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Inorganica Chimica Acta 358 (2005) 4423-4430

Inorganica Chimica Acta

www.elsevier.com/locate/ica

# Synthesis, structure and ethylene oligomerization behavior of non-symmetric bidentate neutral arylnickel(II) phosphine complexes

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Received 28 January 2005; received in revised form 20 July 2005; accepted 6 August 2005 Available online 21 September 2005

### Abstract

A series of new neutral arylnickel(II) phosphine complexes bearing non-symmetric bidentate chelate ligands, 3-aryliminomethyl-5chloro-2-hydroxybenzaldehyde, have been synthesized, and the structure of representative complexes (**2b** and **2d**) has been confirmed by X-ray crystallographic analysis. These neutral arylnickel(II) phosphine complexes have been investigated as catalysts for ethylene oligomerization. Using methylaluminoxane (MAO) as a cocatalyst, these complexes display high ethylene oligomerization activities. A catalytic activity of up to  $4.6 \times 10^6$  g mol<sup>-1</sup> h<sup>-1</sup> has been observed. The influence of Al/Ni molar ratio, reaction temperature, reaction period and pressure on catalytic activity was investigated.

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Keywords: Neutral nickel(II) complex; X-ray crystallography; Catalyst; Methylaluminoxane; Ethylene oligomerization

### 1. Introduction

Over the past decade, olefin oligomerization and polymerization based on late transition metal catalysts has been one of the most exciting developments in the area of catalysis, organometallic chemistry, and polymer science [1]. For instance,  $\alpha$ -diimine Ni(II) or Pd(II) complexes and bis(imino)pyridyl Fe(II) or Co(II) complexes are two kinds of representative catalysts in this field which could not only polymerize ethylene to high branched polymers but could also copolymerize ethylene and polar-functionalized  $\alpha$ -olefins [2,3]. Recently, neutral nickel(II) complexes have attracted much attention because they are less sensitive to protonic solvents and polar monomers than cationic nickel analogs [4]. The most famous example of neutral nickel(II) catalysts is the SHOP-type [4]. These nickel complexes contain an anionic [P,O] chelate ring and show high activity and selectivity for the conversion of ethylene to linear  $\alpha$ -olefins and polymers. Neutral nickel(II) catalysts containing anionic [N,O] chelate ring were also largely reported in recent years [5]. The most notable example is the neutral salicylaldiminato nickel(II) complexes described by Grubbs and co-workers [5g,5h], which exhibited high catalytic activity and good tolerance of polar functional group in ethylene polymerization. In addition, other ligands such as phosphinooxazoline [6], dithio- $\beta$ -diketonate [7], iminophosphine [8], monoiminopyridine [9], bis(pyrazolyl)methane [10],  $\alpha$ -nitroketonate [11], and bis(2-diphenylphosphinoethyl) methylamine [12] have also been employed with late-metals as homogeneous catalysts.

Owing to the fact that linear ethylene oligomers in  $C_4$  to  $C_{20}$  range are very useful materials for the preparation of detergents, plasticizers, linear low-density polyethlene and other fine chemicals [13], the research on ethylene oligomerization is receiving increased attention in ethylene chemistry. There are tremendous amounts of literatures which documented the achievement in this area. Among them, SHOP catalytic systems of  $\alpha$ -keto-ylid nickel catalysts [4a,14] and Brookhart's Ni(II) and Fe(II) bearing

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diimine ligands [3a,3b,3c] systems are the two famous examples. Being interested in obtaining short-chain aolefins, our group carried out a series of works to develop the ethylene oligomerization catalysts. As a part of these works, a series of nickel complexes containing 8-aminoquinoline, 2-(2-pyridyl)quinoxaline, 2,6-bis(imino)phenol, 2,9-bis(imino)-1,10-phenanthroline, pyridylcarboxamide and hydrazone derivatives were investigated [15]. Almost all of them have moderate to high ethylene oligomerization activity. To investgate the effect of introducing an aldehyde group in neutral salicylaldiminato nickel(II) system, in this contribution, a series of neutral arylnickel(II) phosphine complexes bearing non-symmetric bidentate chelate ligands. 3-aryliminomethyl-5-chloro-2-hydroxybenzaldehyde, have been synthesized. The structure of them (2b and 2d) has been confirmed by X-ray crystallographic analysis and the catalytic properties of these complexes for ethylene oligomerization are reported.

#### 2. Results and discussion

## 2.1. Synthesis and spectroscopic characterization

The 3-aryliminomethyl-5-chloro-2-hydroxybenzaldehyde ligands **1a–1f** were prepared as yellow or orange solids in moderate yields through the condensation reaction of 1 equivalent of 4-chloro-2, 6-diformylphenol with 1 equivalent of the appropriate aniline (Scheme 1). Compounds **1a–1f** were characterized by elemental analyses, IR and <sup>1</sup>H NMR.

In view of the high acidity of the hydroxyl proton on the ligands, the target complexes 2a-2f were synthesized from reacting 3-aryliminomethyl-5-chloro-2-hydroxybenzalde-hyde ligands with *trans*-[NiCl(Naph)(PPh<sub>3</sub>)<sub>2</sub>] in THF in the presence of NEt<sub>3</sub> (Scheme 1). Owing to the low polarity of the target complexes, the solubility of them in diethyl ether is very good and the target complexes can be extracted from the reaction mixture by diethyl ether; there-

fore, it is very easy to separate and purify them. The target complexes were obtained from good to excellent yields. All of the complexes were characterized by elemental analyses, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR.

