DOI: 10.1002/ejic.200700392

Nickel Complexes Bearing 2-(Benzimidazol-2-yl)-1,10-phenanthrolines: Synthesis, Characterization and Their Catalytic Behavior Toward Ethylene Oligomerization

Min Zhang,[a] Shu Zhang,[a] Peng Hao,[a] Suyun Jie,[a] Wen-Hua Sun,*[a] Peizhou Li,[b] and Xiaoming Lu[b]

Keywords: Nickel / Tridentate complexes / Phenanthrolines / Ethylene oligomerization / Oligomerization

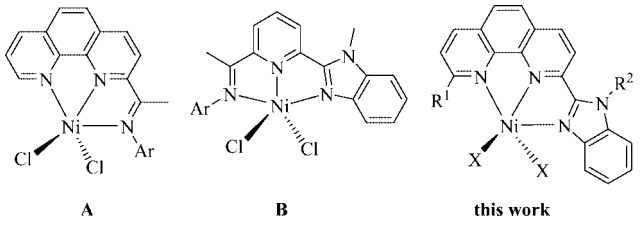
A series of 2-(benzimidazol-2-yl)-1,10-phenanthrolines and their nickel(II) complexes were synthesized and characterized by elemental and spectroscopic analysis along with single-crystal X-ray crystallography. X-ray diffraction analysis revealed that complexes **1a** and **6a** have a six-coordinate distorted octahedral geometry due to the coordination of solvent molecules, whereas **3a** is a centrosymmetric dimer in the solid state and **5b** displays a five-coordinate distorted trigonal-bipyramidal geometry. Upon activation with diethylaluminum chloride (Et_2AlCl), high catalytic activity up to 1.27×10^7 g·mol^{-1}(Ni)·h^{-1} and high selectivity for 1-butene (90.5%) could be achieved. A higher activity up to 3.95×10^7 g·mol^{-1}(Ni)·h^{-1} was observed in the **7a**/Et_2AlCl system with addition of 20 equiv. of PPh_3 as an auxiliary ligand. Reaction conditions and the ligand environment significantly influenced the catalytic properties of the complexes.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Ethylene oligomerization is a major industrial process, and developing new catalysts for ethylene oligomerization is of academic and industrial interest for the synthesis of α-olefins, which are feedstocks for the preparation of detergents, plasticizers, and fine chemicals, as well as comonomers for the production of linear low-density polyethylene (LLDPE).[1] One of the major industrial processes in ethylene oligomerization, named the SHOP process, employs nickel complexes as catalysts.[2] Over the past decades, considerable research effort has been devoted to the design of new nickel complexes as catalysts for olefin reactivity.[3,4] A large number of nickel complexes have been described as active species in ethylene oligomerization. However, limited examples among them could selectively produce α-olefins, because of their fast β-hydrogen elimination and chain immigration.[5] Therefore, the current challenges of nickel complexes in ethylene oligomerization are to find suitable catalysts for better α-olefin selectivity and to improve their catalytic activities. The fundamental research in designing novel homogeneous catalysts will rely on synthesizing ligands possessing environmental coordination to metal atoms that is favorable to the formation of suitable active species. In addition to the P^O chelating nickel complexes used in the SHOP process,[2,6] there are numerous nickel catalysts being investigated with bidentate ligands, such as N^O,[7,8] P^N,[9,10] and N^N,[3,11–13] and tridentate ligands, such as N^N^O,[14] N^P^N,[15] P^N^P,[16] P^N^N,[13d,16] and N^N^N,[17,18] as well as organometallic compounds.[15a]

Considering N^N^N tridentate nickel complexes as catalysts for ethylene oligomerization, several models with high activities have been developed in our group by using 2-imino-1,10-phenanthrolines (**A**),[18b] 2-(2-benzimidazole)-6-iminopyridine (**B**) ligands,[19] and 6-imino-2-quinoxalinylpyridines.[20] Inspired by these model catalysts, our strategy for ethylene activation is to synthesize 2-(benzimidazol-2-yl)-1,10-phenanthrolines and their metal complexes (Scheme 1). A new synthetic methodology for 2-(benzimidazol-2-yl)-1,10-phenanthrolines has been developed, and a further coordination reaction with nickel halides produced their nickel complexes with dichlorides or dibromides. By



Scheme 1.

[a] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080, China
Fax: +86-10-62618239
E-mail: whsun@iccas.ac.cn
[b] Department of Chemistry, Capital Normal University, Beijing 100037, China

© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

tuning the bulkiness and electronic effects of their substituents (R^1 and R^2), these nickel complexes are investigated for ethylene oligomerization, including their catalytic activities and the oligomers produced.

In the presence of Et_2AlCl, these nickel complexes show good catalytic activity towards ethylene oligomerization, especially with high selectivity of ethylene dimerization to 1-butene. In addition, the introduction of PPh_3 as an auxiliary ligand in the catalytic system greatly enhances the activity of the nickel complexes. Herein, we report the synthesis and characterization of 2-(benzimidazol-2-yl)-1,10-phenanthrolines and their nickel complexes; moreover, ethylene oligomerization of these nickel complexes is investigated in detail, along with the influence of reaction conditions and ligand environment.

Results and Discussion

Synthesis and Characterization of Ligands L1–L10 and Complexes 1a–10a, 1b–10b

The original organic compound 2-(1*H*-benzimidazol-2-yl)-9-methyl-1,10-phenanthroline (**L1**) is not yet reported in the literature. According to our previous work and the literature,[19,21] **L1** was synthesized by the reaction of 2,9-dimethyl-1,10-phenanthroline and *o*-phenylenediamine with sulfur as an oxidant. Another original compound, 2-(1*H*-benzimidazol-2-yl)-1,10-phenanthroline (**L6**), was synthesized by the condensation reaction of *o*-phenylenediamine with 1,10-phenanthroline-2-carboxylic acid in the presence of polyphosphoric acid (ppa) under microwave radiation.[22] The modified literature procedure was employed for the preparation of ligands **L2**–**L5** and **L7**–**L10** through the *N*-alkylation of **L1** and **L6** (Scheme 2).[19,23] All the synthesized compounds were well characterized and confirmed by elemental analysis, and ^1H and ^{13}C NMR, and IR spectroscopy. Their nickel complexes **1a**–**10a** and **1b**–**10b** were obtained in high yields by the equimolar reaction of the corresponding ligand and $NiCl_2·6H_2O$ or $(dme)NiBr_2$. These complexes were characterized by IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction techniques (Figures 1–5). Some elemental data showed incorporation of solvent molecules because the samples were prepared by recrystallization. To understand their real structures, ligand **L7** and complexes **1a**, **3a**, **6a**, and **5b** were analyzed by single-crystal X-ray diffraction.

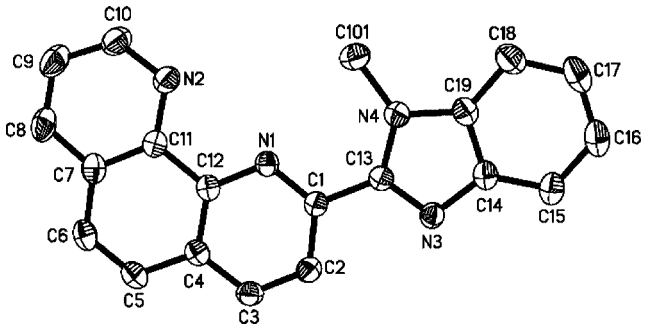
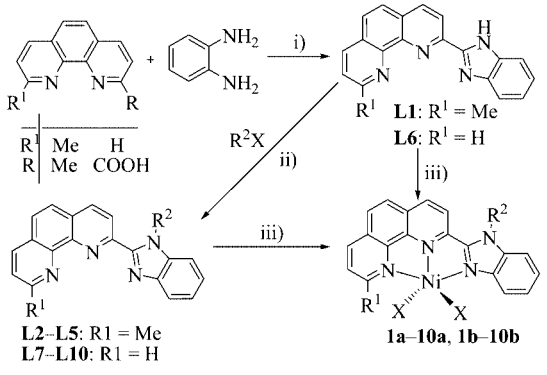


Figure 1. ORTEP drawing of ligand **L7** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N3–C13 1.3204(2), N3–C14 1.3822(2), N4–C13 1.3746(2), N4–C19 1.3863(2); N3–C13–N4 113.00(1), C13–N3–C14 105.13(1), C13–N4–C19 106.10(1).

Single crystals of ligand **L7** suitable for X-ray diffraction analysis were obtained by slow concentration of its ethyl acetate solution at room temperature. In the structure of ligand **L7** (Figure 1), the dihedral angle between the phenanthrolinyl plane and the benzimidazole plane is 7.6°, which indicates all the atoms of the ligand are almost coplanar. The N3–C13 bond [1.3204(2) Å] is longer than the typical imino C=N bond. The methyl group on the imidazole nitrogen atom stretches to the inner side of the phenanthroline ring because of the flexibility of the C1–C13 single bond.

