Inorganica Chimica Acta 362 (2009) 89-96



Contents lists available at ScienceDirect

# Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

# Synthesis, structure, and catalytic ethylene oligomerization of nickel(II) and cobalt(II) complexes with symmetrical and unsymmetrical 2,9-diaryl-1,10-phenanthroline ligands

Peiju Yang<sup>a</sup>, Yue Yang<sup>a,d</sup>, Cui Zhang<sup>a,d</sup>, Xiao-Juan Yang<sup>a,\*</sup>, Huai-Ming Hu<sup>b</sup>, Yici Gao<sup>c</sup>, Biao Wu<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China <sup>b</sup> Department of Chemistry, Northwest University, Xi'an 710069, China <sup>c</sup> College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

<sup>d</sup> Graduate University of Chinese Academy of Sciences, Beijing 100049, China

#### ARTICLE INFO

Article history: Received 27 April 2007 Received in revised form 28 February 2008 Accepted 5 March 2008 Available online 18 March 2008

Keywords: Nickel(II) Cobalt(II) 1,10-Phenanthroline Ethylene oligomerization

# ABSTRACT

A series of nickel(II) and cobalt(II) complexes, NiX<sub>2</sub>L (X = Cl, Br; 1-6) and CoCl<sub>2</sub>L (7-9), with 2,9-diaryl-1,10-phenanthroline ligands  $(L^1-L^3)$  have been synthesized and characterized by elemental analysis, UV-Vis, IR spectroscopy, and X-ray crystal structural study (for 1, 4-7, 9). The solid-state structures of 1, 5–7 and 9 show four-coordinate, slightly flattened tetrahedral geometry at the Ni(II) or Co(II) center, while 4 is five-coordinated (square-pyramidal), containing a THF molecule as an auxiliary ligand. The title complexes (1-9) display good catalytic activities in ethylene oligomerization when activated with methylaluminoxane (MAO). While the Co(II) precatalysts produce primarily  $C_4$  isomers, the Ni(II) complexes give ethylene dimers and trimers at normal pressure. The activities and yields of linear  $\alpha$ -olefins increase with increasing ethylene pressure for the Ni(II) complexes, leading to more high-molar-mass products  $(C_8-C_{18})$ . Complex **6** displays the best catalytic activity among the complexes studied (up to 1518 kg/ mol[Ni] h at 10 atm).

© 2008 Elsevier B.V. All rights reserved.

# 1. Introduction

Linear  $\alpha$ -olefins in the range of C<sub>4</sub>-C<sub>20</sub> are important industrial materials and are widely used for the preparation of detergents, plasticizers and as co-monomers for linear low-density polyethylene (LLDPE) [1-4]. One of the major processes for the production of linear  $\alpha$ -olefins is the oligomerization of ethylene, for example, the SHOP process [5]. Late transition metal complexes are supposed to have a strong propensity for undergoing  $\beta$ -hydrogen elimination process on the central metal, which would facilitate ethylene oligomerization [6]. Particularly, aryl-substituted  $\alpha$ -diimine Ni(II) and Pd(II) complexes [7], and 2,6-bis(imino)pyridyl Fe(II) and Co(II) complexes [8,9] have been found to have high catalytic activities for the polymerization and oligomerization of ethylene, which has inspired much research interest in the late transition metal catalysis systems. Extensive studies have proved that the productivity and physical properties of polyolefins are strongly affected by the coordination environment around the metal atom, such as the coordination atom, the ligand backbone, as well as the substitute groups on the ligands of the precatalysts [10,11]. Therefore, it

Corresponding authors. Tel./fax: +86 931 4968286 (B. Wu).

E-mail addresses: yangxj@lzb.ac.cn (X.-J. Yang), wubiao@lzb.ac.cn (B. Wu).

has been a focus to explore novel polyolefin materials via the design and synthesis of late transition metal catalysts with a deliberate tuning of the ligand backbone.

1,10-Phenanthroline and its derivatives are well-established ligands for late transition metal coordination chemistry because their steric and electronic environment can be conveniently tailored by varying the substituents [12]. The 2,9-diaryl-1,10-phenanthrolines and their complexes, due to their rich chemical and physical properties, have been frequently used in the field of molecular biology and supramolecular self-assembly (e.g., the catenates) [13–15]. However, as typical  $\alpha$ -diimines, late transition metal complexes of bidentate 1,10-phenanthrolines, have rarely been reported for catalytic ethylene oligomerization/polymerization [16,17], although some work of complexes with bis(imino)or mono(imino)-1,10-phenanthroline ligands in a tridentate  $(N^{\wedge}N^{\wedge}N)$  coordination fashion has appeared recently [18–24]. In the present work, we have studied a series of nickel(II) and cobalt(II) dihalide complexes with bidentate (N^N) 1,10-phenanthroline ligands bearing symmetrical or unsymmetrical aryl substituents on the 2,9-positions. Such ligands may provide sufficient protecting shield for the transition metal center, thus benefiting olefin oligomerization to produce high-molar oligomers. Herein, we report the synthesis and crystal structure of these novel Ni(II) and Co(II) complexes, as well as their catalytic activities for ethylene oligomerization with the assistance of methylaluminoxane (MAO).

#### 2. Results and discussion

# 2.1. Syntheses

Ligands  $L^1 - L^3$  were prepared by the modified literature procedures [25–28]. According to the method utilized by Sauvage [26]. a two-step synthetic approach can be applied for the preparation of 2.9-substituted phenanthrolines: 1.10-phenanthroline is first reacted with a slightly excess of the aryllithium reagent (RLi) at room temperature, and the procedure is then repeated once using the monoarylated phenanthroline as the reactant. This method was adopted in our work to prepare the unsymmetrical ligand  $L^2$ , 2phenyl-9-naphthyl-1,10-phenanthroline, where 2-phenyl-1,10phenanthroline was reacted with naphthyllithium to afford the product. For the preparation of the symmetrical 2,9-disubstituted 1,10-phenanthrolines ( $\mathbf{L}^1$  and  $\mathbf{L}^3$ ), an alternative one-step synthesis was employed, as shown in Scheme 1. In this modified procedure 1,10-phenanthroline was reacted directly with 4 equiv. aryllithium reagents at room temperature, followed by hydrolysis and oxidation with activated MnO<sub>2</sub> to give the desired diarylated ligands. The crude products could be purified by column chromatography and subsequent recrystallization. It should be noted that in the reaction of 1,10-phenanthroline with phenyl lithium, both 2,9-diphenyl-1,10-phenanthroline ( $\mathbf{L}^1$ , 50%) and the monoarylated product, 2-phenyl-1,10-phenanthroline (39%), were obtained. The two compounds, with a total yield of 89%, could be well separated by column chromatography using ethyl acetate/petroleum ether as eluent. Changing the stoichiometry of phenyllithium and 1,10-phe-