In IR spectra of ligands 1a-1f, the C=N stretching vibration is distributed in the range from 1620.7 to 1629.6 cm<sup>-1</sup>, while in the corresponding complexes **2a–2f** the C=N stretching vibration is distributed in the range from 1605.4 to 1608.8  $\text{cm}^{-1}$ ; these shifts are contributed to the formation of N-Ni complex bonds. Owing to the fact that C=O groups do not form complex bonds with Ni, the shifts of stretching vibration of C=O in IR spectra are very slight between ligands 1a–1f and complexes 2a–2f. The <sup>1</sup>H NMR spectra of the complexes show the peaks in the range 9.25-9.94 ppm, confirming the existence of the hydrogen of formyl and the peaks in the range 8.45-8.52 according to the hydrogen on carbon in imino groups. In the <sup>13</sup>C NMR spectra of these complexes, the chemical shifts of C atoms in formyl groups are distributed in the range from 189.2 to 190.3 ppm, while the C atoms in imino groups are distributed in the range from 163.7 to 167.7 ppm. In the <sup>31</sup>P NMR spectra of these complexes, the chemical shifts of P atoms are distributed in the range from 25.15 to 26.39 ppm.

#### 2.2. Crystal structure

Single crystals of **2b** and **2d**, suitable for X-ray analysis, were obtained by slow evaporation of diethyl ether from their diethyl ether and ethanol mixed solutions. The crystal data are listed in Table 1 and the selected bond lengths and angles are listed in Table 2. As depicted in Fig. 1, complex **2d** contains a chelating [N,O] ligand, a triphenylphosphine group (PPh<sub>3</sub>) and a naphthyl group. The formyl [2,4,6-Me<sub>3</sub>(C<sub>6</sub>H<sub>2</sub>)–N] moiety occupies the position *trans* to PPh<sub>3</sub> with a nearly linear N(1)–Ni(1)–P(1) angle [177.42(7)°], and the naphthyl group bonded to Ni(1) also lies in a position *trans* to O(1) with an O(1)–Ni(1)–C(21) angle of



Table 1 Crystal data and structure refinement for **2b** and **2d** 

| Complexes                                                                | 2b                             | 2d                             |
|--------------------------------------------------------------------------|--------------------------------|--------------------------------|
| Formula                                                                  | C46H39ClNNiO2P                 | C45H37CINNiO2P                 |
| Formula weight                                                           | 748.90                         | 762.93                         |
| Crystal size (mm)                                                        | $0.38 \times 0.16 \times 0.12$ | $0.40 \times 0.20 \times 0.15$ |
| Crystal system                                                           | monoclinic                     | triclinic                      |
| Space group                                                              | C2/c                           | $P\overline{1}$                |
| a (Å)                                                                    | 37.94190(10)                   | 9.7914(5)                      |
| b (Å)                                                                    | 9.5483(2)                      | 15.1311(11)                    |
| <i>c</i> (Å)                                                             | 23.7550(5)                     | 18.3347(13)                    |
| α (°)                                                                    | 90.00                          | 104.630(2)                     |
| β (°)                                                                    | 99.1790(10)                    | 103.790(2)                     |
| γ (°)                                                                    | 90.00                          | 95.413(2)                      |
| $V(\text{\AA}^3)$                                                        | 8495.8(3)                      | 2517.8(3)                      |
| Ζ                                                                        | 8                              | 2                              |
| $D_{\rm calc} ({\rm g}{\rm cm}^{-3})$                                    | 1.224                          | 1.293                          |
| Diffractometer                                                           | Siemens Smart CCD              | Mercury70                      |
| $\mu (\mathrm{mm}^{-1})$                                                 | 0.595                          | 0.516                          |
| <i>F</i> (000)                                                           | 3276                           | 1026                           |
| $T(\mathbf{K})$                                                          | 293(2)                         | 293(2)                         |
| $\theta$ Range (°)                                                       | 1.74-22.00                     | 3.1005-27.4835                 |
| Total number of reflections                                              | 10263                          | 19594                          |
| Number of unique data $(R_{int})$                                        | 5180 (0.0475)                  | 11375 (0.0161)                 |
| Number of parameters                                                     | 490                            | 631                            |
| R                                                                        | 0.0880                         | 0.0608                         |
| $R_{ m w}$                                                               | 0.2229                         | 0.1509                         |
| Goodness-of-fit on $F^2$                                                 | 1.33                           | 1.030                          |
| $\Delta \rho_{\rm min}$ and $\Delta \rho_{\rm max}$ (e Å <sup>-3</sup> ) | 0.992 and -0.301               | 1.831 and -1.421               |

Table 2

| Selected bond | lengths (Å) | and | angles (°) | for | complexes | 2b | and | 2d |
|---------------|-------------|-----|------------|-----|-----------|----|-----|----|
|---------------|-------------|-----|------------|-----|-----------|----|-----|----|

| Complex 2b       |            |
|------------------|------------|
| Ni(1) - O(1)     | 1.893(5)   |
| Ni(1)-C(51)      | 1.903(9)   |
| Ni(1)–N(1)       | 1.934(7)   |
| Ni(1)–P(1)       | 2.188(2)   |
| O(1)-C(4)        | 1.286(10)  |
| O(2)–C(7)        | 1.198(11)  |
| N(1)-C(8)        | 1.300(10)  |
| N(1)–C(9)        | 1.443(11)  |
| O(1)-Ni(1)-C(51) | 174.1(3)   |
| O(1)-Ni(1)-N(1)  | 92.6(3)    |
| C(51)–Ni(1)–N(1) | 93.2(3)    |
| O(1)–Ni(1)–P(1)  | 86.07(19)  |
| C(51)–Ni(1)–P(1) | 88.1(3)    |
| N(1)–Ni(1)–P(1)  | 176.5(2)   |
| Complex 2d       |            |
| Ni(1) - O(1)     | 1.9017(19) |
| Ni(1)-C(21)      | 1.922(3)   |
| Ni(1)–N(1)       | 1.947(2)   |
| Ni(1)–P(1)       | 2.1768(7)  |
| O(1)–C(1)        | 1.288(3)   |
| O(2)–C(8)        | 1.212(4)   |
| N(1)-C(7)        | 1.287(4)   |
| N(1)-C(9)        | 1.449(3)   |
| O(1)-Ni(1)-C(21) | 167.68(12) |
| O(1)-Ni(1)-N(1)  | 93.00(9)   |
| C(21)–Ni(1)–N(1) | 93.45(11)  |
| O(1)-Ni(1)-P(1)  | 89.29(6)   |
| C(21)–Ni(1)–P(1) | 84.08(9)   |
| N(1)-Ni(1)-P(1)  | 177.42(7)  |



