Dalton Transactions

PAPER

Cite this: Dalton Trans., 2013, 42, 9166

Received 4th October 2012, Accepted 23rd November 2012 DOI: 10.1039/c2dt32343e

www.rsc.org/dalton

Introduction

Late transition metal pre-catalysts bearing α -diimines have attracted great attention over the past two decades for the polymerization/oligomerization of ethylene and α -olefins.¹ This stems from the pioneering work on nickel(II) and palladium(II) complexes by Brookhart and co-workers.² Due to the significant influence exerted by the nature of ancillary ligands present on the catalytic activities of such complexes, a variety of nickel pre-catalysts have been explored *via* the development of new bidentate ligand sets of the types $N^{\Lambda}N$,³ $N^{\Lambda}P$,⁴ $N^{\Lambda}O$,⁵ and tridentate ligand sets comprising $N^{\Lambda}P^{\Lambda}N$,⁶ $O^{\Lambda}N^{\Lambda}N$,⁷ $P^{\Lambda}N^{\Lambda}N$,⁸ $N^{\Lambda}N^{\Lambda}N$,⁹ and $P^{\Lambda}N^{\Lambda}P$.¹⁰ Driven by the demand for advanced polyolefins and new metal pre-catalyst systems (*i.e.*, new IP), alternative ligand sets and the complexes thereof have been explored and extensively reviewed.^{1m,11} A unique

Nickel(II) complexes bearing 4,5-bis(arylimino)pyrenylidenes: synthesis, characterization, and ethylene polymerization behaviour†

Kuifeng Song,^{a,b} Wenhong Yang,^b Baixiang Li,^c Qingbin Liu,*^a Carl Redshaw,*^d Yuesheng Li^c and Wen-Hua Sun*^b

A series of nickel(II) dihalides complexes bearing 4,5-bis(arylimino)pyrenylidenes, NiX₂(2,6-R¹-4-R²C₆H₂N)₂C₁₆H₈, was synthesized and characterized by FT-IR spectroscopy, elemental analysis, and single crystal X-ray diffraction for the organic compounds (L2 and L3) and the nickel complexes (C1 and C2). The molecular structures of C1 (R¹ = Me, R² = H, X = Br) and C2 (R¹ = R² = Me, X = Br) revealed a distorted tetrahedral geometry around the nickel centre. Upon treatment with the co-catalysts MAO, EASC and MMAO, all the nickel pre-catalysts exhibited high activities (of up to 4.42 × 10⁶ g(PE) mol(Ni)⁻¹ h⁻¹) for ethylene polymerization, and produced polyethylene products with a high degree of branching (up to 130 branched per 1000 carbons) and narrow molecular weight distribution. The influence of the reaction parameters and the nature of the ligands on the catalytic behavior of the title nickel complexes have been investigated.

feature of the resultant polyethylenes obtained by these nickel catalytic systems is the highly branched nature of the polymers, which are formed via the 'chain-walking' mechanism.^{2a,12} To date, observed catalytic activities and the properties of the polyethylene products have been tuned/controlled to some degree by changing the substituents at the aryl groups^{1b,13} or by modifying the ligand backbone,^{13,14} including more recent studies on 9,10-phenanthrenequinone-based diimine ligands.¹⁵ In order to target new diimine-based ligands, pyrene-4,5-dione has successfully been prepared and used in preparing 4,5-bis(arylimino)pyrenylidenes and the nickel complexes thereof. These nickel(II) complexes exhibit high activities towards ethylene polymerization and produce highly branched polyethylene, with narrow molecular dispersity, indicative of a single-site catalytic system. Herein, the synthesis and characterization of 4,5-bis(arylimino)pyrenylidenes and their nickel complexes is reported. Furthermore, the impact of the polymerization parameters and the nature of the ligands present on the observed catalytic activity as well as the properties of the polyethylene produced, has been investigated.

Results and discussion

Synthesis and characterization of 4,5-bis(arylimino) pyrenylidenes (L1–L4)

The condensation reactions of the pyrene-4,5-dione with various aniline derivatives were conducted in the presence of

RSCPublishing

View Article Online

^aInstitute of Chemistry and Chemical Engineering, Hebei Normal University, Shijiazhuang 050091, China. E-mail: liuqingb@heinfo.net;

Fax: +86 (10) 80787432; Tel: +86 (10) 80787432

^bKey Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: whsun@iccas.ac.cn; Fax: +86 (10) 62618239; Tel: +86 (10) 62557955

^cState Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China ^dDepartment of Chemistry, University of Hull, Hull, HU6 7RX, UK.

E-mail: c.redshaw@hull.ac.uk; Fax: +44 (0) 1482 466410; Tel: +44 (0) 1482 465219 †CCDC 903462–903465. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32343e

Paper



Scheme 1 Synthesis of ligands (L1–L4) and nickel complexes (C1–C5).

TiCl₄ and Et₃N in toluene, and the corresponding 4,5-bis-(arylimino) pyrenylidenes (L1–L4) were formed in acceptable yields (Scheme 1). The reaction of pyrene-4,5-dione with 2,6-diisopropyl benzamine did not occur, despite various conditions and differing reagents being explored. Organic compounds L1–L4 were characterized by elemental analysis, NMR and IR spectroscopy.

Synthesis and characterization of nickel complexes

Further reactions of 4,5-bis(arylimino)pyrenylidenes L1 and L2 with (DME)nickel(II) dihalide (bromide or chloride) smoothly afforded the corresponding diiminonickel halides (Scheme 1), in varying yields: 66-74% for bromides C1-C2 and <38% for chlorides C4 and C5. However, the 4,5-bis(2,6-diethylphenylimino)pyrenylidene L3 could react with (DME)nickel(II) bromide to form the corresponding nickel complex C3, the nickel bromide complex was not accessible. Even worse, the reaction trials of 4,5-bis(2,6-diethyl-4-methylphenylimino)pyrenylidene L4 with (DME)nickel(II) dihalide in various solvents have not been successful in obtaining its nickel complexes. All isolated nickel complexes were characterized by elemental analysis and IR spectroscopy. To confirm the structures of the nickel complexes, single crystals of complexes C1 and C2 were obtained and the molecular structures were determined by single crystal X-ray diffraction.

X-Ray crystallography

Single crystals of L2, L3, C1 and C2 suitable for X-ray crystallographic analysis were grown by slow diffusion of diethyl ether into the respective dichloromethane solutions. The molecular structures of each are shown in Fig. 1–4, respectively, with selected bond lengths and angles tabulated in Table 1. In the solid-state structures of compounds L2 and L3, the double bonding features are illustrated by N1–C1 1.279(3) and N2–C14 1.282(3) Å in L2 and 1.295(6) and 1.288(6) Å in L3,



Fig. 1 ORTEP drawing of L2. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.



