Synthesis and characterization of novel nickel(II) complexes bearing N,P ligands and their catalytic activity in ethylene oligomerization

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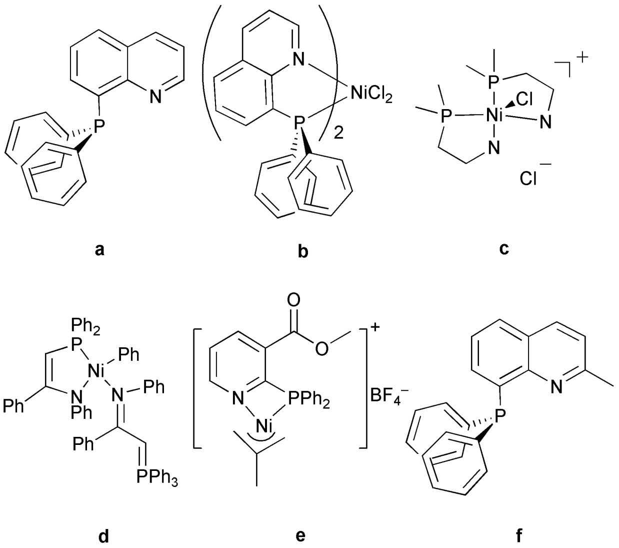
The novel chloro(1-naphthyl)[8-(diphenylphosphino)quinoline]nickel(II) (**1**), chloro(1-naphthyl)[2-methyl-8-(diphenylphosphino)quinoline]nickel(II) (**2**), and [2-methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride (**3**) complexes were synthesized in satisfactory yield and fully characterized. The structures of complexes **1** and **3** were determined by single crystal X-ray analysis, which indicated that complex **1** exists in a square planar configuration, while complex **3** is dimeric square pyramidal. In the presence of MAO cocatalyst, complexes **1–3** displayed good catalytic activities for ethylene oligomerization in toluene, up to 2.45×10^5 g ethylene (mol Ni·h·atm)$^{-1}$ by complex **3**.

The electron-donating roles of nitrogen, oxygen and phosphorus in hetero-organic compounds make such species good ligands for transition metals.[1] Bidentate ligands containing these donor atoms are of great importance in organometallic chemistry for their wide application in chemical industry and material science. Representative of these achievements, the highly active transition metal based precursors for ethylene oligomerization, neutral nickel(II) complexes with chelating P,O ligands, are successfully used in the Shell Higher Olefin Process (SHOP)[2] to produce linear α-olefins. Recently, the catalytic properties of late transition metal complexes containing N^N,[3] N^O,[4] N^P,[5] O^P,[5a,6] P^P[7] or N^N^N[8] ligands have been considerably investigated for ethylene polymerization or oligomerization. These works have demonstrated that the ligands architecture plays a crucial role in adapting the activity of the coordinated metal center. It is generally considered that ethylene oligomerization catalyzed by the family of transition metal complexes, the activity and selectivity are strongly dependent on the coordination environment around the metal center.[6b] Therefore, our interests focus on designing efficient chelating N^P ligands to modify the environment around the nickel center on the basis of their special electronic and steric effects as mixed-donor ligands.[1] Herein we report the initial results of our studies on ethylene oligomerization catalyzed by novel nickel-based catalysts that incorporate quinolyl and diphenylphosphinyl moieties in a single ligand.

Results and discussion

Synthesis of complexes

The preparation of 8-(diphenylphosphino) quinoline (**a**) was reported along with its reaction with NiX_2 to form the six-coordinated L_2NiX_2 type bis[8-(diphenylphosphino)quinoline]Ni(II) dihalide **b**[9] (Scheme 1). It was found that the complex was sensitive to air in solution due to insertion of oxygen into the phosphorus–nickel bond with oxidation of P(III) to P(V).[10] Neither of these compounds showed catalytic activity for ethylene oligomerization or polymerization. However, attempts to prepare mono-bidentate $LNiX_2$ type complex failed when using ligand **a** with either $NiCl_2$ or $(Ph_3P)_2NiCl_2$[11] in various solvents. This may be attributed to the minimal steric bulk of ligand **a**, which favors the formation of a six-coordinated nickel(II) complex with two bidentate ligands. On the other hand, the two small chloride ligands on the metal center are also unfavorable for the formation of four-coordinated complexes. Accordingly, it is expected to obtain mono-bidentate nickel(II) species with a low coordination number by increasing the steric hindrance either of the bidentate ligand or of the metal center with other bulky ligands.