Single crystals of complexes **1a**, **3a**, and **6a** suitable for X-ray diffraction analysis were individually grown by slow layering diffusion of diethyl ether into their methanol solutions. However, single crystals of **5b** were grown from its



	1a	2a	3a	4a	5a	6a	7a	8a	9a	10a	1b	2b	3b	4b	5b	6b	7b	8b	9b	10b
R^1	Me	Me	Me	Me	Me	H	H	H	H	H	Me	Me	Me	Me	Me	H	H	H	H	H
R^2	H	Me	Et	*i*Pr	Bn	H	Me	Et	*i*Pr	Bn	H	Me	Et	*i*Pr	Bn	H	Me	Et	*i*Pr	Bn
X	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br

Scheme 2. Synthesis of ligands **L1**–**L10** and nickel complexes **1a**–**10a**, **1b**–**10b**. (i) S_8, 170 °C for **L1**; ppa, microwave for **L6**. (ii) K_2CO_3, CH_3CN. (iii) $NiCl_2·6H_2O$, EtOH; $(dme)NiBr_2$, CH_2Cl_2.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

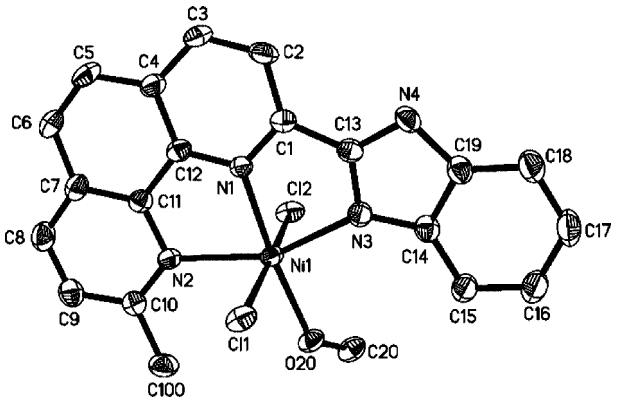


Figure 2. ORTEP drawing of complex **1a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

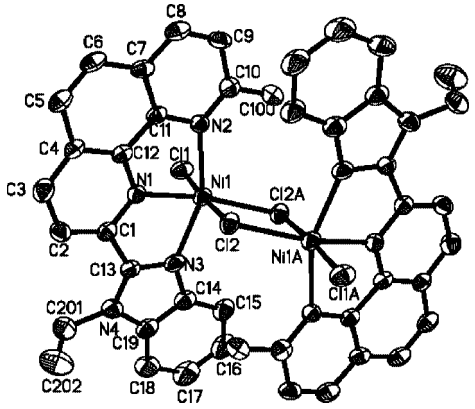


Figure 3. ORTEP drawing of complex **3a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and one molecule of H_2O have been omitted for clarity.

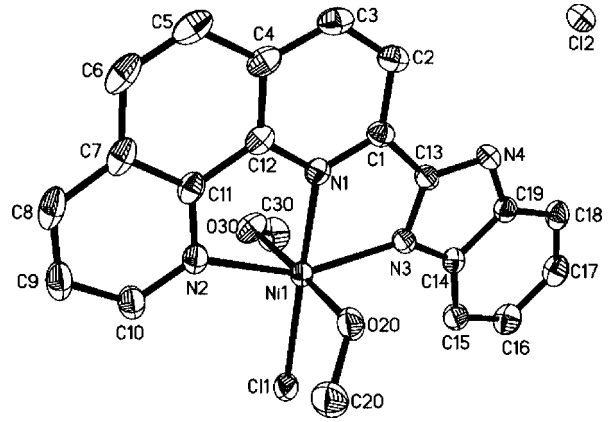


Figure 4. ORTEP drawing of complex **6a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

acetonitrile solution layered with diethyl ether. Their structures are depicted in Figures 2–5, and selected bond lengths and angles are collected in Table 1.

In the structure of **1a** (Figure 2), the coordination geometry around the nickel center can be described as a distorted octahedron because of the coordination of the solvent. The

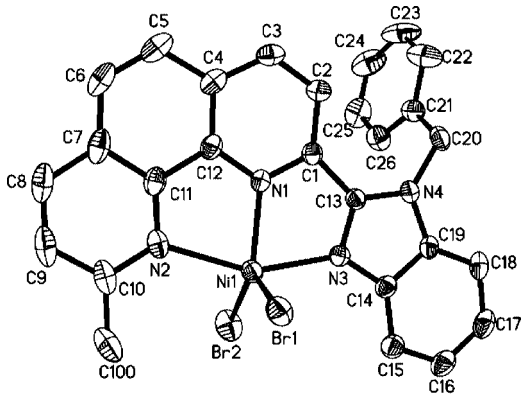


Figure 5. ORTEP drawing of complex **5b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

nickel center is coordinated to N1, N2 (1,10-phenanthroline), and N3 (benzimidazole), forming two fused five-membered rings with acute Ni–N angles: 77.85(1)° (N1–Ni1–N2) and 76.88(1)° (N1–Ni1–N3). The Ni1 atom deviates by 0.1149 Å from the coordinated plane. The dihedral angle between the phenanthrolinyl plane and the benzimidazole plane decreases to 5.8°, which is smaller than that of **L7** (7.6°). The bond lengths of Ni–N and Ni–Cl are significantly different: the Ni1–N1 bond [2.006(4) Å] is shorter than Ni1–N2 [2.208(4) Å] and Ni1–N3 [2.158(4) Å]; the Ni1–Cl2 bond [2.4460(2) Å] is longer than Ni1–Cl1 [2.3823(2) Å].

The structure of **3a** shows a centrosymmetric dinuclear nickel center (Figure 3) in a slightly distorted octahedral geometry. Each nickel atom is coordinated by three nitrogen atoms of the ligand, one terminal chlorine atom (Cl1), and two bridged chlorine atoms (Cl2 and Cl2A). The Ni1 atom deviates by 0.0785 Å from the plane of Cl1–N1–Cl2 and 0.0488 Å from the coordination plane (N1–N2–N3). The coordination plane incorporating N1, N2, and N3 is nearly perpendicular to the Ni1–Ni1A–Cl2–Cl2A plane, with a dihedral angle of 87.9°. The intramolecular distance of Ni···Ni is 3.658 Å, which is shorter than that in other dinuclear nickel complexes.[8c,12a] The dihedral angle between the phenanthrolinyl plane and the benzimidazole plane in **3a** (R^2 = Et) is 7.9°, which is wider than that in **1a** (R^2 = H) (5.8°). The bond lengths of Ni–N and Ni–Cl in **3a** are also different: the Ni1–N2 bond [2.202(3) Å] is longer than Ni1–N1 [2.006(3) Å] and Ni1–N3 [2.129(3) Å]; the bridged Ni1–Cl2 bond [2.5200(1) Å] is longer than Ni1–Cl1 [2.3846(1) Å].

As previously reported,[17a,18b] crystals of N^N^N tridentate nickel complexes contain not only five-coordinate species (**5b**), which are often observed in similar nickel complexes, but also six-coordinate ones, which can be realized through either the formation of dimers with bridged halogen atoms (**3a**) or the coordination of an additional solvent molecule to the metal atom (**1a**). Complex **6a** demonstrates another way of realizing the distorted octahedral coordination geometry of the Ni center (Figure 4). The six-coordinate structure of **6a** is similar to that of complexes **1a** and

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1a**, **3a**, **6a**, and **5b**.

	1a (X = Cl)	**3a** (X = Cl)	**6a** (X = Cl)	**5b** (X = Br)
Bond lengths [Å]				
Ni1–N1	2.006(4)	2.006(3)	2.0328(2)	1.994(3)
Ni1–N2	2.208(4)	2.202(3)	2.1722(2)	2.181(3)
Ni1–N3	2.158(4)	2.129(3)	2.1338(2)	2.094(3)
Ni1–X1	2.3823(2)	2.3846(1)	2.3389(6)	2.4217(7)
Ni1–X2	2.4460(2)	2.5200(1)		2.3969(8)
N3–C13	1.324(6)	1.335(5)	1.328(2)	1.324(4)
N3–C14	1.383(6)	1.396(5)	1.381(2)	1.384(4)
N4–C13	1.349(6)	1.369(5)	1.346(2)	1.364(4)
N4–C19	1.394(6)	1.387(5)	1.378(3)	1.388(4)
Bond angles [°]				
N2–Ni1–N1	77.85(1)	78.11(1)	77.55(6)	78.40(1)
N2–Ni1–N3	154.29(1)	154.60(1)	153.97(6)	154.55(1)
N1–Ni1–N3	76.88(1)	76.57(1)	76.49(6)	76.67(1)
N2–Ni1–X1	86.05(1)	89.27(9)	102.28(5)	94.87(8)
N1–Ni1–X1	96.46(1)	95.71(1)	177.77(5)	103.33(8)
N3–Ni1–X1	92.18(1)	91.26(1)	103.73(5)	95.76(8)
N1–Ni1–X2	88.59(1)	85.40(9)		127.54(8)
N2–Ni1–X2	88.41(1)	87.32(9)		97.49(8)
N3–Ni1–X2	95.56(1)	92.61(1)		93.63(8)
X1–Ni1–X2	171.55(5)	176.12(4)		129.06(3)

3a. However, one chlorine atom (Cl2) is replaced by one methanol molecule and acts as a counterion relatively far from the nickel atom Ni1, with an Ni1···Cl2 distance of 6.892 Å. The nickel atom and the mutually *trans*-disposed oxygen atoms are almost in the same line, with an angle of 174.85° (O20–Ni1–O30). Also, the nickel atom, N1, and Cl1 are almost in the same line, with an angle of 177.77 ° (N1–Ni1–Cl1). The Ni atom deviates slightly from the coordination plane, by 0.0459 Å. The dihedral angle between the phenanthrolinyl plane and the benzimidazole plane in **6a** is 7.5°, which is wider than that in **1a** (5.8°).