Fig. 2 ORTEP drawing of L3. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.



Fig. 3 ORTEP drawing of C1. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

whilst the single bonds for N1–C17 and N2–C23 are 1.424(3) and 1.427(3) Å in L2 and 1.421(6) and 1.451(7) Å in L3. The dihedral angle formed by the two imino-phenyl rings connected to the nitrogen atoms is 72.67° in L2 and is 70.7° in L3. Similar characteristics were observed in analogues bearing 9,10-bis(2,6-dimethylphenylimino)phenanthrenylidene with



Fig. 4 ORTEP drawing of C2. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for compounds L2, L3, C1 and C2

	L2	L3	C1	C2
Bond lengths (Å)				
Ni(1)-N(1)	_	_	1.994(6)	1.987(6)
Ni(1) - N(2)	_	_	1.998(5)	2.003(6)
Ni(1) - Br(1)	_	_	2.3541(14)	2.3488(18)
Ni(1)-Br(2)	—	—	2.3648(13)	2.3615(16)
N(1)-C(1)	1.279(3)	1.295(6)	1.303(8)	1.313(9)
N(1)-C(17)	1.424(2)	1.421(6)	1.444(8)	1.456(9)
N(2)-C(14)	1.282(3)	1.288(6)	1.291(8)	1.309(9)
N(2)-C(23)	1.427(3)	1.451(7)	1.426(8)	1.430(9)
Bond angles (°)				
N(1)-Ni(1)-N(2)	_	_	79.9(2)	80.0(3)
N(1)-Ni(1)-Br(1)	_	_	116.38(18)	112.57(18)
N(1)-Ni(1)-Br(2)	—	—	113.16(19)	112.32(18)
N(2)-Ni(1)-Br(1)	—	—	111.35(17)	120.85(18)
N(2)-Ni(1)-Br(2)	—	—	111.89(16)	109.32(19)
Br(1)-Ni(1)-Br(2)		_	118.02(5)	116.38(6)
C(17)-N(1)-Ni(1)		—	118.4(4)	115.6(4)
C(1)-N(1)-Ni(1)		—	115.6(4)	117.3(5)
C(23)-N(2)-Ni(1)		—	116.1(4)	116.4(5)
C(14)-N(2)-Ni(1)			116.5(4)	115.1(5)
C(1)-N(1)-C(17)	123.63(17)	126.7(4)	126.0(6)	127.1(6)
C(14)-N(2)-C(23)	123.74(18)	127.0(4)	127.4(5)	115.1(5)

double-bonding for C=N at 1.2839(19) and 1.271(2) Å and single bonding for C-N at 1.4099(19) and 1.417(2) Å.¹⁵

As shown in Fig. 3 and 4, the complexes C1 and C2 possess similar structures, that is, the distorted tetrahedral geometry at the nickel centre is comprised of two nitrogen atoms (of the chelate) and two bromine atoms. On comparison of analogous bond lengths and angles, there is evidence of some substituent effects, such as the bond lengths of Ni1–N1, Ni1–N2, Ni1– Br1 and Ni1–Br2 in C1 [1.994(6), 1.998(5), 2.3541(14) and 2.3648(13) Å] *versus* those of C2 [1.987(6), 2.003(6), 2.3488(18) and 2.3615(16) Å]. The distances from the nickel atom to the plane formed by N1, N2 and Br1 and to the plane formed by N1, N2 and Br2 are 0.894 and 0.834 Å in C1, respectively, whilst these values are 0.834 and 0.834 Å for C2, respectively. The dihedral angle between the plane formed by N1, N2 and N11 and the plane formed by N1, N2 and Br2 is 35.75° in C1 and 33.08° in C2. The dihedral angles formed by the two imino-phenyl rings connected to the nitrogen atoms are 148.2° in C1 and 140.61° in C2, respectively.

There are obvious changes of the dihedral angles involving the two imino-phenyl rings at 72.67° in L2 and 140.61° in C2, the difference being attributed to the efficient coordination to the nickel center in C2.

Ethylene polymerization

To ascertain a suitable co-catalyst, pre-catalyst C2 was employed with different activators such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), diethylaluminium chloride (Et₂AlCl) or ethylaluminium sesquichloride (Et₃Al₂Cl₃, EASC) at a temperature of 40 °C and under 10 atm ethylene. The results are summarized in Table 2, from which it can be seen that EASC, MAO and Et₂AlCl are all effective as activators. Different co-catalysts also affect the property of the obtained polyethylenes; the polyethylene via C2/MAO exhibited lower molecular weight but higher branching than that from C2/MMAO (entries 1 and 2 in Table 2). According to Table 2, all polyethylenes exhibited narrow molecular polydispersity and significant branching (from 21 to 53 per 1000 carbons) as well as potentially useful molecular weights (2.0 to 6.4 \times 10^5 g mol⁻¹). Each of these co-catalysts, in combination with C2, was then investigated in more detail.

Ethylene polymerization using the C1-C5/EASC systems

Using EASC as co-catalyst, the polymerization reaction parameters, including Al:Ni molar ratio, reaction time and temperature, were varied, and the results are collected in Table 3. In the case of the Al:Ni molar ratio (entries 1–4 in Table 3), on increasing the ratio from 250 to 500, the catalytic activity first increased and then decreased, whilst the increase of the Al/Ni molar ratio led to polyethylene of lower molecular weight (GPC curves shown in Fig. 5).

