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Synthesis of cobalt(II) and iron(II) complexes with the ligand bis(2-diphenylphosphinoethyl)methylamine and their catalytic action on ethylene oligomerization. X-ray crystal structure of $[CoCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$

Mei Wang [a,*], Xiaomin Yu [a], Zhan Shi [b], Mingxing Qian [a], Kun Jin [a], Jiesheng Chen [b], Ren He [a]

[a] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, Zhongshan Road 158-46, Dalian 116012, People's Republic of China*

[b] *Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Jiefang Road 119, Changchun 130023, People's Republic of China*

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Abstract

Complexes $[MCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ (**1**, M = Co; **2**, Fe) were prepared by a modified procedure. The X-ray structural determination of **1** reveals that the cobalt(II) complex is four-coordinate with a distorted tetrahedral coordination geometry. The tertiary amine $CH_3N(CH_2CH_2PPh_2)_2$ acts as a bidentate ligand through two phosphorus atoms. The Co–P distances of 2.3666(14) and 2.3731(15) Å found in **1** are significantly longer than general Co–P bond lengths. The incoordinate N atom of the ligand locates at the apical position *trans* to one of the chlorides. The catalytic properties of **1** and **2** in combination with ethylaluminoxane (EAO) as cocatalyst for ethylene oligomerization were studied. The activities of 89.4 kg oligomers mol^{-1} Co h^{-1} for **1** and 81.2 kg oligomers mol^{-1} Fe h^{-1} for **2** (100 equivalents of EAO, 180 °C and 1.8 MPa ethylene) were observed with high selectivity to linear C_{4-10} olefins.

Keywords: Cobalt and iron complexes; Bis(2-diphenylphosphinoethyl)methylamine; Ethylene oligomerization

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1. Introduction

The synthesis and chemistry of transition metal complexes containing mixed nitrogen–phosphorus polydentate ligands have received considerable attention for decades. The preparation and magnetic as well as spectroscopic properties of the complexes were extensively studied in the sixties and the seventies [1–4]. Afterward interest in the transition metal complexes containing nitrogen–phosphorus polydentate ligands arises mainly from their potential as homogeneous or water-soluble catalysts [5,6]. Recently, the oligomerization of ethylene to C_6–C_{16} olefins catalyzed by a series of uni-component catalysts of palladium(II) complexes with bidentate iminophosphine (N,P) ligands has been reported [7]. It is noteworthy that the oligomerization of ethylene catalyzed by the palladium(II) complexes with diphosphine (P,P) ligands gives only dimers [8], whereas palladium(II)-based uni-component catalysts with α-diimine (N,N) ligands catalyzes the reaction of ethylene to high polymers at 25 °C [9]. The sharply contrasting results show that proper combinations of the soft P and the hard N donor atoms in the ligands and subtle ligand modifications have an effect on tuning product distributions in ethylene oligomerization and polymerization.

To explore the impact of mixed nitrogen–phosphorus polydentate ligands on ethylene oligomerization, a cobalt(II) and an iron(II) complex containing the ligand bis(2-diphenylphosphinoethyl)methylamine were prepared by a modified procedure [4]. Here we wish to

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* Corresponding author. Fax: +86-411-263-3041.
E-mail address: symbueno@mail.dlptt.ln.cn (M. Wang).

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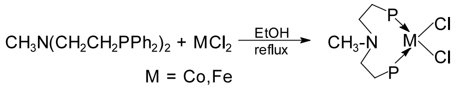
report the synthesis, characterization of the complexes, the X-ray crystal structure of [$CoCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}$], and the catalytic action of the complexes in combination with ethylaluminoxane (EAO) as cocatalyst for ethylene oligomerization. So far as we know, although many complexes of the potentially tridentate ligands $RN(CH_2CH_2PPh_2)_2$ (R–PNP, R = H, alkyl) with a wide variety of transition metals have been prepared and characterized, none of the stereostructures of these complexes has been well established by X-ray crystallographic evidences, and the iron complex with an R–PNP ligand has not been known.

