Transformation of 2-alkoxyimidate-1,10-phenanthroline metal (Mn^{2+}, Co^{2+} and Ni^{2+}) chlorides from bis(2-cyano-1,10-phenanthroline) metal chlorides: Syntheses, characterizations and their catalytic behavior toward ethylene oligomerization

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ABSTRACT

The 2-alkoxyimidate-1,10-phenanthroline complexes of manganese, cobalt and nickel have been synthesized by the reaction of 2-cyano-1,10-phenanthroline with metal dichloride in the corresponding alcohol. The metal complexes bearing two 2-cyano-1,10-phenanthrolines were isolated in non-protonic solvent as the coordination around metal core with two ligands and two chlorides. The alkoxyimidation of nitrile linked on ligand was speeded in forming the 2-alkoxyimidate-1,10-phenanthrolinyl metal complexes. All the complexes have been characterized by FT-IR spectra and elemental analysis, and some of their structures have also been confirmed by single-crystal X-ray diffraction analysis. All the metal complexes were evaluated in the catalytic oligomerization of ethylene with some alkylaluminums as co-catalyst; in which manganese complexes were less active, cobalt complexes showed low to moderate activities, and nickel complexes gave moderate to good activities.

1. Introduction

Nitriles are very important organic intermediates and could be directly transformed to carboxylic acids, esters, amines, and so on. The addition reaction of alcohols to nitriles was discovered by Nef in 1895 [1], in which the reaction of cyanogen with an aqueous ethanol solution of potassium cyanide gave ethyl 1-cyanoformimidate and diethyl oxalimidate. Such reaction was extended to other alcohols [2], and could be catalyzed by alkoxide in the presence of electron-withdrawing groups in the nitrile [3]. The resultant imidate products were found useful in organic synthesis [4,5], for example, the phenanthroline derivatives bearing chiral 2-oxazolinyl groups were prepared by the condensation reaction of 2-cyano-1,10-phenanthroline with the suitable optically active β-aminoalcohol [4,6].

Oligomerization and polymerization of ethylene by late-transition metal catalysts have attracted a great deal of interest since emergence of highly active catalysts of α-diimine nickel and palladium [7], and new catalyst systems covering nearly most late-transition metals have been reported [8,9]. Various metal complexes bearing phenanthroline derivatives were investigated as catalysts in ethylene reactivity in our group [10–18], and showed good catalytic activities. Manganese compounds are frequently used as catalytic precursors in epoxidation of alkenes [19–21], oxidation of sulfides [22,23] and hydrocarbons [24,25] as well as various asymmetric reactions [26]. Recently, a few of manganese complexes have also been reported in olefin polymerization [27–30]. Therefore, the relevant complexes of manganese, cobalt and nickel would be interestingly investigated together. The 2-cyano-1,10-phenanthroline easily reacted with metal (manganese, cobalt and nickel) halides in non-protonic solvents in forming bis(2-cyano-1,10-phenanthroline) metal complexes, however, 1,10-phenanthroline-2-imidate metal complexes were readily isolated in the presence of alcohols. All metal complexes were well characterized, and also investigated for their catalytic behaviors in ethylene oligomerization. Herein we report the preparation and characterization of these manganese, cobalt and nickel complexes, and their catalytic properties in ethylene oligomerization under different conditions.

2. Results and discussion

2-Cyano-1,10-phenanthroline and 2-carboxyl-1,10-phenanthroline were prepared from 1,10-phenanthroline according to

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the literature method [31,32]. The reaction of 2 equivalent 2-cyano-1,10-phenanthroline and $MnCl_2 \cdot 4H_2O$, $CoCl_2$ or $NiCl_2 \cdot 6H_2O$ in CH_2Cl_2 or THF at room temperature led to the formation of corresponding bis(2-cyano-1,10-phenanthroline)metal complexes 1–3, in which 2-cyano-1,10-phenanthroline functioned as a bidentate ligand with its two nitrogen atoms of phenanthroline coordinating with the metal center along with retaining the cyano group free (Scheme 1). The infrared $v(C\equiv N)$ stretching vibration bands in Mn(II), Co(II) and Ni(II) complexes shifted to 2240, 2236 and 2238 cm^{-1} from 2229 cm^{-1} (free ligand), individually, indicating that the coordination interaction between phenanthroline with metal caused a change of an electronic density of the ligand including the nitrile group.

When the reaction of 2-cyano-1,10-phenanthroline and $MnCl_2 \cdot 4H_2O$ was carried out in methanol at room temperature, a pale yellow precipitate formed at the beginning, which was known as complex 1. However, longer reaction time, such as 30 h or longer, resulted in the formation of a new manganese complex 4 as a yellow powder (Scheme 2). That means that the formation of complex 1 is kinetically favorable, however, the phenanthroline-imidate complex would be thermodynamically more stable. The formation of methoxyimidate cobalt complex 5 and nickel complex 6 from 2-cyano-1,10-phenanthroline and $CoCl_2$ or (DME)-$NiCl_2$ required in refluxing methanol (Scheme 2). They could be also readily prepared by reaction of the methoxyimidate ligand 10 and anhydrous $CoCl_2$ or (DME)$NiCl_2$ as a green (5) or yellow-green (6) powder. In their IR spectra, the stretching vibration bands of N–H bond and C=N double bond appeared at 3169 and 1639 cm^{-1} (5), 3178 and 1638 cm^{-1} (6), respectively.

Similar addition reaction is also occurred in the refluxing ethanol solution, ethyl carboxyimidate metal complexes, manganese complex 7 and cobalt complex 8, were isolated (Scheme 2). The infrared stretching vibration bands of N–H bond and C=N double bond in these ethoxyimidate complexes showed up at 3279 and 1640 cm^{-1} (7), 3271 and 1636 cm^{-1} (8), respectively.