**Scheme 1.** Synthesis of the ligands  $(L^1-L^3)$  and complexes **1–9**. Reagents and conditions: (i) (a)  $R^1Li$ , diethyl ether/toluene; (b)  $H_2O$ ; (c)  $MnO_2$ . (ii) (a)  $R^2Li$ , diethyl ether/toluene; (b)  $H_2O$ ; (c)  $MnO_2$ . (iii)  $MX_2 \cdot 6H_2O$ , THF.

nanthroline had a significant effect on the yield of 2-phenyl-1,10phenanthroline, which increased gradually when the molar ratio of phenyllithium to 1,10-phenanthroline was decreased from 4:1 to 1:1, reaching a maximum of 52% when 1,10-phenanthroline was reacted with a slight excess of phenyllithium. Since 2-phenyl-1,10-phenanthroline [29] is an important starting material for the synthesis of the unsymmetrical ligand  $L^2$ , this procedure proved to be a facile, one-pot way to both **L**<sup>1</sup> and the intermediate monophenyl 1,10-phenanthroline. In contrast, when 1,10-phenanthroline was reacted with 4 equiv. of naphthyllithium at room temperature, only 2,9-bis(1-naphthyl)-1,10-phenanthroline  $(L^3)$ was isolated, with neglectable monoarylated phenanthroline. The yield of the 2,9-substituted-1,10-phenanthrolines was dependent on the steric bulk of the substituents ( $L^1$ : 50%;  $L^3$ : 31.5%). The 2,9-diaryl-1,10-phenanthrolines  $(L^1-L^3)$  were characterized with elemental analysis. <sup>1</sup>H NMR, ESI-MS and IR spectroscopy.

The nickel(II) and cobalt(II) complexes **1–9** were prepared by the reaction of the ligands  $L^1-L^3$  with NiCl<sub>2</sub> · 6H<sub>2</sub>O, NiBr<sub>2</sub> · 6H<sub>2</sub>O, or CoCl<sub>2</sub> · 6H<sub>2</sub>O in THF (Scheme 1), followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN. They were characterized by elemental analysis, UV–Vis and IR spectroscopy, and the solid-state structures of **1**, **4–7**, and **9** were confirmed by X-ray diffraction analysis.

#### 2.2. X-ray crystal structures

#### 2.2.1. Nickel(II) complexes

Dark-red single crystals of the Ni(II) complexes **1**, **5**, **6** could be obtained through slow evaporation of a mixed solution of dichloromethane/acetonitrile (50:50). Growth of single crystals of complexes **3** and **4**, which contain the unsymmetrical ligand  $L^2$ , is very difficult, as many attempts to crystallize them have been unsuccessful. Finally, pale green crystals of complex **4** suitable for X-ray analysis were obtained from its solution in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN in the presence of THF, and it turned out that the solid-state structure of **4** incorporates a THF molecule as an auxiliary ligand (vide infra).

X-ray structural studies show that all of the Ni(II) complexes have a metal to phenanthroline ratio of 1:1. The coordination geometry of the three complexes (**1**, **5**, and **6**) that contain symmetrical ligands is similar to one another, with the nickel center being four-coordinated by the two nitrogen donors of the bidentate ligand and two halide ions (Figs. 1–3). Complex **1** contains a NiCl<sub>2</sub>L<sup>1</sup> molecule in an asymmetrical unit, while there are two independent halves of NiCl<sub>2</sub>L<sup>3</sup> molecules in **5**, and half NiBr<sub>2</sub>L<sup>3</sup> molecule in **6** per asymmetrical unit. The coordination environment around the Ni(II) ion in these three compounds is slightly flattened tetrahedral, and the dihedral angle of the N–Ni–N and X–Ni–X (X = Cl or Br) planes is 78.0°, 78.3/79.8° and 78.3° for **1**, **5**, and **6**, respectively. Similar coordination geometry has also been



Fig. 1. The molecular structure of complex 1 with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 2. The molecular structure of 5, showing the two independent molecules.



Fig. 3. The molecular structure of 6.

observed in some copper(II) complexes [30,31]. There exist minor differences of the N–Ni–N bite angle (1,  $84.42(7)^{\circ}$ ; 5,  $83.0(2)/83.6(2)^{\circ}$ ; 6,  $83.8(3)^{\circ}$ ).

The molecular structure of complex **4** bearing unsymmetrical ligand ( $\mathbf{L}^2$ ) is different from those with symmetrical phenanthrolines. As mentioned above, this compound could be crystallized only in the presence of THF, and a THF molecule was found to participate in the coordination with Ni(II) center. This "extra" ligand might be critical in the stabilization of the solid-state structure, as there is a rather strong intramolecular C-H··· $\pi$  interaction between the THF (C32H32B) and the naphthyl moiety (C19–C28) (H···Cg distance: 2.21 Å; C···Cg: 3.14 Å; H···plane: 2.17 Å; C-H···Cg angle: 160.0°; Cg is the centroid of the naphthyl moiety). As shown in Fig. 4, the nickel atom in compound **4** is five-coordinated by the bidentate ligand  $\mathbf{L}^2$ , two bromide ions and a THF molecule. The coordination configuration around nickel(II) is best

described as distorted square pyramidal, with the atoms N1, Br1, Br2 and O1 of the THF molecule defining the basal plane and atom N2 occupying the apical site. The four basal atoms are efficiently coplanar (mean deviation of N1, Br1, Br2, O1: 0.007 Å), and the nickel atom is located slightly above this tetragonal plane by 0.291 Å, leading to the distortion of the bond angles between the apical and basal atoms from 90°. Furthermore, the Ni–N2 bond is bent to N1 and Br2 to adapt to the chelating coordination of N1 and N2. As a result, the N2–Ni–N1 (81.4(1)°) and N2–Ni–Br2 (90.82(9)°) angles are more acute than the N2–Ni–Br1 (101.59(9)°) and N2–Ni–O1 (115.0(1)°) angles. The two Ni–N bond lengths are slightly different, with the axial Ni–N2 being longer than the equatorial Ni–N1 by about 0.015 Å, while the two Ni–Br bonds differ by 0.07 Å.