Fig. 1. Molecular structure of 2d, showing 30% probability displacement ellipsoids with hydrogen atoms omitted for clarity.

167.68(12)°. Due to the repulsion among the naphthyl ring, phenyl ring on chelating [N,O] ligand and the PPh<sub>3</sub> ligand, the *cis* angles at nickel are in the range from 84.08(9)° to 93.45(11)°. Thus, the four coordinate atoms [P(1), O(1), N(1), and C(21)] have an almost exact square-planar geometry with the Ni(1) approximately 0.0776 Å from the plane in complex **1**. Because of the obvious structural similarity, complex **2b** has a molecular structure (Fig. 2) similar to complex **2d**. The four-coordinate atoms [N(1), O(1), P(1), and C(51)] and the central Ni atom are also almost in the same planar; the mean deviation from plane is 0.022 Å. The *trans* N(1)–Ni(1)–P(1) [C(51)–Ni(1)–O(1)] angle and *cis* O(1)–Ni(1)–N(1) [C(51)–Ni(1)–N(1)] angle are 176.5 (2)° [174.1(3)°] and 86.07(19)° [93.2(3)°].



Fig. 2. Molecular structure of 2b, showing 15% probability displacement ellipsoids with hydrogen atoms omitted for clarity.

## 2.3. Ethylene oligomerization

Upon treatment with methylaluminoxane (MAO), all of the complexes 2a-2f are active for ethylene oligomerization. Table 3 lists their activity and molecular weight distribution of the oligomers produced by these neutral nickel catalysts. From these data, we can find that the electronic factor of ligands has more influence on catalysts' activity than the steric factor: the catalytic activity of complexes 2a-2d is very similar, but the catalytic activity of 2e-2f is much lower than 2a-2d.

Owing to the fact that 2d has the highest activity in the same conditions among these complexes, we selected 2d as the precatalyst and carefully investigated its catalytic activity. The influence of cocatalyst MAO on catalytic activities and the distribution of resulting oligomers are summarized in Table 4. The best Al/Ni molar ratio for this catalytic system is 1250. The influence of reaction temperature and time on catalytic activities and the distribution of resulting oligomers are listed in Tables 5 and 6. The best reaction temperature is 25 °C and the best reaction time is 1 h. After investigating the catalytic conditions, the highest catalytic activity in 1 atm was obtained as  $5.73 \times 10^5 \text{ g mol}^{-1} \text{ h}^{-1}$ under the conditions of 5 µmol catalyst (2d), 30 ml toluene, Al/Ni 1250, 1 h, 25 °C and the distribution of C<sub>4</sub> is 72.1% (2-butene >98%), C<sub>6</sub> is 27.9%. When the reaction pressure raised to 10 atm (conditions: 10 µmol catalyst (2d), 1000 ml toluene, Al/Ni 1250, 1 h, 20 °C), the catalytic activity im-

Table 3 Ethylene oligomerization using **2a–2f/MAO** systems and their oligomers' distribution

| Entry | Complexes | Activity<br>(×10 <sup>5</sup> g mol <sup>-1</sup> h <sup>-1</sup> ) | Distribution of oligomers (%) |       |  |
|-------|-----------|---------------------------------------------------------------------|-------------------------------|-------|--|
|       |           |                                                                     | $\overline{C_4}$              | $C_6$ |  |
| 1     | 2a        | 2.92                                                                | 81.4                          | 18.6  |  |
| 2     | 2b        | 3.00                                                                | 80.1                          | 19.9  |  |
| 3     | 2c        | 2.78                                                                | 82.5                          | 17.5  |  |
| 4     | 2d        | 3.70                                                                | 79.0                          | 21.0  |  |
| 6     | 2e        | 1.92                                                                | 80.0                          | 20.0  |  |
| 7     | 2f        | 1.12                                                                | 81.5                          | 18.5  |  |

Reaction conditions: 5  $\mu mol$  catalyst, 30 ml toluene, Al/Ni 1000, 0.5 h, 25 °C, 1 atm ethylene.

Table 4 Influence of Al/Ni molar ratio on **2d**/MAO catalytic systems and their oligomers' distribution

| Entry | Al/Ni | Activity<br>(×10 <sup>4</sup> g mol <sup>-1</sup> h <sup>-1</sup> ) | Distribution of oligomers (%) |                |  |
|-------|-------|---------------------------------------------------------------------|-------------------------------|----------------|--|
|       |       |                                                                     | C <sub>4</sub>                | C <sub>6</sub> |  |
| 1     | 250   | 7.01                                                                | 86.3                          | 13.7           |  |
| 2     | 500   | 8.74                                                                | 91.2                          | 8.8            |  |
| 3     | 750   | 12.5                                                                | 81.2                          | 18.8           |  |
| 4     | 1000  | 37.0                                                                | 79.0                          | 21.0           |  |
| 5     | 1250  | 39.6                                                                | 76.6                          | 27.9           |  |
| 6     | 1500  | 23.6                                                                | 97.9                          | 2.1            |  |

Reaction conditions: 5  $\mu$ mol catalyst, 30 ml toluene, 0.5 h, 25 °C, 1 atm ethylene.

