Chromium(III) complexes bearing 2-imino-1,10-phenanthrolines: Synthesis, molecular structures and ethylene oligomerization and polymerization

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Abstract

A series of chromium(III) complexes ligated by tridentate ligands of 2-imino-1,10-phenanthrolines, LCrCl$_3$ (L = 2-(2,6-(R^1)$_2$C$_6$H$_3$N=CR)-1,10-phen) was synthesized and characterized by elemental and spectroscopic analyses as well as single-crystal X-ray crystallography. X-ray crystallographic analysis of **2** (R = Ph, R^1 = Et), **4** (R = Me, R^1 = Me) and **12** (R = H, R^1 = i-Pr) reveals that the geometry around the chromium atom is octahedral. Upon activation with MAO, these complexes exhibited high activities for ethylene oligomerization (up to 1.15×10^7 g mol^{-1} (Cr) h^{-1}) and moderate activities for ethylene polymerization. The oligomers and polymers obtained were α-olefins, and the distribution of oligomers resembled the Schultz–Flory rule. Various reaction parameters were investigated in detail, and the results revealed that both the steric and electric effects of ligands affected the catalytic activities of their chromium complexes as well as the distribution of the products.
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Keywords: N^N^N tridentate ligands; 2-Imino-1,10-phenanthrolines; Chromium complex; Ethylene oligomerization; Ethylene polymerization

1. Introduction

Olefin polymerization using transition-metal complex catalysts has received great attention over the past decade [1]. Especially, the development of chromium-based catalysts for olefin oligomerization/polymerization has received considerable attention [1a,1c,2]. In general, two classes of chromium-based catalysts are commercially used: Phillips catalyst [3] and Union Carbide catalyst [4]. The Phillips catalysts are inorganic chromium catalysts supported on silica; therefore their active species have not been fully established due to their heterogeneity [2b]. Recently, soluble chromium complexes including Cp-based ligands [1a,1c,5] and other ligands [1a,1c,2a] have been reported as catalysts for ethylene polymerization. Cp-free complexes have begun to figure prominently among chromium-based catalysts due to the fact that carefully tuning of the ligand environment can tremendously affect the catalytic activities and properties of products [1a,1c,2a]. Vari-

ous chromium complexes coordinated by anionic ligands such as N^O (salicylaldiminato (**A**, Scheme 1) [6], amino-phenol 3,5-(^{t}Bu)$_2$-2-(OH)C$_6$H$_2$CH$_2$NH(2,6-Me$_2$C$_6$H$_3$) [7]), N^N (imino-pyrrolide [8], β-diketiminate [8b,9], bis(phosphoranimine)-methanide [10]) and N^N^N (salicylaldiminato [6b]) have been reported. Chromium complexes coordinated to various N^N (bis(imidazole) [11]), P^P or P^N^P (bridged-diphosphine (**B** and **C**, Scheme 1) [12]), P^P^P (triphosphacyclodode-cane [13]), S^N^S (amine bis(thioether) [12c,12d,14]), C^N^C (bis(carbine)pyridine (**D**, Scheme 1) [15]), N^N^O (2-acetyl-6-iminopyridine (**E**, Scheme 1) [16], 2-(ethylcarboxylato)-6-iminopyridine (**F**, Scheme 1) [17]), N^N^N^N (tris(2-pyridylmethyl)amine [18]) and N^S^N (iminodiphenylsulfide [19]) ligands have also been investigated. When combined with appropriate cocatalyst, some of those chromium complexes catalyze ethylene to form polymeric and oligomeric products with high catalytic activities. Chromium complexes coordinated to N^N^N ligands, such as bis(imino)pyridines (**G**, Scheme 1) [16,20], (2-pyridylmethyl)amines (**H**, Scheme 1) [21], tri-azacyclohexane (**I**, Scheme 1) [22], bis(oxazolinyl)pyridine (**J**, Scheme 1) [23] and 2,6-bis(benzimidazolyl)pyridines (**K**, Scheme 1) [24], have attracted great attentions due to their

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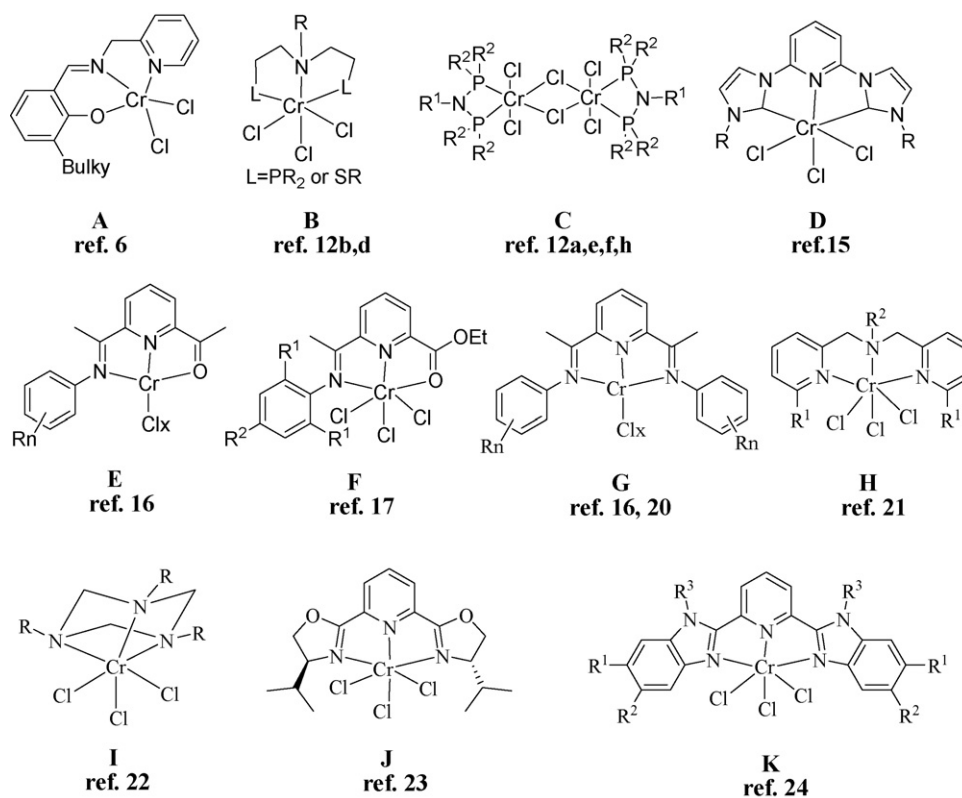
Scheme 1. Representative chromium catalysts.

potential catalytic activities for ethylene oligomerization and polymerization.