The Ni–N bond distances in these complexes (**1**, **4**–**6**) fall into the range of 1.998–2.060 Å (Table 1), which is normal for nickel(II) phenanthroline and bipyridine complexes [32]. Although each of **1**, **5** or **6** has two identical substitute groups on the phenanthroline backbone, the molecule of complex **1** is not symmetrical, while the molecules of **5** and **6** have a two-fold axis bisecting the N–Ni–N and X–Ni–X angles. The dihedral angle between the phenanthroline moiety and the attached phenyl or naphthyl substituent is 28.1° and 43.4° for **1**, 64.9/53.3° (two independent molecules) for **5** and 57.9° for **6**. In the asymmetrical complex **4**, the two dihedral angles of phenanthroline-phenyl and phenanthroline-naphthyl are 50.6° and 67.7°, respectively.

# 2.2.2. Cobalt(II) complexes

The structures of two cobalt(II) complexes (**7**, **9**) with the symmetrical diphenyl- or dinaphthyl-ligands ( $L^1$  and  $L^3$ ) have been determined, which are similar to the nickel(II) analogs (**1**, **5**) with the corresponding ligands. The coordination geometry about the Co(II) center is distorted tetrahedral, with the dihedral angle of the N–Co–N and Cl–Co–Cl planes being 77.9° and 79.4/80.4°, respectively. In an asymmetrical unit, complex **7** contains a CoCl<sub>2</sub> $L^1$  molecule, while **9** has two independent halves of CoCl<sub>2</sub> $L^3$  molecules (Figs. 5 and 6). The Co–N bond distances in the complexes (**7**, **9**) are in the range of 2.049–2.237 Å. The dihedral angle between the phenanthroline moiety and the attached phenyl or naphthyl substituent is 28.0°, 39.8° for **7**, and 52.7/68.0° for **9**. There is no significant intermolecular  $\pi$ – $\pi$  stacking in these complexes.

#### 2.3. Spectroscopic properties

The UV–Vis spectra of the Ni(II) and Co(II) complexes were studied in dichloromethane with various concentrations. In the





Fig. 4. The molecular structure of 4, showing the square pyramidal, five-coordinate Ni(II) center.



Fig. 5. The molecular structure of 7.



Fig. 6. The structure of 9, showing the two independent molecules.

#### Table 1

Selected bond lengths (Å) and bond angles (°) for  $1,\,4\text{--}7$  and 9

	Ni	$\operatorname{Cl}_{2}\mathbf{L}^{1}(1)$	
Ni–N(1) 2.028(2)	Ni-Cl(1) 2.223(1)	N(2)-Ni-N(1)84.42(7)	N(1)-Ni-Cl(1) 99.80(5)
Ni-N(2) 2.008(2)	Ni-Cl(2) 2.2308(8)	N(2)-Ni-Cl(1)114.90(6)	N(2)-Ni-Cl(2) 96.65(6)
		N(1)-Ni-Cl(2)112.43(6)	Cl(1)-Ni-Cl(2)136.86(3)
	NiBr <sub>2</sub>	<b>L</b> <sup>2</sup> (THF) ( <b>4</b> )	
Ni-N(1) 2.045(3)	Ni-N(2) 2.060(3)	N(1)-Ni-Br(1) 89.61(9)	O(1)-Ni-Br(1) 90.3(1)
Br(1)-Ni 2.4920(7)	Br(2)-Ni 2.5649(7)	N(2)-Ni-Br(1) 101.59(9)	N(1)-Ni-Br(2) 88.74(9)
Ni-O(1) 2.077(3)		O(1)-Ni-Br(2) 87.6(1)	N(1)-Ni-O(1) 163.3(1)
N(1)-Ni-N(2) 81.4(1)	Br(1)-Ni-Br(2) 167.09(3)	N(2)-Ni-Br(2) 90.82(9)	N(2)-Ni-O(1) 115.0(1)
	Ni	$Cl_2 L^3$ (5)	
Ni(1)-N(1) 1.998(4)	Ni(1)-Cl(1) 2.212(1)	N(2)-Ni(2)-Cl(2) 101.1(1)	$N(1)-Ni(1)-Cl(1)^{a}$ 115.8(1)
Ni(2)-N(2) 2.020(4)	Ni(2)-Cl(2) 2.205(1)	Cl(1)–Ni(1)–Cl(1) <sup>a</sup> 127.62(9)	$Cl(2)-Ni(2)-Cl(2)^{b}$ 130.0(1)
$N(1)-Ni(1)-N(1)^{a}$ 83.0(2)	N(2)-Ni(2)-N(2) <sup>b</sup> 83.6(2)	N(1)-Ni(1)-Cl(1) 103.0(1)	$N(2)-Ni(2)-Cl(2)^{b}$ 115.9(1)
	Ni	$Br_2 L^3 (6)$	
Ni-N 2.028(5)	Ni-Br 2.3459(8)	N-Ni-N <sup>c</sup> 83.8(3)	N-Ni-Br <sup>c</sup> 116.19(11)
		N-Ni-Br 101.31(12)	$Br(1)-Ni-Br(1)^{c}$ 129.29(5)
	Ca	$Cl_2L^1$ (7)	
Co(1)-N(2) 2.049(2)	Co(1)-Cl(1) 2.2370(8)	N(2)-Co(1)-N(1) 83.21(7)	N(2)-Co(1)-Cl(2) 101.19(6)
Co(1)-N(1) 2.070(2)	Co(1)-Cl(2) 2.2395(9)	N(2)-Co(1)-Cl(1) 118.25(6)	N(1)-Co(1)-Cl(2) 116.90(6)
		N(1)-Co(1)-Cl(1) 103.60(6)	Cl(1)-Co(1)-Cl(2) 126.11(3)
	Co	$Cl_2 L^3$ (9)	
Co(1)-N(1) 2.066(3)	Co(2)-N(2) 2.078(3)	N(2)-Co(2)-Cl(2) 106.81(7)	N(1)-Co(1)-Cl(1) 107.77(8)
Co(1)-Cl(1) 2.222(1)	Co(2)-Cl(2) 2.196(1)	$N(1)-Co(1)-Cl(1)^{d}$ 119.29(8)	$N(2)-Co(2)-N(2)^{e}$ 117.28(6)
$N(1)-Co(1)-N(1)^{d}$ 80.5(2)	$Cl(1)-Co(1)-Cl(1)^{d}$ 81.5(2)	N(2)-Co(2)-Cl(2) <sup>e</sup> 119.71(7)	Cl(2)-Co(2)-Cl(2) <sup>e</sup> 117.63(7)

#### Symmetry code:

UV region, the ligands displayed typical ligand-centered  $\pi$ - $\pi$ <sup>\*</sup> transitions at ~260 and 308 nm for L<sup>1</sup>, and ~230 and 290 nm for L<sup>2</sup> and L<sup>3</sup>, respectively (Fig. 7a). Upon coordination with metal ions, there are minor changes of these bands.