To understand the formation of phenanthroline-imidate metal complexes, the representative 2-methoxyimidate-1,10-phenanthroline manganese complex 4 demonstrates the three accesses (Scheme 3). As the previously mentioned procedure, complex 4 was effectively prepared by reaction of 2-cyano-1,10-phenanthroline and $MnCl_2 \cdot 4H_2O$ in methanol (method A). In addition, the 2-methoxyimidate-1,10-phenanthroline (10), prepared by the methanol addition reaction of 2-cyano-1,10-phenanthroline in presence of sodium methoxide [3,4], directly reacts with $MnCl_2 \cdot 4H_2O$ to form complex 4 in good isolated yield (method B). In the IR spectra, the strong peak at 3195 and 1644 cm^{-1} of complex 4 corresponded to the stretching vibration bands of N–H bond and C=N double bond, respectively, which appeared at 3287 and 1645 cm^{-1} for the corresponding free 2-methoxyimidate-1,10-phenanthroline 10. Moreover, the recrystallization of complex 1 in methanol readily gave the crystals of complex 4 in good yield (method C). This means the methanol addition reaction of nitrile group is accelerated in the presence of manganese dichloride within its metal complex. In fact, complexes 2 and 3 also transformed into their correspondent 2-alkoxyimidate-1,10-phenanthroline complexes 5,6 during recrystallizating them in alcohols; these indicate the transformation of imidate from cyano group favored in presence of metal salts. That could be explain that the coordination interaction between phenanthroline with metal caused a change of an electronic density of the ligand and resulted to make C≡N bond weak. Moreover, in the metal-induced alkoxylation of nitrile, the acidic protonation quickly leads to the enol of an amide (alkoxyimidate). However, the trial for developing catalytic process in forming 2-alkoxyimidate-1,10-phenanthroline
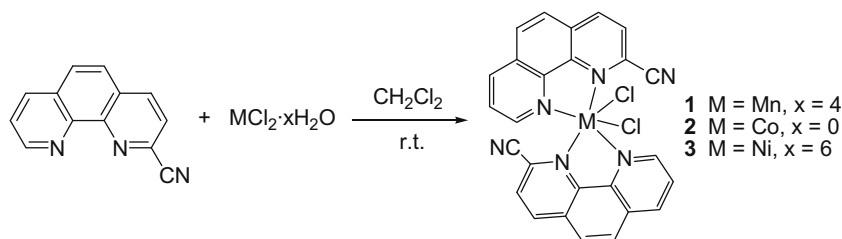
Scheme 1. Syntheses of complexes 1–3 bearing two 2-cyano-1,10-phenanthrolines.
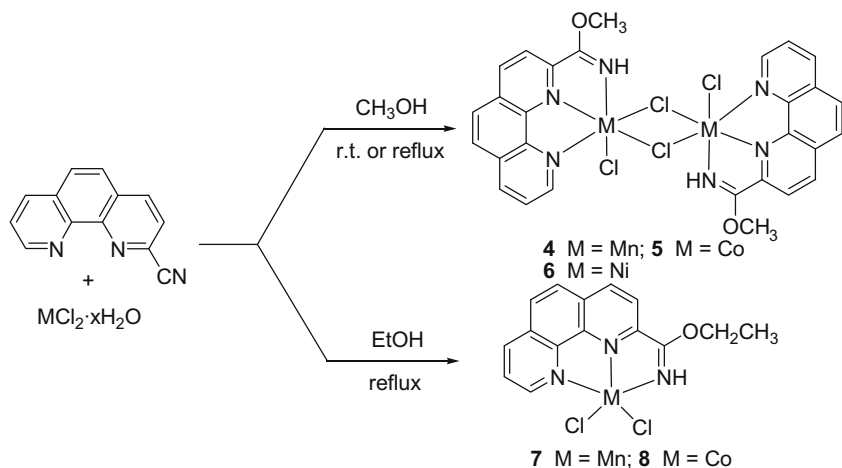
Scheme 2. Syntheses of 2-alkoxyimidate-1,10-phenanthroline metal complexes 4–8.
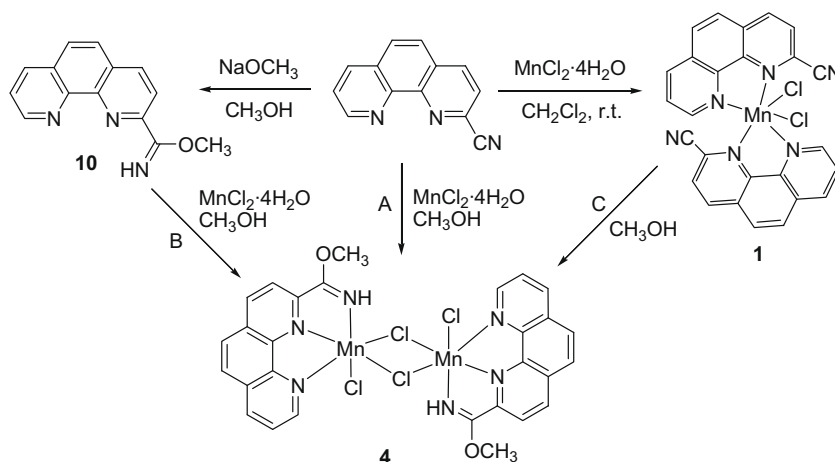
Scheme 3. Alternative formations of 2-methoxyimidate-1,10-phenanthroline manganese complex **4**.

from 2-cyano-1,10-phenanthroline was not successful in the presence of 0.1 equivalent $MnCl_2 \cdot 4H_2O$. It could be plausible the strong coordination happened in forming 2-alkoxyimidate-1,10-phenanthroline manganese complex.

Complex **4** is an air-stable powder in the solid state, however, exposing its methanol solution in the air for several days or being treated with water could lead to the formation of manganese carboxylate complex **9** due to the nucleophilic attack by water and forming carboxylate compound with the lowest enthalpy. Alternatively, the manganese carboxylate complex **9** could be also prepared in the reaction of 2-carboxy-1,10-phenanthroline with $MnCl_2 \cdot 4H_2O$ in base aqueous solution (Scheme 4).

Single crystals of complex **1** suitable for X-ray diffraction analysis were obtained by layering diethyl ether onto its CH_2Cl_2-DMF solution. Crystals of complexes **4** and **5** were grown through layering diethyl ether onto their CH_3OH-DMF solutions individually. Crystals of complex **7** were obtained by slow diffusion of diethyl ether into its EtOH-DMF solution. When complex **4** was treated with water, and the resultant yellow solution was then layered with methanol to give the yellow crystals of complex **9**.

The molecular structure of complex **1** is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. In the structure, the central manganese atom is coordinated by two chlorides and two phenanthrolines derivatives as bidentate ligands. The coordination geometry around the metal center can be described as a distorted octahedron, which is similar to other manganese complexes containing phenanthroline ligands [33–35]. The two phenanthroline rings form a dihedral angle of 78.43°. The two chlorides are located in the *cis*-positions. There is a large difference in bond lengths of the two Mn–N bonds with the distances of 2.237(5) Å and 2.469(4) Å, respectively, because of the existence of the free cyano group at the 2-position of phenanthroline ring.

And the Mn–Cl bond length is 2.4269(2) Å. The bond angles around the metal center are in the range of 69.91(2)–163.3(2)°. The cyano group retained free of coordination with metal core along with the typical triple bond character of C≡N with the distance of 1.125(9) Å.

Both methoxyimidate manganese complex **4** and cobalt complex **5** show a centrosymmetric dimeric structure in the solid state as shown in Figs. 2 and 3, respectively, and their selected bond lengths and angles are collected in Table 2.