Such observations are consistent with the previous conclusion that high molar ratios of Al/Ni enhance chain transfer from nickel species to aluminium, which results in lower molecular weight polymers.¹⁶ The optimum Al/Ni molar ratio was found to be 300:1 with activities of up to 3.53×10^6 g(PE) mol $(Ni)^{-1}$ h⁻¹ observed. According to the entries 2 and 5-6 in Table 3, the optimum reaction temperature in the present study was found to be 40 °C; higher or lower temperatures led to a slight decrease of the catalytic activity, similar to the previously observed situation for reported a-diimine catalyst systems.^{13a-e} In addition, when elevating the temperature from 30 to 50 °C, a marked decrease in the polymer molecular weight was observed. Lifetime studies indicated that higher activities were observed over shorter reaction times (entry 7 in Table 3), i.e. the activities decreased on prolonging the period of polymerization. This suggested that there was no induction period, and that the active species was rather short-lived. Moreover, both the $M_{\rm w}$ and $M_{\rm w}/M_{\rm n}$ values of the obtained PEs increased slightly on extending the reaction time; the $M_{\rm w}$ changes are shown by GPC (Fig. 6). Given that the optimum conditions for the C2/EASC system were found to be an Al/Ni ratio of 300 at 40 °C over 30 min, further investigations using

Table 2 Ethylene polymerization by pre-catalyst C2 with various co-catalysts^a

Entry	Co-cat.	Al/Ni	$T/^{\circ}\mathrm{C}$	Activity ^b	$T_{\rm m}/^{\rm o}{\rm C}$ ^c	$M_{\rm w}/10^5 {\rm ~g~mol^{-1}} {}^{d}$	$M_{\rm w}/M_{\rm n}^{\ d}$	Branches/1000C ^e
1	MAO	1000	40	3.23	113.7	3.85	2.4	29
2	MMAO	1000	40	1.11	121.6	6.38	2.2	21
3	Et_2AlCl	300	40	2.47	97.1	1.98	2.1	53
4	EASC	300	40	3.53	103.1	3.56	2.4	46

^{*a*} Conditions: 3 µmol of C2; 30 min; 10 atm of ethylene; 100 ml toluene. ^{*b*} 10^6 g(PE) mol(Ni)⁻¹ h⁻¹. ^{*c*} Determined by DSC. ^{*d*} Determined by GPC. ^{*e*} Determined by FT-IR.

Table 3	Ethylene po	lymerization b	y pre-catalys	ts C1–C5 with EASC ^a
---------	-------------	----------------	---------------	--

Entry	Pre-cat.	Al/Ni	$T/^{\circ}\mathrm{C}$	<i>t</i> /min	Activity ^b	$T_{\rm m}/^{\rm o}{\rm C}^{\ c}$	$M_{\rm w}/10^5 {\rm ~g~mol^{-1}} {}^{d}$	$M_{ m w}/M_{ m n}^{\ d}$	Branches/1000 C ^{<i>e</i>}
1	C2	250	40	30	2.67	102.4	4.04	2.5	42
2	C2	300	40	30	3.53	103.1	3.56	2.4	46
3	C2	400	40	30	2.56	117.3	3.13	2.4	18
4	C2	500	40	30	2.25	107.5	2.95	3.2	26
5	C2	300	30	30	3.23	102.5	3.73	2.5	40
6	C2	300	50	30	3.07	56.5	1.52	2.3	130 ^f
7	C2	300	40	15	4.42	103.9	2.30	2.2	49
8	C2	300	40	45	1.96	99.7	3.91	2.5	79
9	C1	300	40	30	3.03	106.6	4.68	2.4	26
10	C3	300	40	30	3.63	107.5	7.29	2.1	44
11	C5	250	40	30	1.26	115.5	3.87	2.1	33
12	C5	300	40	30	2.81	107.5	3.18	2.3	34
13	C5	400	40	30	4.41	99.9	2.01	2.1	32
14	C5	500	40	30	2.16	103.3	1.89	2.1	58
15	C5	400	30	30	2.45	110.7	4.13	2.4	5
16	C5	400	50	30	2.29	87.4	2.05	2.2	49
17	C4	400	40	30	0.18	117.4	3.20	2.0	12

^{*a*} Conditions: 3 µmol of complex; 10 atm of ethylene; 100 ml toluene. ^{*b*} 10⁶ g(PE) mol(Ni)⁻¹ h⁻¹. ^{*c*} Determined by DSC. ^{*d*} Determined by GPC. ^{*e*} Determined by FT-IR. ^{*f*} Determined by ¹³C NMR spectroscopy.



Fig. 5 GPC curves of polyethylene obtained at different molar ratios of Al to Ni (entries 1–4 in Table 3).



Fig. 6 GPC curves of polyethylene obtained at different times (entries 2, 7 and 8 in Table 3).

the other pre-catalysts (C1 and C3) were conducted under such conditions. Shown in entries 2, 9 and 10 of Table 3, results reveal the activity order of C3 > C2 > C1, in line with the decreasing bulk of the aniline-derived aryl groups. As illustrated by the above structural features for C1 with C2, efficient coordination to the nickel center in C2 can stabilize the active species and thereby result in better activity, which is consistent with previous observations.^{2a,17} As shown in entries 2, 5 and 6

of Table 3, the degree of branching for the obtained PE products increased on increasing the temperature.

A representative chain of PE formed by the C2/EASC catalytic system (entry 6 in Table 3) was characterized by ¹³C NMR spectroscopic measurements, which revealed 130 branches per 1000 carbons (Fig. 7) according to the interpretation reported by Galland *et al.*¹⁸ These highly branched PEs were obtained due to β -hydrogen migration at the active nickel species.^{1k,m,19}

In a similar way, the chloride complex C5 was used to determine the optimum reaction conditions for the ethylene polymerization and the data are tabulated in Table 3. Accordingly, the highest activities were observed when the Al/Ni molar ratio was increased to 400 (entries 11–14 in Table 3), and the optimum temperature remained at 40 °C (entries 13, 15 and 16 in Table 3).

These optimum conditions were also employed on the C4 system to study the ethylene polymerization behaviour (entry 17 in Table 3); the activity order C5 > C4 was observed. The influence of the substituents on the catalytic activities of these nickel chlorides followed the same trend as observed for the bromide systems, *i.e.* the bulkier the substituent, the higher the activity. Ligated by the same ligand, 4,5-bis(2,6-dimethylphenylimino)pyrenylidene (L1), the bromonickel complex C1 shows much higher activity than did the chloronickel complex C4 (entries 9 and 17 in Table 3);^{9d} this is thought to be due to the low solubility of the chloro-complex. Under the same tendency was observed for the bromo-complex C2 and the chloro-complex C5 (entries 2 and 12 in Table 3); a better activity was achieved for the chloro-complex C5 by further increasing the



Fig. 7 ¹³C-NMR spectrum of polyethylene (entry 6 in Table 3).

Table 4	Ethylene	polymerizati	on by pr	e-catalysts	C1–C5	with MAO
---------	----------	--------------	----------	-------------	-------	----------

molar ratio of Al: Ni at 400 (entry 13 in Table 3). There is no general approach for adapting complex pre-catalysts for better catalytic property, and this emphasizes the importance of finely tuning ligands with different substituents and using different anionic ions.