In the structure of **5b** (Figure 5), the coordination geometry of the nickel center can be best described as distorted trigonal-bipyramidal; the phenanthroline nitrogen atom (N1) and the two bromine atoms (Br1 and Br2) form the equatorial plane. The nickel atom slightly deviates from the plane, by 0.0347 Å, and equatorial angles range between 103.33(8)° and 127.54(8)°. The two axial Ni–N bonds subtend an angle of 154.55(1)°. This equatorial plane is essentially perpendicular to the phenanthrolinyl plane, with a dihedral angle of 90.1°. The sterically bulky benzyl group (R^2) is nearly perpendicular to the phenanthrolinyl plane, with a dihedral angle of 76.8°. It is notable that different R^2 substituents in the ligands have some influence on the Ni1–N3 bond length, and the Ni1–N3 bond of complex **5b** [2.094(3) Å] is shorter than those of complex **1a** [2.158(4) Å] and complex **3a** [2.129(3) Å]. The Ni1–N1 (phenanthroline) bond is shorter by about 0.1 Å than the Ni1–N3 (benzimidazole) (2.0943 Å) bond and by 0.187 Å than the Ni1–N2 (phenanthroline) (2.1813 Å) bond, which is similar to the (2-imino-1,10-phenanthrolinyl)nickel complexes.[18b] The two Ni–Br bond lengths show a slight difference between Ni1–Br2 [2.3969(8) Å] and Ni1–Br1 [2.4217(7) Å].

Catalytic Properties of Complexes 1a–10a and 1b–10b for Ethylene Oligomerization

Ethylene oligomerization catalyzed by these nickel complexes using different cocatalysts has been systematically investigated. Treatment of complexes **6a** and **5b** with MAO, MMAO, Et_3Al, or Et_2AlCl in toluene generates active ethylene oligomerization catalysts. The results are summarized in Table 2. In each case, the reaction produced a mixture of C_4 and C_6 components. Et_2AlCl was found to be the most effective cocatalyst, which was similar to our previous N^N^N nickel system.[18b] Meanwhile, Et_2AlCl generally led to slightly higher selectivities for 1-butene (Entries 4 and 8, Table 2).

In the presence of Et_2AlCl, complexes **6a** and **5b** were typically investigated for further optimization by varying the Al/Ni molar ratio, ethylene pressure, reaction temperature, and reaction time. The detailed results are shown in Table 3.

For the nickel chloride complex **6a**, the highest activity [1.27×10^7 g·mol^{-1}(Ni)·h^{-1}] was observed at an Al/Ni ratio of 300 (Entry 2, Table 3), and greater loading of Et_2AlCl (500–1000 equiv.) led to lower activities (Entries 3–5, Table 3). For the nickel bromide complex **5b**, the enhancement of the Al/Ni molar ratio from 200 to 800 resulted in an increase of catalytic activity (Entries 14–17, Table 3). With an Al/Ni molar ratio of 800, the catalytic activity of **5b** peaked at 4.00×10^6 g·mol^{-1}(Ni)·h^{-1} (Entry 17, Table 3). A further increase of the Al/Ni molar ratio resulted in decreased oligomerization activity (Entry 18, Table 3). The α-C_4 selectivity was also affected by the Al/Ni molar ratio. When the Al/Ni molar ratio was enhanced from 200 to 1000, α-C_4 selectivity for both **6a** and **5b** monotonously and

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 2. Ethylene oligomerization with different cocatalyst.[a]

Entry	Complex	Cocatalyst	Activity[b]	Oligomer distribution[c] [%]		α-C_4 [%]
				$C_4/\Sigma C$	$C_6/\Sigma C$	
1	**6a**	Et_3Al	1.22	91.9	8.1	61.2
2	**6a**	MAO	0.92	93.7	6.3	54.4
3	**6a**	MMAO	1.13	93.0	7.0	59.1
4	**6a**	Et_2AlCl	8.80	89.9	10.1	66.0
5	**5b**	Et_3Al	1.01	91.3	8.7	68.4
6	**5b**	MAO	0.87	93.2	6.8	62.3
7	**5b**	MMAO	0.94	92.4	7.6	65.4
8	**5b**	Et_2AlCl	3.40	90.2	9.8	72.5

[a] General conditions: 5 μmol of complex, 100 mL of toluene, T = 20 °C, 30 atm of C_2H_4, 20 min, Al/Ni = 1000. [b] 10^6 g·mol^{-1}(Ni)·h^{-1}. [c] Determined by GC.

Table 3. Ethylene oligomerization with **6a**/Et_2AlCl and **5b**/Et_2AlCl systems.[a]

Entry	Complex	Al/Ni	T [°C]	P [atm]	t [min]	Activity[b]	Oligomer distribution[c] [%]		α-C_4 [%]
							$C_4/\Sigma C$	$C_6/\Sigma C$	
1	**6a**	200	20	30	20	8.81	93.2	6.8	77.5
2	**6a**	300	20	30	20	12.69	90.1	9.9	72.6
3	**6a**	500	20	30	20	9.97	91.3	8.7	70.2
4	**6a**	800	20	30	20	9.73	89.4	10.6	68.7
5	**6a**	1000	20	30	20	8.80	89.9	10.1	66.0
6	**6a**	300	40	30	20	10.09	89.1	10.9	46.1
7	**6a**	300	60	30	20	1.51	94.0	6.0	40.8
8	**6a**	300	80	30	20	0.52	93.8	6.2	20.1
9	**6a**	300	20	20	20	3.55	90.5	9.5	61.4
10	**6a**	300	20	10	20	2.16	91.6	8.4	54.1
11	**6a**	300	20	30	30	9.84	91.0	9.0	70.5
12	**6a**	300	20	30	40	8.25	96.5	3.5	68.3
13	**6a**	300	20	30	60	6.17	90.3	9.7	64.2
14	**5b**	200	20	30	20	0.90	95.5	4.5	85.3
15	**5b**	300	20	30	20	1.50	94.0	6.0	81.1
16	**5b**	500	20	30	20	2.03	94.9	5.1	75.4
17	**5b**	800	20	30	20	4.00	91.0	9.0	74.2
18	**5b**	1000	20	30	20	3.40	90.2	9.8	72.5
19	**5b**	800	40	30	20	3.60	92.5	7.5	50.9
20	**5b**	800	60	30	20	0.83	97.1	2.9	43.8
21	**5b**	800	80	30	20	0.16	96.6	3.4	21.4
22	**5b**	800	20	20	20	1.03	96.5	3.5	70.4
23	**5b**	800	20	10	20	0.75	92.9	7.1	63.1
24	**5b**	800	20	30	30	2.67	90.3	9.7	73.1
25	**5b**	800	20	30	40	1.96	94.7	5.3	72.5
26	**5b**	800	20	30	60	1.28	92.2	7.8	72.0

[a] General conditions: 5 μmol of complex; 100 mL of toluene; Et_2AlCl as cocatalyst. [b] 10^6 g·mol^{-1}(Ni)·h^{-1}. [c] Determined by GC.

gradually decreased. However, the varied amounts of cocatalyst had no apparent influence on the proportion of the C_4 component in the oligomers produced.

As is apparent, the ethylene concentration significantly affects the catalytic behaviors of the complexes. When the ethylene pressure increased from 10 atm to 30 atm, the ethylene oligomerization activity increased sharply for both **6a** and **5b**. In addition, the α-C_4 selectivity also increased slightly (Entries 2, 9, 10 and Entries 17, 22, 23, Table 3). Elevating the reaction temperature of the **6a**/Et_2AlCl and **5b**/Et_2AlCl systems from 20 °C to 80 °C resulted in a sharp decrease of activity and α-C_4 selectivity, which may be attributed to the decomposition of the active catalytic sites and lower ethylene concentration at higher temperature (Entries 2, 6–8 and Entries 17, 19–21, Table 3).

The catalyst lifetime is a significant factor in industrial considerations. The oligomerization activities and selectivities for 1-butene were monitored at different time intervals in the ethylene oligomerization promoted by **6a**/Et_2AlCl and **5b**/Et_2AlCl systems. A slight decrease in activity was determined over a period of 20 min to 1 h for complex **6a**, indicating a rather long catalyst lifetime. Meanwhile, the α-C_4 selectivity decreased slightly with prolonged reaction time. This observation may be attributed to the isomerization reaction of the produced 1-butene catalyzed by the nickel complex.[9c,17b,24] However, for complex **5b**, the catalytic species showed almost no activity after 20 min.

The results of ethylene oligomerization with all the nickel complexes as precatalysts are collected in Table 4. It can be observed that the ligand environment has considerable ef-

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

fects on the catalytic behaviors, such as activity and α-C_4 selectivity. The introduction of a methyl group on the 9-position of the phenanthroline ring led to a dramatic decrease in oligomerization activity and a slight increase in α-C_4 selectivity. This could be demonstrated by comparing complexes **1a**–**5a** (R^1 = Me) with **6a**–**10a** (R^1 = H). As shown in Table 4, complexes **6a**–**10a** (Entries 6–10, Table 4) displayed higher activities and lower α-C_4 selectivities than their analogues **1a**–**5a** (Entries 1–5, Table 4). The same trend was also observed for the nickel dibromide complexes **1b**–**10b** (compare Entries 16–20 with Entries 11–15, Table 4).