Scheme 1

To pursue the latter strategy we introduced a bulky ligand, naphthyl, onto the nickel center. *trans*-Chloro(1-naphthyl) bis(triphenylphosphine)nickel(II)[12] was employed to react with ligand **a**, giving the deep yellow nickel(II) complex **1** in high

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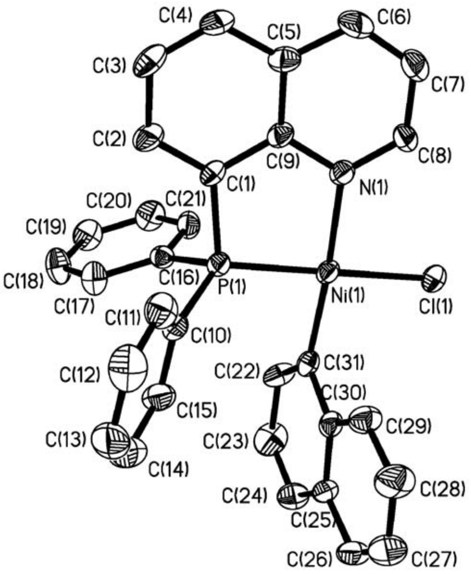


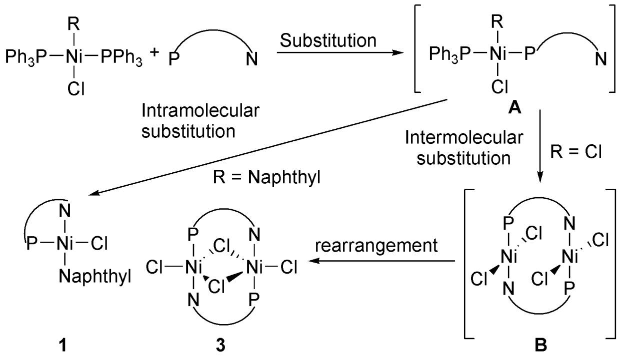
Fig. 1 Molecular structure of complex **1**.

yield. Complex **1** was very sensitive to air in solution and even gradually decomposed during storage. Recrystallization from CH$_2$Cl$_2$–hexane gave red-purple crystals suitable for X-ray diffraction. It was confirmed that the ML complex crystallized in a distorted square planar geometry (see Fig. 1).

For the purpose of increasing the ligand dimension, 2-methyl-8-(diphenylphosphino)quinoline (**f**), a derivative of ligand **a**, was selected as a bidentate ligand, bearing an addition methyl group on the quinoline ring. After many efforts, ligand **f** was synthesized, and reacted with *trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel(II) to give the deep red powder of complex **2** in high yield, which was characterized by IR, ^{1}H NMR and elemental analysis. It is stable in the solid state but unstable in solution.

The reaction of ligand **f** with (Ph$_3$P)$_2$NiCl$_2$ or NiCl$_2$ gave the stable light green nickel(II) complex **3** in high yield, but the former proceeded more easily because of the higher solubility of (Ph$_3$P)$_2$NiCl$_2$ in CH$_2$Cl$_2$ solvent. Characterization of complex **3** was difficult because of its poor solubility in organic solvents, and NMR spectroscopic analysis was not possible due to its paramagnetism. Fortunately, crystals of **3** suitable for X-ray analysis were obtained by recrystallization from CH$_2$Cl$_2$.

On the basis of the structures of **1** and **3** (see Fig. 2), the complexation reaction would likely take the following pathway (Scheme 2). One PPh$_3$ on the nickel substrate was substituted by the bidentate N^P ligand to form the corresponding intermediate **A**. When R = naphthyl, the quinonyl nitrogen replaced another PPh$_3$, due to the steric bulk of the naphthyl, that is intramolecular substitution, to give the bidentate chelating complex **1**. In addition, the naphthyl prefers to locate *cis* to the phosphine ligand due to the π-π stacking between the phenyl and naphthyl rings. However, when R = Cl and the ligand was **f**, intermediate **A** underwent intermolecular substitution to form **B**, and rearrangement gave the dimeric square pyramidal complex **3**.