They have very similar geometries and structural features, therefore, the manganese **4** will be discussed as a representative in detail below. The coordination geometry of each manganese center can be described as a distorted octahedron. Each manganese atom is coordinated to three nitrogen atoms from the imidate ligand, one terminal chloride and two bridging chlorides. The bridges and the two metal centers are coplanar and a Mn···MnA distance of 3.878 Å is observed, suggesting that there is no direct metal–metal interaction. Each manganese atom forms two five-membered chelate rings with three coordinated nitrogen atoms; and the bite angles of N2–Mn–N1 and N2–Mn–N3 are 71.03(4)° and 71.28(4)°, respectively. The distance between the metal center

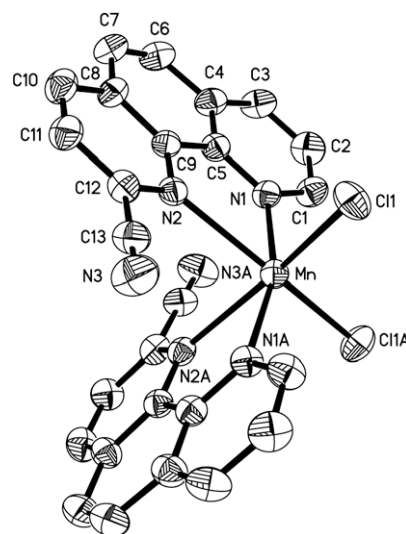**Scheme 4.** Synthesis of 2-carboxylate-1,10-phenanthroline manganese complex **9**.
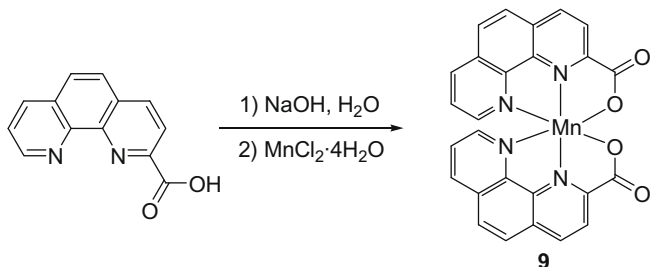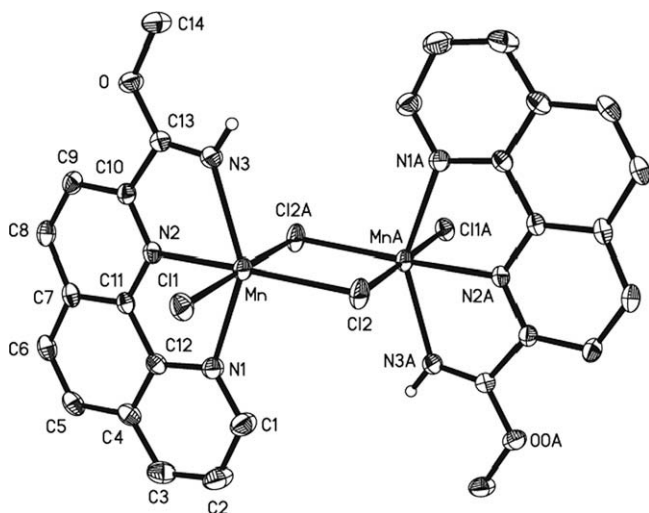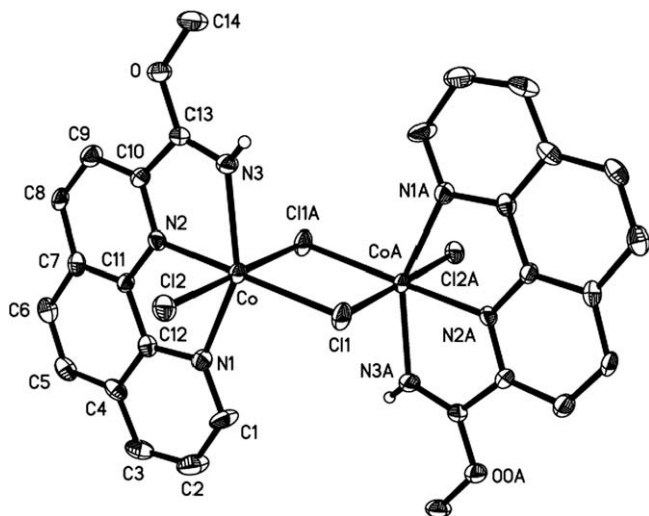

Fig. 1. Molecular structure of complex **1** with thermal ellipsoids at 30% probability level. Hydrogen atoms and solvent dichloromethane molecules have been omitted for clarity.

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

Bond lengths			
Mn–N1	2.237(5)	Mn–Cl1	2.427(2)
Mn–N2	2.469(5)	C13–N3	1.123(10)
Bond angles			
N1–Mn–N1A	163.2(3)	N1–Mn–Cl1	94.40(13)
N2–Mn–N2A	83.7(2)	N1–Mn–Cl1A	95.99(14)
Cl1–Mn–Cl1A	103.26(11)	N2–Mn–Cl1	88.68(12)
N1–Mn–N2	69.91(2)	N2–Mn–Cl1A	161.37(13)
N1–Mn–N2A	97.31(18)		

Table 2
Selected bond lengths (Å) and angles (°) for complexes **4**, **5** and **7**.

4		5		7	
Bond lengths					
Mn–N1	2.3699(1)	Co–N1	2.252(6)	Mn–N1	2.378(2)
Mn–N2	2.2199(1)	Co–N2	2.075(5)	Mn–N2	2.2030(2)
Mn–N3	2.2853(1)	Co–N3	2.197(6)	Mn–N3	2.249(2)
Mn–Cl1	2.4730(4)	Co–Cl1	2.350(2)	Mn–Cl1	2.3651(9)
Mn–Cl2	2.4252(4)	Co–Cl2	2.429(2)	Mn–Cl2	2.3469(7)
Mn–Cl2A	2.7595(4)	Co–Cl1A	2.632(2)		
C13–N3	1.2677(2)	C13–N3	1.264(9)	C13–N3	1.255(3)
C13–O	1.3382(2)	C13–O	1.340(8)	C13–O1	1.335(3)
Bond angles					
N2–Mn–N1	71.03(4)	N2–Co–N1	74.8(2)	N2–Mn–N1	70.73(7)
N2–Mn–N3	71.28(4)	N2–Co–N3	74.2(2)	N2–Mn–N3	71.52(8)
N3–Mn–N1	142.28(4)	N3–Co–N1	149.0(2)	N3–Mn–N1	141.72(8)
N1–Mn–Cl1	90.80(3)	N1–Co–Cl1	99.75(2)	N1–Mn–Cl1	98.75(6)
N1–Mn–Cl2	101.08(3)	N1–Co–Cl2	89.94(2)	N1–Mn–Cl2	97.09(6)
N2–Mn–Cl1	95.59(3)	N2–Co–Cl1	168.73(2)	N2–Mn–Cl1	110.38(6)
N2–Mn–Cl2	163.52(3)	N2–Co–Cl2	93.12(2)	N2–Mn–Cl2	132.67(6)
N3–Mn–Cl1	94.12(4)	N3–Co–Cl1	110.67(2)	N3–Mn–Cl1	99.99(7)
N3–Mn–Cl2	114.95(3)	N3–Co–Cl2	92.00(2)	N3–Mn–Cl2	103.70(6)
Cl2–Mn–Cl1	99.025(2)	Cl1–Co–Cl2	96.79(7)	Cl2–Mn–Cl1	116.72(3)
N1–Mn–Cl2A	85.30(3)	N1–Co–Cl1A	87.63(2)		
N2–Mn–Cl2A	81.59(3)	N2–Co–Cl1A	85.45(2)		
N3–Mn–Cl2A	87.98(4)	N3–Co–Cl1A	89.66(2)		
Cl1–Mn–Cl2A	175.764(1)	Cl1–Co–Cl1A	84.45(7)		
Cl2–Mn–Cl2A	83.381(1)	Cl2–Co–Cl1A	177.43(6)		

Fig. 2. Molecular structure of complex **4** with thermal ellipsoids at 30% probability level. Hydrogen atoms except imidato-hydrogen have been omitted for clarity.