Ethylene polymerization with the C1-C5/MAO systems

Using MAO as the co-catalyst, all the nickel complexes also exhibited good catalytic activities for ethylene polymerization. The results using different Al/Ni molar ratios, temperatures, and pressures are presented in Table 4. Under ambient pressure of ethylene at 40 °C, good activities were observed for ethylene polymerization in the presence of MAO (entry 8 in Table 4).

As seen from the entries 2, 8 and 9 in Table 4, the $T_{\rm m}$ value of the polyethylene increased on increasing the ethylene pressure, and the trend of decreased branching with increasing ethylene pressure here reinforced earlier observations.^{13*a*} The current nickel pre-catalysts based on the pyrene unit produced polyethylene of higher molecular weight than did their nickel analogues derived from α -diimino^{13*a*} and phenanthrene;¹⁵ all nickel pre-catalysts produced highly branched polyethylene as a characteristic property. Moreover, the molecular weight of the polyethylene increased on increasing the pressure of ethylene (shown in Fig. 8).

The catalytic activity was enhanced on increasing the Al/Ni molar ratios from 750 to 1000 (entries 1 and 2 in Table 4) for the C2/MAO catalytic system and from 1250 to 1500 (entries 10 and 11 in Table 4) for the C5/MAO catalytic system. For the C2/MAO catalytic system (entries 2 and 3 in Table 4) and the C5/MAO catalytic system (entries 11 and 12 in Table 4), a clear decrease of activity was observed on further increasing the Al/Ni molar ratios. Thus, the optimum Al/Ni molar ratio was found to be 1000:1 for the C2/MAO catalytic system and 1500:1 for the C5/MAO catalytic system, which afforded the highest activities of 3.23×10^6 g(PE) mol(Ni)⁻¹ h⁻¹ and 3.43×10^6 g(PE) mol(Ni)⁻¹ h⁻¹, respectively over 30 min. Along with increasing the Al/Ni molar ratio, the molecular weight polydispersity became wider with slightly differing molecular weights

Entry	Pre-cat.	Al/Ni	$T/^{\circ}C$	Activity ^b	$T_{\rm m}^{\ \ c}$ /°C	$M_{\rm w}^{~d}/10^5~{\rm g~mol^{-1}}$	$M_{ m w}/M_{ m n}^{\ d}$	Branches/1000C ^e
1	C2	750	40	1.89	106.9	5.21	2.3	31
2	C2	1000	40	3.23	113.7	3.85	2.4	29
3	C2	1250	40	2.57	115.6	3.63	2.1	28
4	C2	1000	30	2.83	117.6	3.50	2.2	27
5	C2	1000	50	1.58	104.4	2.86	2.0	42
6	C1	1000	40	2.07	114.4	4.57	2.5	8
7	C3	1000	40	3.53	115.8	7.33	2.2	29
8 ^f	C2	1000	40	0.22	95.2	1.80	2.3	47
9 ^g	C2	1000	40	1.26	101.4	2.70	1.9	35
10	C5	1250	40	2.27	112.3	3.56	2.2	29
11	C5	1500	40	3.43	116.2	3.49	2.3	35
12	C5	1750	40	1.23	117.6	4.69	2.4	38
13	C4	1500	40	0.36	120.3	2.94	2.1	23

^{*a*} Conditions: 3 µmol of complex; 30 min; 10 atm of ethylene; total volume 100 ml. ^{*b*} 10^6 g(PE) mol(Ni)⁻¹ h⁻¹. ^{*c*} Determined by DSC. ^{*d*} Determined by GPC. ^{*e*} Determined by FT-IR. ^{*f*} 1 atm of ethylene. ^{*g*} 5 atm of ethylene.

(entries 10, 11 and 12 in Table 4), indicating that the higher the Al/Ni ratio, the more chain transfer and termination occurs. The best performance was observed at 40 °C (entries 2, 4 and 5 in Table 4), and the other pre-catalysts were employed under such conditions. When MAO was used as co-catalyst, the order of the catalytic activity performance decreases in the order C3 > C2 > C1 for the bromides, and C5 > C4 for the chlorides.

Ethylene polymerization with C1-C5/Et₂AlCl system

Similarly using Et_2AlCl as co-catalyst, catalytic screening results were also obtained at different Al/Ni molar ratios and reaction temperatures. For the C2/Et₂AlCl system, elevating the reaction temperature from 30 to 40 °C resulted in enhanced activity (entries 4 and 2 in Table 5).

Elevating the reaction temperature further from 40 to 50 °C resulted in a reduction in the activity (entries 2 and 5 in Table 5). Meanwhile, the M_w/M_n values of the obtained polyethylene decreased when the temperature was increased. Over the Al/Ni molar ratio range 100 to 300 for the C2/Et₂AlCl system, the highest polymerization activity and molecular weight were observed at the Al/Ni molar ratio of 200 (entries 1,



Fig. 8 GPC curves of polyethylene obtained at different the pressure of ethylene.

2 and 3 in Table 5). In the C5/Et₂AlCl system, the optimum Al/ Ni molar ratio at 40 °C was found to be 400 : 1 (entries 8, 9 and 10 in Table 5). Moreover, the M_w and M_w/M_n values for polyethylene decreased on increasing the Al/Ni molar ratio (entries 8, 9 and 10 in Table 5). All the products obtained possessed a relatively high degree of branching, which increased on increasing the temperature. At the optimum reaction conditions, the catalytic activity of the C5 system is higher than that of C4. Also, from the data in Table 5, the catalytic activity was found to decrease in the order C3 > C2 > C1 (Table 5).

Conclusions

The newly designed 4,5-bis(arylimino)pyrenylidenes were successfully synthesized and used to form nickel halide complexes. The resulting nickel complex pre-catalysts showed high activities for ethylene polymerization with various co-catalysts such as EASC, Et_2AlCl and MAO. Reaction parameters such as the Al/Ni molar ratio, the reaction temperature and time have a significant influence on the catalytic activity and properties of the obtained polyethylene. The polyethylene products were confirmed to be highly branched.