Recently, two different kinds of chromium complexes containing 2,6-bis(benzimidazolyl) pyridines **K** [24b] and 2-(ethylcarboxylato)-6-iminopyridines **F** [17] were investigated for ethylene reactivity with moderate to high catalytic activities in our group. The new achievement of designing and synthesizing 2-imino-1,10-phenanthroline derivatives and their metal complexes of iron(II), cobalt(II) and nickel(II) provides alternative model catalysts with high activities [25]. Subsequently, it is necessary to investigate the scope of their chromium analogues and their catalytic behavior. These chromium complexes were synthesized by reactions of 2-imino-1,10-phenanthrolines with chromium(III) trichloride. In the presence of methylaluminoxane (MAO), all the chromium complexes showed high ethylene oligomerization activities and moderate polymerization activities. Herein, the synthesis, characterization of these chromium complexes are reported with their catalytic properties for ethylene activation investigated under various reaction conditions.

2. Experimental

2.1. General

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Elemental analyses were performed on a Flash EA 1112 microanalyzer. The IR spectra were obtained as KBr pellets on a Bruker DMX-300 spectrometer. GC analyses were performed with a Carlo Erba Strumentazione gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) DM-1 silica capillary column. The yield of oligomers was calculated by referencing with the mass of the solvent. GC–MS analyses were performed with HP 5890 SERIES II and HP 5971 SERIES mass detectors. ^{1}H NMR and ^{13}C NMR of the polymer samples were recorded on a Bruker DMS-300 instrument at 110 °C in 1,2-dichlorobenzene-d_4 using TMS as an internal standard.

Solvents were dried by the appropriate drying reagents and distilled under nitrogen prior to use. Methylaluminoxane (MAO) was purchased from Albemarle as a 1.4 M solution in toluene. Modified methylaluminoxane (MMAO, 1.93 M in heptane) was purchased from Akzo Corp. Triethylaluminum (2 M in toluene) and diethylaluminum chloride (Et$_2$AlCl, 1 M in hexane) were purchased from Arcros Chemicals. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

2.2. Synthesis of Complexes 1–12

2.2.1. General procedure

All the 2-imino-1,10-phenanthrolines used as ligands were prepared according to our reported procedure [25]. A solution of CrCl$_3$·3THF in dichloromethane was dropwise added to a solution of the ligand in dichloromethane. The color of the solution changed immediately and some precipitate was formed. The reaction mixture was stirred at room temperature for 9 h and then
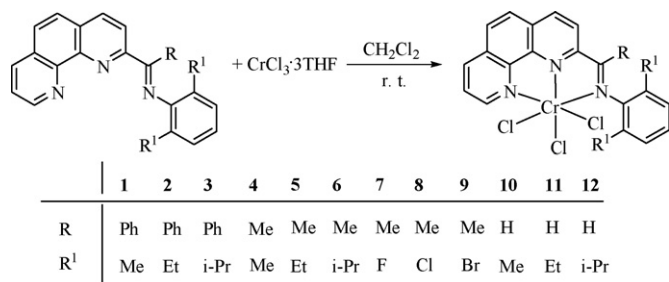
Scheme 2. The synthesis of complexes **1–12**.

diethyl ether was added. The green precipitate was collected with filtration, washed with diethyl ether and dried in vacuum. All the complexes were prepared in high yield (Scheme 2).

2.2.2. 2-Benzoyl-1,10-phenanthroline(2,6-dimethylanil) CrCl$_3$ (1)

Green powder in 83% yield. FT-IR (KBr disc, cm^{-1}): 3047, 1591, 1542, 1487, 1450, 1405, 1294, 866, 702. Anal. Calc. for C$_{27}$H$_{21}$Cl$_3$CrN$_3$ (545.83): C, 59.41; H, 3.88; N, 7.70. Found: C, 59.62; H, 3.65; N, 7.54.

2.2.3. 2-Benzoyl-1,10-phenanthroline(2,6-diethylanil)CrCl$_3$ (2)

Green powder in 82% yield. FT-IR (KBr disc, cm^{-1}): 3057, 2962, 1602, 1544, 1489, 1441, 1403, 1294, 866, 785, 703. Anal. Calc. for C$_{29}$H$_{25}$Cl$_3$CrN$_3$ (572.05): C, 60.69; H, 4.39; N, 7.32. Found: C, 60.91; H, 4.30; N, 7.33.

2.2.4. 2-Benzoyl-1,10-phenanthroline(2,6-diisopropylanil) CrCl$_3$ (3)

Green powder in 87% yield. FT-IR (KBr disc, cm^{-1}): 3058, 2967, 1602, 1531, 1489, 1460, 1439, 1402, 1292, 871, 785, 701. Anal. Calc. for C$_{31}$H$_{29}$Cl$_3$CrN$_3$ (601.94): C, 61.86; H, 4.86; N, 6.98. Found: C, 61.56; H, 4.70; N, 6.96.

2.2.5. 2-Acetyl-1,10-phenanthroline(2,6-dimethylanil)CrCl$_3$ (4)

Green powder in 85% yield. FT-IR (KBr disc, cm^{-1}): 3056, 2967, 1602, 1511, 1455, 1403, 1293, 865, 775. Anal. Calc. for C$_{22}$H$_{19}$Cl$_3$CrN$_3$ (483.76): C, 54.62; H, 3.96; N, 8.69. Found: C, 54.35; H, 4.28; N, 8.35.