Table 5

Table 6

Influence of reaction time on 2d/MAO catalytic systems and their oligomers' distribution

| Entry Time | Time (min) | Activity                                            | Distribution of oligomers (%) |                |  |
|------------|------------|-----------------------------------------------------|-------------------------------|----------------|--|
|            |            | $(\times 10^{5} \text{ g mol}^{-1} \text{ h}^{-1})$ | C <sub>4</sub>                | C <sub>6</sub> |  |
| 1          | 15         | 1.47                                                | 97.23                         | 2.77           |  |
| 2          | 30         | 3.96                                                | 76.7                          | 23.3           |  |
| 3          | 45         | 4.99                                                | 78.3                          | 21.7           |  |
| 4          | 60         | 5.73                                                | 72.1                          | 27.9           |  |
| 5          | 75         | 3.42                                                | 70.9                          | 29.1           |  |

Reaction conditions: 5 µmol catalyst, 30 ml toluene, Al/Ni 1250, 25 °C, l atm ethylene.

Influence of temperature on 2d/MAO catalytic systems and their oligomers' distribution

| Entry | <i>T</i> (°C) | Activity                                          | Distribution of oligomers (%) |                |  |
|-------|---------------|---------------------------------------------------|-------------------------------|----------------|--|
|       |               | $(\times 10^4 \text{ g mol}^{-1} \text{ h}^{-1})$ | C <sub>4</sub>                | C <sub>6</sub> |  |
| 1     | 0             | 8.37                                              | 74.9                          | 25.1           |  |
| 2     | 25            | 49.9                                              | 78.3                          | 21.7           |  |
| 3     | 50            | 32.3                                              | 66.6                          | 33.4           |  |
| 4     | 75            | 7.11                                              | 60.0                          | 40.0           |  |

Reaction conditions: 5  $\mu$ mol catalyst, 30 ml toluene, Al/Ni 1250, 45 min, 1 atm ethylene.

proved to  $4.6 \times 10^6$  g mol<sup>-1</sup> h<sup>-1</sup>. In the resulting oligomers, the distribution of C<sub>4</sub> is 92.5% (the distribution of 1-butene is 57.3% and that of 2-butene is 42.7%) and that of C<sub>6</sub> is 7.5%.

## 3. Experimental

#### 3.1. General procedures and materials

All manipulations for air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Melting points (m.p.) were determined with a digital electrothermal apparatus without calibration. The IR spectra were recorded on a Perkin–Elmer FT-IR 2000 spectrophotometer using KBr disc in the range of 4000–400 cm<sup>-1</sup>. The NMR spectra were recorded on a Bruker DMX-300 instrument with TMS as the internal standard. The <sup>31</sup>P NMR spectra were recorded on a Varian XL-200 instrument with H<sub>3</sub>PO<sub>4</sub> (85%) as the external standard. The elemental analyses were performed on a Flash EA 1112 microanalyzer. Distribution of oligomers obtained was measured on a Varian VISTA 6000 GC spectrometer and a HP 5971A GC–MS detector.

THF, diethyl ether and toluene were refluxed over sodium-benzophenone until purple color appeared and were distilled under nitrogen atmosphere prior to use. EtOH was purified according to literature methods. 4-Chloro-2, 6-diformylphenol [16] and *trans*-[NiCl(Naph)(PPh<sub>3</sub>)<sub>2</sub>] [17] were prepared according to the literature method. Methylaluminoxane (MAO, 1.4 mol  $1^{-1}$  in toluene) was purchased from Albemarle Corp. (USA). All of the anilines were purchased from Aldrich Chemical Co or Acros Chemical Co. All other chemicals were obtained commercially and used without further purification unless stated otherwise.

## 3.2. Synthesis of ligands (1a–1f)

2,6-Dimethyl aniline (2.0 mmol) in 10 ml dried ethanol was added dropwise to a stirred solution of 4-chloro-2, 6-diformylphenol (2.1 mmol) and catalytic amount of *p*toluenesulfonic acid in dried ethanol (20 ml) for 1 h. The reaction mixture was stirred and refluxed for 24 h under N<sub>2</sub>, and then cooled. After the evaporation of ethanol, the resulting mixture was purified by column chromatography on silica gel using light petroleum/ethyl acetate (50/1) as an eluent. **1a** was obtained as orange crystal in 46.9% yield. The other ligands **1b–1f** were prepared via the same procedure.

## 3.2.1. 3-(2,6-Dimethylphenylimino)methyl-5-chloro-2hydroxybenzaldehyde (1a)

Yield: 46.9%; m.p. 184–186 °C. <sup>1</sup>H NMR:  $\delta = 10.53$  (s, 1H, O=CH), 8.36 (s, 1H, N=CH), 7.91 (d, J = 2.7 Hz, 1H, Ar–H), 7.57 (s, 1H, Ar–H), 7.06–7.09 (m, 3H, Ar– H), 2.22 (s, 6H, CH<sub>3</sub>). IR (KBr): 3429.8 (wb, O–H), 3067.8 (w, Ar–H), 1677.7 (s, C=O), 1625.9 (s, C=N), 1579.2 (s, C=C), 1455.4 (s, C=C), 1259.9 (m, Ar–O) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>16</sub>H<sub>14</sub>CINO<sub>2</sub>: C, 66.79; H, 4.90; N, 4.87. Found: C, 66.58; H, 4.96; N, 4.64%.