Scheme 2

Crystal structure of complexes 1 and 3

The crystallographic structure illustrates that complex **1** has a four-coordinated, distorted square planar geometry around the nickel center. Its molecular structure is shown in Fig. 1. The naphthyl and diphenylphosphino groups are located in *cis* position, and no *trans* isomer could be found (Scheme 3). The Ni–N distance 2.010 Å is a little longer by 0.037, 0.036 and 0.089 Å, and the Ni–P distance (2.107 Å) is a little shorter by 0.062, 0.012 and 0.086 Å than those of the known structures of complex **c**^{13} {*cis*-[Ni(edmp)$_2$]Cl$_2$ (edmp = Me$_2$PCH$_2$CH$_2$NH$_2$, Scheme 1), mean Ni–N 1.973 Å, Ni–P 2.169 Å}, complex **d**^{5a} (Ni–N 1.974 Å, Ni–P 2.119 Å), and complex **e**^{5b}(Ni–N 1.921 Å, Ni–P 2.193 Å), respectively. However, the Ni–Cl distance (2.211 Å) is significantly shorter, by 0.63 Å, than that in **c** (mean Ni–Cl 2.841 Å). On the other hand, the N–Ni–P angle (87.69°) is larger by 1.5°, 2.07° and 13.8° than those of **c** (mean 86.2°), **d** (85.62°) and **e** (73.9°), respectively. Probably, since the quinolyl and phosphorus form a conjugated system, the phosphorus becomes electron rich and attracts the adjacent nickel closer, which consequently extends the Ni–N distance and N–Ni–P angle. Selected bond lengths and angles are listed in Table 1.

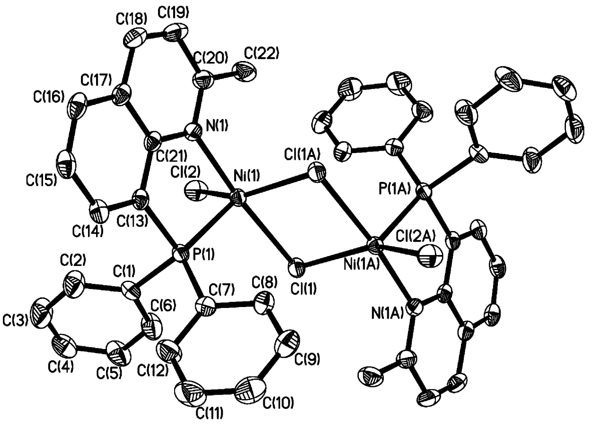
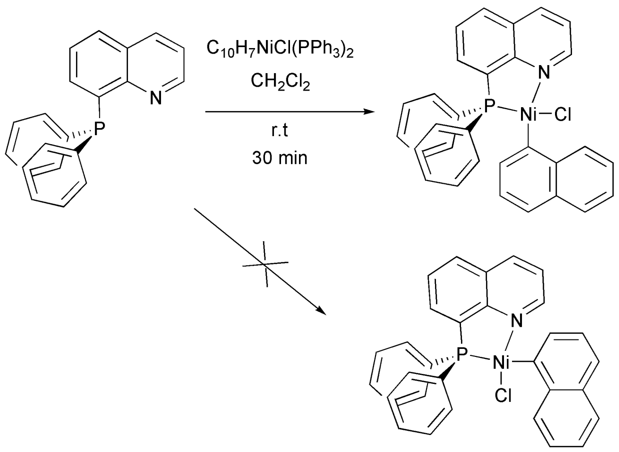


Fig. 2 Molecular structure of complex **3**.