2.2.6. 2-Acetyl-1,10-phenanthroline(2,6-diethylanil)CrCl$_3$ (5)

Green powder in 74% yield. FT-IR (KBr disc, cm^{-1}): 3056, 2966, 1602, 1510, 1456, 1405, 1290, 862, 790. Anal. Calc. for C$_{24}$H$_{23}$Cl$_3$CrN$_3$ (511.81): C, 56.32; H, 4.53; N, 8.21. Found: C, 56.26; H, 4.89; N, 7.97.

2.2.7. 2-Acetyl-1,10-phenanthroline(2,6-diisopropylanil) CrCl$_3$ (6)

Green powder in 83% yield. FT-IR (KBr disc, cm^{-1}): 3055, 2968, 1604, 1519, 1460, 1410, 861, 770. Anal. Calc. for

C$_{26}$H$_{27}$Cl$_3$CrN$_3$ (539.87): C, 57.84; H, 5.04; N, 7.78. Found: C, 57.55; H, 5.37; N, 7.79.

2.2.8. 2-Acetyl-1,10-phenanthroline(2,6-difluoroanil)CrCl$_3$ (7)

Green powder in 70% yield. FT-IR (KBr disc, cm^{-1}): 3053, 2969, 1605, 1531, 1460, 1413, 863, 709. Anal. Calc. for C$_{20}$H$_{13}$Cl$_3$CrF$_2$N$_3$ (491.69): C, 48.85; H, 2.66; N, 8.55. Found: C, 48.66; H, 2.38; N, 8.35.

2.2.9. 2-Acetyl-1,10-phenanthroline(2,6-dichloroanil) CrCl$_3$ (8)

Green powder in 86% yield. FT-IR (KBr disc, cm^{-1}): 3059, 2960, 1607, 1529, 1462, 1402, 877, 780. Anal. Calc. for C$_{20}$H$_{13}$Cl$_5$CrN$_3$ (524.60): C, 45.79; H, 2.50; N, 8.01. Found: C, 45.69; H, 2.32; N, 7.74.

2.2.10. 2-Acetyl-1,10-phenanthroline(2,6-dibromoanil) CrCl$_3$ (9)

Green powder in 97% yield. FT-IR (KBr disc, cm^{-1}): 3058, 2965, 1609, 1522, 1457, 1405, 867, 779. Anal. Calc. for C$_{20}$H$_{13}$Br$_2$Cl$_3$CrN$_3$ (613.50): C, 39.15; H, 2.14; N, 6.85. Found: C, 39.43; H, 2.22; N, 6.55.

2.2.11. 2-Formyl-1,10-phenanthroline(2,6-dimethylanil) CrCl$_3$ (10)

Green powder in 84% yield. FT-IR (KBr disc, cm^{-1}): 3060, 2922, 1605, 1506, 1464, 1442, 1405, 863, 776. Anal. Calc. for C$_{21}$H$_{17}$Cl$_3$CrN$_3$·THF (541.84): C, 53.70; H, 3.65; N, 8.95. Found: C, 53.54; H, 3.41; N, 9.26.

2.2.12. 2-Formyl-1,10-phenanthroline(2,6-diethylanil) CrCl$_3$ (11)

Green powder in 69% yield. FT-IR (KBr disc, cm^{-1}): 3051, 2972, 1604, 1507, 1458, 1406, 859. Anal. Calc. for C$_{23}$H$_{21}$Cl$_3$CrN$_3$ (497.79): C, 55.49; H, 4.25; N, 8.44. Found: C, 55.38; H, 3.96; N, 8.13.

2.2.13. 2-Formyl-1,10-phenanthroline (2,6-diisopropylanil)]CrCl$_3$ (12)

Green powder in 78% yield. FT-IR (KBr disc, cm^{-1}): 3061, 2957, 2867, 1607, 1511, 1461, 1407, 864. Anal. Calc. for C$_{25}$H$_{25}$Cl$_3$CrN$_3$ (525.84): C, 57.10; H, 4.79; N, 7.99. Found: C, 57.15; H, 4.80; N, 7.66.

2.3. General procedure for ethylene oligomerization and polymerization

Ethylene oligomerization and polymerization at 1 atm of ethylene pressure was carried out as follows: The catalyst precursor was dissolved in toluene in a Schlenk tube and the reaction solution was stirred at 1 atm of ethylene with the reaction temperature being controlled by water bath. The reaction was initiated by adding the desired amount of cocatalyst. After the desired period of time, the catalytic reaction mixture was quenched with 5% hydrochloric acid in an ice-water bath in accordance with

the oligomers of C_4 and C_6 produced. An analysis by gas chromatography (GC) was carried out to determine the distribution of oligomers obtained. The remaining solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, dried in a vacuum at 60 °C until constant weight.

Ethylene oligomerization at higher ethylene pressure was carried out in a 250-mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Briefly, toluene, the desired amount of cocatalyst and toluene solution of the catalyst precursor (the total volume was 100 mL) was added to the reactor in this order under an ethylene atmosphere. Reaching the desired reaction temperature, ethylene with the desired pressure was introduced to start the reaction, and the ethylene pressure was kept by constant feeding of ethylene. After 1 h, the reaction was stopped. The catalytic reaction mixture was quenched with 5% hydrochloric acid in an ice-water bath in accordance with the oligomers of C_4 and C_6 produced. Then the solution was analyzed by gas chromatography (GC) for determining the distribution of oligomers obtained. The remaining solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, dried in a vacuum at 60 °C until constant weight.