The incorporation of an alkyl group on the nitrogen atom of the benzimidazole ligand in the complex led to a decrease in oligomerization activity and α-C_4 selectivity. Complexes **1a** and **1b** or **6a** and **6b** containing the N–H group showed much higher activities than their *N*-alkylated analogues (compare Entry 1 with Entries 2–5, Entry 11 with Entries 12–15, Entry 6 with Entries 7–10, and Entry 16 with Entries 17–20, Table 4). Tentatively, these results suggest that N–H functionality is essential for high activity and selectivity with this ligand system, which could be caused by their deprotonation to give anionic amide ligands when activated by Et_2AlCl. The anionic amide ligands could be free or form N–Al species (anion–cation pair) to increase their catalytic activity. This observation is consistent with a previous report, although the mechanism is not clear.[22a,25] Different alkyl groups such as methyl, ethyl, isopropyl, and benzyl groups had no obvious influence on α-C_4 selectivity. Meanwhile, the steric bulk effects of these groups on oligomerization activities are not very regular, which could be attributed to the longer distance between the alkyl group and the metal center.

The effect of the coordinated halide X (X = Cl or Br) on the ethylene reactivity seems to be rather small. With the exception of complexes **6a** and **6b**, each nickel bromide complex showed slightly higher activity than the corresponding chloride ones, which may be attributed to the better solubility in toluene for the bromide complexes.

Previous studies on nickel catalysts have demonstrated that incorporating PPh_3 into the catalytic system can lead to higher activity and longer lifetime. Meanwhile, the potential catalytic intermediates incorporating PPh_3 were observed and the relationship between the amounts of PPh_3 and the catalytic activity was explored.[8c,12e,18b] Complexes **2a**, **6a**, **7a**, and **1b** were selected to further study the effect of PPh_3 on the α-C_4 selectivity. The detailed results are summarized in Table 5. In the presence of 20 equiv. of PPh_3,

Table 4. Ethylene oligomerization with **1a**–**10a** and **1b**–**10b**/Et_2AlCl systems.[a]

Entry	Complex	Activity[b]	Oligomer distribution[c] [%]		α-C_4 [%]
			$C_4/\Sigma C$	$C_6/\Sigma C$	
1	**1a**	2.33	92.3	7.7	90.5
2	**2a**	1.06	93.4	6.6	85.7
3	**3a**	0.97	95.9	4.1	86.2
4	**4a**	0.91	97.1	2.9	83.6
5	**5a**	1.22	95.0	5.0	84.2
6	**6a**	12.69	90.1	9.9	72.6
7	**7a**	2.77	96.6	3.4	70.8
8	**8a**	4.03	96.2	3.8	66.4
9	**9a**	4.21	92.9	7.1	67.9
10	**10a**	2.00	95.7	4.3	70.3
11	**1b**	2.52	91.1	8.9	89.2
12	**2b**	1.27	92.5	7.5	82.8
13	**3b**	1.14	97.4	2.6	80.9
14	**4b**	1.02	94.4	5.6	86.4
15	**5b**	1.50	94.0	6.0	81.1
16	**6b**	10.08	90.4	9.6	71.3
17	**7b**	3.28	96.9	3.1	68.9
18	**8b**	4.24	94.6	5.4	67.2
19	**9b**	4.68	95.2	4.8	66.1
20	**10b**	2.16	95.6	4.4	69.0

[a] General conditions: 5 μmol of complex and 100 mL of toluene; Et_2AlCl as cocatalyst and Al/Ni = 300. T = 20 °C, 30 atm of C_2H_4, 20 min. [b] 10^6 g·mol^{-1}(Ni)·h^{-1}. [c] Determined by GC.

Table 5. Ethylene oligomerization with **2a**, **6a**, **7a**, and **1b**/Et_2AlCl/Ph_3P systems.[a]

Entry	Complex	Activity[b]	Oligomer distribution[c] [%]		α-C_4 [%]
			$C_4/\Sigma C$	$C_6/\Sigma C$	
1	**2a**	3.78	92.5	7.5	19.5
2	**6a**	3.21	88.4	11.6	20.8
3	**7a**	3.95	91.8	8.2	12.1
4	**1b**	2.67	91.3	8.7	26.7

[a] General conditions: 5 μmol of complex; Et_2AlCl as cocatalyst and Al/Ni = 300; 20 equiv. of PPh_3 and 100 mL of toluene; T = 20 °C, 30 atm of C_2H_4, 20 min. [b] 10^7 g·mol^{-1}(Ni)·h^{-1}. [c] Determined by GC.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

the activities of all investigated complexes are much higher [up to 10^7 g·mol^{-1}(Ni)·h^{-1}] than those of catalytic systems without PPh_3. For complex **7a**, a more than 10 times higher activity was achieved, reaching 3.95×10^7 g·mol^{-1}(Ni)·h^{-1} (Entry 7 in Table 4 vs. Entry 3 in Table 5). The plausible role of PPh_3 is that of association and dissociation with the nickel core to activate and protect the active sites. However, it is noteworthy that analysis of the products shows that the selectivities for 1-butene are much lower (≤26.7%). Further studies to understand the effects of the auxiliary ligand on the ethylene oligomerization are in progress.

Conclusions

A series of nickel catalysts ligated by 2-(benzimidazol-2-yl)-1,10-phenanthroline derivatives have been found to possess several characteristics that make them attractive catalysts for ethylene oligomerization. On treatment with Et_2AlCl, these complexes oligomerize ethylene to dimers and trimers with high activities and α-olefin selectivities. Further experimental results illustrate their sensitivity toward different ligand environments, reaction temperatures, and ethylene pressures. Complexes **1a**–**5a** and **1b**–**5b**, with a methyl group on the 9-position of the phenanthrolinyl ring (R^1 = Me), showed lower activities but higher selectivities for α-olefins than complexes **6a**–**10a** and **6b**–**10b** (R^1 = H). The incorporation of an alkyl group (R^2) on the nitrogen atom of the benzimidazole led to a decrease in oligomerization activity and selectivity for 1-butene (complexes **1a**, **1b**, **6a**, and **6b**). In general, higher ethylene pressure and lower temperature resulted in higher activities and α-olefin selectivities of the catalysts. Additionally, in the presence of 20 equiv. of PPh_3, the activities of all investigated complexes increased dramatically with lower selectivities for 1-butene.

Experimental Section

General Procedure: All air- or moisture-sensitive manipulations were carried out under nitrogen using standard Schlenk techniques. Melting points were determined with a digital electrothermal apparatus without calibration. IR spectra were obtained with a Perkin–Elmer FTIR 2000 spectrophotometer by using KBr disks in the range of 4000–400 cm^{-1}. NMR spectra were recorded with a Bruker DMX-300 or Bruker ARX 400 spectrometer with TMS as the internal standard. Elemental analyses were performed with a Flash EA 1112 microanalyzer. GC was 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 column. Toluene was refluxed in the presence of sodium/benzophenone and distilled under nitrogen prior to use. The polymerization-grade ethylene was supplied by Beijing Yansan Petrochemical Co. Et_2AlCl (1.90 M) solution in toluene and triethylaluminum (diluted to 2 M in toluene for usage) were purchased from Acros Chemicals, while methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. All other commercial chemicals were used without further purification.

Synthesis of Ligands: New synthetic procedures were developed to prepare the original organic compounds, 2-(1*H*-benzimidazol-2-yl)-9-methyl-1,10-phenanthroline (**L1**) and 2-(1*H*-benzimidazol-2-yl)-1,10-phenanthroline (**L6**). The *N*-alkylation of **L1** and **L6** was subjected to different modified conditions to synthesize their derivatives, **L2**–**L5** and **L7**–**L10**, individually.

2-(1*H*-Benzimidazol-2-yl)-9-methyl-1,10-phenanthroline (L1): A mixture of 2,9-dimethyl-1,10-phenanthroline ($2C_{14}H_{12}N_2 \cdot H_2O$) (1.00 g, 4.80 mmol), *o*-phenylenediamine (0.58 g, 5.36 mmol), and sulfur (3.00 g, 11.70 mmol) was heated and kept at 170 °C for 8 h. After the mixture had cooled to room temperature, 200 mL of methanol was added to extract the product, and the precipitated solid was filtered off. The filtrate was concentrated and the residual brown oil was purified by column chromatography (silica gel, chloroform/ethyl acetate/methanol as elute, v/v/v = 20:20:1) to give an ivory-white powder (0.60 g) in 42% yield. M.p. 138–140 °C. IR (KBr disk): $\tilde{\nu}$ = 3419, 3051, 2950, 1620, 1590, 1466, 1435, 1337, 1189, 1065, 889, 768, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.60 (s, 1 H, NH), 8.58 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.18 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.06 (d, ^1J = 8.4 Hz, 1 H, Phen), 7.82 (d, ^1J = 6.0 Hz, 1 H, Phen), 7.66 (s, 2 H, Phen), 7.49 (d, ^1J = 6.0 Hz, 1 H, benzimidazole), 7.36 (d, ^1J = 8.4 Hz, 1 H, benzimidazole), 7.24 (dd, ^1J = 6.0 Hz, 2 H, benzimidazole), 2.80 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 151.9, 150.6, 147.2, 143.7, 143.5, 135.8, 135.6, 127.7, 126.0, 125.5, 124.5, 123.0, 119.8, 111.9, 23.5 ppm. $C_{20}H_{14}N_4$ (310.35): calcd. C 77.06, H 4.39, N 18.55; found C 77.40, H 4.55, N 18.05.