Scheme 3

Table 1 Selected bond lengths (Å) and angles (degree) for complex **1**

Ni(1)–P(1)	2.1071(15)	Ni(1)–Cl(1)	2.2113(15)
Ni(1)–N(1)	2.010(4)	Ni(1)–C(31)	1.903(5)
N(1)–Ni(1)–P(1)	87.69(13)	C(31)–Ni(1)–N(1)	174.01(19)
N(1)–Ni(1)–Cl(1)	94.81(13)	P(1)–Ni(1)–Cl(1)	172.97(6)
C(31)–Ni(1)–Cl(1)	90.49(14)	P(1)–Ni(1)–C(31)	87.38(14)

Different from **1**, complex **3** in the solid state is a centrosymmetric dimer bridged by two chlorine atoms, Cl(1) and Cl(1)^{i} (symmetry code *i*: $-x$, $-y$, $-z$) as shown in Fig. 2. Each nickel is coordinated in a square pyramidal environment by nitrogen and phosphorus atoms of ligand **f** and two bridging chlorine atoms, and a terminal chlorine atom at the apical position. The Ni–N distance (2.093 Å) is a little longer by 0.12, 0.119 and 0.172 Å, but contrary to **1**, the Ni–P distance (2.287 Å) is also longer by 0.118, 0.167 and 0.094 Å than those in **c**, **d** and **e**, respectively. Unlike that of complex **1**, the N–Ni–P angle (84.48°) is smaller by 1.72° and 1.14° than those of **c** and **d**, respectively. Moreover, the Ni(1)–N(1) distance is longer by 0.083 Å, the Ni(1)–P(1) distance longer by 0.179 Å and the Ni–Cl average distance longer by 0.142 Å, than those of complex **1**, while the N–Ni–P angle is less (3.21°). This phenomenon indicates that there may be some repulsive interaction between the two closely located ligands, especially between the 2-methyl group of quinoline ring and the *P*-phenyl group in another ligand, which enables the bridged structure of complex **3** to slightly stretch along the Ni–Ni axis, and thus extends the relevant bond distances and angles. Selected bond lengths and angles are listed in Table 2.

Ethylene oligomerization

The ethylene oligomerization catalytic behavior of complexes **1–3** was investigated using an excess of MAO as the cocatalyst in toluene. As shown in Table 3, complex **1** shows moderate activity [$(0.13–2.05)\times10^5$ g C_2H_4 (mol Ni·h·atm)$^{-1}$] for ethylene oligomerization at 25 °C, while the six-coordinated ML_2 type **b**[9] displays no activity under similar conditions, which may be due to the electron deficiency of the four-coordinate nickel(II). This result provides an effective way to obtain an active center through altering the electronic and steric environment around the nickel cation. The products are mainly C_4 and C_6 olefins, and the selectivity to 1-C_4 is very high while appreciably lower for 1-C_6. Moreover, lower reaction temperatures seem to increase the catalytic activity, giving activities up to 2.05×10^5 g C_2H_4 (mol Ni·h·atm)$^{-1}$ at 0 °C for **1**. However, even lower temperatures limit the formation of the active species, and thus decrease the activity to some extent. On the other hand, the activity significantly decreases at temperatures above 80 °C, which may be caused by the decrease of ethylene solubility in toluene at high temperature. Complexes **2** and **3** show higher catalytic activities than **1**, probably the result of the greater stability of their cationic active centers in toluene. For complex **3**, in contract to **1** and **2**, the products are mainly C_4, C_6 and C_8 and the activity for ethylene oligomerization increases with increasing MAO : Ni molar ratio. Additionally, the activity reaches as high as 2.45×10^5 g C_2H_4 (mol Ni·h·atm)$^{-1}$ at 50 °C with a 500 MAO/Ni ratio, but the selectivity for α-olefin decreases as the temperature increases.

Table 2 Selected bond lengths (Å) and angles (degree) for complex **3**

Ni(1)–P(1)	2.2865(10)	Ni(1)–Cl(1)	2.4490(10)
Ni(1)–N(1)	2.093(3)	Ni(1)–Cl(2)	2.2653(10)
Ni(1)–Cl(1A)^{i}	2.3439(9)		
N(1)–Ni(1)–Cl(2)	93.37(9)	N(1)–Ni(1)–P(1)	84.48(9)
Cl(2)–Ni(1)–P(1)	104.64(4)	N(1)–Ni(1)–Cl(1)^{i}	89.37(8)
Cl(1)^{i}–Ni(1)–Cl(2)	146.99(4)	P(1)–Ni(1)–Cl(1)^{i}	108.37(4)
N(1)–Ni(1)–Cl(1)	173.11(8)	Cl(1)–Ni(1)–Cl(2)	92.69(4)
P(1)–Ni(1)–Cl(1)	97.15(4)	Cl(1)–Ni(1)–Cl(1)^{i}	83.76(3)

Symmetry code *i*: $-x$, $-y$, $-z$.