2.4. X-ray crystal structural determination of 2, 4 and 12

Intensity data for complexes **2** and **4** were collected on a Brucker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Single-crystal X-ray diffraction studies for complex **12** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods, and refined by full-matrix least-square on F^2. Each hydrogen atom was placed in a calculated position, and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed using SHELXL-97 package [26]. Crystal data and processing parameters were summarized in Table 1. CCDC-631242 (**2**), -631243 (**4**) and -631244 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Synthesis of the chromium complexes (1–12)

The ligands were efficiently synthesized according to our reported procedure [25a]. Their chromium complexes were easily synthesized by the reaction of $CrCl_3 \cdot 3THF$ and corresponding ligands of 2-imino-1,10-phenanthrolines in dichloromethane (Scheme 2). The resultant products were

Table 1
Crystal data and structure refinement for **2**, **4** and **12**

	2	**4·CH₂Cl₂**	**12·2H₂O**
Empirical formula	$C_{29}H_{25}Cl_3CrN_3$	$C_{22}H_{19}Cl_3CrN_3 \cdot CH_2Cl_2$	$C_{25}H_{25}Cl_3CrN_3 \cdot 2H_2O$
Formula weight	573.87	568.68	557.83
Crystal color	Green	Green	Green
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	10.3895(6)	8.0117(2)	10.362(2)
b (Å)	17.8363(1)	24.9597(6)	11.376(2)
c (Å)	14.6809(1)	12.4017(3)	23.634(6)
β (°)	92.275(4)	94.8900(1)	108.30(3)
Volume (Å³)	2718.4(3)	2470.94(1)	2645.0(1)
Z	4	4	4
D_{calc} (Mg m⁻³)	1.402	1.529	1.401
μ (mm⁻¹)	0.739	1.021	0.762
$F(000)$	1180	1156	1148
Crystal size (mm)	$0.30 \times 0.10 \times 0.10$	$0.33 \times 0.10 \times 0.06$	$0.39 \times 0.13 \times 0.04$
θ range (°)	1.80–28.36	1.63–28.30	2.07–27.40
Limiting indices	$-12 \leq h \leq 13$, $-23 \leq k \leq 23$, $-19 \leq l \leq 19$	$-10 \leq h \leq 10$, $-33 \leq k \leq 31$, $-15 \leq l \leq 16$	$0 \leq h \leq 13$, $-14 \leq k \leq 0$, $-30 \leq l \leq 28$
Completeness to θ (%)	98.8 ($\theta = 28.36$)	99.9 ($\theta = 28.30$)	97.5 ($\theta = 27.40$)
Absorption correction	Empirical	Empirical	Empirical
Data/restraints/parameters	6723/0/325	6139/0/289	5871/0/297
Goodness-of-fit on F^2	0.796	1.109	1.012
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0574, wR2 = 0.1403	R1 = 0.0363, wR2 = 0.1030	R_1 = 0.0618, wR_2 = 0.1668
R indices (all data)	R1 = 0.1845, wR2 = 0.1842	R1 = 0.0477, wR2 = 0.1074	R_1 = 0.0942, wR_2 = 0.1848
Largest diff peak and hole (e Å⁻³)	0.623 and −0.346	0.484 and −0.603	1.652 and −0.669

isolated as green air-stable powders in good yields and characterized by IR spectra and elemental analysis. In the IR spectra, the stretching vibration bands of C=N of these chromium complexes (1591–1609 cm^{-1}) apparently shifted to lower wave numbers and the peak intensity was greatly reduced, as compared to the corresponding ligands (1618–1646 cm^{-1}) [25a], which indicates the coordination interaction between the imino nitrogen atom and the metal cation. The molecular structures of complexes **2**, **4** and **12** were confirmed by the single-crystal X-ray diffraction studies.

3.2. Molecular structures

Crystals of complexes **2**, **4** and **12** suitable for X-ray structure determination were obtained through the slow diffusion of diethyl ether into their dichloromethane solution. Analysis of X-ray crystallography reveals that all complexes display the distorted octahedronal geometry, in which the chromium center is coordinated to the tridentate ligand and three chlorides. Their selected bond lengths and angles are collected in Table 2, and meanwhile their molecular structures are shown in Figs. 1 and 2.

In the molecular structure of complex **2** (Fig. 1), three coordinated nitrogen atoms and three chlorides are situated around the chromium center in a meridianal manner. The N1, N3, Cl1 and Cl3 atoms could be located in an equatorial plane and the two axial bonds nearly form a straight angle (N2−Cr−Cl2, 178.48(1)°). Most of bond
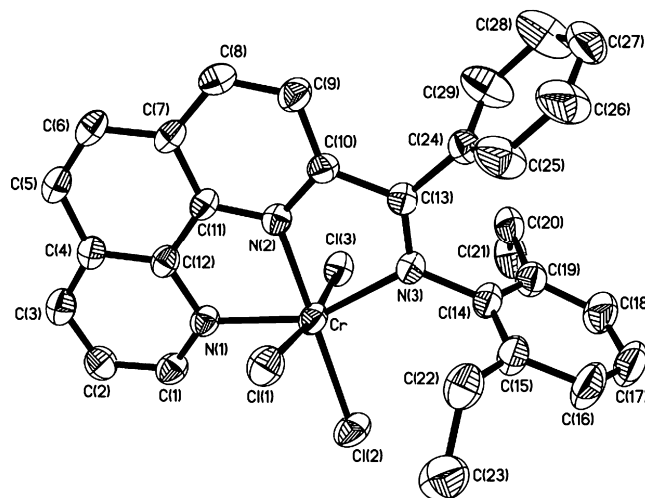

Fig. 1. Molecular structure of complex **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

angles in the equatorial plane are very close to a right angle (N(1)−Cr−Cl(1), 86.02(1)°; N(1)−Cr−Cl(3), 86.81(1)°; N(3)−Cr−Cl(1), 92.58(1)°; N(3)−Cr−Cl(3), 91.80(1)°). The axial Cr−N(2) (phenanthrolinyl) bond length (1.993(3) Å) is shorter about 0.11 Å than the Cr−N(1) (phenanthrolinyl) bond length (2.101(3) Å) and about 0.16 Å than the Cr−N(3) (imino) bond length (2.151(3) Å). The Cr−Cl bond lengths span a relatively narrow range, with the Cr−Cl(2) bond (2.2701(1) Å) located at *trans* position to N(2) being shorter than the Cr−Cl(1)