Experimental

General procedure

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified and dried under nitrogen by conventional methods prior to use unless otherwise stated. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Diethyl-aluminium chloride (Et₂AlCl, 0.79 M in toluene) and ethylaluminium sesquichloride (EASC, 0.87 M in toluene) were purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Arcos, or local suppliers. ¹H and ¹³C NMR spectra were recorded on a

ry	Pre-cat.	Al/Ni	$T/^{\circ}\mathrm{C}$	Activity ^b	$T_{\rm m}^{\ \ c}/^{\rm o}{\rm C}$	$M_{\rm w}^{~d}/10^5~{\rm g~mol^{-1}}$	$M_{\rm w}/{M_{\rm n}}^d$	Branches/1000C ^e
	C2	100	40	0.79	120.3	2.68	2.3	29
	C2	200	40	2.81	105.7	3.32	2.5	39
	C2	300	40	2.47	97.1	1.98	2.1	53
	C2	200	30	2.24	109.0	2.97	2.9	31
	C2	200	50	0.20	107.1	1.98	2.1	37
	C1	200	40	1.29	119.5	3.90	2.2	27
	C3	200	40	3.22	107.6	6.70	2.2	52
	C5	300	40	2.31	103.6	3.28	2.3	47
	C5	400	40	2.65	110.3	3.02	2.2	33
	C5	500	40	2.39	106.7	2.86	1.9	38
	C4	400	40	0.068	115.3	6.08	2.6	19

^{*a*} Conditions: 3 µmol of complex; 30 min; 10 atm of ethylene; total volume 100 ml. ^{*b*} 10^6 g(PE) mol(Ni)⁻¹ h⁻¹. ^{*c*} Determined by DSC. ^{*d*} Determined by GPC. ^{*e*} Determined by FT-IR.

Table 6 Crystal data and structure refinements for L2, L3, C1 and C2

	L2	L3	C1	C2
Empirical formula	$C_{34}H_{30}N_2$	C38H38N2	C ₃₂ H ₂₇ Br ₂ N ₂ Ni	C34H30Br2N2Ni
Cryst. color	Red	Red	Brown	Red
Fw	466.60	522.70	658.05	685.13
$T(\mathbf{K})$	446(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Cryst. syst.	Triclinic	Triclinic	Triclinic	Triclinic
Space group	PĪ	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a(A)	8.8655(18)	8.0890(16)	11.613(2)	14.873(3)
$b(\dot{A})$	11.826(2)	18.545(4)	15.244(3)	16.510(3)
$c(\dot{A})$	13.450(3)	19.786(4)	18.470(4)	16.616(3)
α (°)	88.28(3)	79.56(3)	106.33(3)	99.21(3)
$\beta(\check{\circ})$	75.63(3)	86.95(3)	98.48(3)	101.46(3)
γ (°)	70.27(3)	88.80(3)	96.40(3)	113.54(3)
$V(A^3)$	1283.6(4)	2914.6(10)	3063.0(10)	3533.6(12)
Z	2	4	4	4
$D_{\text{calcd}} (\text{mg m}^{-3})$	1.207	1.191	1.368	1.288
$\mu (\text{mm}^{-1})$	0.070	0.069	3.262	2.832
F(000)	496	1120	1216	1384
Cryst size (mm)	0.20 imes 0.13 imes 0.09	0.25 imes 0.20 imes 0.10	0.25 imes 0.23 imes 0.21	0.26 imes 0.24 imes 0.10
θ range (°)	1.83-27.42	1.05 - 25.00	1.17-27.46	1.30 - 27.41
Limiting indices	$-11 \le h \le 11$	$-9 \le h \le 9$	$-15 \le h \le 14$	$-19 \le h \le 19$
C C	$-15 \le h \le 15$	$-22 \le h \le 22$	$-19 \le h \le 19$	$-21 \le h \le 21$
	$-17 \le h \le 12$	$-23 \le h \le 22$	$-18 \le h \le 23$	$-21 \le h \le 21$
No. of rflns collected	12 718	22 029	29 319	45 507
No. unique rflns [R(int)]	5801(0.0541)	10 223 (0.1117)	13 734 (0.0787)	15 927 (0.1035)
Completeness to θ (%)	99.0 $(\theta = 27.42)$	99.6 $(\theta = 25.00)$	98.0 $(\theta = 27.46)$	98.9 $(\theta = 27.41)$
Goodness of fit on F^2	1.022	1.098	1.075	1.049
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0820$	$R_1 = 0.1339$	$R_1 = 0.0831$	$R_1 = 0.0995$
	$wR_2 = 0.2297$	$wR_2 = 0.3404$	$wR_2 = 0.1903$	$wR_2 = 0.2617$
R indices (all data)	$R_1 = 0.0951$	$R_1 = 0.1793$	$R_1 = 0.1115$	$R_1 = 0.1506$
	$wR_2 = 0.2475$	$wR_2 = 0.3873$	$wR_2 = 0.2112$	$wR_2 = 0.2991$
Largest diff. peak and hole (e ${\rm \AA}^{-3})$	0.388 and -0.331	0.552 and -0.461	0.760 and -1.022	0.985 and –0.959

Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; δ values were given in ppm and *J* values in Hz. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were carried out using a Flash EA 1112 microanalyzer. Molecular weights and molecular weight distribution (MWD) of polyethylene were determined by a PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. DSC trace and melting points of polyethylene were obtained from the second scanning run on Perkin-Elmer DSC-7 at a heating rate of 10 °C min⁻¹.

Syntheses and characterization

4,5-Bis(2,6-dimethylphenylimino)pyrenylidene (L1). To a mixture of 2,6-dimethylaniline (15.00 mmol, 1.81 g) and triethylamine (45.00 mmol, 4.54 g) in toluene (50 ml) was added dropwise 1.6 ml of the 9.0 M solution of TiCl₄ in toluene over 10 min at 90 °C, followed by addition of a suspension of pyrene-4,5-dione (5.00 mmol, 1.18 g) in 15 ml of toluene. The reaction mixture was heated to reflux for 30 min, and the precipitate was removed by hot filtration. The filtrate was evaporated *in vacuo*. Finally, 0.47 g of deep red crystalline solid was isolated by silica gel column chromatography (petroleum ether–dichloromethane = 5 : 1, v/v) and re-crystallization in petroleum ether. Yield: 21%. Mp: 181–182 °C. FT-IR (KBr, cm⁻¹): 3056 (m), 2940 (m), 1637 (s, C=N), 1593 (s), 1461 (s), 1236 (m),

827 (s), 758 (vs), 716 (vs). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.66 (d, J = 7.2 Hz, 1H, Pyrene H), 8.09 (d, J = 7.6 Hz, 1H, Pyrene H), 7.78–7.76 (m, 4H, Pyrene H), 7.72 (t, J = 7.6 Hz, 1H, Ph H), 7.04–7.01 (m, 3H, Pyrene H, Ph H), 6.91–6.81 (m, 4H, Pyrene H, Ph H), 2.11 (s, 6H, Ph–CH₃), 1.33 (s, 6H, Ph–CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 159.27, 157.50, 149.53, 148.15, 133.06, 131.87, 131.61, 130.97, 130.73, 128.06, 127.83, 127.63, 127.39, 127.22, 126.77, 126.28, 125.34, 125.05, 124.33, 123.03, 122.45, 18.62, 17.35. Anal. Calcd for C₃₂H₂₆N₂: C, 87.64; H, 5.98; N, 6.39. Found: 87.46; H, 5.78; N, 6.76.