2. Results and discussion

2.1. Preparation and spectroscopic characterization of [$MCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}$] (**1**, M = Co; **2**, Fe)

The title complexes **1** and **2** were prepared directly by simple assembly of one equivalent of MCl_2 and the free tertiary amine in absolute ethanol (Eq. (1)). Since the complexes **1** and **2** have rather low solubility in ethanol, the products can directly precipitate in the ethanolic solution during the reactions. The advantages of convenient separation and high yields of products encouraged us to use ethanol as solvent, instead of 1-butanol which was used in the literature [4] for the preparations of analogous Co(II) and Ni(II) complexes. The Co(II) complex is blue and the Fe(II) complex is colorless. Both of the complexes are air-stable in the solid state, but in solution they are sensitive to a trace amount of water and oxygen. Decomposition occurred gradually for complex **1** and quickly for **2** when they are dissolved in untreated solvents. The magnetic properties of complexes **1** and **2**, being paramagnetic and having a high spin electronic configuration, are the same as the reported iron(II) and cobalt(II) complexes bearing 2,6-bis(imino)pyridyl ligands, which are known to be highly active catalysts for ethylene polymerization [10].



(1)

Table 1
X-ray crystallographic data for **1**

Empirical formula	$C_{29}H_{31}Cl_2CoNP_2$
Formula weight	585.32
Temperature (K)	293
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	8.7267(7)
b (Å)	15.3372(13)
c (Å)	20.8864(16)
V (Å^3)	2795.5(4)
Z	4
D_{calc} (g cm^{-3})	1.391
Absorption coefficient (mm^{-1})	0.938
Total reflections	13 787
Observed reflections [$I > 2\sigma(I)$]	4012
Goodness-of-fit on F^2	1.044
R (observed data, %)	$R_1 = 0.0479$ [a], $wR_2 = 0.1224$ [b]
R (all data, %)	$R_1 = 0.0564$ [a], $wR_2 = 0.1291$ [b]

[a] $R_1 = (\Sigma\|F_o| - |F_c\|)/(\Sigma|F_o|)$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Although some complexes of [$MX_2\{RN(CH_2CH_2PPh_2)_2\}$] (M = Co, Ni; X = Br, I; R = H, CH_3, Cy) were prepared in the late sixties [3,4], no IR and NMR data relative to these complexes have been reported. All typical bands in the IR spectrum of the free ligand appeared with small shifts in the spectra of complexes **1** and **2**. The common characters of the IR spectra of **1** and **2** were that the band at 1490 cm^{-1} was split and the intensity of the bands in the 1000–1200 cm^{-1} region increased evidently. The $^{31}P\{^1H\}$-NMR spectrum of **1** showed an intense singlet at δ 23.2, which differs by 43.6 ppm from the resonance (δ −20.4) of the phosphorus atoms in the $^{31}P\{^1H\}$-NMR spectrum of the ligand [6], indicating that in solution the two coordinating phosphorus atoms of the complex are eqivalent on the NMR time scale. In the ^1H-NMR spectrum of **1**, besides the signals (δ 7.60–7.40) for the phenyl groups of the ligand, there were a broad singlet at δ 2.71 for the methyl group on the nitrogen atom and two broad humps without clear fine structures centered at ca. δ 4.63 and 2.92. The Co(II) complex **1** manifested a considerable downfield shift of the resonance (δ 4.63) for the protons of CH_2 groups attached to the diphenylphosphino groups (δ 2.9 for the same protons in the free ligand) [6], which is caused by the coordination of the two phosphorus atoms to the Co(II) center. In contrast, the resonance for the protons of CH_2 groups attached to the nitrogen atom in complex **1** shifted downfield only by ca. 0.4 ppm compared with the signal arising from the same protons (δ 2.5) in the free ligand. Attempts to obtain the ^1H- and ^{31}P-NMR spectra of the Fe(II) complex **2** were thwarted because of the poor solubility of **2** in organic solvents and quick decomposition in solution.