9-Methyl-2-(1-methyl-1*H*-benzimidazol-2-yl)-1,10-phenanthroline (L2): K_2CO_3 (0.50 g, 3.62 mmol) was added to a solution of **L1** (0.25 g, 0.80 mmol) in acetonitrile (50 mL). After the mixture was refluxed for 12 h, iodomethane (0.07 mL, 1.12 mmol) was added and the mixture was stirred at room temperature for 24 h. After filtration and concentartion, an orange oil was obtained; thereafter it was dissolved in $CHCl_3$ (50 mL) and washed with water (50 mL × 3). The organic phase was separated, dried with anhydrous $MgSO_4$, and the solvents were evaporated. The residue was purified by column chromatography (silica gel, triethylamine/petroleum ether as elute, v/v = 2:1) to give a white powder (0.12 g) in 46% yield. M.p. 170–172 °C. IR (KBr disk): $\tilde{\nu}$ = 2919, 1614, 1588, 1438, 1414, 1326, 1258, 1096, 855, 728 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.38 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.17 (d, ^1J = 8.4 Hz, 1 H, Phen), 7.89 (d, ^1J = 8.0 Hz, 1 H, Phen), 7.83 (d, ^1J = 8.8 Hz, 1 H, Phen), 7.79 (d, ^1J = 8.8 Hz, 1 H, Phen), 7.55 (t, ^1J = 7.2 Hz, 2 H, benzimidazole), 7.40 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 7.35 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 4.78 (s, 3 H, CH_3), 2.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 150.4, 150.1, 145.7, 145.0, 142.8, 137.8, 136.7, 136.3, 127.2, 127.0, 125.3, 123.7, 123.4, 122.7, 120.2, 110.2, 33.2, 26.0 ppm. $C_{21}H_{16}N_4$ (324.38): calcd. C 77.45, H 5.23, N 17.32; found C 77.76, H 4.97, N 17.27.

2-(1-Ethyl-1*H*-benzimidazol-2-yl)-9-methyl-1,10-phenanthroline (L3): Ligands **L3**–**L5** and **L7**–**L10** were prepared using a similar method to that for **L2**. Iodoethane (0.09 mL, 1.12 mmol) reacted with deprotonated **L1** at 60 °C for 12 h. **L3** was obtained as a pink solid in 60% yield after purification by column chromatography (silica gel, triethylamine as elute). M.p. 128–130 °C. IR (KBr disk): $\tilde{\nu}$ = 2962, 1615, 1588, 1488, 1416, 1329, 1264, 1097, 849, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.37 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.16 (d, ^1J = 8.4 Hz, 1 H, Phen), 7.90 (d, ^1J = 8.0 Hz, 1 H, Phen), 7.83 (d, ^1J = 8.8 Hz, 1 H, Phen), 7.79 (d, ^1J = 8.8 Hz, 1 H, Phen), 7.55 (t, ^1J = 7.2 Hz, 2 H, benzimidazole), 7.39 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 7.34 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 5.34 (q, ^1J = 7.2 Hz, 2 H, CH_2CH_3), 2.92 (s, 3 H, CH_3), 1.77 (t, ^1J = 7.2 Hz, 3 H, CH_2CH_3) ppm. ^{13}C

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

NMR (75 MHz, $CDCl_3$): δ = 159.5, 150.2, 150.0, 145.9, 145.3, 143.1, 136.8, 136.6, 136.1, 128.4, 127.2, 127.0, 125.3, 123.6, 123.3, 122.6, 120.3, 110.3, 41.4, 25.8, 15.8 ppm. $C_{22}H_{18}N_4$ (338.41): calcd. C 77.81, H 5.66, N 16.53; found C 78.08, H 5.36, N 16.56.

2-(1-Isopropyl-1*H*-benzimidazol-2-yl)-9-methyl-1,10-phenanthroline (L4): 2-Iodopropane (0.11 mL, 1.12 mmol) reacted with deprotonated **L1** and was refluxed for 12 h. **L4** was obtained as yellow crystals in 43% yield by column chromatography (silica gel, triethylamine as elute). M.p. 130–132 °C. IR (KBr disk): $\tilde{\nu}$ = 2967, 1617, 1588, 1493, 1419, 1404, 1387, 1132, 855, 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.63 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.36 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.12 (d, ^1J = 8.1 Hz, 1 H, Phen), 7.91 (d, ^1J = 8.4 Hz, 1 H, Phen), 7.78–7.75 (m, 3 H, 2 H-Phen, 1 H-benzimidazole), 7.51 (d, ^1J = 8.4 Hz, 1 H, benzimidazole), 7.33 (m, 2 H, benzimidazole), 6.67 (sept, ^1J = 6.6 Hz, 1 H, C*H*$(CH_3)_2$), 2.90 (s, 3 H, C*H*$_3$), 1.90 (d, ^1J = 6.6 Hz, 6 H, CH(C*H*$_3)_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 145.0, 149.5, 144.9, 144.1, 142.8, 135.9, 135.3, 134.3, 127.4, 126.4, 126.1, 124.4, 123.2, 122.8, 122.1, 121.4, 119.8, 112.3, 48.7, 25.0, 20.9 ppm. $C_{23}H_{20}N_4$ (352.43): calcd. C 77.98, H 6.03, N 15.99; found C 78.38, H 5.72, N 15.90.

2-(1-Benzyl-1*H*-benzimidazol-2-yl)-9-methyl-1,10-phenanthroline (L5): Benzyl bromide (0.13 mL, 1.12 mmol) reacted with deprotonated **L1** and was refluxed for 12 h. **L5** was obtained by column chromatography (silica gel, triethylamine as elute) as an ivory-white powder in 55% yield. M.p. 122–124 °C. IR (KBr disk): $\tilde{\nu}$ = 3038, 3004, 1616, 1587, 1495, 1442, 1414, 1329, 864, 740, 720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.36 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.17 (d, ^1J = 8.0 Hz, 1 H, Phen), 7.94 (dd, ^1J = 6.0 Hz, 1 H, Phen), 7.80 (dd, ^1J = 8.4 Hz, 2 H, Phen), 7.55 (d, ^1J = 8.0 Hz, 2 H, benzimidazole), 7.37 (dd, ^1J = 6.0 Hz, 2 H, benzimidazole), 7.31 (d, ^1J = 6.0 Hz, 2 H, Ph), 7.13 (m, 3 H, Ph), 6.90 (s, 2 H, C*H*$_2$), 2.89 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 158.5, 149.1, 145.2, 143.9, 143.6, 143.2, 142.0, 137.2, 136.4, 135.7, 135.2, 127.4, 126.2, 124.3, 122.7, 122.3, 121.9, 119.4, 110.0, 48.1, 24.8 ppm. $C_{27}H_{20}N_4$ (400.47): calcd. C 80.53, H 5.23, N 14.24; found C 80.98, H 5.03, N 13.99.

2-(1*H*-Benzimidazol-2-yl)-1,10-phenanthroline (L6): A mixture of 1,10-phenanthroline-2-carboxylic acid (1.12 g, 5.00 mmol), *o*-phenylenediamine (0.58 g, 5.40 mmol), and polyphosphoric acid (ppa) (7.00 g) was irradiated in a microwave oven (450 W) three times, for 2 min each time. The heated reaction mixture was poured into ice-cold water (300 mL), and the pH was adjusted to 9 by the addition of $NaHCO_3$. The precipitated solid was filtered off. After purification of the solid by column chromatography (silica gel, ethyl acetate/methanol as elute, v/v = 1:1), **L6** was obtained as white crystals (0.36 g) in 26% yield. M.p. 126–128 °C. IR (KBr disk): $\tilde{\nu}$ = 3399, 3059, 1619, 1587, 1502, 1431, 1315, 1275, 856, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.43 (s, 1 H, NH), 9.06 (dd, ^1J = 4.4 Hz, 1 H, Phen), 8.74 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.35 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.24 (dd, ^1J = 8.0 Hz, 1 H, Phen), 7.88 (t, ^1J = 6.4 Hz, 1 H, benzimidazole), 7.82 (dd, ^1J = 8.8 Hz, 2 H, Phen), 7.64 (dd, ^1J = 8.0 Hz, 1 H, Phen), 7.57 (m, 1 H, benzimidazole), 7.30 (m, 2 H, benzimidazole) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.3, 149.0, 148.4, 145.2, 144.8, 144.2, 136.6, 136.5, 134.7, 128.8, 128.5, 126.4, 123.6, 123.0, 122.0, 120.9, 119.6, 111.6 ppm. $C_{19}H_{12}N_4$ (296.33): calcd. C 77.38, H 3.83, N 18.79; found C 77.01, H 4.08, N 18.91.

2-(1-Methyl-1*H*-benzimidazol-2-yl)-1,10-phenanthroline (L7): L7 was obtained as a white powder in 51% yield by column chromatography (silica gel, triethylamine as elute). M.p. 186–188 °C. IR (KBr disk): $\tilde{\nu}$ = 2936, 1617, 1590, 1496, 1463, 1439, 1414, 1259, 1100, 855, 736 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.23 (d, ^1J = 3.9 Hz, 1 H, Phen), 8.77 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.42 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.31 (d, ^1J = 8.0 Hz, 1 H, Phen), 7.92–7.88 (m, 3 H, 2 H-Phen, 1 H-benzimidazole), 7.70 (dd, ^1J = 7.8 Hz, 1 H, Phen), 7.55 (d, ^1J = 7.4 Hz, 1 H, benzimidazole), 7.41 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 7.36 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 4.72 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 149.2, 145.1, 144.3, 144.0, 141.6, 138.0, 136.4, 135.6, 134.9, 127.9, 126.1, 125.2, 122.7, 122.4, 122.0, 121.5, 119.0, 109.0, 29.7 ppm. $C_{20}H_{14}N_4$ (310.35): calcd. C 77.18, H 4.88, N 17.94; found C 77.40, H 4.55, N 18.05.