Experimental

Materials and physical measurements

All operations were performed in Schlenk tubes under nitrogen, using vacuum-line techniques. The solvents were purified and dried under nitrogen by conventional methods. The ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz on a Brucker dmx300 spectrometer at room temperature, using $SiMe_4$ as internal standard. IR spectra were recorded on a Perkin Elmer 2000 FI-IR instrument. Microanalyses were obtained from a Carlo Erba 1106. The oligomerization products of ethylene were analyzed by gas chromatography with a Beifen 3400 instrument on a SE-54 column (methylsilicone, diameter 0.32 mm, length 25 m) using a temperature program from 35–250 °C. 8-Chloroquinoline (Acros), MAO (methylaluminoxane, Aybemarle Co., 1.4 M) and high purity ethylene (Beijing Yanshan Petrochemical Co.) were used as received. 2-Methyl-8-chloroquinoline[14] and Ph_2PLi[15] were prepared according to the published methods.

Synthesis

2-Methyl-8-(diphenylphosphino)quinoline (f). A solution of 2-methyl-8-chloroquinoline (1.77 g, 10 mmol) in THF (10 mL) was added dropwise to a solution of Ph_2PLi (1.92 g, 10 mmol) in THF (30 mL) at −78 °C. The mixture was stirred for 1 h, then the reaction mixture was gradually warmed up to room temperature and allowed to stand for 24 h. After the volatiles were removed in vacuum, 20 mL of water was added. The resultant solution was extracted by diethyl ether (3 × 20 mL). The combined organic layer was concentrated to about 10 mL and hexane (30 mL) was added to deposit **f** as a white powder (2.62 g, 80%), mp 168 °C. Found: C, 80.84; H, 5.58; N, 4.17. $C_{22}H_{18}NP$ requires C, 80.72; H, 5.54; N, 4.28%. MS (EI): *m*/*z* 327 (M^+, 100%), 250 ($[M-Ph]^+$, 56). IR (KBr): ν/cm^{-1} 3055.5(s), 2999.9(m), 2957.4(w), 2915.5(m), 2856.0(w), 1951.3(w), 1885.2(w), 1823.9(w), 1769.8(w), 1675.0(w), 1601.1(vs), 552.6(w), 1496.2(s), 1478.8(m), 1429.9(vs), 1370.3(m), 1312.8(s), 1274.2(w), 244.6(m), 1205.3(w), 1181.4(w), 1141.0(m), 1094.3(m), 1069.3(m), 1025.5(m), 1000.3(w), 976.4(w), 915.5(w), 833.7(s), 797.0(m), 763.3(m), 745.9(vs), 698.1(vs), 660.6(m), 549.6(m), 499.8(s), 472.0(m), 444.3(m), 399.2(m). ^{1}H NMR($CDCl_3$): δ 2.49 (3H, s, CH_3), 6.98 (1H, m), 7.14–7.28 (12H, m), 7.66 (1H, d, quinolyl-5-*H*), 7.93 (1H, d, quinolyl-4-*H*). ^{13}C NMR($CDCl_3$): δ 25.2 (CH_3), 122.0 (quinolyl-3-*C*), 125.4 (quinolyl-6-*C*), 125.7 (quinolyl-10-*C*), 128.0, 128.1, 128.3, 133.7, 133.9, 134.1, 135.8 (quinolyl-8-*C*), 137.5 [P–C (of Ph)], 137.7 (quinolyl-9-*C*), 158.2 (quinolyl-2-*C*).