Table 2
Selected Bond Lengths (Å) and Angles (°) for **2**, **4** and **12**

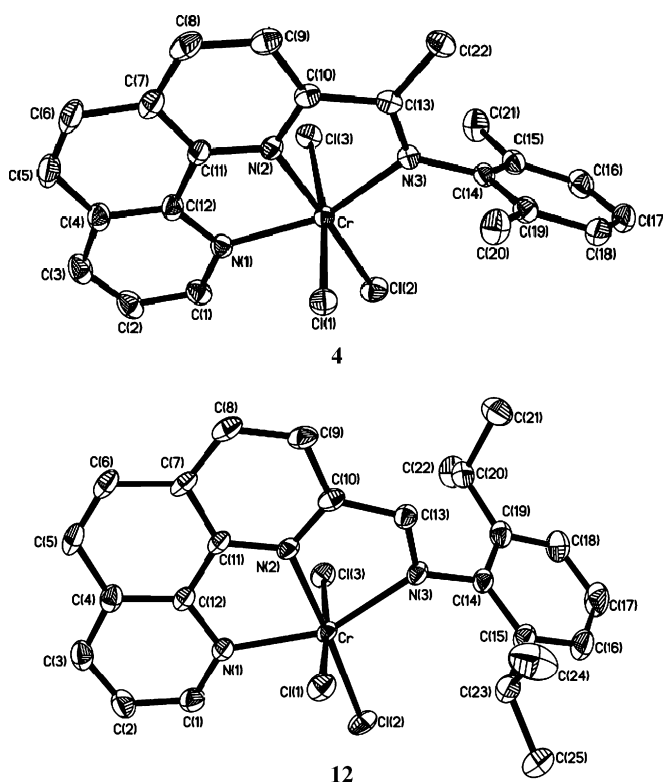|	2	4	12
Bond lengths			
Cr−N(1)	2.101(3)	2.1079(2)	2.101(3)
Cr−N(2)	1.993(3)	1.9873(2)	1.989(3)
Cr−N(3)	2.151(3)	2.1474(2)	2.158(3)
Cr−Cl(1)	2.3270(1)	2.3048(6)	2.3319(1)
Cr−Cl(2)	2.2701(1)	2.2834(6)	2.2731(1)
Cr−Cl(3)	2.3088(1)	2.3311(6)	2.3160(1)
N(1)−C(1)	1.320(5)	1.325(3)	1.334(5)
N(1)−C(12)	1.366(5)	1.360(3)	1.369(5)
N(2)−C(10)	1.337(5)	1.327(2)	1.329(5)
N(2)−C(11)	1.337(5)	1.340(3)	1.332(5)
N(3)−C(13)	1.295(5)	1.297(2)	1.282(5)
N(3)−C(14)	1.475(5)	1.455(2)	1.454(4)
Bond angles			
N(1)−Cr−N(2)	78.63(1)	79.24(6)	78.61(1)
N(2)−Cr−N(3)	75.90(1)	76.00(6)	76.26(1)
N(1)−Cr−N(3)	154.52(1)	155.16(6)	154.80(1)
N(1)−Cr−Cl(1)	86.02(1)	86.67(5)	86.91(1)
N(1)−Cr−Cl(2)	101.39(1)	98.18(5)	98.43(1)
N(1)−Cr−Cl(3)	86.81(1)	86.76(5)	89.56(1)
N(2)−Cr−Cl(1)	85.32(1)	87.78(5)	84.87(1)
N(2)−Cr−Cl(2)	178.48(1)	177.32(5)	176.85(1)
N(2)−Cr−Cl(3)	88.49(1)	85.34(5)	88.65(1)
N(3)−Cr−Cl(1)	92.58(1)	90.47(4)	92.62(9)
N(3)−Cr−Cl(2)	104.09(1)	106.61(4)	106.73(9)
N(3)−Cr−Cl(3)	91.80(1)	93.08(4)	88.06(1)
Cl(1)−Cr−Cl(2)	93.16(5)	92.79(2)	93.92(5)
Cl(1)−Cr−Cl(3)	171.32(5)	171.26(2)	173.12(4)
Cl(2)−Cr−Cl(3)	93.03(5)	93.85(2)	92.43(5)

Fig. 2. Molecular structures of complexes **4** and **12** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent have been omitted for clarity.
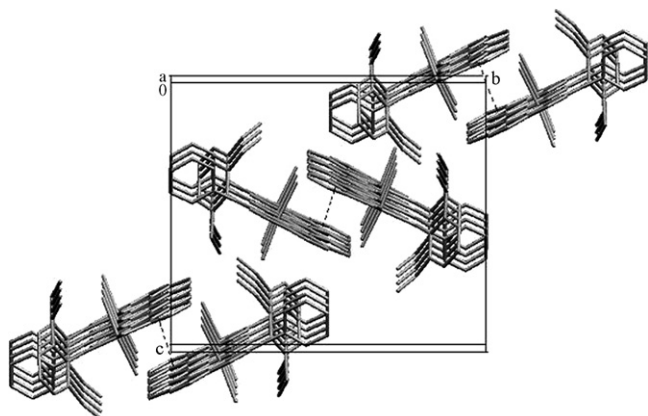
Fig. 3. A view of the crystal packing for complex **2**, projected along the *a*-axis.

(2.3270(1) Å) and Cr–Cl(3) (2.3088(1) Å) bond at *cis* position. The similar phenomenon was observed with the reported bis(imino)pyridine chromium complexes [16,20]. The imino N(2)–C(13) bond length is 1.295(5) Å with the typical character of a C=N double bond. The atoms of 1,10-phenanthroline ring and C(13), N(3) of the imino group as well as the chromium atom form a perfect plane (the mean deviation is 0.0509 Å), with the largest deviation from the plane being 0.1073 Å at N(3). The phenyl ring linking to the imino group is oriented nearly perpendicularly to the coordination plane with the dihedral angle of 82.2°. Interestingly, the C_6 central rings of phenanthroline between two adjacent chromium moieties interact in a "face-to-face" fashion with the relevant plane-to-plane distance of 3.390 Å and center-to-center distance of 3.508 Å. It is noteworthy that the molecular packing of **2**, viewed from the *a*-axis, is in a perfect stacking (Fig. 3). The well-stacked structure in the solid state is formed by self-assembly of molecules, presumably driven by intermolecular π–π stacking and hydrogen bonds. Similar observation was obtained in their nickel analogues [25b].