4,5-Bis(mesitylimino)pyrenylidene (L2). Using the same procedure as for the synthesis of L1, L2 (0.57 g) was obtained as a deep red crystalline solid. Yield: 24.26%. Mp: 180-181 °C. FT-IR (KBr, cm⁻¹): 3053 (w), 2902 (m), 1634 (s, C=N), 1601 (s), 1471 (m), 1272 (m), 1216 (m), 828 (vs), 713 (vs). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.36 (d, J = 7.6 Hz, 1H, Pyrene H), 8.07 (d, J = 7.6 Hz, 1H, Pyrene H), 7.86-7.75 (m, 4H, Pyrene H), 7.22 (d, J = 7.6 Hz, 1H, Pyrene H), 7.06 (d, J = 7.6 Hz, 1H, Pyrene H), 6.82 (s, 2H, Ph H), 6.65 (s, 2H, Ph H), 2.28 (s, 3H, Ph-CH₃), 2.21 (s, 3H, Ph-CH₃), 2.06 (s, 6H, Ph-CH₃), 1.28 (s, 6H, Ph-CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 159.71, 157.66, 147.11, 145.72, 133.31, 132.27, 131.86, 131.60, 131.46, 130.83, 128.77, 128.29, 128.07, 127.81, 127.67, 127.42, 127.21, 126.76, 126.31, 125.26, 124.94, 124.20, 20.85, 20.79, 18.56, 17.21. Anal. Calcd for C₃₄H₃₀N₂: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.24; H, 6.92; N, 5.64.

4,5-Bis(2,6-diethylphenylimino)pyrenylidene (L3). Using the same procedure as for the synthesis of L1, L3 (0.33 g) was obtained as a deep red crystalline solid. Yield: 12.55%. Mp: 178-180 °C. FT-IR (KBr, cm⁻¹): 2964 (s), 2929 (s), 2866 (m), 1639 (s, C=N), 1604 (s), 1454 (vs), 1203 (s), 855 (s), 627 (vs), 712 (vs). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.64 (d, J = 7.6 Hz, 1H, Pyrene H), 8.08 (d, J = 7.6 Hz, 1H, Pyrene H), 7.78-7.75 (m, 4H, Pyrene *H*), 7.21 (t, *J* = 7.6 Hz, 1H, Pyrene *H*), 7.04 (d, *J* = 7.6 Hz, 1H, Pyrene H), 6.89 (s, 2H, Ph H), 6.72 (s, 2H, Ph H), 2.54-2.47 (m, 2H, Ph-CH2-), 2.41-2.32 (m, 5H, Ph-CH2-, Ph-CH₃), 2.26 (s, 3H, Ph-CH₃), 1.60-1.46 (m, 4H, Ph-CH₂-), 1.13 $(t, J = 7.2 \text{ Hz}, 6\text{H}, \text{Ph-C}H_3), 0.743 (t, J = 7.6 \text{ Hz}, 6\text{H}, \text{Ph-C}H_3).$ ¹³C NMR (100 MHz, CDCl₃, TMS): δ 159.05, 157.70, 146.08, 144.77, 133.35, 132.45, 131.55, 130.70, 130.45, 130.39, 129.69, 128.13, 127.77, 127.59, 127.17, 127.12, 126.76, 126.37, 126.16, 125.93, 125.42, 24.97, 23.36, 21.21, 13.41, 13.35. Anal. Calcd for C₃₈H₃₈N₂: C, 87.21; H, 7.33; N, 5.36. Found: C, 86.92; H, 7.41; N, 5.42.

Dalton Transactions

4,5-Bis(2,6-diethyl-4-methylphenylimino)pyrenylidene (L4). Using the same procedure as for the synthesis of L1, L4 (0.23 g) was obtained as a deep red crystalline solid. Yield: 9.24%. Mp: 172-174 °C. FT-IR (KBr, cm⁻¹): 3055 (w), 2965 (m), 1641 (s, C=N), 1507 (m), 1439 (m), 1339 (m), 1190 (m), 1056 (m), 900 (m), 831 (vs), 752 (vs), 7159 (vs). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.63 (d, J = 6.8 Hz, 1H, Pyrene H), 8.09 (d, J = 8 Hz, 1H, Pyrene H), 7.87-7.76 (m, 4H, Pyrene H), 7.18 (t, J = 7.6 Hz, 1H, Pyrene H), 7.08–6.98 (m, 4H, Pyrene H, Ph H), 6.90 (m, 3H, Ph H), 2.56-2.50 (m, 2H, Ph-CH₂-), 2.41-2.36 (m, 2H, Ph-CH2-), 1.61-1.45 (m, 4H, Ph-CH2-), 1.13 $(t, J = 7.2 \text{ Hz}, 6\text{H}, \text{Ph-C}H_3), 0.84 (t, J = 6.3 \text{ Hz}, 6\text{H}, \text{Ph-C}H_3).$ ¹³C NMR (100 MHz, CDCl₃, TMS): δ 158.63, 157.60, 148.51, 147.23, 133.16, 131.85, 131.62, 130.88, 130.63, 130.48, 129.86, 127.96, 127.85, 127.61, 127.27, 127.20, 126.84, 126.19, 125.66, 125.17, 123.34, 122.69, 24.99, 23.39, 13.33, 13.27. Anal. Calcd for C36H34N2: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.44; H, 6.92; N, 5.64.

Synthesis of nickel complexes (C1-C5)

The complexes (C1-C5) were prepared by the reaction of (DME)NiBr₂ and (DME)NiCl₂ with the corresponding ligands (L1–L3) in dichloromethane (L1/L2 afforded the bromides C1/ C2 or the chlorides C4/C5; L3 afforded the bromide C3). A typical synthetic procedure for C2 can be described as follows: the ligand L2 (0.40 mmol, 0.20 g) and (DME)NiBr₂ (0.40 mmol, 0.12 g) were added to a flame-dried Schlenk flask tube, then 20 ml dichloromethane was subsequently added with rapid stirring at room temperature for 24 h. The solvent was removed in vacuo and the residual solid was washed with Et₂O several times. Finally, C2 was isolated as a brown powder (0.20 g, 66.78%). FT-IR (KBr, cm⁻¹): 2910 (w), 2853 (w), 1622 (s, C=N), 1605 (m), 1498 (m), 1466 (m), 1351 (m), 1297 (s), 1205 (m), 1026 (m), 831 (vs), 707 (vs). Anal. Calcd for C34H34Br2N2Ni: C, 59.17; H, 4.97; N, 4.06. Found: C, 59.29; H, 4.86; N, 4.15.