Chloro(1-naphthyl)[8-(diphenylphosphino)quinoline]nickel(II) (1). A solution of 8-(diphenylphosphino)quinoline (1.57 g, 5 mmol) in CH_2Cl_2 (10 mL) was added to a solution of *trans*-chloro(1-naphthyl)bis(triphenylphosphane)nickel(II) (3.72 g, 5 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred for 30 min. The resultant solution was concentrated to about 5 mL and hexane (20 mL) was added to completely precipitate complex **1**. The solid was collected by filtration, washed with diethyl ether (2 × 10 mL) and dried under vacuum to give a deep yellow powder of complex **1** (2.58 g, 97%), mp 233 °C (from CH_2Cl_2). Found: C, 67.85; H, 4.30; N, 2.25. $C_{31}H_{23}ClNNiP\cdot0.75H_2O$ requires C, 67.93; H, 4.50; N, 2.56%. IR (KBr): ν/cm^{-1} 3048.8(s), 2954.7(m), 2864.7(m), 1960.3(w),1894.5(w), 1827.4(w), 760.3(w), 1707.5(w),

Table 3 Oligomerization of ethylene catalyzed by complexes **b**, **1**, **2** and **3**[a]

					Proportion (%)					
Run No.	Complex	MAO : Ni[b]	T/°C	Activity[c]	C_4	1-C_4[f]	C_6	1-C_6[f]	C_8	1-C_8[f]
1	**b**	300 : 1	25	–[d]						
2	**1**	50 : 1	25	0.13	>99	92.7				
3	**1**	100 : 1	25	0.42	88.4	>99	11.6	57.9		
4	**1**	300 : 1	25	1.63	77.3	>99	22.7	65.1		
5	**1**	500 : 1	25	0.93	93.1	>99	6.9	93.7		
6	**1**	1000 : 1	25	0.91	96.3	>99	3.7	94.1		
7	**1**	300 : 1	80	–[e]						
8	**1**	300 : 1	50	0.49	>99	43				
9	**1**	300 : 1	0	2.05	83.6	>99	16.4	83.6		
10	**1**	300 : 1	−10	1.31	>99	>99				
11	**2**	300 : 1	25	2.10	90.7	>99	9.3	80.8		
12	**2**	1000 : 1	25	0.91	96.1	>99	3.9	94.8		
13	**3**	300 : 1	25	0.65	77.6	91.0	13.0	67.1	9.4	58.8
14	**3**	500 : 1	25	1.47	80.2	95.9	15.1	75.8	4.7	64.7
15	**3**	1000 : 1	25	1.53	85.0	95.9	9.4	88.8	5.6	68.4
16	**3**	500 : 1	0	0.86	86.8	98.0	6.8	89.2	6.4	68.9
17	**3**	500 : 1	50	2.45	88.4	96.7	6.4	71.8	5.2	57.4
18	**3**	500 : 1	80	1.75	94.5	94.1	3.5	64.2	2.0	42.0

[a] Reaction conditions: toluene (50 ml), 4 μmol Ni(II) complex, 1 atm ethylene, 30 min. [b] Molar ratio. [c] Activity: $\times 10^5$g C_2H_4 (mol Ni·h·atm)$^{-1}$. [d] No activity. [e] Very low activity. [f] 1-C_n percentage in its corresponding C_n efin.

1588.2(m), 1544.4(m), 1493.6(vs), 1435.8(vs), 1376.0(vs), 1305.7(m),45.2(m),1225.3(m),1198.0(m),1153.3(m),1132.4(m), 1098.5(s), 1069.3(w), 97.2(m), 951.6(m), 852.1(m), 833.0(s), 783.3(vs), 745.6(vs), 695.5(vs), 643.0(w), 69.3(s), 545.3(s), 521.6(w), 495.8(vs), 467.7(s), 419.6(m). ^{1}H NMR($CDCl_3$): δ 6.52 (2H, m), 6.81 (2H, t), 6.89 (2H, t), 7.06 (2H, m), 7.18 (1H, d), 7.39 (1H, d), 7.48 (4H, d), 7.68 (2H, d), 7.83 (1H, t), 8.06 (1H, d), 8.17–8.23 (2H, m), 8.42 (1H, d, quinolyl-5-*H*), 9.11 (1H, d, quinolyl-4-*H*), 10.20 (1H, d, quinolyl-2-*H*).