In complex **4**, the chromium atom is quasi-octahedral, the three coordinated chlorides dispose *mer* in the coordination sphere. It displays nearly equivalent N(2)–Cr–Cl angles (N(2)–Cr–Cl(1) = 87.78(5)° and N(2)–Cr–Cl(3) = 85.34(5)°). The presence of a methyl substituent on the imino-C atom instead of the phenyl group and that of methyl groups on the imino-N phenyl ring instead of ethyl groups confers no obvious influence on the molecular geometry, which can be observed from the similar bond lengths and angles of complexes **2** and **4**. The Cr–N and Cr–Cl bond distances in complex **4** have a similar trend to those in complex **2**: the Cr–N(2) bond distance is the shortest among the three Cr–N bonds and the Cr–Cl(2) bond length is also the shortest among the three Cr–Cl bonds. Both the mean (0.017 Å) and the largest (0.0721 Å) deviations of the plane formed by 1,10-phenanthroline, C(13), N(3) and Cr atoms are smaller than those in complex **2**, which is probably due to the less bulky methyl group (C(22)). The different dihedral angles between the phenyl plane on the imino-N and the coordination plane in **2** (82.2°) and **4** (106.5°) is probably due to the less bulky methyl group on the imino-C atom.

In complex **12**, the Cl–Cr–Cl and N–Cr–N angles are 93.92(5)°, 92.43(5)°, 173.12(4)° and 78.61(1)°, 76.26(1)°,
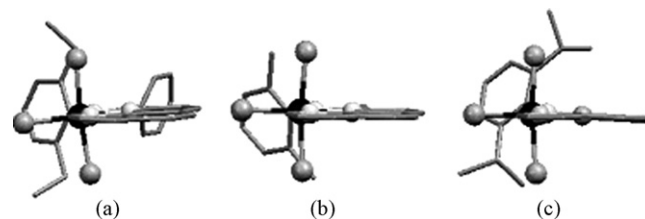

Fig. 4. The different dihedral angles between the coordination plane and the phenyl plane. (a) 82.2° in **2**; (b) 106.5° in **4**; (c) 65.9° in **12**.

154.80(1)°, respectively. The structure is similar to that of **2** and **4**. The observed similarities include the shortest Cr–N(2)(phenanthrolinyl) bond (1.989(3) Å) compared with Cr–N(1)(phenanthrolinyl) bond (2.101(3) Å) and Cr–N(3)(imino) bond (2.158(3) Å). The Cr–Cl(2) bond (opposite N(2)) is the shortest of the three Cr–Cl bonds. The most noticeable differences are the dihedral angle (65.9°) between the coordination plane and the phenyl plane (Fig. 4) and the shorter imino N(3)–C(13) bond length (1.282(5) Å). The differences are probably due to the less bulky hydrogen on the imino-C atom.

3.3. Ethylene oligomerization and polymerization at ambient pressure

The chromium complexes were initially studied for their catalytic activities of ethylene oligomerization and polymerization at ambient pressure (Table 3). Complex **2** was used to select suitable reaction parameters. When combined with various organo-aluminum compounds such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), triethylaluminum (Et_3Al) and diethylaluminum chloride (Et_2AlCl), it showed different catalytic performance. The catalytic system with Et_3Al or Et_2AlCl only produced butenes in lower oligomerization activities. However, complex **2** with MAO or MMAO oligomerized ethylene to obtain oligomers following the Schulz–Flory rule with remarkably higher activities. Further investigations were carried out with MAO as cocatalyst.

3.3.1. Effects of reaction parameters

The influences of the Al/Cr molar ratio and reaction temperature on ethylene reactivity were studied with the **2**/MAO system. Increasing the Al/Cr molar ratio from 300 to 1500 led to great enhancement of ethylene oligomerization activities (entries 5–8, Table 3). A further increase in the Al/Cr molar ratio to 2000 resulted in decreased oligomerization activity (entry 9, Table 3). The decrease in oligomerization activity might be caused by the impurities in commercial MAO such as alkyl aluminum, which led to the deactivation of active catalytic sites. However, the polymerization activities were not strongly affected by the Al/Cr molar ratio. The distribution of oligomers and the α-olefin selectivity were also significantly affected by the Al/Cr molar ratio. Larger amounts of longer chain oligomers were produced and decreased selectivity for α-olefins was observed at higher Al/Cr molar ratios.

Table 3
Ethylene reactivity at ambient pressure with **1–12**[a]

Entry	Complex	Cocat	Al/Cr	T^b (°C)	t^c (min)	Oligomer distribution[d] (%)				A_o[e]	A_p[f]
						$C_4/\sum C$	$C_6/\sum C$	$\geq C_8/\sum C$	α-Olefin (%)[d]		
1	**2**	Et$_3$Al	500	20	60	100	–	–	–	0.03	No
2	**2**	Et$_3$Al	1000	20	60	100	–	–	–	0.27	No
3	**2**	Et$_2$AlCl	500	20	60	100	–	–	–	0.30	No
4	**2**	MMAO	1000	20	60	64.2	19.8	16.0	>90	2.11	Trace
5	**2**	MAO	300	20	60	70.6	25.1	4.3	>97	2.16	0.8
6	**2**	MAO	500	20	60	69.2	26.5	4.3	>96	2.56	2.1
7	**2**	MAO	1000	20	60	50.4	28.4	21.2	>90	7.50	1.9
8	**2**	MAO	1500	20	60	40.4	43.8	15.8	>80	7.91	2.2
9	**2**	MAO	2000	20	60	24.9	55.1	20.0	>79	5.32	2.0
10	**2**	MAO	1000	0	60	74.1	22.2	3.7	>90	2.11	Trace
11	**2**	MAO	1000	40	60	39.2	40.4	20.4	>78	7.42	2.7
12	**2**	MAO	1000	60	60	32.0	37.4	30.6	>79	7.35	1.4
13	**2**	MAO	1000	20	30	60.6	24.2	15.2	>91	9.75	–
14	**2**	MAO	1000	20	90	51.4	28.4	20.2	>94	7.29	–
15	**2**	MAO	1000	20	120	43.2	33.2	23.6	>93	7.01	–
16	**1**	MAO	1000	20	60	72.4	23.6	4.0	>95	4.36	0.8
17	**3**	MAO	1000	20	60	85.1	10.5	4.3	>85	0.71	0.6
18	**4**	MAO	1000	20	60	49.2	25.8	24.9	>90	1.34	2.1
19	**5**	MAO	1000	20	60	55.4	24.1	20.5	>96	1.72	2.1
20	**6**	MAO	1000	20	60	83.7	8.8	7.5	>93	0.45	1.4
21	**7**	MAO	1000	20	60	85.8	11.3	2.9	>90	4.73	2.1
22	**8**	MAO	1000	20	60	33.8	40.4	25.8	>91	5.31	1.6
23	**9**	MAO	1000	20	60	31.9	26.5	41.6	>93	6.16	1.7
24	**10**	MAO	1000	20	60	43.0	34.6	22.4	>91	1.12	1.0
25	**11**	MAO	1000	20	60	45.1	26.5	28.4	>92	1.89	Trace
26	**12**	MAO	1000	20	60	42.1	31.1	26.8	>95	7.35	Trace

