, 1017s (ν_{cycle}).

4.8.4. Chloro(1-naphthyl){8-(dipyrrolidin-1-ylphosphino)quinoline}nickel (II) (16)

A red powder (234 mg) was obtained (90%). ^1H NMR (500 MHz, $CDCl_3$): δ 10.08 (s, 1H, CH=N); 9.70 (s, 1H, NiCCH); 8.30 (s, 1H); 7.98 (s, 1H); 7.72–7.24 (m, 8H); 7.05 (s, 1H); 3.67 (s, 2H, CH_2); 3.38–3.14 (m, 4H, CH_2); 2.64 (s, 2H, CH_2); 1.98–1.57 (m, 8H, CH_2). ^{31}P NMR: δ 95.8. HRMS: Found, 485.2373 (M^+-Cl); calc. for $C_{27}H_{29}N_3NiP$, 485.2329. IR (KBr) cm^{-1}: 1604w ($\nu_{C=C}$); 1152m ($\nu_{\beta(C-H)}$); 954, 915m (ν_{cycle}).

4.9. General procedure for ethylene oligomerization

A Medimex autoclave (100 ml) was loaded with 15 μmol of each of the nickel complexes **13**–**16** and 30 ml toluene. The autoclave was connected to an ethylene source through a *Buchi-bpc* gas-flow controller, which maintained a constant ethylene pressure. It also enabled the monitoring of the ethylene consumption. The mixture was stirred for 10 min; 5 ml of MAO (10% solution in toluene) were then added by a syringe. The autoclave was kept at the same pressure for a limited period of time; the catalytic reaction was terminated by adding acidified water. An aliquot of the organic layer was analyzed by GC and GC–MS.

Table 4
Crystal data and structure refinement of ligand **3**

Empirical formula	$C_{17}H_{14}N_3P$
Formula weight	291.28
T (K)	298(2)
λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.1647(16)
b (Å)	11.852(2)
c (Å)	15.069(3)
α (°)	73
β (°)	78.866(3)
γ (°)	75
V (Å^3)	1501.3(5)
Z	4
D_{calc} (g cm^{-3})	1.289
Absorption coefficient (mm^{-1})	0.179
Crystal size (mm)	$0.57 \times 0.37 \times 0.25$
Reflections collected, unique	13 193, 6091
R_{int}	0.0372
Refinement method	Full-matrix least-squares on F^2
Data, restraints, parameters	6091, 0, 379
Goodness-of-fit	1.101
R, R_w	0.0835, 0.1907
Minimum/maximum residual density (e Å^{-3})	0.728/−0.257

Table 5
Crystal data and structure refinement of complex [Pd(P,N)(CH_3)Cl] (**10**)

Empirical formula	$C_{22}H_{17}ClNO_2PPd$
Formula weight	499.5
T (K)	293(2)
λ (Å)	0.71073
Crystal system	Orthorombic
Space group	*P*/*bca*
Unit cell dimensions	
a (Å)	11.5030(8)
b (Å)	14.1591(9)
c (Å)	29.903(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4870.3(6)
Z	6
D_{calc} (g cm^{-3})	1.690
Absorption coefficient (mm^{-1})	0.288
Crystal size (mm)	$0.39 \times 0.22 \times 0.17$
Reflections collected, unique	30 317, 4975
R_{int}	0.0315
Refinement method	Full-matrix least-squares on F^2
Data, restraints, parameters	4975, 0, 298
Goodness-of-fit	1.116
R, R_w	0.0465, 0.1076
Minimum/maximum residual density (e Å^{-3})	0.726/−0.384

4.10. Structure determination

X-ray structural measurements of the ligand **3** and the complex [Pd(P,N)(CH_3)Cl] (**10**) were carried out on a Bruker CCD diffractometer (SMART PLATFORM, with CCD detector, graphite monochromator, Mo Kα radiation). The program SMART was used for data collection. Integration was performed with SAINT. The structure solution (Patterson method) and refinement on F^2 were accomplished with SHELXTL-97. Model plots were made with ORTEP32. All non-hydrogen atoms were refined freely with anisotropic displacement parameters. The hydrogen atoms were refined at calculated positions riding on their carrier atoms. Weights were optimized in the final refinement cycles. Tables 4 and 5 give the crystallographic data for the compounds **3** and **10**.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 270149 and 270150. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing to data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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