Data for C1 (brown powder, 71.16% yield) are as follows. FT-IR (KBr, cm^{-1}): 2969 (w), 2858 (w), 1623 (s, C=N), 1602 (m),

1464 (m), 1416 (m), 1353 (m), 1299 (s), 1096 (m), 834 (s), 761 (s), 704 (vs). Anal. Calcd for $C_{32}H_{30}Br_2N_2Ni$: C, 58.14; H, 4.57 N, 4.24. Found: C, 58.26; H, 4.55; N, 4.23.

Data for C3 (brown powder, 74.18% yield) are as follows. FT-IR (KBr, cm⁻¹): 2962 (m), 2929 (m), 2873 (m), 1621 (s, C=N), 1601 (m), 1513 (m), 1452 (s), 1350 (s), 1305 (vs), 1203 (m), 852 (vs), 837 (vs), 711 (vs). Anal. Calcd for $C_{38}H_{42}Br_2N_2Ni$: C, 61.24; H, 5.68; N, 3.76. Found: C, 61.08; H, 5.28; N, 3.76.

Data for C4 (brown powder, 38.82% yield) are as follows. FT-IR (KBr, cm⁻¹): 2955 (w), 2931 (m), 2866 (m), 1619 (s, C=N), 1600 (m), 1463 (m), 1421 (m), 1278 (s), 1198 (m), 829 (s), 761 (vs), 713 (vs). Anal. Calcd for $C_{32}H_{26}Cl_2N_2Ni$: C, 67.65; H, 4.61; N, 4.93. Found: C, 67.46; H, 4.69; N, 4.81.

Data for C5 (brown powder, 25.53% yield) are as follows. FT-IR (KBr, cm⁻¹): 2966 (w), 2929 (m), 2870 (m), 1623 (s, C=N), 1604 (m), 1472 (m), 1274 (m), 1206 (m), 824 (s), 811 (vs), 712 (s). Anal. Calcd for $C_{34}H_{30}Cl_2N_2Ni$: C, 68.49; H, 5.07; N, 4.70. Found: C, 68.52; H, 5.02; N, 4.76.

Procedure for ethylene polymerization

Ethylene polymerization was conducted in a stainless steel autoclave (0.25 L capacity) equipped with a mechanical stirrer and a temperature controller. Then, 100 ml of toluene containing the catalyst precursor was transferred to the fully dried reactor under nitrogen atmosphere. The required amount of co-catalyst was then injected into the reactor via a syringe. At the required reaction temperature, the reactor was immediately pressurized to high ethylene pressure, and the ethylene pressure was kept constant with feeding of ethylene. After the reaction mixture was stirred for the desired period, the pressure was released and the mixture was cooled to room temperature. Following this, the residual reaction solution was quenched with 30% hydrochloride acid ethanol, and then the precipitated polymer was collected by filtration, and was adequately washed with ethanol, and was dried in a vacuum until of constant weight.

X-Ray crystallographic studies

Single crystals of L2, L3, C1 and C2 suitable for X-ray diffraction analysis were obtained by layering diethyl ether on their dichloromethane solutions at room temperature. With graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) at 173(2) K, the cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.²⁰ Details of the X-ray structure determinations and refinements are provided in Table 6.

Acknowledgements

This work is supported by NSFC no. 20904059 as well as the MOST 863 program no. 2009AA034601. The RSC and EPSRC are thanked for the awarded of travel grant (to CR).

References

- 1 (a) C. S. Popeney, A. L. Rheingold and Z. Guan, Organometallics, 2009, 28, 4452; (b) D. H. Leung, J. W. Ziller and Z. Guan, J. Am. Chem. Soc., 2008, 130, 7538; (c) S. P. Meneghetti, P. J. Lutz and J. Kress, Organometallics, 1999, 18, 2734; (d) Y. Chen, S. Mandal and A. Sen, Organometallics, 2010, 29, 3160; (e) T. V. Laine, M. Klinga and M. Leskela, Eur. J. Inorg. Chem., 1999, 959; (f) T. V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Lofgren and M. Leskela, Macromol. Rapid Commun., 1999, 20, 487; (g) A. Koppl and H. G. Alt, J. Mol. Catal. A: Chem., 2000, 154, 45; (h) T. Schareina, G. Hillebrand, H. Fuhrmann and R. Kempe, Eur. J. Inorg. Chem., 2001, 2421; (i) D. M. Shin, S. U. Son, B. K. Hong, Y. K. Chung and S.-H. Chun, J. Mol. Catal. A: Chem., 2004, 210, 35; (j) R. Chen, J. Bacsa and S. F. Mapolie, Inorg. Chem. Commun., 2002, 5, 724; (k) R. Chen and S. F. Mapolie, J. Mol. Catal. A: Chem., 2003, 193, 33; (l) M. S. Mohlala, I. A. Guzei, J. Darkawa and S. F. Mapolie, J. Mol. Catal. A: Chem., 2005, 241, 93; (m) S. D. Ittel, L. K. Johnson and M. Brookhart, Chem. Rev., 2000, 100, 1169; (n) S. Mecking, Coord. Chem. Rev., 2000, 203, 325.
- 2 (a) L. K. Johnson, C. M. Killian and M. Brookhart, J. Am. Chem. Soc., 1995, 117, 6414; (b) L. K. Johnson, S. Mecking and M. Brookhart, J. Am. Chem. Soc., 1996, 118, 267.
- 3 (a) S. A. Svejda and M. Brookhart, Organometallics, 1999, 18, 65; (b) T. V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola and M. Leskelä, J. Organomet. Chem., 2000, 606, 112; (c) C. Shao, W.-H. Sun, Z. Li, Y. Hu and L. Han, Catal. Commun., 2002, 3, 405; (d) S. Jie, D. Zhang, T. Zhang, W.-H. Sun, J. Chen, Q. Ren, D. Liu, G. Zheng and W. Chen, J. Organomet. Chem., 2005, 690, 1739; (e) C. Zhang, W.-H. Sun and Z.-X. Wang, Eur. J. Inorg. Chem., 2006, 4895; (f) R. Gao, L. Xiao, X. Hao, W.-H. Sun and F. Wang, Dalton Trans., 2008, 5645; (g) F. Yang, Y. Chen, Y. Lin, K. Yu, Y. Liu, Y. Wang, S. Liu and J.-T. Chen, Dalton Trans., 2009, 1243.
- 4 (a) W. Keim, S. Killat, C. F. Nobile, G. P. Suranna, U. Englert, R. Wang, S. Mecking and D. L. Schröder, J. Organomet. Chem., 2002, 662, 150; (b) W.-H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng and H. Wang, New J. Chem., 2002, 26, 1474; (c) F. Speiser, P. Braunstein, L. Saussine and R. Welter, Organometallics, 2004, 3, 2613; (d) F. Speiser, P. Braunstein and L. Saussine, Organometallics, 2004, 23, 2625; (e) F. Speiser, P. Braunstein, L. Saussine and R. Welter, Inorg. Chem., 2004, 43, 1649; (f) Z. Weng, S. Teo and T. S. A. Hor, Organometallics, 2006, 25, 4878.