[a] Conditions: 5 μmol of catalysts; solvent: toluene (30 mL).
[b] Reaction time.
[c] Reaction temperature.
[d] Determined by GC.
[e] Oligomer activity: 10^5 g mol^{-1} (Cr) h^{-1}.
[f] Polymer activity: 10^4 g mol^{-1} (Cr) h^{-1}.

The butenes have low boiling points and potentially affect the fractional pressure of ethylene over catalytic time course; however, the high solubility of butenes in toluene will keep produced butenes in solution. In fact, oligomerization and polymerization proceed with only solved ethylene, then coordination with active sites in the catalytic system. The resultant observation was the catalytic activity decreasing along with the prolong reaction time (entries 7, 13–15, Table 3), and meanwhile higher order olefins were obtained.

Elevating the reaction temperature from 0 to 20 °C speeded the combined catalytic reactions of oligomerization and polymerization. No significant variation was observed by elevating the reaction temperature to 60 °C, indicating the stability of the catalysts at higher temperature. However, lower α-olefin selectivity was obtained at higher reaction temperature. A similar influence of temperature on the oligomers produced with chromium-based systems had been reported [24].

3.3.2. Effect of the ligand environments

The variation of the R substituent on the imino-C of ligands, 2-(ArN=CR)-1,10-phen, resulted in changes of catalytic performance. Aldimine (R=H) and phenyl-ketimine (R=Ph) complexes showed relatively higher activities than the cor-

responding methyl-ketimine (R=Me) complexes. This was a completely reversed observation compared with iron(II) analogues bearing the same ligands [25a]. Furthermore, the R substituent had different influences on the catalytic performance of methyl- or phenyl-ketimine and aldimine analogues. The phenyl-ketimine complex **2** with 2,6-diethyl groups and the aldimine complex **12** with 2,6-diisopropyl groups showed much higher oligomerization activity than their corresponding analogues. However, for the methyl-ketimine complexes, no obvious difference was observed between **4** (with Me substituents) and **5** (with Et substituents). The α-olefin selectivity and polymerization activities were not greatly affected by the R group.

The R^1 substituents on the imino-N aryl ring had a great influence on the catalytic performance of both ketimine and aldimine complexes. For phenyl-ketimine complexes **1–3**, somewhat reduced catalytic activity was observed for the sterically bulkier catalysts. This was clearly revealed by comparing the 2,6-diisopropyl substituted **3** with 2,6-dimethyl substituted **1** or 2,6-diethyl substituted **2** (entry 17 versus entry 16 or 7, Table 3). The same trend was also observed for the methyl-ketimine complexes **4–6** (entries 18–20, Table 3). The more bulky isopropyl groups at the *ortho*-positions of the imino-N aryl

ring and R (R = Ph, Me) on the imino-C may prevent the insertion of ethylene to the catalytic sites, therefore leading to lower catalytic activity. Complexes **7–9**, containing 2,6-dihalogen-substituted ligands, exhibited relatively higher oligomerization activities than complexes **4–6** bearing alkyl groups (entries 21–23, Table 3). Aldimine complexes **10–12** also displayed high activities for ethylene oligomerization along with considerable activities for ethylene polymerization (entries 24–26, Table 3). Based on these data, their oligomerization activities varied in the orders of **10** (with Me) < **11** (with Et) < **12** (with *i*-Pr), which was different from ketimine complexes. This could be possibly caused by the less bulkiness of hydrogen on the imino-C. In addition, there was no regular influence of ligand environment on the polymerization activities and α-olefin selectivity.

3.4. Ethylene oligomerization and polymerization at 10 atm of ethylene

Upon activation with methylaluminoxane (MAO), all the chromium complexes exhibited high catalytic activities for oligomerization and moderate activities for polymerization at 10 atm of ethylene. The detailed results are listed in Table 4. The distribution of olefin oligomers resembled the Schulz–Flory rule and was characterized by the constant K, where K represented the probability of chain propagation (K = rate of propagation/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of C_n)) [27]. The K values were determined by the molar ratio of C_{14} and C_{12} fractions.

3.4.1. Effects of reaction parameters
Apparently, the ethylene concentration significantly affected the catalytic behavior of all the complexes. Comparing with the catalytic behavior at ambient pressure (Table 3), the higher cat-

alytic activities could be reached with increasing pressure of ethylene. At 10 atm of ethylene, the catalytic activities for both oligomerization and polymerization increased by nearly one order of magnitude. The higher ethylene concentration increased the chain propagation leading to longer chain oligomers up to the range of C_4 to C_{28} along with improved activities.

According to observed data (entries 1–4, Table 4 with 10 atm of ethylene), elevation of the temperature from 20 to 80 °C resulted in an increased catalytic activities and K values. However, lower selectivity of α-olefins was obtained at higher reaction temperature because of the faster chain transformation. In general, the suitable active sites were formed at elevated temperature up to 80 °C. Due to the high activity and acceptable α-olefin selectivity, further investigations were carried out at 80 °C.