Chloro(1-naphthyl)[2-methyl-8-(diphenylphosphino) quinoline]nickel(II) (2). Complex **2** was prepared as a red powder according to a similar procedure as for complex **1** by using **f** instead of 8-(diphenylphosphino)quinoline on the 5 mmol scale (2.65 g, 97%), mp 178 °C (crystallized from CH_2Cl_2). Found: C, 70.18; H, 4.43; N, 2.56. $C_{32}H_{25}ClNNiP$ requires 70.05; H, 4.59; N, 2.55%. IR (KBr): ν/cm^{-1} 3042.9(s), 3004.5(m), 2918.9(w),1966.7(w),1816.7(w),1778.8(w),1667.0(w),1602.6(s), 1544.6(s),1495.4(vs),1436.4(vs),1369.5(s),1308.2(m),1243.5(m), 1220.1(w),1191.0(m),1145.3(m),1101.5(s),1023.3(m),997.3(m), 948.7(m), 893.0(w), 841.9(s), 785.5(vs), 742.2(s), 694.2(vs), 647.6(m), 559.5(s), 541.7(m), 505.9(vs), 481.4(m), 468.2(m), 416.6(m), 393.7(w). ^{1}H NMR($CDCl_3$): δ 3.52 (3H, s, CH_3), 6.73–6.85 (5H, m), 7.15 (6H, s), 7.43 (5H, m), 7.74 (1H, s), 7.93 (1H, s), 8.11 (3H, s), 9.76 (1H, s).

[2-Methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride (3). A solution of **f** (1.64 g, 5 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of $(Ph_3P)_2NiCl_2$ (3.26 g, 5 mmol) in diethyl ether (20 mL) and the resultant mixture was stirred for about 30 min. The precipitate was collected by filtration, washed with diethyl ether and dried under vacuum to give complex **3** as light green crystals (2.16 g, 95%), mp 240 °C (from CH_2Cl_2). Found: C, 50.82; H, 3.61; N, 2.51. $C_{22}H_{18}Cl_2NNiP \cdot CH_2Cl_2$ requires C, 50.98; H, 3.72; N, 2.58%; IR (KBr): ν/cm^{-1} 3053.7(s), 1970.6(w), 1911.2(w), 1825.6(w), 1606.6(vs), 1562.6(s),1502.2(vs),1482.8(s),1434.5(vs),1368.0(m),1313.4(s), 1269.9(m), 1246.1(m), 1206.7(w), 1188.1(w), 1146.4(m), 1098.1(s), 1071.6(w), 1028.2(m), 998.3(m), 930.2(w), 893.3(w), 843.9(vs), 779.0(s), 748.0(vs), 695.1(vs), 655.7(m), 618.9(w), 554.1(s), 519.5(s), 504.4(vs), 478.5(s), 461.0(m), 417.5(m).

Oligomerization of ethylene

A typical oligomerization reaction was carried out as follows: to a three-neck flask (250 mL) containing toluene (50 mL) under ethylene atmosphere (1 atm), was added a dichloromethane solution containing either the nickel(II) precatalyst **b** (10 μmol) or complex **1**, **2** or **3**, and an excess amount of MAO at a given temperature. The solution was stirred for 30 min to allow ethylene oligomerization and the reaction was terminated by adding acidic ethanol (10% HCl in ethanol). The products were subsequently analyzed by gas chromatography or GC-MS analysis.

X-Ray crystallography

Single crystals of **1** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2–hexane, while complex **3** was obtained from its CH_2Cl_2 solution. Intensity data were collected on a CCD area detector at 293(2) K with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Each H atom was placed in a calculated position and refined using a riding model. All nonhydrogen atoms were refined anisotropically. Structure solution and refinement were performed using the SHELXL-97 package.[16]

CCDC reference numbers 183920 and 183730. See http://www.rsc.org/suppdata/nj/b2/b203738f/ for crystallographic files in cif or other electronic format.

Crystal data for complex 1. $C_{31}H_{23}ClNNiP \cdot 0.75H_2O$, $M = 548.15$, red brown block, monoclinic, space group *C*2/*c*, $a = 18.606(5)$, $b = 9.184(2)$, $c = 34.005(9)$ Å, $\alpha = 90°$, $\beta = 96.381(5)°$, $\gamma = 90°$, $U = 5774(3)$ Å^3, $Z = 8$, μ(Mo-K$_\alpha$) = 0.84 mm^{-1}, 11609 reflections collected, 5052 unique ($R_{int} = 0.0750$), $R_1 = 0.0536$ for 2443 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1119$ for all data.