Fig. 3. Molecular structure of complex **5** with thermal ellipsoids at 30% probability level. Hydrogen atoms except imidato-hydrogen have been omitted for clarity.

accordance with the typical C=N double bond, confirming the formation of imine bond during the reaction.

In the solid state, complex **4** displays intermolecular hydrogen bonding interactions between the terminal chloride (Cl1) and the hydrogen atom of N3–H11 bond (Fig. 4). Such hydrogen bondings between the neighboring molecules result in a 1-D infinite chain, as shown in Fig. 3, in which the correspondent phenanthroline rings are approximately in parallel. The hydrogen bonding angle of N3–H11···Cl1 is 164.50° and the distances of H11···Cl1 and N3···Cl1 are 2.462 and 3.327 Å, respectively.

Unlike complex **4**, the ethoxyimidate manganese complex **7** possesses a mononuclear structure with a distorted trigonal bipyramidal geometry around the metal center, in which N2 and two chlorides compose an equatorial plane (Fig. 5), and its selected bond lengths and angles are also listed in Table 2. In the structure of **7**, the manganese atom slightly deviates by 0.0635 Å from the triangular plane of N2, Cl1 and Cl2. The equatorial plane is almost perpendicular to the phenanthroline ring with a dihedral angle of 89.6°. The equatorial bond angles, N2–Mn–Cl1, N2–Mn–Cl2 and Cl2–Mn–Cl1 are 110.38(6)°, 132.67(6)° and 116.72(3)°, respectively. The axial Mn–N1 and Mn–N3 bonds form an angle of 141.72(8)° (N3–Mn–N1). Similarly, the Mn–N2 bond (2.2030 (2) Å) is slightly shorter than Mn–N1 (2.378(2) Å) and Mn–N3 (2.249(2) Å) bonds, whereas the distances of two Mn–Cl bonds are very close. The C13–N3 bond length is 1.255(3) Å, with the typical character of a C=N double bond.

In complex **9**, the manganese atom is coordinated by two oxygen atoms and four nitrogen atoms from two ligands of phenanthroline carboxylate monoanion (Fig. 6). The selected bond lengths and angles are collected in Table 3. The coordination geometry around the manganese center can be described as a distorted octahedron, in which the two oxygens dispose in a *cis*-fashion. The two phenanthroline planes are nearly perpendicular forming a dihedral angle of 87.90°. The bond angles around the metal center change in the range of 70.40(1)° (N2–Mn–N1) to 153.08(1)° (N2–Mn–N2A). There is a large difference between the Mn–N1 (2.439(3) Å) and Mn–N2 (2.174(3) Å) bond length. The distance of Mn–O1 bond is 2.149(3) Å. Because of the delocalization of electrons in the carboxylate group, the two C–O bonds just have a little

and the terminal chloride (Mn–Cl1) is 2.4730(4) Å; whereas, the distances of the manganese atom and the two bridging chlorides differ obviously with the bond lengths of 2.4252(4) and 2.7595(4) Å. The Mn–N2 bond (2.2199(1) Å) is slightly shorter than Mn–N1 (2.3699(1) Å) and Mn–N3 (2.2853(1) Å) bonds, which is similar to other metal complexes ligated by phenanthroline derivatives [11–15,17,18]. The C13–N3 bond distance is 1.2677(2) Å, in
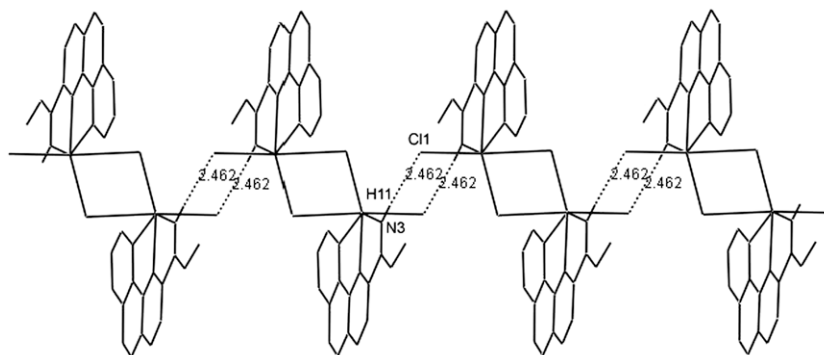
Fig. 4. The 1-D chain formed by intermolecular hydrogen bonding interactions (N3–H11···Cl1) in solid state of complex **4**.
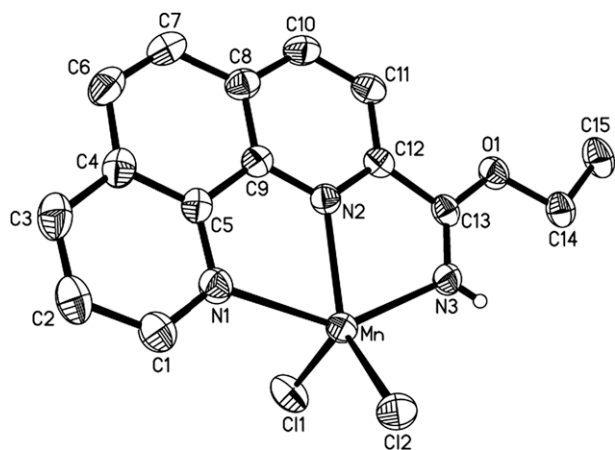

Fig. 5. Molecular structure of complex **7** with thermal ellipsoids at 30% probability level. Hydrogen atoms except imidato-hydrogen and solvent ethanol molecule have been omitted for clarity.

Fig. 6. Molecular structure of complex **9** with thermal ellipsoids at 30% probability level. Hydrogen atoms and water molecules have been omitted for clarity.

difference; the O1–C13 bond (1.273(4) Å) is slightly longer than the O2–C13 bond (1.230(4) Å) due to the coordination of O1 to the metal center weakening the strength of C–O bond.

3. Catalytic ethylene oligomerization

In the presence of some alkylaluminums as co-catalyst, complexes **1–8** were investigated for ethylene oligomerization. On

Table 3
Selected bond lengths (Å) and angles (°) for complex **9**.