2.2. Molecular structure of [$CoCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}$] (**1**)

The stereostructures of the complexes and the problem whether $CH_3N(CH_2CH_2PPh_2)_2$ acts as a tridentate or as a bidentate ligand in the complexes could not be determined by the obtained spectroscopic data. A crystal of [$CoCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}$] was subjected to

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Co–Cl(1)	2.2483(16)	Co–Cl(2)	2.2817(16)
Co–P(1)	2.3666(14)	Co–P(2)	2.3731(15)
P(1)–C(6)	1.820(6)	P(2)–C(24)	1.820(5)
P(1)–C(12)	1.826(6)	P(2)–C(18)	1.824(5)
P(1)–C(1)	1.836(7)	P(2)C(4)	1.825(6)
N–C(2)	1.330(12)	N–C(5)	1.349(10)
N–C(3)	1.375(11)	C(1)–C(2)	1.329(12)
C(3)–C(4)	1.362(11)		
Bond angles			
Cl(1)–Co–Cl(2)	104.73(7)	Cl(1)–Co–P(1)	113.04(7)
Cl(2)–Co–P(1)	102.15(6)	Cl(1)–Co–P(2)	120.04(7)
Cl(2)–Co–P(2)	98.71(6)	P(1)–Co–P(2)	114.57(6)
C(6)–P(1)–C(12)	105.8(2)	C(6)–P(1)–C(1)	106.6(3)
C(12)–P(1)–C(1)	103.8(3)	C(6)–P(1)–Co	110.46(18)
C(12)–P(1)–Co	120.08(18)	C(1)–P(1)–Co	109.3(2)
C(24)–P(2)–C(18)	102.7(2)	C(24)–P(2)–C(4)	104.9(3)
C(18)–P(2)–C(4)	105.5(3)	C(24)–P(2)–Co	114.86(19)
C(18)–P(2)–Co	116.69(18)	C(4)–P(2)–Co	111.10(18)
C(2)–N–C(5)	111.0(13)	C(2)–N–C(3)	108.5(14)
C(5)–N–C(3)	108.3(12)	C(2)–C(1)–P(1)	112.1(5)
C(1)–C(2)–N	135.9(8)	C(4)–C(3)–N	129.8(9)
C(3)–C(4)–P(2)	111.4(5)		

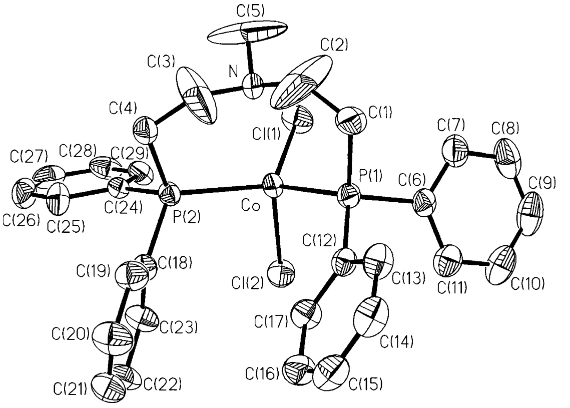


Fig. 1. Perspective view of complex **1**. ORTEP diagram showing 30% probability ellipsoids.

an X-ray diffraction study. Crystallographic details and structure refinements are summarized in Table 1. Selected bond lengths and angles for **1** are shown in Table 2. The molecular structure of **1** with the atom-numbering scheme is depicted in Fig. 1. The complex **1** crystallizes with four molecules in an orthorhombic unit cell. It is interesting to note that the molecular packing of **1**, viewed from the *a*-axis, is in a perfect stacking of phenyl rings and of all bonds of the same kinds (see Fig. 2). The well-laid-out structure in the solid state is formed by the self-assembly of molecules, presumably driven by intermolecular π···π stacking interactions of the neighboring phenyl groups.