2-(1-Ethyl-1*H*-benzimidazol-2-yl)-1,10-phenanthroline (L8): L8 was obtained as a pale yellow powder in 62% yield by column chromatography (silica gel, triethylamine as elute). M.p. 156–158 °C. IR (KBr disk): $\tilde{\nu}$ = 3038, 2961, 1614, 1588, 1555, 1461, 1418, 1379, 1328, 1290, 1105, 845, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.22 (d, ^1J = 4.0 Hz, 1 H, Phen), 8.76 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.42 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.30 (d, ^1J = 8.0 Hz, 1 H, Phen), 7.91 (d, ^1J = 7.6 Hz, 1 H, benzimidazole), 7.88 (s, 2 H, Phen), 7.68 (dd, ^1J = 8.0 Hz, 1 H, Phen), 7.57 (d, ^1J = 8.0 Hz, 1 H, benzimidazole), 7.40 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 7.36 (t, ^1J = 7.2 Hz, 1 H, benzimidazole), 5.38 (q, ^1J = 7.2 Hz, 2 H, C*H*$_2$CH$_3$), 1.61 (t, ^1J = 7.2 Hz, 3 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 149.1, 148.7, 145.3, 144.2, 141.8, 137.5, 135.4, 134.7, 127.8, 126.1, 125.1, 122.4, 122.3, 121.9, 121.3, 119.0, 109.0, 39.8, 14.3 ppm. $C_{21}H_{16}N_4$ (324.38): calcd. C 77.48, H 4.78, N 17.64; found C 77.76, H 4.97, N 17.27.

2-(1-Isopropyl-1*H*-benzimidazol-2-yl)-1,10-phenanthroline (L9): L9 was obtained as a brown powder in 32% yield through column chromatography (silica gel, triethylamine as elute). M.p. 130–132 °C. IR (KBr disk): $\tilde{\nu}$ = 2973, 1617, 1586, 1495, 1457, 1422, 1336, 1282, 1254, 1136, 862, 744 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.18 (d, ^1J = 3.3 Hz, 1 H, Phen), 8.60 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.41 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.27 (d, ^1J = 8.0 Hz, 1 H, Phen), 7.90 (d, ^1J = 5.4 Hz, 1 H, benzimidazole), 7.86 (s, 2 H, Phen), 7.76 (d, ^1J = 6.0 Hz, 1 H, benzimidazole), 7.65 (dd, ^1J = 7.2 Hz, 1 H, Phen), 7.32 (m, 2 H, benzimidazole), 6.45 [sept, ^1J = 6.9 Hz, 1 H, C*H*$(CH_3)_2$], 1.86 [d, 6 H, CH(C*H*$_3)_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 149.5, 149.4, 145.2, 144.1, 142.5, 135.6, 134.7, 133.8, 127.8, 127.0, 126.2, 125.1, 123.2, 122.0, 121.7, 121.0, 119.5, 111.9, 48.2, 20.5 ppm. $C_{22}H_{18}N_4$ (338.41): calcd. C 78.44, H 4.93, N 16.63; found C 78.08, H 5.36, N 16.56.

2-(1-Benzyl-1*H*-benzimidazol-2-yl)-1,10-phenanthroline (L10): L10 was obtained as a brown powder in 47% yield by column chromatography (silica gel, triethylamine as elute). M.p. 108–110 °C. IR (KBr disk): $\tilde{\nu}$ = 2928, 1605, 1588, 1496, 1434, 1351, 1259, 1163, 1078, 857, 735 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.13 (d, ^1J = 3.2 Hz, 1 H, Phen), 8.65 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.27 (d, ^1J = 8.4 Hz, 1 H, Phen), 8.18 (d, ^1J = 7.2 Hz, 1 H, Phen), 7.84 (t, ^1J = 6.0 Hz, 1 H, benzimidazole), 7.74 (s, 2 H, Phen), 7.58 (dd, ^1J = 8.0 Hz, 1 H, Phen), 7.47 (t, ^1J = 6.0 Hz, 1 H, benzimidazole), 7.28 (t, ^1J = 3.2 Hz, 2 H, benzimidazole), 7.22 (s, 1 H, Phen), 7.12 (d, ^1J = 3.2 Hz, 2 H, Ph), 6.99 (m, 3 H, Ph), 6.71 (s, 2 H, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 149.2, 148.9, 145.3, 141.9, 137.0, 136.2, 135.7, 134.9, 128.0, 127.3, 126.3, 126.1, 125.2, 122.9, 122.6, 122.1, 121.8, 119.3, 109.8, 47.9 ppm. $C_{26}H_{18}N_4$ (386.45): calcd. C 81.13, H 4.82, N 14.05; found C 80.81, H 4.69, N 14.50.

Syntheses of Nickel Complexes 1a–10a and 1b–10b: Complexes **1a**–**10a** were prepared according to the following procedure. The corresponding ligand and 1 equiv. of $NiCl_2 \cdot 6H_2O$ were individually dissolved in ethanol and mixed together. The reaction mixture was stirred at room temperature for 8 h. The resulting precipitate was

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

filtered, washed with diethyl ether, and dried in a vacuum. Instead of $NiCl_2·6H_2O$ in the same synthetic procedure, a stoichiometric amount of (dme)$NiBr_2$ and the corresponding ligand in CH_2Cl_2 were stirred under nitrogen to form the nickel bromide complexes **1b**–**10b**.

Characterization Data of Nickel Dichloride Complexes 1a–10a. 1a: Green powder in 87% yield. IR (KBr disk): $\tilde{\nu}$ = 3254, 1624, 1588, 1504, 1429, 1321, 863, 747 cm^{-1}. $C_{20}H_{14}Cl_2N_4Ni·H_2O$ (457.97): calcd. C 52.19, H 3.17, N 12.66; found C 52.45, H 3.52, N 12.23. **2a**: Green powder in 82% yield. IR (KBr disk): $\tilde{\nu}$ = 1622, 1589, 1504, 1486, 1464, 862, 745 cm^{-1}. $C_{21}H_{16}Cl_2N_4Ni$ (453.98): calcd. C 55.14, H 3.07, N 12.55; found C 55.56, H 3.55, N 12.34. **3a**: Green powder in 86% yield. IR (KBr disk): $\tilde{\nu}$ = 3333, 1621, 1585, 1491, 1441, 1334, 862, 746 cm^{-1}. $C_{22}H_{18}Cl_2N_4Ni$ (468.00): calcd. C 56.14, H 3.47, N 11.65; found C 56.46, H 3.88, N 11.97. **4a**: Green powder in 91% yield. IR (KBr disk): $\tilde{\nu}$ = 3371, 2973, 1622, 1586, 1517, 1446, 1334, 1161, 865, 747 cm^{-1}. $C_{23}H_{20}Cl_2N_4Ni$ (482.03): calcd. C 57.62, H 4.46, N 11.33; found C 57.31, H 4.18, N 11.62. **5a**: Green powder in 90% yield. IR (KBr disk): $\tilde{\nu}$ = 3056, 1619, 1586, 1522, 1481, 1447, 1426, 1334, 857, 746 cm^{-1}. $C_{27}H_{20}N_4NiCl_2$ (530.07): calcd. C 61.04, H 3.57, N 10.65; found C 61.18, H 3.80, N 10.57. **6a**: Green powder in 84% yield. IR (KBr disk): $\tilde{\nu}$ = 3273, 3046, 1614, 1581, 1512, 1446, 1321, 859, 742, 706 cm^{-1}. $C_{19}H_{12}Cl_2N_4Ni$ (425.92): calcd. C 53.13, H 2.51, N 13.50; found C 53.58, H 2.84, N 13.15. **7a**: Green powder in 88% yield. IR (KBr disk): $\tilde{\nu}$ = 3273, 1621, 1577, 1530, 1510, 1460, 1418, 1335, 854, 743, 706 cm^{-1}. $C_{20}H_{14}Cl_2N_4Ni$ (439.95): calcd. C 54.11, H 3.59, N 12.47; found C 54.60, H 3.21, N 12.73. **8a**: Green powder in 85% yield. IR (KBr disk): $\tilde{\nu}$ = 3340, 1621, 1607, 1579, 1526, 1482, 1442, 1334, 853, 745 cm^{-1}. $C_{21}H_{16}Cl_2N_4Ni$ (453.98): calcd. C 55.17, H 3.88, N 12.11; found C 55.56, H 3.55, N 12.34. **9a**: Green powder in 89% yield. IR (KBr disk): $\tilde{\nu}$ = 2976, 1620, 1577, 1522, 1440, 1334, 857, 746 cm^{-1}. $C_{22}H_{18}Cl_2N_4Ni$ (468.00): calcd. C 56.09, H 3.51, N 12.32; found C 56.46, H 3.88, N 11.97. **10a**: Green powder in 90% yield. IR (KBr disk): $\tilde{\nu}$ = 3055, 1621, 1605, 1577, 1523, 1467, 1436, 1333, 857, 739 cm^{-1}. $C_{26}H_{18}Cl_2N_4Ni$ (516.05): calcd. C 60.14, H 3.13, N 10.59; found C 60.51, H 3.52, N 10.86.