Bond lengths			
Mn–O1	2.149(3)	Mn–O1A	2.160(3)
Mn–N1	2.439(3)	Mn–N1A	2.374(3)
Mn–N2	2.174(3)	Mn–N2A	2.174(3)
O1–C13	1.273(4)	O1A–C13A	1.268(4)
O2–C13	1.230(4)	C13A–O2A	1.239(4)
Bond angles			
N2–Mn–N1	70.40(1)	O1–Mn–O1A	105.60(1)
N1A–Mn–N1	91.51(1)	O1A–Mn–N1A	143.58(1)
N2A–Mn–N1	86.51(1)	O1–Mn–N2	73.93(1)
O1–Mn–N1	144.33(1)	O1A–Mn–N2	119.76(1)
O1A–Mn–N1	91.94(1)	N2–Mn–N2A	153.08(1)
N2–Mn–N1A	95.46(1)	O1–Mn–N2A	127.96(1)
N2A–Mn–N1A	70.81(1)	O1A–Mn–N2A	73.24(1)
O1–Mn–N1A	92.08(1)	O2A–C13A–O1A	126.0(4)
O2–C13–O1	126.9(4)		

activation with methylaluminoxane (MAO), modified methylaluminoxane (MMAO), or diethylaluminum chloride (Et_2AlCl), manganese complexes **1**, **4** and **7** only showed low activities for ethylene dimerization ($\leqslant$1200 g mol^{-1} h^{-1}). Therefore, manganese complexes were not interested in ethylene oligomerization. Under the same conditions, fortunately, cobalt complexes **2**, **5** and **8** gave higher activities for ethylene oligomerization (Table 4); among them, complex **2** coordinating two 1,10-phenanthroline

Table 4
Ethylene oligomerization with cobalt and nickel complexes.[a]

Entry	Complex	Cocat	Al/M	Activity[b]	% Oligomer distribution[c]		% 1 – C$_4$[c]
					C$_4$/$\sum$C	C$_6$/$\sum$C	
1	**2**	MAO	500	0.10	100	–	40.2
2	**2**	MMAO	500	0.80	96.5	3.5	32.4
3	**2**	Et$_2$AlCl	200	0.24	100	–	6.7
4	**3**	MAO	500	1.77	86.9	13.1	57.2
5	**3**	MMAO	500	3.58	86.8	13.2	56.7
6	**3**	Et$_2$AlCl	200	4.25	88.7	11.3	51.8
7	**5**	MAO	500	1.06	100	–	40.4
8	**5**	MMAO	500	2.60	100	–	80.4
9	**5**	Et$_2$AlCl	200	5.34	87.1	12.9	61.7
10	**6**	MAO	500	4.61	85.0	15.0	53.0
11	**6**	MMAO	500	4.43	82.7	17.3	67.2
12	**6**	Et$_2$AlCl	200	32.3	83.4	16.6	19.1
13	**8**	MAO	500	0.58	100	–	56.0
14	**8**	MMAO	500	2.11	100	–	>99
15	**8**	Et$_2$AlCl	200	0.62	92.2	7.8	61.9

[a] *Conditions*: 5 μmol metal; 30 mL toluene; 25 °C; 30 min; 1 atm ethylene.
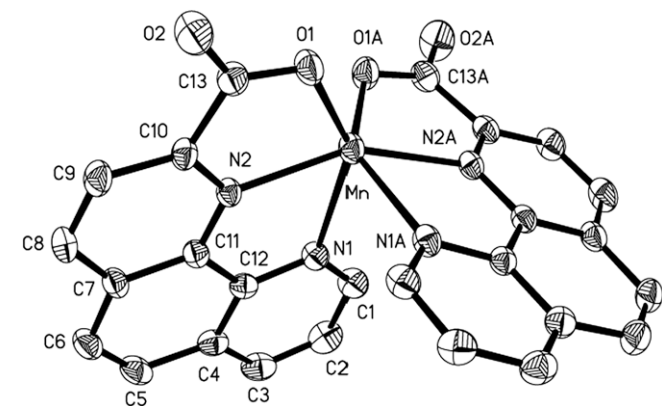[b] 10^4 g mol^{-1} h^{-1}.
[c] Weight percentage determined by GC.

ligands with nitrile group was less active and the activities were not more than 2400 g mol^{-1} h^{-1}; whereas 2-methoxyimidate-1,10-phenanthroline complex **5** was the most active one in the presence of Et$_2$AlCl (Al/Co = 200:5.34 × 10^4 g mol^{-1} h^{-1}, entry 9 in Table 4). For the ethoxyimidate-1,10-phenanthroline complex **8**, MMAO was found to be the most active co-catalyst. In employing MAO or Et$_2$AlCl as co-catalyst, complex **8** showed much lower activity than complex **5** did. For the nickel complexes with 2-cyano- and 2-methoxyimidate-1,10-phenanthroline ligands, the complexes **3** and **6** were more active in ethylene oligomerization (Table 4) than the corresponding manganese and cobalt complexes were, and some amount of hexenes were also produced. For instance, in the presence of 200 equiv. of Et$_2$AlCl at 1 atm of ethylene pressure, nickel complex **6** exhibited the highest activity up to 3.23 × 10^5 g mol^{-1} h^{-1} for ethylene oligomerization with the selectivity of 19.1% for 1-butene (entry 12 in Table 4).

In both of cobalt and nickel catalytic systems, complexes (**2** and **3**) bearing 2-cyano-1,10-phenanthroline showed lower catalytic activities than complexes (**5**, **6** and **8**) did; that could be caused that two ligands in complexes **2** and **3** occupied space around active metal center and hindered the coordination of ethylene for reaction. It should be also addressed, there was no polyethylene observed in all catalytic systems.

Based on the above results, nickel complex **6** was investigated for optimum reaction condition, and the results were given in Table 5. Increasing the Al/Ni molar ratio in the range of 100–500 resulted in an increase in the activity to 3.85 × 10^5 g mol^{-1} h^{-1} at the optimal Al/Ni molar ratio of 300 and then a gradual decrease; however, the distribution of oligomers and the selectivity for 1-butene did not have a great change. The reaction temperature was found to have a remarkable influence on the catalytic activity and the distribution of oligomers. The highest activity within 30 min of reaction time was obtained at 5 °C and 91.2% of butanes were observed in the oligomeric products with the selectivity of 41.9% for 1-butene. At lower temperature, the consumption of ethylene could last longer time, and the activity was slightly decreased within 60 min with increasing amount of hexenes, whereas the selectivity for 1-butene decreased dramatically (2.0%). An elevated reaction temperature led to a decrease of the catalytic activity and an increase of the butene content. When the reaction temperature was increased to 60 °C, the activity decreased to 1.28 × 10^4 g mol^{-1} h^{-1} including 93.2% of butenes in the products with the selectivity of 42.3% for 1-butene. The catalytic activity could also be improved with an increase of ethylene pressure. When the ethylene pressure was increased to 10 atm from 1 atm, the catalytic activity of complex **6** increased to 8.71 × 10^5 g mol^{-1} h^{-1} with 84.1% selectivity for 1-butene (entry 10 in Table 5).

It is necessary to understand the scope of metal complexes with various 1,10-phenanthroline derivatives for ethylene reactivity. In comparison with metal complexes ligated with other 1,10-phenanthroline derivatives [10–18], however, the titled complexes showed much lower catalytic activities towards ethylene oligomerization, and the high flexibilities of nitrile and alkoxyimidate groups in their ligands would be the cause.

4. Conclusion

The metal (Mn, Co or Ni) complexes ligated by 2-carboxyimidate-1,10-phenanthroline were formed in the reaction of 2-cyano-1,10-phenanthroline with metal dichloride in alcohol, meanwhile the metal complexes bearing two 2-cyano-1,10-phenanthrolines were isolated in the reactions with non-protonic solvents. The alkoxyimidation of nitrile linked on ligand was speeded in the presence of metal salt with forming the 2-alkoxyimidate-1,10-phenanthrolinyl metal complexes. The investigation for ethylene oligomerization displayed that manganese complexes showed low activities, cobalt complexes showed low to moderate activities, while nickel complexes gave moderate to good catalytic activities. In the presence of Et$_2$AlCl, methoxyimidate nickel complex **6** was most active and produced butenes and hexenes.