- 5 (a) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben and M. W. Day, Organometallics, 1998, 17, 3149; (b) C. Carlini, M. Isola, V. Liuzzo, A. M. R. Galletti and G. Sbrana, Appl. Catal., A, 2002, 231, 307; (c) S. Wu and S. Lu, Appl. Catal., A, 2003, 246, 295; (d) F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song and W.-H. Sun, J. Organomet. Chem., 2004, 689, 936; (e) T. Hu, L.-M. Tang, X.-F. Li, Y.-S. Li and N.-H. Hu, Organometallics, 2005, 24, 2628.
- 6 F. Speiser, P. Braunstein and L. Saussine, *Dalton Trans.*, 2004, 1539.
- 7 (a) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen and W. Chen, *J. Organomet. Chem.*, 2005, 690, 1570;
 (b) Q.-Z. Yang, A. Kermagoret, M. Agostinho, O. Siri and P. Braunstein, *Organometallics*, 2006, 25, 5518.
- 8 J. Hou, W.-H. Sun, S. Zhang, H. Ma, Y. Deng and X. Lu, *Organometallics*, 2006, 25, 236.
- 9 (a) L. Wang, W.-H. Sun, L. Han, H. Yang, Y. Hu and X. Jin, *J. Organomet. Chem.*, 2002, 658, 62; (b) N. Ajellal, M. C. A. Kuhn, A. D. G. Boff, M. Hörner, C. M. Thomas, J.-F. Carpentier and O. L. Casagrande, *Organometallics*, 2006, 25, 1213; (c) S. Adewuyi, G. Li, S. Zhang, W. Wang, P. Hao, W.-H. Sun, N. Tang and J. Yi, *J. Organomet. Chem.*, 2007, 692, 3532; (d) M. Zhang, S. Zhang, P. Hao, S. Jie, W.-H. Sun, P. Li and X. Lu, *Eur. J. Inorg. Chem.*, 2007, 3816.
- 10 P. Braunstein, Y. Chauvin, S. Mercier and L. Saussine, C. R. Chim., 2005, 8, 31.
- 11 V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
- 12 H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang and W.-H. Sun, *Organometallics*, 2011, **30**, 2418.
- 13 (a) D.P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, Macromolecules, 2000, 33, 2320; (b) R. J. Maldanis, J. S. Wood, A. Chandrasekaran, M. D. Rausch and J. C. W. Chien, J. Organomet. Chem., 2002, 645, 158; (c) H. Zou, F. M. Zhu, Q. Wu, J. Y. Ai and S. A. Lin, J. Polym. Sci., Part A: Polym. Chem., 2005, 43, 1325; (d) B. K. Bahuleyan, G. W. Son, D.-W. Park, C.-S. Ha and I. Kim, J. Polym. Sci., Part A: Polym. Chem., 2008, 46, 1066; (e) M. M. Wegner, A. K. Ott and B. Rieger, Macromolecules, 2010, 43, 3624; (f) C.-L. Song, L.-M. Tang, Y.-G. Li, X.-F. Li, J. Chen and Y.-S. Li, J. Polym. Sci., Part A: Polym. Chem., 2006, 44, 1964; (g) H.-R. Liu, P. T. Gomes, S. I. Costa, M. T. Duarte, R. Branquinho, A. C. Fernandes, J. C. W. Chien, R. P. Singh and M. M. Marques, J. Organomet. Chem., 2005, 690, 1314; (h) C. S. Popeney and Z. Guan, Macromolecules, 2010, 43, 4091; (i) M. Helldörfer, J. Backhus, W. Milius and H. G. Alt, J. Mol. Catal. A: Chem., 2003, 193, 59.
- 14 F.-S. Liu, H.-B. Hu, Y. Xu, L.-H. Guo, S.-B. Zai, K.-M. Song, H.-Y. Gao, L. Zhang, F.-M. Zhu and Q. Wu, *Macromolecules*, 2009, 42, 7789.
- 15 L. Li, M. Jeon and S. Y. Kim, J. Mol. Catal. A: Chem., 2009, 303, 110.
- 16 (a) L. C. Simon, R. S. Mauler and R. F. de Souza, J. Polym. Sci., Part A: Polym. Chem., 1999, 37, 4656;

(b) G. J. P. Britovsek, M. Bruce, V. C. Gibson,
B. S. Kimberley, P. J. Maddox, S. Mastroianni,
S. J. McTavish, C. Redshaw, G. A. Solan, S. Stromberg,
A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999,
121, 8728; (c) D.-J. Byun and S. Y. Kim, *Macromolecules*,
2000, 33, 1921; (d) G. J. P. Britovsek, S. A. Cohen,
V. C. Gibson and M. van Meurs, *J. Am. Chem. Soc.*, 2004,
126, 10701; (e) M. van Meurs, G. J. P. Britovsek, V. C. Gibson
and S. A. Cohen, *J. Am. Chem. Soc.*, 2005, 127, 9913.

17 (*a*) W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking and R. Fröhlich, *J. Organomet. Chem.*,

2006, **691**, 4196; (*b*) L. Xiao, R. Gao, M. Zhang, Y. Li, X. Cao and W.-H. Sun, *Organometallics*, 2009, **28**, 2225; (*c*) M. Zhang, K. Wang and W.-H. Sun, *Dalton Trans.*, 2009, 6354.

- 18 G. B. Galland, R. F. de Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*, 1999, **32**, 1620.
- 19 B. K. Bahuleyan, B. R. Jermy, I. Y. Ahn, H. Suh, D.-W. Park, C. S. Ha and I. Kim, *Catal. Commun.*, 2009, **11**, 252.
- 20 G. M. Sheldrick, *SHELXTL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.