The visible spectra of the complexes were obtained at higher concentration ( $10^{-3}$  M) and Fig. 7b presents the absorption bands of complexes NiCl<sub>2</sub>L<sup>3</sup> (**5**), NiBr<sub>2</sub>L<sup>3</sup> (**6**) and CoCl<sub>2</sub>L<sup>3</sup> (**9**). In all cases, the Ni(II) complexes (**1–6**) showed a broad peak with the maximum absorption at 500–520 nm and  $\varepsilon$  value around 100 M<sup>-1</sup> cm<sup>-1</sup>, which is assigned to the MLCT charge transfer of the complexes. The cobalt(II) complexes **7–9**, however, showed very different absorption bands from the nickel(II) compounds: their absorptions appeared in much longer wavelengths. All the three Co(II) complexes at ~575 nm ( $\varepsilon$  ~ 300 M<sup>-1</sup> cm<sup>-1</sup>) and a relatively broad band at ~675 nm accompanied by a shoulder. These long wavelength

absorptions could be attributed to the  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$  transition, corresponding to a tetrahedral cobalt(II) center [33]. Compared to the ligand-centered absorption bands, the molar absorption coefficients of the visible transitions are much lower. The MLCT band of **7–9** could not be resolved, probably due to overlap with the higher-energy d–d transition. On the other hand, the d–d transitions of the Ni(II) complexes in the visible region were not observed.

# 2.4. Oligomerization of ethylene

In the present work, complexes 1-9 are active for ethylene oligomerization using MAO as cocatalyst. It should be noted that although complex **4** crystallized as a THF adduct in the solid-state structure, samples used in the ethylene oligomerization experiments were obtained from  $CH_2Cl_2$  and have the composition of

<sup>&</sup>lt;sup>a</sup> (-1 - x, -y, z).

<sup>&</sup>lt;sup>b</sup> (-x, -y, z).

<sup>&</sup>lt;sup>c</sup> (1 - x, 1 - y, z).

<sup>&</sup>lt;sup>d</sup> (-x, -y, z).

<sup>&</sup>lt;sup>e</sup> (-x, 1 - y, z).



Fig. 7. The UV–Vis spectra of (a) ligands  $L^1-L^3$  (concd.  $1 \times 10^{-5}$  M) and (b) complexes 5, 6 and 9 (concd.  $1 \times 10^{-3}$  M).

NiX<sub>2</sub>L as confirmed by elemental analysis. All the experiments were repeated three times and the mean values were taken as the final results. The results of ethylene oligomerization at 1 atm are listed in Table 2. As analyzed by GC and GC–MS, ethylene dimers and trimers are the main oligomeric products for the nicke-I(II) precatalysts (**1–6**), while the cobalt(II) complexes (**7–9**) lead to mainly C<sub>4</sub> isomers. The activities of Ni(II) complexes are slightly higher than those of the Co(II) analogs.

Under normal pressure (1 atm), the nickel(II) complexes bearing different steric-demanding ligands and different halide ions showed slightly different catalytic activities for ethylene oligomerization to yield isomers of the short-chain dimers and trimers (Table 2, run 1–6). Sterically bulkier catalysts resulted in higher activities, i.e., the activity increased gradually from the diphenylsubstituted catalysts **1** and **2** to the phenyl/naphthyl (**3**, **4**), and then to the dinaphthyl-substituted compounds (**5**, **6**) under the same conditions. The properties of the oligomer products also displayed some differences: the complexes (**5** and **6**) containing dinaphthyl groups (Table 2, run 5 and 6) led to a higher yield of ethylene trimers (C<sub>6</sub> about 29–45%) than the less bulky compounds

 Table 2

 Ethylene oligomerization with 1–9/MAO at 1 atm

Run	Complex	Al/M (mol/mol)	Time (min)	Т (°С)	Activity (kg/mol <sup>*</sup> h)	Produ distri	Product distribution (wt%)	
						C <sub>4</sub>	C <sub>6</sub>	Linear α-olefins
1	1	1000	30	15	58	82	18	24
2	2	1000	30	15	72.5	79	21	8
3	3	1000	30	15	86	78	22	10
4	4	1000	30	15	90	83	17	37
5	5	1000	30	15	94	71	29	19
6	6	1000	30	15	136	58	42	22
7	6	250	30	15	21	96	4	78
8	6	500	30	15	82	73	27	8
9	6	1500	30	15	112	60	40	13
10	6	2000	30	15	118	60	40	26
11	6	1000	15	15	121	61	39	16
12	6	1000	45	15	108	63	37	20
13	6	1000	60	15	103	60	40	14
14	6	1000	75	15	98	60	40	14
15	6	1000	90	15	93	61	39	17
16	6	1000	30	0	85	62	38	22
17	6	1000	30	30	149	73	27	27
18	6	1000	30	45	134	74	25	32
19	6	1000	30	60	144	76	24	32
20	7	1000	30	15	39	>99	-	74
21	8	1000	30	15	42	>99	-	43
22	9	1000	30	15	40	>99	-	64

General conditions: 10 µmol precatalyst; 40 mL toluene as solvent.

**1–4** ( $C_6$  about 17–22%) under the identical reaction conditions (run 1–4). Furthermore, the catalytic activities of the dibromides are better than those of the dichloride analogs. The cobalt(II) complexes (**7–9**) exhibited slightly lower activities than the nickel(II) analogs; however, the distribution of the ethylene oligomers is significantly different, with  $C_4$  isomers as the only products.

# 2.4.1. Effects of Al/M molar ratio, oligomerization temperature and time

It is well known that the catalytic performance of a given catalyst is greatly dependent on the oligomerization conditions. To probe the effects of reaction parameters on the ethylene oligomerization behavior, the precatalyst **6** was investigated under varying conditions, such as the amount of MAO (i.e., the molar ratio of Al/M), the reaction temperature and reaction time. The catalytic activity of complex **6** increased rapidly when the Al/Ni ratio was increased from 250 to 1000 (Table 2, run 6–8), but there were no significant changes with larger Al/Ni ratios (from 1000 to 2000, run 6 and 9, 10). However, at Al/Ni = 250 (Table 2, run 7) the precatalyst led to a better yield of linear  $\alpha$ -olefins (78%) and ethylene dimers ( $C_4$  about 96%) than at Al/Ni = 500–2000 ( $C_4$  about 55–73%, linear  $\alpha$ -olefins about 8–26%) at 15 °C (run 6 and 8–10).