5. Experimental

5.1. General considerations

IR spectra were recorded on a Thermo Nicolet 6700 instrument by using KBr disc in the range 4000–650 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker DMX-300 instrument with TMS as the internal standard. Elemental C, H, N analyses were performed on a Flash EA 1112 microanalyzer. GC analyses were performed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB capillary column. The yield of oligomers was calculated by referencing to the mass of solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated area in the GC trace.

Toluene was refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Corp (USA). Diethylaluminum chloride (Et$_2$AlCl, 2 mol/L M in hexane) were purchased from Acros Chemicals. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

Table 5
Ethylene oligomerization with complex **6** under various reaction conditions.[a]

Entry	Al/Ni	T (°C)	P (atm)	Activity[b]	% Oligomer distribution[c]			% 1 − C$_4$[c]
					C$_4$/$\sum$C	C$_6$/$\sum$C	C$_{\geqslant 8}$/$\sum$C	
1	100	25	1	29.5	85.2	14.8	–	17.5
2	200	25	1	32.3	83.4	16.6	–	19.1
3	300	25	1	38.5	84.2	15.8	–	17.7
4	400	25	1	34.1	86.1	13.9	–	17.2
5	500	25	1	29.9	89.3	10.7	–	16.0
6	300	5	1	40.3	91.2	8.8		41.9
7[d]	300	5	1	39.4	75.4	21.0	3.6	2.0
8	300	40	1	20.2	90.6	9.4	–	23.2
9	300	60	1	1.28	93.2	6.8	–	42.3
10	200	30	10	87.1	91.1	5.6	3.3	84.1

[a] *Conditions*: 5 μmol Ni; cocat: Et$_2$AlCl; 30 min; toluene: 30 mL for 1 atm and 100 mL for 10 atm.
[b] 10^4 g mol^{-1} h^{-1}.
[c] Weight percentage determined by GC.
[d] Reaction time: 60 min.

5.2. Synthesis of the complexes **1**–**10**

*[2-CN-1,10-phen]$_2$MnCl$_2$ (**1**):* The 2 equiv. of 2-cyano-1,10-phenanthroline (0.449 g, 2.2 mmol) was dissolved in 15 mL of dichloromethane, to which 1 equiv. of solid MnCl$_2 \cdot$ 4H$_2$O (0.217 g, 1.1 mmol) was added. The reaction mixture was stirred at room temperature for 1 day and a pale yellow precipitate formed. It was isolated by filtration, washed with diethyl ether, and dried under vacuum giving the final product as a pale yellow powder (0.495 g, 85.0% yield). FT-IR (KBr disk, cm^{-1}): 3060 (s), 3013 (m, sh), 2240 (s, $v_{C\equiv N}$), 1622 (vs), 1603 (m), 1588 (m), 1566 (m), 1510 (vs), 1491 (vs), 1451 (m), 1416 (s), 1395 (vs), 1318 (m), 1299 (s), 1146 (s), 1096 (s), 906 (m), 886 (vs), 871 (vs, sh), 840 (m), 770 (m), 741 (vs), 727 (s). Anal. Calc. for C$_{26}$H$_{14}$Cl$_2$MnN$_6$ (536.27): C, 58.23; H, 2.63; N, 15.67. Found: C, 57.88; H, 2.72; N, 15.19%.

*[2-CN-1,10-phen]2CoCl$_2$ (**2**):* In a manner similar to that described for complex **1**, complex **2** was prepared from 2-cyano-1,10-phenanthroline (0.206 g, 1.0 mmol) and CoCl$_2$ (0.065 g, 0.5 mmol) as a pale red powder (0.243 g) in 89.5% of yield. FT-IR (KBr disk, cm^{-1}): 3058 (s), 2236 (s, $v_{C\equiv N}$), 1623 (vs), 1604 (m), 1569 (m), 1510 (vs), 1491 (vs), 1452 (m), 1426 (s), 1397 (vs), 1321 (m), 1301 (s), 1145 (s), 1096 (s), 867 (vs), 775 (s), 740 (vs). Anal. Calc. for C$_{26}$H$_{14}$Cl$_2$CoN$_6$ (540.27): C, 57.80; H, 2.61; N, 15.56. Found: C, 57.78; H, 2.68; N, 15.58%.

*[2-CN-1,10-phen]2NiCl$_2$ (**3**):* In a manner similar to that described for complex **1**, complex **3** was prepared from 2-cyano-1,10-phenanthroline (0.103 g, 0.5 mmol) and NiCl$_2 \cdot$ 6H$_2$O (0.060 g, 0.25 mmol) as a pale green powder (0.119 g) in 87.3% of yield. FT-IR (KBr disk, cm^{-1}): 3064 (vs), 2974 (s), 2238 (s, $v_{C\equiv N}$), 1624 (vs), 1604 (m), 1582 (s), 1568 (m, sh), 1509 (vs), 1492 (vs), 1452 (m), 1419 (s), 1395 (vs), 1301 (s), 1224 (s), 1206 (m), 1144 (s), 1107 (m), 1094 (s), 866 (vs), 774 (s), 739 (vs), 730 (vs). Anal. Calc. for C$_{26}$H$_{14}$Cl$_2$N$_6$Ni (540.03): C, 57.83; H, 2.61; N, 15.56. Found: C, 57.37; H, 2,67; N, 15.46%.

*{[2-(HN=COCH$_3$)-1,10-phen]MnCl$_2$}$_2$ (**4**):* There are three procedures used in preparing this complex, and detail illustrated in the followings:

Method A: To a suspension of 2-cyano-1,10-phenanthroline (0.206 g, 1.0 mmol) in 10 mL of methanol, 1 equiv. of solid MnCl$_2 \cdot$ 4H$_2$O (0.110 g, 1.0 mmol) was added. A pale yellow precipitate formed quickly and then the reaction mixture was refluxed for 30 h. During the stirring, the precipitate changed to yellow color gradually. The final product was isolated by filtration, washed with diethyl ether, dried under vacuum and obtained as a yellow powder (0.283 g, 78.3% yield).

Method B: Sodium (0.030 g, 1.25 mmol) was added to 50 mL of methanol to make a solution of sodium methoxide and then 2-cyano-1,10-phenanthroline (2.052 g, 10.0 mmol) was added. The reaction mixture was heated up until the entire solid dissolved into a brown-yellow solution. This solution was then allowed to be stirred overnight at room temperature. Acetic acid (4 drops) was added to neutralize the solution and then the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane and filtered to remove the inorganic salt. After the evaporation of dichloromethane, orange oil was obtained, which was treated with diethyl ether to afford an orange solid. The final product, 2-methoxyimidate-1,10-phenanthroline (**10**), was collected by filtration, washed with diethyl ether and dried under vacuum as a slightly orange solid (1.660 g, 70.0% yield). FT-IR (KBr disk, cm^{-1}): 3287 (s, v_{N-H}), 3026 (s), 2993 (s), 2948 (s, sh), 1645 (vs, $v_{C=N}$), 1616 (m), 1554 (s), 1505 (m), 1494 (s), 1458 (m), 1440 (s), 1393 (vs), 1347 (s), 1192 (s), 1105 (s), 1083 (m), 970 (s), 865 (vs), 707 (vs). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.75 (br, 1H, N*H*); 9.24 (d, *J* = 3.2 Hz, 1H); 8.33 (d, *J* = 8.4 Hz, 1H); 8.26 (d, *J* = 8.0 Hz, 1H); 8.18 (d, *J* = 8.4 Hz, 1H); 7.82 (s, 2H); 7.67 (dd, *J* = 7.6 Hz, 1H); 4.11 (s, 3H, OC*H*$_3$).