As shown in Fig. 1, the Co(II) complex **1** is four-coordinate with a distorted tetrahedral geometry. The result is not in agreement with the early suggestion that the $[CoX_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ (X = Br, I) complexes each be five-coordinate with a distorted square-pyramidal coordination polyhedron in the solid state [4]. In spite of the presence of three potentially coordinating atoms, the CH_3–PNP ligand is bidentate through two phosphorus atoms to the center Co(II) of complex **1**. The Co–P bond lengths of 2.3666(14) and 2.3731(15) Å are considerably longer than the general Co–P bond lengths (2.1–2.3 Å) reported for many cobalt(II) phosphine complexes [2,11–13]. Only a few examples of cobalt(II) complexes with Co–P coordination bonds longer than 2.35 Å were reported, such as the Co–P length of 2.369(5) Å for $[Cy_3PCo(dmgH)_2Cl]$ (dmgH = dimethylglyoximate), 2.418(1) Å for $[Ph_3PCo(dmgH)_2CH_3]$ [14], and 2.520(2) Å for $[CoL_2(O_3SCF_3)_2]$ (L = $P(CH_2Ph)(CH_2CH_2OC_2H_5)_2$ [13]. The lengthenings of Co–P distances in these octahedral cobalt complexes are caused by the *trans* effect of other ligands. In contrast to these cobalt complexes, the *trans* effect of ligands on the Co–P bond lengths does not exist in complex **1** with a tetrahedral coordination configuration. It is reasonable to assume that the significant lengthening of Co–P bonds in complex **1** is provoked by the steric size of two phosphorus terminals in the CH_3–PNP ligand. To our knowledge, the Co–P distances found in complex **1** are the largest values so

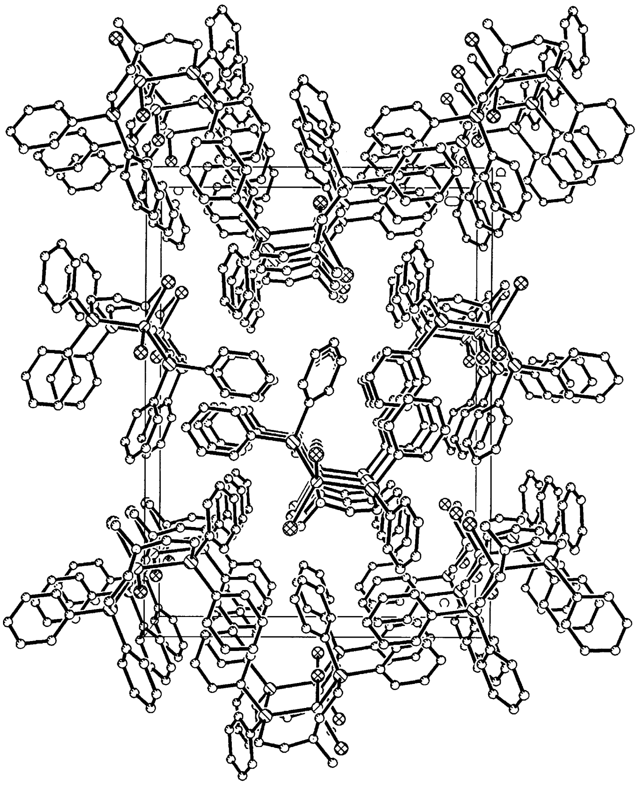


Fig. 2. A view of the crystal packing for complex **1**, projected along the *a*-axis.

Table 3
Results of ethylene oligomerization by **1** and **2** in toluene [a]

Compound no.	Temperature (°C)	Activity (kg mol^{-1} M^{-1} h^{-1})	Olefins [b]	Linear olefins [b]		α
			$C^{=}_{4-10}/\Sigma C^{=}$	$C^{=}_{4-10}/\Sigma C^{=}_{4-10}$	α-$C^{=}_{6-10}/\Sigma C^{=}_{6-10}$	
1	150	38.6	90.2	97.0	73.2	0.63
1	160	63.7	90.7	97.2	75.5	0.64
1	170	88.1	91.9	97.3	74.7	0.57
1	180	89.4	92.9	93.6	63.6	0.54
1	210	85.4	95.5	97.9	38.5	0.42
2	150	36.0	89.8	95.3	64.4	0.60
2	180	81.2	90.3	96.5	62.3	0.53
2	210	66.1	94.9	97.9	35.4	0.40

[a] Reaction conditions: $[MCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ (M = Co, Fe) 0.05 mmol, Al/M = 100, reaction time 2 h, pressure of ethylene 1.8 MPa, toluene 30 ml.