3.4.2. Effect of ligands environment
Changes in the ligand environments [2-(ArN=CR)-1,10-phen] of these systems led to different catalytic behavior. Changing the substituent on the imine functional group from ketimine (R = Ph, **1–3**; R = Me, **4–9**) to aldimine (R = H, **10–12**) resulted in the differences in productivity, K value and α-olefin selectivity. Methyl-ketimine catalysts were less productive than their phenyl-ketimine and aldimine analogues. The phenyl-ketimine precatalyst **2** gave the highest activity of 1.15×10^7 g mol^{-1} (Cr) h^{-1} (entry 4, Table 4). The corresponding aldimines **10–12** displayed productivities in the range $(2.73–5.00) \times 10^6$ g mol^{-1} (Cr) h^{-1} (entries 13–15, Table 4). However, the highest activity obtained from methyl-ketimine was 2.14×10^6 g mol^{-1} (Cr) h^{-1} of **4** (entry 7, Table 4). Furthermore, the phenyl-ketimine complexes displayed larger K value and methyl-ketimine complexes showed higher α-olefin selectivity.

Table 4
Ethylene reactivity at 10 atm[a]

Entry	Complex	T^{b} (°C)	Oligomers						A_p^{e}
			A_o^{c}	K	$C_4/\sum C$	$C_6/\sum C$	$\geq C_8/\sum C$	α-Olefin (%)[d]	
1	**2**	20	1.76	0.38	32.7	42.8	24.5	>96	2.2
2	**2**	40	2.42	0.38	32.4	47.4	20.2	>96	1.0
3	**2**	60	5.15	0.42	17.6	46.3	36.1	>92	2.7
4	**2**	80	11.5	0.48	20.9	38.6	40.5	>87	4.1
5	**1**	80	6.66	0.58	15.3	31.2	53.5	>86	3.6
6	**3**	80	0.46	0.74	31.3	16.4	52.3	>86	4.5
7	**4**	80	2.14	0.34	26.7	44.0	29.3	>89	3.4
8	**5**	80	2.02	0.40	34.7	36.7	28.6	>93	3.6
9	**6**	80	1.69	0.30	28.2	41.2	30.6	>91	3.1
10	**7**	80	1.57	0.50	39.2	30.4	30.4	>88	2.6
11	**8**	80	1.72	0.43	40.5	35.2	24.3	>78	2.8
12	**9**	80	1.98	0.55	29.1	31.2	39.7	>80	2.5
13	**10**	80	2.73	0.36	29.8	34.0	36.2	>89	1.9
14	**11**	80	4.29	0.38	18.3	45.3	36.4	>84	1.7
15	**12**	80	5.00	0.27	30.6	40.2	29.2	>79	Trace

[a] Conditions: 5 μmol of catalysts; cocatalyst: MAO; Al/Cr = 1000; reaction time: 1 h; solvent: toluene (100 mL).
[b] Reaction temperature.
[c] Activity for oligomers: 10^6 g mol^{-1} (Cr) h^{-1}.
[d] % α-olefin content determined by GC and GC–MS.
[e] Activity for polymers: 10^5 g mol^{-1} (Cr) h^{-1}.

At 10 atm of ethylene, the influence of the substituent on the imino-N aryl ring on the oligomerization activity was similar to the results obtained at 1 atm of ethylene. The phenyl-ketimine complex **2** with ethyl groups on the imino-N aryl ring displayed the highest oligomerization activity among its corresponding analogues (entry 4, Table 4). For aldimine complexes, it was observed that an increase in the steric hindrance of the R^1 group led to an enhanced activity (entries 13–15, Table 4); however, no significant effect was noticed for methyl-ketimine complexes (entries 7–9, Table 4). The introduction of electron-withdrawing halogen groups to the methyl-ketimine complexes resulted in a little influence on the oligomerization activities, which were different from the results at 1 atm of ethylene. The complexes containing halogen groups gave the higher K values and lower α-olefin selectivity. In addition, the polymerization activities were also affected by the substituents on the imino-N aryl ring. For the phenyl-ketimine complexes **1**–**3**, somewhat increased activity was observed for the sterically bulkier catalyst system (entries 4–6, Table 4), which was different from the aldimine complexes **10**–**12** (entries 13–15, Table 4). Complexes **4**–**6**, bearing alkyl groups, displayed higher polymerization activities than their analogues bearing halogen groups.

3.4.3. Characterization of low-molecular-weight waxes

In most cases of the ethylene reactivity with the titled complexes/MAO system, some polyethylene waxes were obtained in addition to the oligomers. As characterized by IR spectra recorded with a KBr disk in the range of 4000–400 cm^{-1}, the waxes could be confirmed to be mainly linear α-olefins from the characteristic vibration absorption bands of various C—H and C=C bonds. The ^{1}H NMR and ^{13}C NMR spectra of the waxes obtained were recorded in *o*-dichlorobenzene-*d₄* using TMS as the internal standard. Like our previous results obtained with chromium [24] and iron catalysts [25a,28], the ^{13}C NMR spectra demonstrated absolute predominance of linear α-olefins with a vinyl-unsaturated chain end. The average molecular weights based on ^{1}H NMR indicated that the carbon numbers of the waxes were in the ranges of 40–75.

4. Conclusions

Following the highly active iron complexes bearing 2-imino-1,10-phenanthrolinyl ligands, corresponding chromium complexes were also synthesized and fully characterized. Upon treatment with MAO, these chromium complexes displayed high activities up to 1.15×10^7 g mol^{-1} (Cr) h^{-1}. The distributions of obtained oligomers resembled the Schulz–Flory rule. In addition, some low-molecular-weight waxes were produced with moderate activities and proved to be long linear olefins with vinyl end groups. Both the R on the imino-C and R^1 substituents on the imino-N aryl ring had an obvious influence on the catalytic behavior including catalytic activities, distribution of oligomers and selectivity for α-olefins. Chromium complexes bearing aldimine (R = H) or phenyl-ketimine (R = Ph) showed relatively higher activities than complexes with methyl-ketimine (R = Me). For the phenyl-ketimine complexes, the sterically bulkier isopropyl groups on the imino-N aryl ring resulted in

lower activity; however, reversed results were observed for the aldimine complexes. In addition, the substituents on the N-aryl ring imino-N aryl showed no significant effect for the methyl-ketimine complexes.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.07.012.

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