2-Methoxyimidate-1,10-phenanthroline (0.236 g, 1.0 mmol) and 1 equiv. of MnCl$_2 \cdot$ 4H$_2$O (0.200 g, 1.0 mmol) were mixed together and then 6 mL of methanol was added as a solvent. The reaction mixture was stirred at room temperature for 9 h. The resulting yellow precipitate was isolated by filtration, washed with diethyl ether, and dried under vacuum yielding the final product as a yellow powder (0.319 g, 88.2% yield).

Method C: The isolated complex **1** (0.117 g, 0.2 mmol) was suspended in 10 mL of methanol and the mixture was stirred at room temperature. The pale yellow solid changed to yellow gradually. After being stirred for 6 h, the resulting yellow solid was filtered, washed with methanol and diethyl ether, and dried under vacuum to give complex **4** as a yellow solid (0.047 g, 58.6% yield). FT-IR (KBr disk, cm^{-1}): 3195 (s, v_{N-H}), 3045 (s), 2946 (s), 1644 (s, $v_{C=N}$), 1615 (vs), 1605 (s, sh), 1586 (s), 1574 (m), 1511 (m), 1499 (vs), 1462 (vs), 1446 (m, sh), 1431 (m), 1410 (m), 1355 (s), 1343 (w, sh), 1302 (s), 1213 (m), 1196 (s), 1139 (m), 1094 (s), 976 (s), 888 (m), 867 (vs), 835 (s), 787 (s), 724 (vs), 703 (m, sh). Anal. Calc. for C$_{28}$H$_{22}$Cl$_4$Mn$_2$N$_6$O$_2$ (726.20): C, 46.31; H, 3.05; N, 11.57. Found: C, 46.36; H, 3.16; N, 11.29%.

*{[2-(HN=COCH$_3$)-1,10-phen]CoCl$_2$}$_2$ (**5**):* 2-Cyano-1,10-phenanthroline (0.103 g, 0.5 mmol) was dissolved in 10 mL of methanol under heating, to which solid CoCl$_2$ (0.065 g, 0.5 mmol) was added. The reaction mixture was refluxed for 9 h to produce a deep-red solution. The solvent was evaporated and the green residue was washed with dichloromethane and diethyl ether and dried under vacuum to give a green powder (0.176 g, 95.3% yield). FT-IR (KBr disk, cm^{-1}): 3169 (s, v_{N-H}), 3049 (s), 3004 (s), 2945 (s), 1639 (s, $v_{C=N}$), 1616 (vs), 1607 (s, sh), 1577 (m), 1512 (m), 1500 (vs), 1463 (vs), 1411 (m), 1364 (s), 1346 (m, sh), 1307 (s), 1214 (m), 1199 (s), 1145 (m), 1104 (m), 1096 (s), 976 (s), 866 (vs), 789 (s), 724 (vs), 700 (m, sh). Anal. Calc. for C$_{28}$H$_{22}$Cl$_4$Co$_2$N$_6$O$_2$ (734.19): C, 45.81; H, 3.02; N, 11.45. Found: C, 46.07; H, 2.79; N, 11.24%.

*{[2-(HN=COCH$_3$)-1,10-phen]NiCl$_2$}$_2$ (**6**):* In a manner similar to that described for complex **5**, complex **6** was prepared from 2-cyano-1,10-phenanthroline (0.170 g, 0.83 mmol) and (DME)NiCl$_2$ (0.182 g, 0.83 mmol) in refluxed methanol as a yellow-green powder (0.280 g) in 92.2% of yield. FT-IR (KBr disk, cm^{-1}): 3178 (s, v_{N-H}), 3050 (s), 2944 (s), 1638 (s, $v_{C=N}$), 1616 (vs), 1609 (s, sh), 1580 (s), 1512 (m), 1463 (vs), 1414 (m), 1365 (s), 1348 (m, sh), 1307 (s), 1214 (s), 1198 (s), 1144 (m), 1098 (s), 877 (s, sh), 866 (vs), 789 (s), 724 (vs), 700 (s, sh). Anal. Calc. for C$_{28}$H$_{22}$Cl$_4$N$_6$Ni$_2$O$_2$ (733.71): C, 45.84; H, 3.02; N, 11.45. Found: C, 45.59; H, 3.14; N, 11.03%.

*[2-(HN=COCH$_2$CH$_3$)-1,10-phen]MnCl$_2$ (**7**):* 2-Cyano-1,10-phenanthroline (0.103 g, 0.5 mmol) was dissolved in 10 mL of ethanol under heating, to which solid MnCl$_2 \cdot$ 4H$_2$O (0.098 g, 0.5 mmol) was added. A pale yellow precipitate formed immediately and then the reaction mixture was refluxed for 6 h. During the reflux, the precipitate changed to yellow gradually. The resulting precipitate was isolated by filtration, washed with ethanol and diethyl ether, and dried under vacuum to yield a yellow powder (0.145 g, 77.5% yield). FT-IR (KBr disk, cm^{-1}): 3279 (s, v_{N-H}), 1640 (s, $v_{C=N}$), 1616 (vs), 1603 (s, sh), 1573 (s), 1510 (m), 1457 (vs), 1416 (m), 1400 (m), 1376 (s), 1348 (m), 1308 (s), 1192 (s), 1156 (m), 1133 (m), 1102 (s), 1009 (m), 875 (vs), 805 (s), 725 (vs), 702 (m). Anal. Calc. for C$_{15}$H$_{13}$Cl$_2$MnN$_3$O (377.13): C, 47.77; H, 3.47; N, 11.14. Found: C, 47.80; H, 3.58; N, 10.94%.

*[2-(HN=COCH$_2$CH$_3$)-1,10-phen]CoCl$_2$ (**8**):* In a manner similar to that described for complex **7**, complex **8** was prepared from 2-cyano-1,10-phenanthroline (0.104 g, 0.5 mmol) and CoCl$_2$ (0.067 g, 0.5 mmol) in refluxed ethanol as a green powder (0.140 g, 72.6% yield). FT-IR (KBr disk, cm^{-1}): 3271 (s, v_{N-H}), 3048 (s), 2983 (s), 1636 (s, $v_{C=N}$), 1616 (vs), 1604 (s, sh), 1574 (s), 1511 (m), 1457 (vs), 1417 (m), 1401 (m), 1376 (s), 1349 (m), 1339 (m), 1308 (s), 1191 (s), 1156 (m), 1133 (m), 1103 (s), 1010 (m), 875 (vs), 806

(s), 725 (vs), 701 (m). Anal. Calc. for $C_{15}H_{13}Cl_2CoN_3O$ (381.12): C, 47.27; H, 3.44; N, 11.03. Found: C, 46.99; H, 3.48; N, 11.05%.