[b] Determined by GC analysis (OV 101, 30 m × 0.25 mm) with *n*-heptane as an internal standard and GC–MS spectra.

far reported for the Co–P coordination bonds without the influence of the *trans* effect. These data practically show the importance of steric effect on the M–L bond lengths in transition metal complexes. Although the nitrogen atom of the ligand stays very close to the Co(II) center, the distance of 2.665 Å between the cobalt(II) and the nitrogen atom is out of the range (1.9–2.3 Å) expected for a direct coordination bond donating from a nitrogen atom to a Co(II) center [15]. This bidentate coordination model of the CH_3–PNP ligand is similar with those of the CH_3–NNN ligands ($CH_3N(CH_2CH{=}NAr)_2$) in the analogous Co(II) and Fe(II) dichloride complexes, which proved to be active catalysts for ethylene polymerization [16]. Considering the outer-electron configuration of Co(II) with a P_2X_2 donor set, the center cobalt(II) has only 15 electrons in its valence shell and it should be quite electron-deficient. Therefore, the cause for the fact that the amine $CH_3N(CH_2CH_2PPh_2)_2$ in complex **1** acts as a bidentate ligand should be attributed to the steric effect of the methyl group and the relative low coordinating power of the tertiary nitrogen. The Co–Cl distances of 2.2483(16) and 2.2817(16) Å fall well within the range of Co–Cl bond lengths reported for cobalt complexes [11,14,17].

The bond angles subtended at the cobalt atom vary from 98.71 to 120.04°. It is noticeable that enlarged are the angles of P(1)–Co–P(2) (114.57(6)°), P(2)–Co–Cl(1) (120.04(7)°) and Cl(1)–Co–P(1) (113.04(7)°), which form a wide cone with the bottom facing to the coordination ring of the molecule, while the remaining angles (P(2)–Co–Cl(2) 98.71(6)°, P(1)–Co–Cl(2) 102.15(6)° and Cl(1)–Co–Cl(2) 104.73(7)°) concerning with the Co–Cl(2) bond of complex **1** are all decreased from the value in a standard tetrahedral configuration. The eight-membered ring of complex **1** may be primarily responsible for the large distortion of the coordination configuration. Furthermore, the cobalt atom is displaced of 0.4780 Å from the plane of P(1), P(2) and Cl(1) towards the Cl(2) atom. If the nitrogen atom is considered into the coordination sphere, the stereostructure of complex **1** is a pseudo-trigonal bipyramid with the Cl(2) and the N atom at each apex of the bipyramid, which may give a rational expression to the fact that the Co–Cl(2) distance is 0.0334 Å longer than the Co–Cl(1) bond. Although, the nitrogen atom of the CH_3–PNP ligand does not directly bind with the center cobalt in complex **1**, it indeed plays an important role in the coordination configuration of the complex.

2.3. Ethylene oligomerization

It has been reported that the analogous iron(II) and cobalt(II) complexes containing CH_3–NNN ligands with MAO as cocatalyst are highly active catalysts for ethylene polymerization [16]. Ethylene oligomerization catalyzed by $LFeCl_2$, $LCoCl_2$ (L = *N*,*N*,*N*-tridentate ligands)/MAO affords oligomers with high average molecular weight [10b], while α-diimine iron(II) and cobalt(II) complexes in combination with EAO are moderately active for ethylene oligomerization with good selectivity to C_{4-10} olefins [18]. It has been found that in comparison with $LMCl_2$ (M = Fe, Co)/MAO catalysts, the catalytic systems formed by the replacement of MAO with EAO has a preference for low-carbon olefins. One of the unrevealed problems in this field is the influence by the replacement of hard N donor atoms with soft ones on the catalytic activity and selectivity of the iron(II) and cobalt(II) complexes. The catalytic activities and product distributions of **1** and **2** in combination with EAO as cocatalyst for ethylene oligomerization were tested, respectively, at different temperatures. The results are collected in Table 3. Without cocatalyst, complexes **1** and **2** are inactive in ethylene oligomerization. The active catalysts were generated in situ by the addition of 100 equivalents of EAO to the precursor complexes in toluene. The catalytic reactions were carried out under a constant pressure of ethylene (1.8 MPa). At the temperature below 120 °C, the activities of catalytic systems **1**/EAO and **2**/EAO were very low. The activities of **1** and **2**, which increased apparently as the reaction temperature was raised from 150 to 180 °C, are comparable to those of the cobalt(II) and iron(II) dichloride complexes with an *N*,*N*-ligand ($PhHC{=}NCH_2CH_2N{=}CHPh$) in this temperature range. The further enhancement of temperature resulted in a trend of decreased activities for the catalytic systems of **1** and **2**. In contrast, the activities of α-diimine cobalt(II) and iron(II) complexes with EAO kept a strongly growing trend even at 200 °C, which was found in our previous studies [18]. The results imply that the active catalysts derived from the cobalt and iron dichloride complexes with a CH_3–PNP ligand are less thermostable than those derived from the complexes with α-diimine ligands. Complexes **1** and **2** both displayed high selectivities to the low-carbon olefins. A Schulz–Flory distribution of olefin oligomers was observed in all catalytic runs (GC analysis). The data presented in Table 3 illustrate that the α-value, which represents the probability of chain propagation, is sensitive to the reaction temperature. For example, the α-value changed from 0.63 to 0.42 for **1**/EAO and from 0.6 to 0.4 for **2**/EAO when the reaction temperature was increased from 150 to 210 °C. The experimental facts showed that the replacement of an α-diimine ligand $PhHC{=}NCH_2CH_2N{=}CHPh$ with $CH_3N(CH_2CH_2Ph_2)_2$ in cobalt(II) and iron(II) dichloride precursors led to a higher selectivity to the low-carbon linear olefins in ethylene oligomerization reaction, but with no obvious improvement of the selectivity to linear α-olefins.

3. Experimental

3.1. General procedures

The reactions and operations related to organometallic complexes were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. Toluene and THF were distilled from sodium–benzophenone ketyl and methylene chloride from phosphorus pentoxide. Anhydrous EtOH was further dried by distillation from sodium–diethyl phthalate before use. Ethylene was purified by passage through a column of molecular sieves (4 Å). Triethyl aluminum was carefully distilled in vacuo and then partially hydrolyzed by the reaction with $Al_2(SO_4)_3 \cdot 18H_2O$ ($AlEt_3$–$H_2O = 1:1$, mol mol^{-1}) in toluene at 0–5 °C. Anhydrous $CoCl_2$ was obtained by dehydration of $CoCl_2 \cdot 6H_2O$ in vacuo at 120–130 °C for 6 h. Iron(II) dichloride was prepared as the method reported in the literature [19]. Other commercially available chemical reagents were used without further purification.

Infrared spectra were recorded from KBr disk by using a Nicolet AVATAR-360 IR spectrophotometer. ^{31}P- and ^{1}H-NMR spectra were recorded on a JEDLFX-90Q apparatus. The ^{31}P-NMR spectra were referenced to external 85% H_3PO_4 and the ^{1}H-NMR spectra to internal Me_4Si. Elemental analyses were performed on a CARLO ERBA MOD-1106 elemental analyzer and GC–MS analyses of oligomers were made by using an HP6890GC/5973MS instrument.

3.2. Preparation of the ligand $CH_3N(CH_2CH_2PPh_2)_2$

The starting compound $CH_3N(CH_2CH_2Cl)_2$ was obtained from the reaction of $SOCl_2$ and $CH_3N(CH_2CH_2OH)_2$ [20], which was prepared by Eschweiler–Clarke reaction from $HN(CH_2CH_2OH)_2$. Instead of $KPPh_2$ as reported in the literature [4,6], $LiPPh_2$ was used in the preparation of the ligand $CH_3N(CH_2CH_2PPh_2)_2$. The free tertiary amine $CH_3N(CH_2CH_2Cl)_2$ (7.8 g, 0.05 mol) was dissolved in THF (40 ml) and added dropwise at −5–0 °C to a deep red solution of $LiPPh_2$, which was obtained freshly through the reaction of lithium (1.4 g, 0.2 mol) with PPh_3 (26.2 g, 0.1 mol) in THF at 0–5 °C. The further operations were made according to the published procedure [6]. The ligand $CH_3N(CH_2CH_2PPh_2)_2$ in its hydrochloride form was obtained (yield, 18 g, 75%); m.p. 121–123 °C. IR (KBr, cm^{-1}): 3447 (w), 3009 (m), 2989 (w), 2964 (m), 2921 (w), 2565 (m), 2458 (s br), 2396 (m), 1490 (m), 1432 (s), 749 (s), 698 (s), 509 (m), 481 (m), 415 (m). $^{31}P\{^{1}H\}$-NMR ($CHCl_3$): δ −20.4 (s).

3.3. Preparation of $[MCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ (**1**, M = Co; **2**, Fe)

Bis(2-diphenylphosphinoethyl)methylamine hydrochloride (9.2 g, 18.8 mmol) was treated with a stoichiometric amount of 10% NaOH. The insoluble oil was separated and the inorganic layer was extracted with toluene (10 ml × 3). The merged organic portion was dried with Na_2SO_4 overnight. The free amine (7.0 g, 15.4 mmol) was obtained as a light-yellow dense oil after the solvent was removed in vacuo. The ligand was dissolved in absolute EtOH (15 ml) and dropped with stirring to a deep blue solution of $CoCl_2$ (1.8 g, 13.8 mmol) in the same solvent. The mixture was stirred at 20 °C for 30 min and then refluxed for 1 h. A large amount of blue microcrystalline was precipitated during the reaction. After the solution was concentrated in vacuo and cooled to −5 °C, the crude product was filtered off, washed with cold EtOH (10 ml × 3) and dried in vacuo at 60 °C. The pure blue crystal (rectangular prism) of $[CoCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ was obtained by recrystallization from CH_2Cl_2–petroleum ether (60–90 °C). Yield: 6.0 g (75%), m.p. 162–164 °C.

IR (KBr, cm^{-1}): 3081 (m), 2975 (w), 2913 (w), 2866 (w), 1486 (m), 1438 (s), 1162 (m), 1118 (m), 1098 (m), 749 (s), 697 (s), 504 (m), 486 (w), 422 (w). ^{1}H-NMR (Me_2SO-d_6): δ 7.58–7.46 (m, 20H, 4Ph), 4.63 (br., 4H, $2CH_2P$), 2.92 (br., 4H, $2CH_2N$), 2.71 (s, 3H, NCH_3). $^{31}P\{^1H\}$-NMR (Me_2SO-d_6): δ 23.2 (s). Anal. Calc. for $C_{29}H_{31}NP_2Cl_2Co$: C, 59.54; H, 5.35; N, 2.39. Found: C, 59.58; H, 5.41; N, 2.26%.

The analogous iron(II) complex (**2**) was prepared by the same procedure as above. The colorless microcrystalline of $[FeCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ was obtained in 61% yield (4.9 g), m.p. 170 °C (dec.). IR (KBr, cm^{-1}): 3048 (m), 2973 (w), 2908 (w), 2815 (m), 1480 (m), 1459 (m), 1430 (s), 1306 (m), 1184 (m), 1097 (m), 746 (s), 696 (s), 504 (s), 472 (m), 431 (m). Anal. Calc. for $C_{29}H_{31}NP_2Cl_2Fe$: C, 59.84; H, 5.38; N, 2.41. Found: C, 59.76; H, 5.27; N, 2.29%.

3.4. Crystal structure determination of $[CoCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ (1)

A deep blue crystal (0.80 × 0.04 × 0.04 mm) of $[CoCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ was used for X-ray measurement. The data were measured on a Siemens SMART CCD diffractometer using graphite monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT processing program [21]. Intensity data were corrected for absorption with empirical methods. In the solution and refinement of the structure, the SHELXTL crystallographic software package was used [22]. The structure was solved by direct method, and refined on F_o^2 with full-matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically.

3.5. Oligomerization of ethylene

The ethylene oligomerization reactions catalyzed by $[MCl_2\{CH_3N(CH_2CH_2PPh_2)_2\}]$ (**1**, M = Co; **2**, Fe) were made as our previous reports [18]. Both of the complexes exhibited poor solubility in toluene. When the cocatalyst EAO was added to the suspension of the precursor complex in toluene, all solids were dissolved instantly and the solution turned brown–yellow for **1** and black for **2**. No pre-reaction was needed for these catalytic systems. After the reaction was quenched, the distribution and structures of the oligomers were determined by GC analysis and GC–MS spectra of the obtained solution with *n*-heptane as an internal standard.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 167311 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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