# *3.2.2. 3-(2,6-Diethylphenylimino)methyl-5-chloro-2hydroxybenzaldehyde (1b)*

Yellow crystal, Yield: 30.6%; m.p. 116–118 °C. <sup>1</sup>H NMR:  $\delta = 10.53$  (s, 1H, O=CH), 8.36 (s, 1H, N=CH), 7.91 (d, J = 2.7 Hz, 1H, Ar–H), 7.57 (s, 1H, Ar–H), 7.16 (s, 3H, Ar–H), 2.56 (q, J = 7.6 Hz, 4H, CH<sub>2</sub>), 1.17 (t, J = 7.6 Hz, CH<sub>3</sub>). IR (KBr): 3427.4 (wb, O–H), 3068.2 (w, Ar–H), 1680.5 (s, C=O), 1629.6 (s, C=N), 1579.8 (s, C=C), 1450.6 (s, C=C), 1251.6 (m, Ar–O) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>18</sub>H<sub>18</sub>ClNO<sub>2</sub>: C, 68.46; H, 5.84; N, 4.44. Found: C, 68.35; H, 5.84; N, 4.34%.

# *3.2.3. 3-(2,6-Diisopropylphenylimino)methyl-5-chloro-2hydroxybenzaldehyde (1c)*

Yellow crystal, Yield: 44.1%; m.p. 180–181 °C. <sup>1</sup>H NMR:  $\delta$  14.10 (s, 1H, Ar–OH), 10.53 (s, 1H, O=CH), 8.32 (s, 1H, N=CH), 7.93 (d, J = 2.8 Hz, 1H, Ar–H), 7.58 (s, 1H, Ar–H), 7.22 (s, 3H, Ar–H), 2.94 (q, J = 6.9 Hz, 2H, CH), 1.2 (d, J = 6.9 Hz, 12H, CH<sub>3</sub>). IR (KBr): 3434.7 (wb, O–H), 3065.0 (w, Ar–H), 1680.2 (s, C=O), 1629.5 (s, C=N), 1580.2 (s, C=C), 1454.5 (s, C=C), 1250.7 (m, Ar–O) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>20</sub>H<sub>22</sub>ClNO<sub>2</sub>: C, 69.86; H, 6.45; N, 4.07. Found: C, 69.50; H, 6.46; N, 3.85%.

# *3.2.4. 3-(2,4,6-Trimethylphenylimino)methyl-5-chloro-2hydroxybenzaldehyde (1d)*

Orange crystal, Yield: 61.0%; m.p. 174–176 °C. <sup>1</sup>H NMR:  $\delta$  10.53 (s, 1H, O=CH), 8.34 (s, 1H, N=CH), 7.91 (d, J = 3.0 Hz, 1H, Ar–H), 7.55 (d, J = 2.1 Hz, 1H, Ar–H), 6.95 (s, 2H, Ar–H), 2.31 (s, 3H, CH<sub>3</sub>), 2.19 (s, 6H, CH<sub>3</sub>). IR (KBr): 3442.3 (b, O–H), 3337.5 (w, O–H), 1676.9 (s, C=O), 1620.7 (s, C=N), 1574.2 (s, C=C), 1456.1 (s, C=C), 1265.9 (m, Ar–O) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>17</sub>H<sub>16</sub>ClNO<sub>2</sub>: C, 67.66; H, 5.34; N, 4.64. Found: C, 67.45; H, 5.40; N, 2.97%.

# 3.2.5. 3-(2,6-Dibromo-4-methylphenylimino)methyl-5chloro-2-hydroxybenzaldehyde (1e)

Yellow crystal, Yield: 45.2%; m.p. 234–235 °C. <sup>1</sup>H NMR:  $\delta = 13.20$  (s, 1H, Ar–OH), 10.51 (s, 1H, O=CH), 8.51 (s, 1H, N=CH), 7.94 (d, J = 2.8, Hz, 1H, Ar–H), 7.65 (s, 1H, Ar–H), 7.45 (s, 2H, Ar–H), 2.35 (s, 3H, CH<sub>3</sub>); IR: 3448.8 (wb, O–H), 1680.4 (s, C=O), 1623.3 (s, C=N), 1579.1 (s, C=C), 1452.0 (m, C=C) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>15</sub>H<sub>10</sub>Br<sub>2</sub>CINO<sub>2</sub>: C, 41.75; H, 2.34; N, 3.25. Found: C, 41.74; H, 2.41; N, 3.25%.

# 3.2.6. 3-(2,6-Difluorophenylimino)methyl-5-chloro-2hydroxybenzaldehyde (1f)

Orange crystal, Yield: 55.7%; m.p. 232–233 °C. <sup>1</sup>H NMR:  $\delta = 10.51$  (s, 1H, O=CH), 8.95 (s, 1H, N=CH), 7.92 (d, J = 2.8 Hz, 1H, Ar–H), 7.65 (s, 1H, Ar–H), 7.07–7.01 (m, 3H, Ar–H); IR: 3440.4 (w, O–H), 3080.4 (w, Ar–H), 1679.6 (s, C=O), 1622.7 (s, C=N), 1574.8 (s, C=C), 1456.3 (m, C=C), 1267.7 (m, Ar–O) cm<sup>-1</sup>. Anal. Calc. for C<sub>14</sub>H<sub>8</sub>ClF<sub>2</sub>NO<sub>2</sub>: C, 56.87; H, 2.73; N, 4.74. Found: C, 56.81; H, 2.83; N, 4.72%.