Crystal data for complex 3. $C_{44}H_{36}Cl_4N_2Ni_2P_2 \cdot 2CH_2Cl_2$, $M = 1083.76$, light green block, triclinic, space group *P*-1, $a = 10.9073(7)$, $b = 11.0443(3)$, $c = 11.5761(5)$ Å,

$\alpha = 95.605(4)°$, $\beta = 103.724(6)°$, $\gamma = 114.101(6)°$, $U = 1206.46(10)$ Å^3, $Z = 2$, μ(Mo-K$_\alpha$) = 1.32 mm^{-1}, 8314 reflections collected, 5387 unique ($R_{\text{int}} = 0.0417$), $R_1 = 0.0564$ for 4221 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1497$ for all data.

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References

1 H. A. Hudali, J. V. Kingston and H. A. Tayim, *Inorg. Chem.*, 1979, **18**, 1391.

2 (*a*) W. Keim, F. H. Kowaldt, R. Goddard and C. Krgüer, *Angew. Chem., Int. Ed. Engl.*, 1987, **17**, 466; (*b*) W. Keim, A. Behr, B. Gruber, B. Hoffmann, F. H. Kowaldt, U. Kürschner, B. Limbäcker and F. P. Sistig, *Organometallics*, 1986, **5**, 2356; (*c*) W. Keim, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235; (*d*) W. Keim, *J. Mol. Catal.*, 1989, **52**, 19.

3 (*a*) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (*b*) C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664; (*c*) C. M. Killian, L. K. Johnson and M. Brookhart, *Organometallics*, 1997, **16**, 2005; (*d*) S. A. Svejda and M. Brookhart, *Organometallics*, 1999, **18**, 65; (*e*) S. P. Meneghetti, P. J. Lutz and J. Kress, *Organometallics*, 1999, **18**, 2734; (*f*) Z. Li, W. Sun, Z. Ma, Y. Hu and C. Shao, *Chin. Chem. Lett.*, 2001, **12**, 691.

4 (*a*) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben and M. W. Day, *Organometallics*, 1998, **17**, 3149; (*b*) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science*, 2000, **287**, 460; (*c*) F. M. Bauers and S. Merking, *Angew. Chem., Int. Ed.*, 2001, **40**, 3020.

5 (*a*) P. Braunstein, J. Pietsch, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1996, 3571; (*b*) M. C. Bonnet, F. Dahan, A. Ecke, W. Keim, R. P. Schulz and I. Tkatchenko, *J. Chem. Soc., Chem. Commun.*, 1994, 615; (*c*) P. Braunstein, J. Pietsch, Y. Chauvin, A. DeCian and J. Fischer, *J. Organomet. Chem.*, 1997, **529**, 387; (*d*) E. K. V. D. Beuken, W. J. J. Smeets, A. L. Spek and B. L. Feringa, *Chem. Commun.*, 1998, 223.

6 (*a*) M. D. Fryzuk, X. Gao and S. J. Rettig, *Can. J. Chem.*, 1995, **73**, 1175; (*b*) J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.*, 1998, **22**, 467.

7 N. A. Cooley, S. M. Green, D. F. Wass, K. Heslop, A. G. Orpen and P. G. Pringle, *Organometallics*, 2001, **20**, 4769.

8 (*a*) B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049; (*b*) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728; (*c*) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, S. Mastroianni, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 1639.

9 V. K. Issleib and M. Haftendorn, *Z. Anorg. Allg. Chem.*, 1970, **376**, 79.

10 Z. Li, W.-H. Sun, L. Wang, B. Wu, C. He and C. Yan, *J. Chem. Crystallogr.*, 2002, **32**, 107.

11 K. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1954, **27**, 501.

12 J. V. Soolingen, H. D. Verkruijsse, M. A. Keegstra and L. Brandsma, *Synth. Commun.*, 1990, **20**, 3153.

13 T. Suzuki, A. Morikawa and K. Kashiwabara, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2539.

14 E. Bartow and E. W. McCollum, *J. Am. Chem. Soc.*, 1904, **26**, 700.

15 K. Sommer, *Z. Anorg. Allg. Chem.*, 1970, **376**, 37.

16 G. M. Sheldrick, SHELXTL ver 5.1, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998.