The catalytic lifetime of complex **6** was investigated with Al/ Ni = 1000 and reaction temperature at 15 °C (Table 2, run 6 and 11–15) in the range of 15–90 min. The precatalyst showed a relatively stable activity, only slightly decreasing when the reaction time exceeded 60 min, and was still active when prolonged to 90 min. On the other hand, the temperature factor was tested for complex **6** ranging from 0 to 60 °C with Al/Ni = 1000 (run 6 and 16–19). The catalytic activity increased when the temperature was raised from 0 to 15 °C and then to 30 °C, but it remained nearly constant at further elevated temperature, up to 60 °C. The yield of the linear  $\alpha$ -olefins showed a slight increase (run 6 and 16–19) with the increase is not yet clear. In general, the selectivity for linear  $\alpha$ -olefins is low for the nickel(II) precatalysts (Table 2) due to their ability to isomerize  $\alpha$ -olefins [34].

#### 2.4.2. Effects of ethylene pressure on the catalytic behavior

The ethylene oligomerization and polymerization behaviors of precatalysts **1–9** were investigated under 10 atm of ethylene (Table 3). At this pressure, the activities of the nickel(II) dibromide complexes were significantly higher than those of the dichloride analogs (Table 3, run 23–28), which is in contrast to the minor differences between the bromides and chlorides at 1 atm (Table 2). It can be seen that the catalytic activities of the Ni(II) and Co(II) complexes were considerably enhanced at higher pressure, and the oligomer distribution was also impacted, as GC–MS analysis revealed

Table 3 Ethylene oligomerization with 1–9/MAO at different pressures

Run	Complex	Pressure (atm)	Activity (kg/mol[M] h)	Produ	Product distribution (wt%)			
				C <sub>4</sub>	C <sub>6</sub>	$C \ge 8$	Linear α-olefins	
23	1	10	257	33	38	21	25	
24	2	10	766	61	27	12	26	
25	3	10	235	48	24	28	27	
26	4	10	747	38	35	27	34	
27	5	10	233	35	36	30	28	
28	6	10	1518	46	44	11	40	
29	6	7.5	652	28	44	28	45	
30	6	5	294	33	51	16	45	
31	6	2.5	113	73	22	5	41	
32	7	10	39	>99	-	-	59	
33	8	10	104	>99	-	-	13	
34	9	10	118	>99	-	-	28	
35	9	7.5	111	>99	-	-	14	
36	9	5	58	>99	-	-	14	
37	9	2.5	46	>99	-	-	22	

General conditions: 10  $\mu mol$  precatalyst; 100 mL toluene as solvent; Al/M = 1000; 60 min.

an increase of the yield of linear  $\alpha$ -olefins and ethylene trimers. The best catalytic activities of the complexes at 10 atm were obtained for complex **6** (1518 kg/mol[Ni] h). It is noteworthy that higher carbon-number olefins ( $C_8-C_{18}$ ) were also produced together with ethylene dimers and trimers at 10 atm pressure for the Ni(II) complexes, while the Co(II) analogs gave only dimers at higher pressure, the same as at normal pressure. Finally, the precatalysts **6** and **9** were chosen to test the change of the catalytic activity with the ethylene pressure (run 28–30, 34–37). The activities of the two compounds increased gradually with increasing ethylene pressure.

#### 3. Conclusions

The synthesis, structure, and catalytic ethylene oligomerization properties of six nickel(II) halide and three cobalt(II) chloride complexes with symmetrical and unsymmetrical 2,9-disubstituted phenanthroline ligands are reported. All complexes exhibit good catalytic activities for ethylene oligomerization, with Ni(II) complexes being slightly better than the Co(II) ones. At normal pressure, the major products of the Ni(II) complexes are ethylene dimers and trimers, while the Co(II) analogs give only dimers at either normal or higher pressure. The ethylene oligomerization activities are influenced by the Al/M molar ratio, reaction time, and ethylene pressure, and complexe **6** displays the best catalytic activity among the series of complexes (up to 1518 kg/mol[Ni] h at 10 atm).

# 4. Experimental

#### 4.1. General considerations

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk vacuum line techniques. Solvents were refluxed over an appropriate drying agent and distilled under nitrogen prior to use. MAO solution (1.65 M) in toluene was purchased from Albemarle Corp (USA). 1,10-Phenanthroline, 1-bromonaphthalene, bromobenzene, the nickel(II) and cobalt(II) salts, and other chemicals were commercially available and were used without further purification. <sup>1</sup>H NMR spectra were obtained on a Mercury plus-400 spectrometer with TMS as the internal standard. IR spectra were recorded as KBr pellets with an HP5890 II GC/ NEXUS-870 spectrometer. ESI-MS spectra were measured on a Waters ZQ 4000 instrument. Element analyses were performed with an Elementar VarioEL instrument. Electronic spectra were recorded with an HP 8453 spectrometer. Oligomerization activity measurements and oligomer distribution analysis were carried out on an Agilent 6890N/5973N GC/MS spectrometer (Hp-1 ms column) and Sp-2100 detectors.

# 4.2. Synthesis of the ligands $L^1-L^3$

# 4.2.1. 2,9-Diphenyl-1,10-phenanthroline $(L^1)$ and 2-phenyl-1,10-phenanthroline

A solution of bromobenzene (18.84 g, 120 mmol) in 20 mL of dry diethyl ether was added dropwise under nitrogen to a suspension of lithium (2.48 g, 360 mmol) in 150 mL of diethyl ether at 0 °C. The solution was allowed to stir for 1 h, and was slowly added to a suspension of 1,10-phenanthroline (5.40 g, 30 mmol) in 80 mL of toluene at 0 °C. The mixture first became yellow and then dark violet, which was stirred overnight at room temperature. After addition of water (60 mL) the organic layer was separated, and the aqueous phase was extracted three times with dichloromethane  $(3 \times 15 \text{ mL})$ . The combined organic extracts were stirred with 110 g of activated MnO<sub>2</sub> for 2 h. After filtration, the solution was dried over MgSO<sub>4</sub>, and the solvent removed by rotary evaporation to give a solid of the mixture of the desired di- and monoarylated 1,10-phenanthroline. The two products were then separated by column chromatography on silica gel using ethyl acetate/petroleum ether (2:1, v/v) as the eluent. The disubstituted 2,9-diphenyl-1,10-phenanthroline was eluted first (yield 50%), followed by the 2-phenyl-1,10-phenanthroline (39%). Both products were recrystallized from toluene. Total yield: 89% (based on 1,10-phenanthroline). The characterization of the two compounds showed identical results to the literature reports [29,35].

#### *4.2.2.* 2-*Phenyl-9-(1-naphthyl)-1,10-phenanthroline* (**L**<sup>2</sup>)

Similar to the above procedure, 1-bromonaphthalene (4.97 g, 24 mmol) was reacted with lithium (0.48 g, 69.5 mmol) in diethyl ether. Then the aryllithium agent was reacted with 2-phenyl-1,10-phenanthroline (1.53 g, 6 mmol) in 55 mL of toluene. After hydrolysis with 30 mL of water and extraction with CH<sub>2</sub>Cl<sub>2</sub>, the organic extracts were stirred with 50 g of activated MnO<sub>2</sub>. The solvent was removed and the resulting yellow solid was purified by column chromatography (ethyl acetate/petroleum ether = 1:4), and the product was recrystallized from ethyl acetate/petroleum ether. Yield: 1.45 g (68.0%). Mp: 172-173 °C. ESI-MS: m/z 357  $[M+H]^+$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta = 8.86$  (d, I = 9.2 Hz, 1H, naphthyl-H2), 8.85 (d, J = 8.4 Hz, 2H, H4, H7), 8.32–8.36 (m, 2H, Ph-o-H), 8.13 (d, J = 8.4 Hz, 1H, H3), 8.01 (d, J = 8.0 Hz, 1H, H8), 7.92-7.96 (m, 3H, naphthyl-H4,5,8), 7.85 (s, 2H, H5, H6), 7.54-7.61 (m, 3H, Ph-*m*-H + naphthyl-H3), 7.40-7.46 (m, 3H, Ph*p*-H + naphthyl-H6,7). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  = 158.9, 156.8, 146.2, 146.0, 139.4, 138.3, 136.7, 136.2, 134.2, 131.6, 129.4, 129.3, 128.7, 128.3, 127.7, 127.4, 126.6, 126.4, 126.1, 125.9, 125.8, 125.3, 124.4, 119.9. IR (KBr, v/cm<sup>-1</sup>): 3034, 1586, 1577, 1539, 1505, 1483, 852, 779, 696, 517. Anal. Calc. for C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>: C, 87.93; H, 4.74; N, 7.32. Found: C, 88.31; H, 4.61; N, 7.03%.

#### 4.2.3. 2,9-Bis(1-naphthyl)-1,10-phenanthroline (*L*<sup>3</sup>)

The same reaction and work-ups employed for  $L^1$  and  $L^2$  were followed for  $L^3$ , with 1-bromonaphthalene (28.98 g, 140 mmol), lithium (2.48 g, 360 mmol), 1,10-phenanthroline (5.40 g, 30 mmol), and activated MnO<sub>2</sub> (120 g) being used in the preparation. The product was purified by column chromatography (ethyl acetate/petroleum ether = 4:1) and recrystallized from ethyl acetate/petroleum ether. Yield: 4.08 g (31.5%). Mp: 209–210 °C. ESI-MS: m/z 433.6 [M+H]<sup>+</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  = 8.61 (d, J = 6.8 Hz, 2H, H4, H7), 8.39 (d, J = 8.0 Hz, 2H, naph-thyl-H2), 7.99 (d, J = 8.8 Hz, 2H, naphthyl-H4), 7.91 (s, 2H, H5,

H6), 7.88 (d, *J* = 6.4 Hz, 6H, H3, H8 + naphthyl-H5,8), 7.56 (t, *J* = 7.6, 8.0 Hz, 2H, naphthyl-H3), 7.46 (m, 4H, naphthyl-H6,7). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  = 159.1, 146.2, 138.6, 136.1, 134.0, 131.5, 129.1, 128.6, 128.2, 127.4, 126.4, 126.2, 126.1, 125.6, 125.2, 124.7. IR (KBr, *v*/cm<sup>-1</sup>): 3041, 1618, 1582, 1541, 1509, 1499, 1152, 797, 776, 746, 731, 706, 667, 651, 625, 607, 584, 558, 507, 494, 495, 442, 415. *Anal.* Calc. for C<sub>32</sub>H<sub>20</sub>N<sub>2</sub>: C, 88.86; H, 4.66; N, 6.48. Found: C, 88.69; H, 4.75; N, 6.51%.

# 4.3. Synthesis of the complexes 1-9

The title complexes were prepared by reaction of nickel or cobalt dichloride or dibromide with the corresponding ligands. The typical synthesis is described below for **1** and **7**, and complexes **2–6** and **8**, **9** were synthesized following similar procedures.

#### 4.3.1. NiCl<sub>2</sub> $L^1$ (1)

The ligand 2,9-diphenyl-1,10-phenanthroline (33.2 mg, 0.1 mmol) and NiCl<sub>2</sub> ·  $6H_2O$  (23.9 mg, 0.1 mmol) in THF (10 mL) were refluxed for 8 h to obtain a pink precipitate, which was filtered and washed with ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL). The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>. Yield: 40.2 mg (87%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3045, 1622, 1585, 1551, 1508, 1487, 1422, 1361, 1155, 869, 775, 740, 703, 660, 521, 439. *Anal.* Calc. for C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>2</sub>Ni: C, 62.39; H, 3.49; N, 6.06. Found: C, 62.15; H, 3.46; N, 5.86%. ESI-MS: 425.4 [M-Cl]<sup>+</sup>.

# 4.3.2. $NiBr_2 L^1$ (2)

Yield: 45.1 mg (82.1%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3059, 1622, 1588, 1553, 1512, 1488, 1152, 862, 776, 702, 661, 601. *Anal.* Calc. for C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>Br<sub>2</sub>Ni: C, 52.32; H, 2.93; N, 5.09. Found: C, 52.18; H, 2.78; N, 4.92%. ESI-MS: 471.4  $[M-Br]^{+}$ .

# 4.3.3. $NiCl_2 L^2$ (3)

Yield: 29.3 mg (60.2%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3057, 1625, 1587, 1556, 1514, 1488, 1152, 804, 781, 705, 663, 519. *Anal.* Calc. for C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>Cl<sub>2</sub>Ni: C, 65.68; H, 3.54; N, 5.47. Found: C, 65.47; H, 3.50; N, 5.22%. ESI-MS: 475.4 [M–Cl]<sup>+</sup>.

#### 4.3.4. NiBr<sub>2</sub> $L^2$ (4)

Yield: 33.6 mg (58.4%). Mp > 300 °C. IR (KBr, v/cm<sup>-1</sup>): 3057, 1625, 1587, 1555, 1513, 1499, 1487, 1364, 1154, 876, 803, 781,

#### Table 4

Crystallographic data for compounds 1, 4–7, and 9

705, 663, 519. *Anal.* Calc. for C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>Br<sub>2</sub>Ni: C, 55.96; H, 3.02; N, 4.66. Found: C, 55.78; H, 3.25; N, 4.58%. ESI-MS: 521.3 [M–Br]<sup>+</sup>.

# 4.3.5. $NiCl_2 L^3$ (5)

Yield: 46.4 mg (82.6%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3054, 1625, 1588, 1558, 1515, 1495, 1365, 1152, 879, 861, 802, 777, 665, 517. *Anal.* Calc. for C<sub>32</sub>H<sub>20</sub>N<sub>2</sub>Cl<sub>2</sub>Ni: C, 68.37; H, 3.59; N, 4.98. Found: C, 67.98; H, 3.32; N, 4.76%. ESI-MS: 525.4 [M–Cl]<sup>+</sup>.

#### 4.3.6. $NiBr_2 L^3$ (6)

Yield: 49.9 mg (76.7%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3055, 1625, 1587, 1557, 1514, 1494, 1156, 873, 797, 778, 664, 515. *Anal.* Calc. for C<sub>32</sub>H<sub>20</sub>N<sub>2</sub>Br<sub>2</sub>Ni: C, 59.04; H, 3.10; N, 4.30. Found: C, 58.88; H, 2.96; N, 4.15%. ESI-MS: 571.4 [M–Br]<sup>+</sup>.

# 4.3.7. $CoCl_2 L^1$ (7)

The ligand 2,9-diphenyl-1,10-phenanthroline (33.2 mg, 0.1 mmol) and  $CoCl_2 \cdot 6H_2O$  (23.8 mg, 0.1 mmol) in THF (10 mL) were refluxed for 8 h to obtain a blue precipitate, which was filtered and washed with ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL). The product was then recrystallized from  $CH_2Cl_2/CH_3CN$ . Yield: 37.2 mg (80.5%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3046, 1620, 1586, 1576, 1549, 1506, 1487, 1445, 1419, 1358, 1276, 1179, 1156, 1121, 1021, 907, 869, 851, 776, 759, 741, 703, 658. *Anal.* Calc. for  $C_{24}H_{16}N_2Cl_2Co: C, 62.36; H, 3.49; N, 6.06.$  Found: C, 62.59; H, 3.25; N, 6.26%. ESI-MS: 426.4 [M-Cl]<sup>+</sup>.

# 4.3.8. $CoCl_2 L^2$ (8)

Yield: 39.1 mg (76.4%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3444, 3058, 2922, 1623, 1587, 1555, 1512, 1496, 1424, 1395, 1363, 1343, 1298, 1245, 1188, 1152, 1132, 1103, 1062, 1023, 975, 907, 868, 800, 779, 759, 665, 612. *Anal.* Calc. for C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>Cl<sub>2</sub>Co: C, 65.65; H, 3.54; N, 5.47. Found: C, 65.27; H, 3.75; N, 5.61%. ESI-MS: 476.5 [M-Cl]<sup>+</sup>.

#### 4.3.9. $CoCl_2 L^3$ (9)

Yield: 39.2 mg (69.7%). Mp > 300 °C. IR (KBr,  $\nu/cm^{-1}$ ): 3426, 3057, 2923, 1623, 1586, 1552, 1511, 1490, 1420, 1395, 1361, 1240, 1187, 1150, 1023, 986, 907, 873, 803, 779, 757, 661, 606, 550, 433. *Anal.* Calc. for C<sub>32</sub>H<sub>20</sub>N<sub>2</sub>Cl<sub>2</sub>Co: C, 68.35; H, 3.58; N, 4.98. Found: C, 68.62; H, 3.41; N, 4.79%. ESI-MS: 526.6 [M–Cl]<sup>+</sup>.

	1	4	5	6	7	9
Formula	C24H16Cl2N2Ni	C32H26Br2N2NiO	C32H20Cl2N2Ni	C32H20Br2N2Ni	C <sub>24</sub> H <sub>16</sub> Cl <sub>2</sub> CoN <sub>2</sub>	$C_{32}H_{20}Cl_2CoN_2$
Fw	462.00	673.08	562.11	651.04	462.22	562.33
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	Pba2	P2 <sub>1</sub> 2 <sub>1</sub> 2	$P2_1/n$	Pba2
a (Å)	7.808(2)	9.634(2)	15.784(3)	15.981(3)	7.918(2)	15.422(3)
b (Å)	13.836(3)	17.400(4)	17.441(4)	8.728(2)	13.770(2)	17.208(3)
c (Å)	19.122(4)	15.805(3)	9.354(2)	9.402(2)	19.148(3)	9.678(2)
α (°)	90	90	90	90	90	90
β(°)	101.47(3)	98.93(3)	90	90	101.262(8)	90
γ (°)	90	90	90	90	90	90
V (Å <sup>3</sup> )	2024.4(7)	2617.3(9)	2575.1(9)	1311.5(5)	2047.5(6)	2568.3(9)
Ζ	4	4	4	2	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.516	1.708	1.450	1.649	1.499	1.454
F(000)	944	1352	1152	648	940	1148
$\mu ({\rm mm^{-1}})$	1.235	3.825	0.986	3.811	1.112	0.901
θ Range (°)	1.83-27.34	1.75-27.48	1.74-28.08	2.17-28.30	1.83-26.81	1.77-28.60
Reflection collected $(R_{int})$	17879 (0.0379)	24504 (0.0501)	15833 (0.0910)	8347 (0.0520)	11913 (0.0337)	15836 (0.0445)
Independent reflections	4396	6000	5082	3185	4334	5643
Observed reflections $[I > 2\sigma(I)]$	3458	4039	2168	1704	3067	2938
$R_1; wR_2 [I > 2\sigma(I)]$	0.0310; 0.0828	0.0440; 0.1128	0.0398; 0.0719	0.0464; 0.1010	0.0374; 0.0845	0.0352; 0.0787
$R_1$ ; $wR_2$ (all data)	0.0441; 0.0866	0.0706; 0.1227	0.1299; 0.0854	0.1115; 0.1198	0.0605; 0.0956	0.0834; 0.0870
Goodness-of-fit (F <sup>2</sup> )	1.094	0.977	0.794	1.007	1.027	0.809

#### 4.4. X-ray crystal structure determination

Diffraction data for the complexes were collected with a Rigaku RAXIS-RAPID IP diffractometer (**1**, **4**) or a Bruker SMART CCD area detector (**5–7**, **9**) at room temperature (293 K) with graphite-monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). An empirical absorption correction using sADABS [36] was applied for all the data. The structures were solved by direct methods using the SHELXS program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on  $F^2$  by the use of the program SHELXL [37]. The hydrogen atoms were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data for the complexes are listed in Table 4.

# 4.5. General procedure for ethylene oligomerization

#### 4.5.1. Oligomerization at 1 atm

In a typical experiment, the complex ( $10 \mu$ mol) was added to a glass reactor, which was evacuated and filled three times with nitrogen and twice with ethylene. Freshly distilled toluene (40 mL) was added to the reactor, followed by methylaluminoxane (MAO) toluene solution via a syringe. The reaction mixture was stirred under 1 atm ethylene for a given period while the temperature was maintained by a water bath. A small amount of the reaction mixture was taken out with a syringe and quenched by ice-cooled 10% HCl solution, and the product was analyzed by GC and GC–MS. Then the reaction was terminated by adding HCl/EtOH solution, and no polymers were found. The yield of oligomers was calculated by referencing with the mass of the used solvent based on the prerequisite that the mass of each fraction is approximately proportional to its integrated areas in the GC trace [38].

#### 4.5.2. High-pressure oligomerization

A 1 L stainless-steel autoclave equipped with an electronically controlled stirrer was evacuated and filled three times with nitrogen and twice with ethylene. Freshly distilled toluene (100 mL) was added. After the temperature reached a certain point, MAO was injected and then a toluene solution (20 mL) of the catalyst was added. The reactor pressure was kept constant throughout the oligomerization process by manually controlled addition of ethylene. After 30 min the reactor was cooled in an ice bath, the extra ethylene was vented off and the reaction was quenched by 10% HCl. Quantitative GC analysis of the product was performed immediately after the termination of the reaction.

#### Acknowledgment

We thank the "Bairen Jihua" program of Chinese Academy of the Sciences for financial support.

# Appendix A. Supplementary material

CCDC 620348–620351, 631891 and 631892 contain the supplementary crystallographic data for **1**, **4–7** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.03.018.

#### References

- [1] D.H. Camacho, E.V. Salo, J.W. Ziller, Z. Guan, Angew. Chem., Int. Ed. Engl. 43 (2004) 1821.
- [2] S.M. Pillai, M. Ravindranathan, S. Sivaram, Chem. Rev. 86 (1986) 353.
- [3] J. Skupinska, Chem. Rev. 91 (1991) 613.
- [4] G. Wilke, Angew. Chem., Int. Ed. Engl. 27 (1988) 185.
- [5] W. Keim, F.H. Kowalt, R. Goddard, C. Kruger, Angew. Chem., Int. Ed. Engl. 17 (1978) 466.
- [6] F. Speiser, P. Braunstein, L. Saussine, Acc. Chem. Res. 38 (2005) 784.
- [7] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
  [8] G.J.P. Britovsek, V.C. Gibson, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, B.S. Kimberley, P.J. Maddox, Chem. Commun. (1998) 849.
- [9] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
- [10] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 428.
- [11] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
- [12] J.P. Sauvage, Acc. Chem. Res. 23 (1990) 319.
- [13] V. Kalsani, M. Schmittel, A. Listorti, G. Accorsi, N. Armaroli, Inorg. Chem. 45
- (2006) 2061. [14] M. Meyer, A.M. Albrecht-Gary, C.O. Dietrich-Buchecker, J.P. Sauvage, J. Am. Chem. Soc. 119 (1997) 4599.
- [15] G. Rapenne, C.O. Dietrich-Buchecker, J.P. Sauvage, J. Am. Chem. Soc. 121 (1999) 994.
- [16] H. Tanaka, Y. Kin, M. Nakano, A. Usuki, Patent No. JP 2000344815.
- [17] M.D. Doherty, S. Trudeau, P.S. White, J.P. Morken, M. Brookhart, Organometallics 26 (2007) 1261.
- [18] W.-H. Sun, S. Jie, S. Zhang, W. Zhang, Y. Song, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, Organometallics 25 (2006) 666.
- [19] W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, J. Organomet. Chem. 691 (2006) 4196.
- [20] L. Wang, W.-H. Sun, L. Han, H. Yang, Y. Hu, X. Jin, J. Organomet. Chem. 658 (2002) 62.
- [21] J.D.A. Pelletier, Y.D.M. Champouret, J. Cadarso, L. Clowes, M. Ganete, K. Singh, V. Thanarajasingham, G.A. Solan, J. Organomet. Chem. 691 (2006) 4114.
- [22] G.J.P. Britovsek, S.P.D. Baugh, O. Hoarau, V.C. Gibson, D.F. Wass, A.J.P. White, D.J. Williams, Inorg. Chim. Acta 345 (2003) 279.
- [23] S. Jie, S. Zhang, W.-H. Sun, X.-F. Kuang, T.-F. Liu, J.-P. Guo, J. Mol. Catal., A: Chem. 269 (2007) 85.
- [24] S. Jie, S. Zhang, K. Wedeking, W. Zhang, H. Ma, X. Lu, Y. Deng, W.-H. Sun, C.R. Chimie 9 (2006) 1500.
- [25] F. Barigelletti, B. Ventura, J.-P. Collin, R. Kayhanian, P. Gaviña, J.-P. Sauvage, Eur. J. Inorg. Chem. (2000) 113.
- [26] C.O. Dietrich-Buchecker, P.A. Marnot, J.P. Sauvage, Tetrahedron Lett. 23 (1982) 5291.
- [27] P.A. Marnot, University of Louis Pasteur, Strasbourg, France 1984.
- [28] M. Schmittel, C. Michel, S.-X. Liu, D. Schildbach, D. Fenske, Eur. J. Inorg. Chem. (2001) 1155.
- [29] G.J.T. Brink, I.W.C.E. Arends, M. Hoogenraad, G. Verspui, R.A. Sheldon, Adv. Synth. Catal. 345 (2003) 1341.
- [30] M. Gelbert, C. Koerber, O. Friedrich, F. Fahrenkrug, M. Keller, U. Luening, Supramol. Chem. 14 (2002) 199.
- [31] B. Wu, P. Yang, X. Huang, Y. Liu, X. Liu, C. Xia, Z. Anorg. Allg. Chem. 632 (2006) 684.
   [32] P. Cillard, J.A. McCharata, C. Milliana, Computing Conditioning
- [32] R.D. Gillard, J.A. McCleverty, G. Wilkinson, Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, 1987. p. 80.
- [33] R.D. Gillard, J.A. McCleverty, G. Wilkinson, Comprehensive Coordination Chemistry, vol. 1, Pergamon Press, 1987. pp. 254–255.
- [34] F. Speiser, P. Braunstein, L. Saussine, Organometallics 23 (2004) 2633.
- [35] M.S. Goodman, A.D. Hamilton, J. Weiss, J. Am. Chem. Soc. 117 (1995) 8447.
- [36] G.M. Sheldrick, Program sADABS: Area-Detector Absorption Correction, University of Göttingen, Germany, 1996.
- [37] G.M. Sheldrick, SHELXS-97, SHELXL-97, Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1997.
- [38] R.L. Grob, Modern Practice of Gas Chromatography, second ed., 1985.