## 3.3. Synthesis of complexes

To a stirred solution of 3-(2,6-dimethylphenylimino) methyl-5-chloro-2-hydroxybenzaldehyde (1.00 mmol) and Et<sub>3</sub>N (1.5 mmol) in THF (10 ml) at room temperature, *trans*-[NiCl(Naph)(PPh<sub>3</sub>)<sub>2</sub>] (0.95 mmol) was added; the reaction mixture was stirred at room temperature for 24 h. After the evaporation of the THF in vacuum, the resulting mixture was extracted by diethyl ether (10 ml × 3). Then, 10 ml ethanol was added to the diethyl ether solution and the solution was evaporated in vacuum to remove the excess diethyl ether; after keeping the solution for several hours at room temperature, rufous crystal of **2a** was obtained in 82.8% yield. The other ligands **2b–2f** were prepared via the same procedure.

# 3.3.1. (1-Naphthyl) {[3-(2,6-dimethylphenylimino)methyl]-5-chloro-2-hydroxybenzaldehyde}(triphenylphosphine) nickel(II) (2a)

Yield: 82.8%; m.p. 177–178 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 9.54 (d, J = 9.0 Hz, 1H, O=CH), 8.49 (s, 1H, N=CH), 7.81 (d, J = 9.0 Hz, 1H, Ar–H), 7.70 (s, 1H, Ar–H), 7.42 (t, J = 9.0, 6H, Ar–H), 7.24–7.29 (m, 6H, Ar–H), 7.02–7.15 (m, 7H, Ar–H), 6.91 (d, J = 6.0 Hz, 1H, Ar–H), 6.71 (q, J = 6.0, 2H, Ar–H), 6.50 (t, J = 6.0 Hz, 1H, Ar– H), 6.21–6.29 (m, 2H, Ar–H), 1.21 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  190.2, 164.7, 150.8, 148.2, 147.7, 139.7, 139.3, 134.2, 133.8, 133.7, 133.0, 132.4, 130.1, 130.0 129.7, 129.4, 128.7, 127.8, 127.7, 127.3, 126.8, 124.8, 124.4, 123.6, 133.7, 118.7, 19.8, 17.9, 15.2. <sup>31</sup>P NMR (H<sub>3</sub>PO<sub>4</sub> as external standard, CDCl<sub>3</sub>/ppm): 25.69. IR (KBr): 3427.3 (wb, O–H), 3051.5 (m, Ar–H), 1674.0 (s, C=O), 1608.7 (s, C=N), 1530.4 (s, C=C), 1439.5 (s, C=C), 1243.3 (m, Ar–O) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>44</sub>H<sub>35</sub>NO<sub>2</sub>CIPNi · CH<sub>2</sub>CH<sub>3</sub>OH: C, 70.75; H, 5.29; N, 1.91. Found: C, 70.39; H, 5.40; N, 2.03%.

# 3.3.2. (1-Naphthyl) {[3-(2,6-diethylphenylimino)methyl]-5-chloro-2-hydroxybenzaldehyde}(triphenylphosphine) nickel(II) (2b)

Rufous crystal, Yield: 89.7%; m.p. 181–182 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.50 (d, J = 6.0 Hz, 1H, O=CH), 8.49 (s, 1H, N=CH), 7.86 (d, J = 9.0 Hz, 1H, Ar-H), 7.73 (d, J = 3, 1H, Ar–H), 7.43 (t, J = 9.0, 6H, Ar–H), 7.30–7.33 (m, 5H, Ar-H), 7.28–7.32 (m, 7H, Ar-H), 7.13–7.15 (m, 1H, Ar–H), 6.83 (d, J = 6.0, 1H, Ar–H), 6.72 (q, J = 3.0 Hz, 2H, Ar–H), 6.64 (t, J = 7.5, 1H, Ar–H), 6.25– 6.29 (m, 2H, Ar-H), 3.24 (7, J = 9.0, 6.0, 3.0 Hz, 2H,  $CH_2$ ), 2.37 (q, J = 9.0, 6.0 Hz, 1H,  $CH_2$ ), 1.90 (q, J = 9.0, 3.0 Hz, 1H, CH<sub>2</sub>), 1.28 (t, J = 6.0 Hz, 3H, CH<sub>3</sub>), 0.60 (t, J = 6.0 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 190.3, 164.6, 149.6, 139.3, 134.3, 133.9, 133.8, 133.1, 130.2, 130.0, 129.8, 128.7, 127.7, 127.3, 125.3, 125.2, 124.5, 123.6, 123.1, 122.8, 121.8, 118.7, 25.9, 24.4, 14.6, 14.1. <sup>31</sup>P NMR (H<sub>3</sub>PO<sub>4</sub> as external standard,  $CDCl_3/$ ppm): 25.46. IR (KBr): 3450.0 (wb, O-H), 3051.0 (m, Ar-H), 1673.9 (s, C=O), 1608.2 (s, C=N), 1530.9 (s, C=C), 1440.9 (s, C=C), 1242.3 (w, Ar-O) cm<sup>-1</sup>. Anal. Calc. for C<sub>46</sub>H<sub>39</sub>ClNNiO<sub>2</sub>P · 1/2EtOH: C, 71.82; H, 5.39; N, 1.78. Found: C, 71.67; H, 5.16; N, 1.43%.