[2-(COO)-1,10-phen]$_2$Mn **(9):** 2-Carboxyl-1,10-phenanthroline (0.114 g, 0.51 mmol) and NaOH (0.040 g, 1.0 mmol) were stirred in 10 mL of water yielding a yellow solution, to which solid $MnCl_2 \cdot 4H_2O$ (0.051 g, 0.26 mmol) was added. A yellow precipitate formed immediately and then the mixture was stirred at room temperature for 2 h. The resulting precipitate was isolated by filtration, washed with water, and dried under vacuum to give a yellow solid (0.123 g, 96.5% yield). FT-IR (KBr disk, cm^{-1}): 3413 (s, br), 1634 (s, $v_{C=O}$), 1574 (s), 1507 (m), 1492 (m), 1400 (m), 1357 (s), 1329 (m), 1298 (s), 1176 (s), 870 (vs), 843 (m), 821 (s), 720 (s). Anal. Calc. for $C_{26}H_{14}MnN_4O_4 \cdot 2H_2O$ (537.38): C, 58.11; H, 3.38; N, 10.43. Found: C, 58.53; H, 3.52; N, 10.81%.

6. General procedure for ethylene oligomerization

At 1 atm ethylene: A flame-dried, three-neck flask was loaded with the precatalyst and purged three times by nitrogen. Ethylene was then charged in the flask along with freshly distilled toluene and the mixture stirred for 30 minutes under 1 atm of ethylene pressure. The reaction temperature was controlled with a water bath and the required amount of co-catalyst was then injected with a syringe. The reaction mixture was stirred for the required time and the mixture was cooled with an ice bath. Then the reaction was quenched by addition of 5% aqueous hydrogen chloride. The contents and distribution of oligomers were determined by GC.

At 10 atm ethylene: A 250-mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller was heated in *vacuo* for at least 2 h at over 80 °C, then cooled to the required reaction temperature under ethylene atmosphere and charged with toluene, the desired amount of co-catalyst, and a toluene solution of the precatalyst; the total volume was 100 mL. The reactor was sealed and pressurized to 10 atm of ethylene pressure at the required reaction temperature, and the ethylene pressure was maintained with a feed of ethylene. After the required time, the autoclave was cooled with an ice bath for one hour, then the pressure was released and a small amount of the reaction solution was collected and quenched by addition of 5% aqueous hydrogen chloride. The organic layer was analyzed by GC to determine the composition and mass distribution of the oligomers obtained. Finally, the remaining reaction solution was quenched with 5% hydrochloric acid in ethanol.

7. X-ray crystallography measurements

Single-crystal X-ray diffraction studies for complexes **1**, **4**, **5**, **7** and **9** were carried out on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 Package [36]. Crystallographic data and processing parameters for complexes **1**, **4**, **5**, **7** and **9** are summarized in Table 6.

Appendix A. Supplementary material

CCDC 696154, 696155, 696156, 696157 and 696158 contain the supplementary crystallographic data for **1**, **4**, **5**, **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.jorganchem.2008.09.052.

Table 6
Crystal data and structure refinement for complexes **1**, **4**, **5**, **7** and **9**.

Data	$1 \cdot 2CH_2Cl_2$	4	5	$7 \cdot C_2H_5OH$	$9 \cdot 2H_2O$
Formula	$C_{26}H_{14}Cl_2MnN_6 \cdot 2CH_2Cl_2$	$C_{14}H_{11}Cl_2MnN_3O$	$C_{14}H_{11}Cl_2CoN_3O$	$C_{15}H_{13}Cl_2MnN_3O \cdot C_2H_5OH$	$C_{26}H_{10}MnN_4O_4 \cdot 2H_2O$
Formula weight	706.12	363.10	367.09	423.19	533.35
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
a (Å)	12.9313(7)	7.94030(10)	7.8244(16)	8.33540(10)	10.0220(4)
b (Å)	16.2653(9)	9.8691(2)	9.866(2)	16.0914(2)	10.5569(4)
c (Å)	14.7494(9)	10.8566(2)	10.781(2)	14.8594(2)	12.1397(4)
α (°)	90	64.7550(10)	64.09(3)	90	71.262(2)
β (°)	106.597(4)	86.3130(10)	85.85(3)	105.3710(10)	68.576(2)
γ (°)	90	70.55510(10)	70.27(3)	90	82.263(3)
Volume (Å^3)	2973.0(3)	722.58(2)	701.9(2)	1921.77(4)	1132.06(7)
Z	4	2	2	4	2
$D_{calcd.}$ (mg m^{-3})	1.578	1.669	1.737	1.463	1.565
μ (mm^{-1})	1.014	1.283	1.603	0.98	0.636
$F(000)$	1420	366	370	868	542
Crystal size (mm)	$0.30 \times 0.25 \times 0.20$	$0.30 \times 0.20 \times 0.20$	$0.21 \times 0.20 \times 0.17$	$0.53 \times 0.22 \times 0.09$	$0.20 \times 0.15 \times 0.12$
θ range (°)	2.07–28.38	2.08–28.30	2.11–25.01	1.90–28.30	1.89–28.33
Limiting indices	$-15 \leqslant h \leqslant 15$	$-10 \leqslant h \leqslant 10$	$-9 \leqslant h \leqslant 9$	$-10 \leqslant h \leqslant 6$	$-13 \leqslant h \leqslant 13$
	$-19 \leqslant k \leqslant 19$	$-12 \leqslant k \leqslant 13$	$-11 \leqslant k \leqslant 11$	$-21 \leqslant k \leqslant 21$	$-12 \leqslant k \leqslant 14$
	$-17 \leqslant l \leqslant 17$	$-14 \leqslant l \leqslant 14$	$-12 \leqslant l \leqslant 12$	$-17 \leqslant l \leqslant 19$	$-16 \leqslant l \leqslant 16$
Reflections collected	12464	14373	3925	20078	17853
Unique reflections	2631	3567	2428	4448	5565
Completeness to θ (%)	99.9 (25.00°)	99.1 (28.30°)	98.0 (25. 01°)	93.2 (28.30°)	0.985(28.33°)
Number of parameters	186	194	194	230	334
Goodness-of-fit (GOF) on F^2	1.295	1.08	1.132	1.094	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0996$	$R_1 = 0.0253$	$R_1 = 0.0784$	$R_1 = 0.0428$	$R_1 = 0.0652$
	$wR_2 = 0.3018$	$wR_2 = 0.07$	$wR_2 = 0.2126$	$wR_2 = 0.1357$	$wR_2 = 0.1526$
R indices(all data)	$R_1 = 0.1291$	$R_1 = 0.0298$	$R_1 = 0.0902$	$R_1 = 0.0563$	$R_1 = 0.1094$
	$wR_2 = 0.3311$	$wR_2 = 0.0726$	$wR_2 = 0.2223$	$wR_2 = 0.145$	$wR2 = 0.174$
Largest difference peak, hole (e Å^{-3})	1.157, −1.288	0.356, −0.352	0.929, −0.774	0.769, −0.381	0.631, −0.364

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