Characterization Data of Nickel Dibromide Complexes 1b–10b: 1b: Green powder in 79% yield. IR (KBr disk): $\tilde{\nu}$ = 3373, 1624, 1588, 1504, 1446, 1321, 1147, 864, 745 cm^{-1}. $C_{20}H_{14}Br_2N_4Ni$ (528.85): calcd. C 45.66, H 2.74, N 10.35; found C 45.42, H 2.67, N 10.59. **2b**: Green powder in 77% yield. IR (KBr disk): $\tilde{\nu}$ = 2963, 1622, 1587, 1486, 1461, 1261, 1097, 1024, 861, 801, 741 cm^{-1}. $C_{21}H_{16}Br_2N_4Ni$ (542.88): calcd. C 46.24, H 2.65, N 10.77; found C 46.46, H 2.97, N 10.32. **3b**: Green powder in 80% yield. IR (KBr disk): $\tilde{\nu}$ = 3333, 1622, 1586, 1486, 1446, 1335, 1200, 1155, 860, 744 cm^{-1}. $C_{22}H_{18}Br_2N_4Ni·0.5H_2O$ (565.91): calcd. C 47.06, H 3.68, N 10.33; found C 46.69, H 3.38, N 9.90. **4b**: Green powder in 82% yield. IR (KBr disk): $\tilde{\nu}$ = 2971, 1622, 1587, 1516, 1457, 1334, 1160, 861, 752 cm^{-1}. $C_{23}H_{20}Br_2N_4Ni$ (570.93): calcd. C 48.67, H 3.98, N 9.41; found C 48.39, H 3.53, N 9.81. **5b**: Green powder in 73% yield. IR (KBr disk): $\tilde{\nu}$ = 3044, 1624, 1589, 1482, 1448, 1333, 1151, 859, 731 cm^{-1}. $C_{27}H_{20}Br_2N_4Ni$ (618.98): calcd. C 52.78, H 3.64, N 9.50; found C 52.39, H 3.26, N 9.05. **6b**: Green powder in 70% yield. IR (KBr disk): $\tilde{\nu}$ = 3363, 1623, 1580, 1514, 1446, 1320, 1144, 980, 858, 743 cm^{-1}. $C_{19}H_{12}Br_2N_4Ni$ (514.83): calcd. C 44.02, H

Table 6. Crystallographic data and refinement for **L7**, **1a**, **3a**, **6a**, and **5b**.

	L7	**1a**·CH_3OH	**3a**	**6a**·$2CH_3OH$	**5b**
Empirical formula	$C_{20}H_{14}N_4$	$C_{21}H_{17}Cl_2N_4NiO$	$C_{44}H_{36}Cl_4N_8Ni_2O_2$	$C_{21}H_{20}Cl_2N_4NiO_2$	$C_{27}H_{20}Br_2N_4Ni$
Formula mass	310.35	471.00	967.99	490.02	619.00
Temperature [K]	293(2)	296(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
Space group	*P*2(1)2(1)2(1)	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a [Å]	6.0912(7)	9.6962(2)	9.7622(1)	10.8359(4)	12.814(3)
b [Å]	12.4134(2)	21.060(4)	10.3016(2)	20.3821(9)	13.114(3)
c [Å]	20.360(2)	10.437(2)	11.6713(2)	10.8855(4)	15.384(3)
α [°]	90	90	72.086(8)	90	90
β [°]	90	113.46(3)	84.125(9)	118.3960(1)	107.29(3)
γ [°]	90	90	70.165(9)	90	90
Volume [Å^3]	1539.4(3)	1955.2(7)	1050.6(3)	2114.89(1)	2468.3(9)
Z	4	4	1	4	4
$D_{calcd.}$ [g m^{-3}]	1.339	1.600	1.530	1.539	1.666
μ [mm^{-1}]	0.082	1.287	1.200	1.196	4.047
F(000)	648	964	496	1008	1232
Crystal size [mm]	0.30 × 0.10 × 0.07	0.13 × 0.11 × 0.10	0.27 × 0.19 × 0.10	0.45 × 0.25 × 0.20	0.32 × 0.16 × 0.10
θ range [°]	1.92–28.28	2.34–27.48	1.83–28.38	2.00–28.38	2.08–28.36
Limiting indices	$-6 \le h \le 8$	$-12 \le h \le 12$	$-13 \le h \le 7$	$-14 \le h \le 12$	$-16 \le h \le 16$
	$-16 \le k \le 13$	$-26 \le k \le 27$	$-13 \le k \le 10$	$-26 \le k \le 27$	$-17 \le k \le 17$
	$-27 \le l \le 26$	$-13 \le l \le 13$	$-15 \le l \le 14$	$-6 \le l \le 14$	$-20 \le l \le 17$
No. of reflections collected	9186	8598	12212	19029	26399
No. of unique reflections	3749	4484	5144	5210	6147
R_{int}	0.0175	0.0593	0.0464	0.0293	0.0569
Completeness to θ (%)	98.6 (θ = 28.28 °)	100.0 (θ = 27.48 °)	97.6 (θ = 28.38 °)	98.2 (θ = 28.38 °)	99.4 (θ = 28.36 °)
Absorption correction	empirical	empirical	empirical	empirical	empirical
No. of parameters	217	268	271	279	307
Goodness-of-fit on F^2	1.068	1.074	0.881	1.040	1.003
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0361	R_1 = 0.0672	R_1 = 0.0522	R_1 = 0.0324	R_1 = 0.0429
	wR_2 = 0.0953	wR_2 = 0.1425	wR_2 = 0.1151	wR_2 = 0.0798	wR_2 = 0.0981
R indices (all data)	R_1 = 0.0480	R_1 = 0.1164	R_1 = 0.1754	R_1 = 0.0490	R_1 = 0.0968
	wR_2 = 0.1008	wR_2 = 0.1595	wR_2 = 0.1457	wR_2 = 0.0858	wR_2 = 0.1164
Largest diff. peak, hole [e Å^{-3}]	0.133, –0.146	0.462, –0.485	0.355, –0.451	0.369, –0.356	0.470, –0.590

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2.59, N 10.51; found C 44.33, H 2.35, N 10.88. **7b**: Green powder in 73% yield. IR (KBr disk): $\tilde{\nu}$ = 3310, 1621, 1576, 1531, 1511, 1480, 1460, 1418, 1335, 1132, 1043, 854, 742, 706 cm^{-1}. $C_{20}H_{14}Br_2N_4Ni$ (528.85): calcd. C 44.97, H 2.28, N 10.11; found C 45.42, H 2.67, N 10.59. **8b**: Green powder in 71% yield. IR (KBr disk): $\tilde{\nu}$ = 3369, 1620, 1607, 1577, 1525, 1481, 1441, 1334, 858, 743 cm^{-1}. Anal. $C_{21}H_{16}Br_2N_4Ni$ (542.88): calcd. C 46.95, H 2.52, N 10.78; found C 46.46, H 2.97, N 10.32. **9b**: Green powder in 81% yield. IR (KBr disk): $\tilde{\nu}$ = 3351, 1622, 1580, 1521, 1441, 1335, 857, 746 cm^{-1}. $C_{22}H_{18}Br_2N_4Ni$ (556.91): calcd. C 46.99, H 3.57, N 10.48; found C 47.45, H 3.26, N 10.06. **10b**: Green powder in 77% yield. IR (KBr disk): $\tilde{\nu}$ = 3374, 1621, 1606, 1576, 1524, 1438, 1334, 854, 737, 697 cm^{-1}. $C_{26}H_{18}Br_2N_4Ni$ (604.95): calcd. C 51.27, H 3.34, N 9.58; found C 51.62, H 3.00, N 9.26.

X-ray Crystallography: Single-crystal X-ray diffraction studies for complex **1a** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data for crystals of ligand **L7** and complexes **3a**, **6a**, and **5b** were collected with a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). 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 of F^2. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed using the SHELXL-97 package.[26] Crystal data and processing parameters are summarized in Table 6. CCDC-643354 (for **L7**), -643355 (for **1a**), -643356 (for **3a**), -643357 (for **6a**), and -643358 (for **5b**) 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.

General Procedure for Ethylene Oligomerization: A 250-mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller was heated in vacuo at 80 °C for 2 h. It was cooled to the required reaction temperature under ethylene, and charged with toluene, the desired amount of cocatalyst, and toluene solution of catalytic precursor; the total volume was 100 mL. The reactor was sealed and pressurized to the desired ethylene pressure, and the ethylene pressure was maintained with feeding of ethylene. After the reaction was carried out for the required period, the pressure was released. A small amount of the reaction solution was collected, the reaction in this small sample was terminated by the addition of 5% aqueous hydrogen chloride, and the organic layer was analyzed by gas chromatography (GC) for determining the composition and mass distribution of oligomers obtained.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant no. 20473099) and the Ministry of Science and Technology (grant no. 2006AA03Z553).

[1] a) D. Vogt in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, Germany, **2002**, vol. 1, pp. 240–253; b) G. W. Parshall, S. D. Ittel in *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, Wiley, New York, **1992**, pp. 68–72; c) J. Skupinska, *Chem. Rev.* **1991**, *91*, 613–648.