# 3.3.3. (1-Naphthyl) {[3-(2,6-diisopropylphenylimino) methyl]-5-chloro-2-hydroxybenzaldehyde} (triphenylphosphine) nickel(II) (2c)

Rufous crystal, Yield: 75.1%; m.p. 180–181 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.94 (d, J = 6.0 Hz, 1H, O=CH), 8.45 (s, 1H, N=CH), 7.94 (d, J = 9.0 Hz, 1H, Ar-H), 7.33– 7.49 (m, 6H, Ar-H), 7.29-7.23 (m, 6H, Ar-H), 7.05-7.18 (m, 7H, Ar-H), 6.88 (q, 6.1 Hz, 2H, Ar-H), 6.69 (d, J = 9.0 Hz, 1H, Ar–H), 6.27 (t, J = 9.0, 1H, Ar–H), 1.77 (d, J = 9.0 Hz, 3H, CH<sub>3</sub>), 1.45 (d, J = 6.0 Hz, 2H, CH), 1.32 (d, J = 6.0 Hz, 3H, CH<sub>3</sub>), 1.13 (d, J = 6.0 Hz, 3H, CH<sub>3</sub>), 0.89 (d, J = 6.0 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 190.2, 164.7, 148.9, 146.8, 140.4, 139.2, 135.1, 133.8, 133.6, 133.1, 131.8, 130.1, 129.9, 129.5, 127.8, 127.7, 125.9, 123.8, 123.5, 123.4, 123.2, 122.1, 118.7, 29.5, 28.1, 26.1, 25.6, 22.7, 20.3.  ${}^{31}P$  NMR (H<sub>3</sub>PO<sub>4</sub> as external standard, CDCl<sub>3</sub>/ppm): 26.22. IR (KBr): 3427.4 (wb, O-H), 3054.2 (m, Ar-H), 1677.3 (s, C=O), 1608.8 (s, C=N), 1531.1 (s, C=C), 1438.9 (s, C=C), 1216.1 (m,

Ar–O) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>48</sub>H<sub>43</sub>ClNNiO<sub>2</sub>P · EtOH: C, 71.74; H, 5.90; N, 1.67. Found: C, 71.78; H, 5.49; N, 1.97%.

# 3.3.4. (1-Naphthyl) {[3-(2,4,6-trimethylphenylimino) methyl]-5-chloro-2-hydroxybenzaldehyde} (triphenylphosphine) nickel(II) (2d)

Rufous crystal, Yield: 94.3%; m.p. 153-154 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.50 (d, J = 6.0 Hz, 1H, O=CH), 8.52 (s, 1H, N=CH), 7.82 (d, J = 6.0 Hz, 1H, Ar-H), 7.72 (d, J = 6.0 Hz, 1H, Ar–H), 7.43 (t, J = 6.1 Hz, 6H, Ar–H), 7.34 (s, 6H, Ar-H), 7.11-7.23 (m, 6H, Ar-H), 6.94 (d, J = 4.7 Hz, 2H, Ar–H), 6.76 (d, J = 5.6, 1H, Ar–H), 6.45 (s, 1H, Ar-H), 6.31 (s, 1H, Ar-H), 6.00 (s, 1H, Ar-H), 2.54 (s, 3H, CH<sub>3</sub>), 1.93 (s, 3H, CH<sub>3</sub>), 1.58 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 189.2, 163.7, 147.2, 138.6, 138.2, 136.2, 136.0, 133.2, 133.1, 132.8, 132.7, 132.5, 131.8, 131.3, 128.9, 127.6, 127.4, 127.3, 127.1, 126.8, 126.4, 126.2, 122.5, 120.7, 19.2, 18.6, 16.9.  $^{31}$ P NMR (H<sub>3</sub>PO<sub>4</sub> as external standard, CDCl<sub>3</sub>/ppm): 25.64. IR (KBr): 3449.9 (wb, O-H), 3051.9 (m, Ar-H), 1665.9 (s, C=O), 1605.4 (s, C=N), 1530.9 (s, C=C), 1479.5 (m, C=C), 1442.6 (s, C=C), 1298.3 (m, Ar–O)  $cm^{-1}$ . Anal. Calc. for C<sub>45</sub>H<sub>37</sub>NO<sub>2</sub>ClPNi: C, 72.17; H, 4.98; N, 1.87. Found: C, 72.17; H, 5.16; N, 1.61%.

# 3.3.5. (1-Naphthyl) {[3-(2,6-dibromo-4-methylphenylimino) methyl]-5-chloro-2-hydroxybenzaldehyde} (triphenylphosphine) nickel(II) (2e)

Rufous crystal, Yield: 89.0%; m.p. 158–159 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.46 (d, J = 8.4 Hz, 1H, O=CH), 8.49 (s, 1H, N=CH), 7.74-7.81 (m, 1H, Ar-H), 7.74 (d, J = 3.0 Hz, 1H, Ar-H), 7.37-7.52 (m, 9H, ArH), 7.28-7.35 (m, 6H, Ar-H), 7.06-7.15 (m, 5H, Ar-H), 6.78-6.83 (m, 2H, Ar–H), 6.40-6.47 (q, J = 7.5, 2H, Ar–H), 1.92 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 190.3, 167.1, 147.3, 146.7, 139.8, 139.7, 137.3, 137.2, 137.1, 134.8, 133.9, 133.8, 133.7, 132.4, 132.1, 132.0, 131.7, 131.1, 130.2, 130.0, 129.7, 129.0, 128.7, 128.5, 128.4, 127.8, 127.7, 126.9, 123.7, 123.8, 123.0, 122.8, 121.9, 118.9, 118.2, 117.6, 19.81.  $^{31}$ P NMR (H<sub>3</sub>PO<sub>4</sub> as external standard, CDCl<sub>3</sub>/ppm): 25.15. IR (KBr): 3439.9 (wb, O–H), 3052.5 (m, Ar-H), 1667.5 (s, C=O), 1608.3 (s, C=N), 1581.7 (m, C=C), 1527.4 (s, C=C), 1480.0 (m, C=C), 1247.3 (m,  $cm^{-1}$ . Anal. Calc. Ar–O) for  $C_{43}H_{31}Br_2ClN$ -NiO<sub>2</sub>P · C<sub>2</sub>H<sub>5</sub>OH · PPh<sub>3</sub>: C, 63.75; H, 4.42; N, 1.18. Found: C, 63.67; H, 3.98; N, 0.92%.

# 3.3.6. (1-Naphthyl) {[3-(2,6-difluorophenylimino)methyl]-5-chloro-2-hydroxybenzaldehyde}(triphenylphosphine) nickel(II) (2f)

Yield: 67.5%; m.p. 135–136 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.25 (dd, J = 8.7, 2.1 Hz, 1H, O=CH), 8.49 (s, 1H, N=CH), 8.05 (d, J = 7.8 Hz, 1H, Ar–H), 7.72 (d, J = 3.0, 1H, Ar–H), 7.48–7.57 (m, 6H, Ar–H), 7.28–7.40 (m, 6H, Ar–H), 7.16–7.19 (m, 3H, Ar–H), 7.02–7.14 (m, 3H, Ar–H), 7.03 (d, J = 6.9, 1H, Ar–H), 6.77 (d, J = 7.1 Hz, 1H

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Ar–H), 6.53 (t, J = 7.5, 1H, Ar–H), 6.38–6.48 (m, 1H, Ar–H), 6.20 (t, J = 5.7 Hz, 1H, Ar–H), 5.94 (t, J = 9.0 Hz, 1H, Ar–H), 5.52 (t, J = 9.0 Hz, 1H, Ar–H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  190.2, 167.7, 166.2, 156.0, 152.6, 149.7, 149.0, 139.8, 139.5, 137.3, 137.1, 134.3, 134.0, 133.9, 133.6, 132.5, 131.8, 130.1, 130.0, 129.9, 129.7, 129.5, 128.9, 128.7, 128.5, 128.4, 127.9, 127.8, 127.1, 125.6, 125.4, 123.8, 123.5, 123.1, 122.3, 119.0, 110.3, 110.0. <sup>31</sup>P NMR (H<sub>3</sub>PO<sub>4</sub> as external standard, CDCl<sub>3</sub>/ppm): 26.39. IR (KBr): 3434.2 (wb, O–H), 3052.3 (m, Ar–H), 1671.3 (s, C=O), 1605.9 (s, C=N), 1527.8 (s, C=C), 1475.0 (m, C=C), 1442.4 (s, C=C), 1242.9 (m, Ar–O) cm<sup>-1</sup>. *Anal.* Calc. for C<sub>42</sub>H<sub>29</sub>ClF<sub>2</sub>NNiO<sub>2</sub>P · PPh<sub>3</sub>: C, 71.70; H, 4.41; N, 1.39. Found: C, 71.84; H, 4.54; N, 1.21%.

#### 3.4. X-ray crystal structure determination of 2b and 2d

Intensity data of **2b** were collected at 293(2) K on a Siemens Smart CCD diffractometer with graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation, using the  $\phi-\omega$ scan mode. Data collection and reduction were performed using the SMART and SAINT softwares [18]. Empirical absorption correction was applied to the raw intensities by using the SADABS program [19]. The structure was solved by direct methods and full-matrix least-squares method based on  $F^2$ using the SHELXTL program package [20]. Non-hydrogen atoms were subjected to anisotropic refinement.

Intensity data of **2d** were collected at 293(2) K on a Mercury70 diffractometer with graphite-monochromated Molybdenum' ( $\lambda = 0.71073$  Å) radiation. Cell parameters were obtained by the global refinement of the positions of all collected reflections. Intensity data were corrected by Lorentz and polarization effects and empirical absorptions were applied by using the CRYSTALCLEAR program. The structure was solved by direct methods. The final refinement was done by full-matrix least-squares on  $F^2$ methods, with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for geometric hydrogen atoms by using the SHELXTL-97 package [21].

#### 3.5. General procedure for ethylene oligomerization

A flame dried three-neck round flask was loaded with the complex (2a-2f) and vacuum-filled three times by nitrogen and then two times by ethylene. Then, the freshly distilled toluene was charged with ethylene and stirred for 10 min. MAO was added by a syringe. The reaction mixture was stirred under 1 atm ethylene pressure for a limited time and the catalytic reaction was terminated with acidified water. An aliquot of the reaction mixture was analyzed by GC and GC–MS. High-pressure ethylene polymerization was performed in a stainless steel autoclave (2000 ml capacity) equipped with gas ballast through a solenoid clave for continuous feeding of ethylene at constant pressure. 1000 ml toluene containing the catalyst precursor was transferred to the fully dried reactor under nitrogen atmosphere. Then, the required amount of cocatalyst (MAO) was injected into the reactor using a syringe. As the prescribed temperature was reached, the reactor was pressurized to 10 atm. After stirring for the desired reaction time, the reaction was quenched and treated using the similar method described above for 1 atm reaction.

# 4. Conclusion

In this contribution, a series of new neutral arylnickel(II) phosphine complexes bearing non-symmetric bidentate chelate ligands, 3-aryliminomethyl-5-chloro-2hydroxybenzaldehyde, have been synthesized in a simple route and acceptable yields and the structure of representative complexes (**2b** and **2d**) has been confirmed by X-ray crystallographic analysis. Moreover, using methylaluminoxane (MAO) as a cocatalyst, these complexes display high ethylene oligomerization activities. After investigating the catalytic conditions, the highest catalytic activity was obtained as  $5.73 \times 10^5$  g mol<sup>-1</sup> h<sup>-1</sup> at 1 atm and  $4.6 \times 10^6$  g mol<sup>-1</sup> h<sup>-1</sup> at 10 atm.

#### 5. Supplementary material

Details of crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 250442 for **2d** and 250421 for **2b**. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc. cam.ac.uk or http://www.ccdc.ac.uk), upon request.

## Acknowledgments

This work was supported by Natural Science Foundation (No. 20371040) of China, the Key Project of Chinese Ministry of Education (No. 205161) and the Youth Science and Technology Foundation of Gansu province (3ZS041-A25-007). We thank Professor W.-H. Sun for valuable help.

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