[2] a) W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 466–467; b) W. Keim, A. Behr, B. Limbäcker, C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 503; c) P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. D. Cian, J. Fisher, *J. Chem. Soc. Chem. Commun.* **1994**, 2203–2204; d) P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, *C. R. Chim.* **2005**, *8*, 31–38.

[3] a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415; b) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267–268; c) C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 11664–11665.

[4] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1204; b) S. Mecking, *Angew. Chem. Int. Ed.* **2001**, *40*, 534–540; c) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315; d) F. Speiser, P. Braunstein, L. Saussine, *Acc. Chem. Res.* **2005**, *38*, 784–793; e) W. Zhang, W.-H. Sun, *Prog. Chem.* **2005**, *17*, 310–319; f) S. Jie, S. Zhang, W.-H. Sun, *Petrochem. Technol. (Shiyou Huagong)* **2006**, *35*, 295–300; g) W.-H. Sun, D. Zhang, S. Zhang, S. Jie, J. Hou, *Kinet. Catal.* **2006**, *47*, 278–283; h) D. H. Camacho, E. V. Salo, J. W. Ziller, Z. Guan, *Angew. Chem. Int. Ed.* **2004**, *43*, 1821–1825.

[5] P. W. Jolly in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, U. K., **1982**, vol. 8, p. 384.

[6] a) W. Keim, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235–244; b) J. Heinicke, M. He, A. Dal, H.-F. Klein, O. Hetche, W. Keim, U. Flörke, H.-J. Haupt, *Eur. J. Inorg. Chem.* **2000**, 431–440.

[7] a) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben, M. W. Day, *Organometallics* **1998**, *17*, 3149–3151; b) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460–462; c) C. Carlini, M. Isola, V. Liuzzo, A. M. R. Galletti, G. Sbrana, *Appl. Catal., A* **2002**, *231*, 307–320; d) L. Wang, W.-H. Sun, L. Han, Z. Li, Y. Hu, C. He, C. Yan, *J. Organomet. Chem.* **2002**, *650*, 59–64.

[8] a) S. Wu, S. Lu, *Appl. Catal., A* **2003**, *246*, 295–301; b) D. Zhang, S. Jie, T. Zhang, J. Hou, W. Li, D. Zhao, W.-H. Sun, *Acta Polym. Sin.* **2004**, *5*, 758–762; c) W.-H. Sun, W. Zhang, T. Gao, X. Tang, L. Chen, Y. Li, X. Jin, *J. Organomet. Chem.* **2004**, *689*, 917–929; d) T. Hu, L.-M. Tang, X.-F. Li, Y.-S. Li, N.-H. Hu, *Organometallics* **2005**, *24*, 2628–2632.

[9] a) W. Keim, S. Killat, C. F. Nobile, G. P. Suranna, U. Englert, R. Wang, S. Mecking, D. L. Schröder, *J. Organomet. Chem.* **2002**, *662*, 150–171; b) W.-H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng, H. Wang, *New J. Chem.* **2002**, *26*, 1474–1478; c) F. Speiser, P. Braunstein, L. Saussine, R. Welter, *Organometallics* **2004**, *23*, 2613–2624; d) F. Speiser, P. Braunstein, L. Saussine, *Organometallics* **2004**, *23*, 2625–2632.

[10] a) F. Speiser, P. Braunstein, L. Saussine, *Organometallics* **2004**, *23*, 2633–2640; b) F. Speiser, P. Braunstein, L. Saussine, R. Welter, *Inorg. Chem.* **2004**, *43*, 1649–1658; c) Z. Weng, S. Teo, T. S. A. Hor, *Organometallics* **2006**, *25*, 4878–4882.

[11] a) C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics* **1997**, *16*, 2005–2007; b) S. A. Svejda, M. Brookhart, *Organometallics* **1999**, *18*, 65–74; c) S. P. Meneghetti, P. J. Lutz, J. Kress, *Organometallics* **1999**, *18*, 2734–2737; d) T. V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Löfgren, M. Leskelä, *Macromol. Rapid Commun.* **1999**, *20*, 487–491.

[12] a) T. V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, *J. Organomet. Chem.* **2000**, *606*, 112–124; b) Z. Li, W.-H. Sun, Z. Ma, Y. Hu, C. Shao, *Chin. Chem. Lett.* **2001**, *12*, 691–692; c) B. Y. Lee, X. Bu, G. C. Bazan, *Organometallics* **2001**, *20*, 5425–5431; d) C. Shao, W.-H. Sun, Z. Li, Y. Hu, L. Han, *Catal. Commun.* **2002**, *3*, 405–410; e) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, *J. Organomet. Chem.* **2005**, *690*, 1570–1580; f) S. Jie, D. Zhang, T. Zhang, W.-H. Sun, J. Chen, Q. Ren, D. Liu, G. Zheng, W. Chen, *J. Organomet. Chem.* **2005**, *690*, 1739–1749.

[13] a) E. Nelkenbaum, M. Kapon, M. S. Eisen, *J. Organomet. Chem.* **2005**, *690*, 2297–2305; b) J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez, P. Gómez-Sal, *Organome-*

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

tallics **2006**, *25*, 3876–3887; c) C.-L. Song, L.-M. Tang, Y.-G. Li, X.-F. Li, J. Chen, Y.-S. Li, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1964–1974; d) C. Zhang, W.-H. Sun, Z.-X. Wang, *Eur. J. Inorg. Chem.* **2006**, *23*, 4895–4902.

[14] Q.-Z. Yang, A. Kermagoret, M. Agostinho, O. Siri, P. Braunstein, *Organometallics* **2006**, *25*, 5518–5527.

[15] a) S. Al-Benna, M. J. Sarsfield, M. Thornton-Pett, D. L. Ormsby, P. J. Maddox, P. Brès, M. Bochmann, *J. Chem. Soc. Dalton Trans.* **2000**, 4247–4257; b) F. Speiser, P. Braunstein, L. Saussine, *Dalton Trans.* **2004**, 1539–1545.

[16] J. Hou, W.-H. Sun, S. Zhang, H. Ma, Y. Deng, X. Lu, *Organometallics* **2006**, *25*, 236–244.

[17] a) L. Wang, W.-H. Sun, L. Han, H. Yang, Y. Hu, X. Jin, *J. Organomet. Chem.* **2002**, *658*, 62–70; b) F. A. Kunrath, R. F. de Souza, O. L. Casagrande Jr, N. R. Brooks, V. G. Young Jr, *Organometallics* **2003**, *22*, 4739–4743; c) N. Ajellal, M. C. A. Kuhn, A. D. G. Boff, M. Hörner, C. M. Thomas, J.-F. Carpentier, O. L. Casagrande Jr, *Organometallics* **2006**, *25*, 1213–1216.

[18] a) W.-H. Sun, S. Jie, S. Zhang, W. Zhang, Y. Song, H. Ma, *Organometallics* **2006**, *25*, 666–677; b) W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, *J. Organomet. Chem.* **2006**, *691*, 4196–4203; c) J. D. A. Pelletier, Y. D. M. Champouret, J. Cadarso, L. Clowes, M. Gañete, K. Singh, V. Thanarajasingham, G. A. Solan, *J. Organomet. Chem.* **2006**, *691*, 4114–4123; d) S. Jie, S. Zhang, K. Wedeking, W. Zhang, H. Ma, X. Lu, Y. Deng, W.-H. Sun, *C. R. Chim.* **2006**, *9*, 1500–1509; e) S. Jie, S. Zhang, W.-H. Sun, X. Kuang, T. Liu, J. Guo, *J. Mol. Catal. A: Chem.* **2007**, *269*, 85–96.

[19] a) P. Hao, S. Zhang, W.-H. Sun, Q. Shi, S. Adewuyi, X. Lu, P. Li, *Organometallics* **2007**, *26*, 2439–2446; b) W.-H. Sun, P. Hao, S. Zhang, Q. Shi, W. Zuo, X. Tang, *Organometallics* **2007**, *26*, 2720–2734.

[20] a) S. Adewuyi, G. Li, S. Zhang, W. Wang, P. Hao, W.-H. Sun, N. Tang, J. Yi, *J. Organomet. Chem.* **2007**, *692*, 3532–3541; b) W.-H. Sun, P. Hao, G. Li, S. Zhang, W. Wang,J. Yi, M. Asma, N. Tang, *J. Organomet. Chem.*; DOI: 10.1016/j.jorganchem.2007.04.027.

[21] a) H. Saikachi, T. Hisano, *Chem. Pharm. Bull.* **1959**, *7*, 347–350; b) G. Tsukamoto, K. Yoshino, T. Kohno, H. Ohtaka, H. Kagaya, K. Ito, *J. Med. Chem.* **1980**, *23*, 734–738.

[22] a) W. Zhang, W.-H. Sun, S. Zhang, J. Hou, K. Wedeking, S. Schultz, R. Fröhlich, H. Song, *Organometallics* **2006**, *25*, 1961–1969; b) A. W. Addison, P. J. Burke, *J. Heterocycl. Chem.* **1981**, *18*, 803–805.

[23] Y. Kikugawa, *Synthesis* **1981**, 124–125.

[24] H.-P. Chen, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *Organometallics* **2003**, *22*, 4893–4899.

[25] D. S. McGuinness, P. Wasserscheid, D. H. Morgan, J. T. Dixon, *Organometallics* **2005**, *24*, 552–556.

[26] G. M. Sheldrick, *SHELXTL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Received: April 10, 2007
Published Online: June 29, 2007

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim