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Synthesis, characterization and ethylene polymerization behaviour of binuclear nickel halides bearing 4,5,9,10-tetra(arylimino)-pyrenylidenes†

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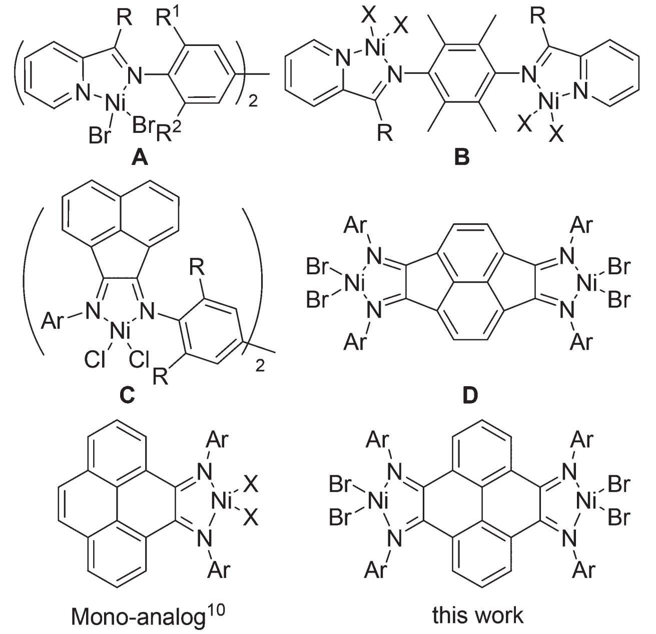
Pyrene-4,5,9,10-tetraone was prepared *via* the oxidation of pyrene, and reacted with various anilines to afford a series of 4,5,9,10-tetra(arylimino)pyrenylidene derivatives (**L1–L4**). The tetraimino-pyrene compounds **L1** and **L2** were reacted with two equivalents of (DME)$NiBr_2$ in CH_2Cl_2 to afford the corresponding dinickel bromide complexes (**Ni1** and **Ni2**). The organic compounds were fully characterized, whilst the bi-metallic complexes were characterized by FT-IR spectra and elemental analysis. The molecular structures of representative organic and nickel compounds were confirmed by single-crystal X-ray diffraction studies. These nickel complexes exhibited high activities towards ethylene polymerization in the presence of either MAO or Me_2AlCl, maintaining a high activity over a prolonged period (longer than previously reported dinickel complex pre-catalysts). The polyethylene obtained was characterized by GPC, DSC and FT-IR spectroscopy and was found to possess branched features.

Introduction

Inspired by the bulky α-diimino nickel/palladium complex pre-catalysts reported by the Brookhart group,[1] the use of nickel complex pre-catalysts in ethylene poly-/oligo-merization has been extensively investigated through the modification of the ligands used[2] and alternative models of the nickel complexes have been reported.[3] High activity and enhanced thermo-stability for nickel pre-catalysts has been pursued and a number of successful examples such as the *ortho*-difurylaryl[4] and bulky unsymmetrical α-diiminonickel complexes have been isolated.[5]

Binuclear metal complexes have been explored in catalysis with the potential of synergistic effects,[6] and have also been considered in ethylene poly-/oligo-merization.[7] A number of dinickel complex pre-catalysts have been employed in olefin polymerization,[8,9] for example, the bridged dinickel complexes **A**,[8a] **B**[8b] and **C**[8c] (Scheme 1) provided two active sites and performed with different catalytic behaviour to their mono-analogs.[1a,8d] In comparison to the good ethylene polymerization achieved by mono-nickel pre-catalysts,[8d] the methyl-bridged



Scheme 1 Representative nickel complex pre-catalysts.

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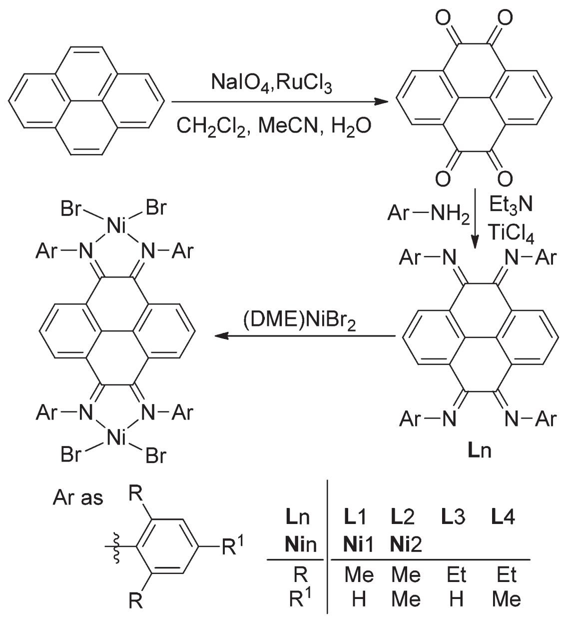
dinickel complexes **A** appeared to act with two active sites producing both polyethylenes and oligomers,[8a] meanwhile phenyl-bridged **B** polymerized ethylene with relative lower activities.[8b] The dinickel complexes **C**[8c] exhibited higher activities than their 'mono' analogs,[1a] whilst **D**, containing a rigid backbone,[9] revealed twice the activities of their 'mono' analogs.[1a] On the basis of the oxidation of pyrene, we achieve the preparation of pyrene-4,5-dione[10] and pyrene-4,5,9,10-tetraone. The mono-nickel complexes ligated by 4,5-diiminopyrenylidenes were found to be highly active pre-catalysts in ethylene polymerization and produced highly branched polyethylenes.[10] Subsequently, herein the 4,5,9,10-tetra(arylimino)pyrenylidene derivatives (**L1–L4**) are prepared and were reacted with (DME) $NiBr_2$ in CH_2Cl_2. In two cases, dinickel complexes (**Ni1** and **Ni2**) were successfully isolated. The obtained nickel complexes exhibited high activity for ethylene polymerization, and more importantly were capable of maintaining the activities over a prolonged reaction period. The synthesis and characterization of the tetraiminopyrenylidenes and their nickel complexes are reported in detail, as well as the ethylene polymerization behaviour of these nickel complex pre-catalysts.



Scheme 2 Synthesis procedures.

Results and discussion

Synthesis and characterization of 4,5,9,10-tetra(arylimino)-pyrenylidenes and their nickel complexes

The precursor pyrene was oxidized to pyrene-4,5,9,10-tetraone using a mixture of ruthenium(III) chloride, sodium periodate, dichloromethane, acetonitrile and water using a modification of the literature procedure.[11] It was found that subsequent condensation of pyrene-4,5,9,10-tetraone with anilines had limited synthetic use, and only the four 4,5,9,10-tetra(arylimino)pyrenylidene derivatives (**L1–L4**)[10] were successfully isolated, *i.e.* less bulky substituents were necessary. For example, prolonged reaction with excessive molar ratios of 2,6-diisopropylaniline was unsuccessful. The reaction of all compounds **L1–L4** using (DME)$NiBr_2$ was, in our hands, limited to the compounds **L1** and **L2**, which afforded the nickel complexes **Ni1** and **Ni2** (Scheme 2). All of the organic compounds and the complexes were fully characterized by elemental analysis and FT-IR spectroscopy as well as by ^1H and ^{13}C NMR measurements for the organic compounds. Moreover, the structures of the representative compounds **L1** and **Ni2** were confirmed by single-crystal X-ray diffraction.

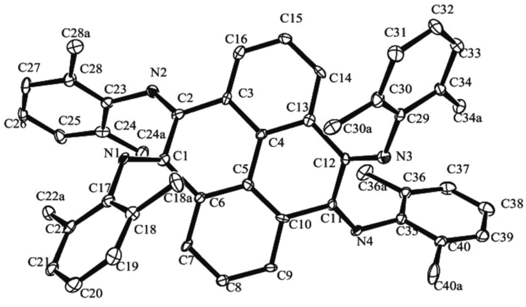


Fig. 1 ORTEP drawing of **L1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

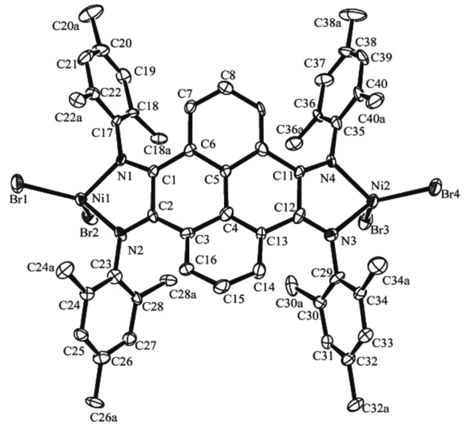


Fig. 2 ORTEP drawing of **Ni2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

X-ray crystallography

Single crystals of **L1** and **Ni2** suitable for single-crystal X-ray crystallographic analysis were individually obtained by layering diethyl ether onto their dichloromethane solutions at room temperature. The molecular structures of **L1** and **Ni2** are shown in Fig. 1 and 2 and selected bond lengths and bond angles are tabulated in Table 1. There is a free dichloromethane molecule in the single crystal of **Ni2**, when drawing in ORTEP, it is neglected. Considering the double bonds within the 4,5,9,10-tetra(arylimino)pyrenylidene derivatives, though the conjugated phenyl rings have been linked through imino-double bonds, the total 2*n* double-bonds result in non-conjugation and non-planarity of the 4,5,9,10-tetraylidenylpyrenes.

Table 1 The selected bond lengths (Å) and angles (°) for **L1** and **Ni2**

	L1	**Ni2**
Bond lengths (Å)		
N(1)–C(1)	1.300(5)	1.312(15)
N(2)–C(2)	1.269(5)	1.300(14)
N(3)–C(12)	1.244(5)	1.284(16)
N(4)–C(11)	1.283(5)	1.257(15)
N(1)–C(17)	1.435(5)	1.433(14)
N(2)–C(23)	1.429(5)	1.451(17)
N(3)–C(29)	1.418(5)	1.472(16)
N(4)–C(35)	1.412(5)	1.449(16)
Ni(1)–N(1)		1.970(9)
Ni(1)–N(2)		2.003(11)
Ni(1)–Br(1)		2.323(2)
Ni(1)–Br(2)		2.355(2)
Ni(2)–N(3)		1.999(11)
Ni(2)–N(4)		1.981(10)
Ni(2)–Br(4)		2.342(2)
Ni(2)–Br(3)		2.355(3)
Bond angles (°)		
C(1)–N(1)–C(17)	120.3(3)	122.9(9)
C(2)–N(2)–C(23)	126.3(3)	124.4(11)
C(12)–N(3)–C(29)	123.0(3)	125.5(11)
C(11)–N(4)–C(35)	122.9(3)	123.6(10)
Br(1)–Ni(1)–Br(2)		118.64(9)
Br(4)–Ni(2)–Br(3)		122.52(9)
N(4)–Ni(2)–Br(4)		114.9(3)
C(29)–N(3)–Ni(2)		119.9(9)
C(11)–N(4)–Ni(2)		116.2(8)

Table 2 Ethylene polymerization with MAO[a]

Entry	Al/Ni	Temp (°C)	Act.[b]	M_w[c]	M_w[c]/M_n	T_m[d]/°C	Brs.[e]/1000C
1	200	30	0.55	2.6	3.8	131.6	11
2	300	30	0.85	2.4	3.7	131.9	8
3	400	30	1.16	2.3	2.9	132.4	8
4	500	30	1.50	2.3	2.2	131.4	9
5	600	30	0.42	4.4	2.9	130.3	10
6	500	20	0.62	2.3	4.0	133.9	8
7	500	40	1.01	2.2	3.2	125.0	11
8	500	50	0.07	1.5	3.1	126.5	12
9[f]	500	30	1.20	2.1	2.0	134.5	7
10[g]	500	30	1.30	2.3	2.4	129.7	8
11[h]	500	30	1.30	2.4	4.2	129.4	10
12	500	30	0.65	2.2	4.7	130.2	9
13[i]	500	30	1.26	4.9	3.0	129.4	14

[a] General conditions: 2 μmol **Ni1**; 100 mL toluene with 10 atm ethylene for entries 1–11 and 13 and 5 atm for entry 12; 30 min. [b] 10^6 g (PE) mol^{-1} (Ni) h^{-1}. [c] Determined by GPC, 10^5 g mol^{-1}. [d] Determined by DSC. [e] Determined by FT-IR. [f] 15 min. [g] 45 min. [h] 60 min. [i] **Ni2**.

Such a feature is consistent with the observed classical single and double C–N bonds to every nitrogen atoms in Table 1. In addition, both molecular structures (**L1** and **Ni2**) do not show any symmetry, and their corresponding bond lengths and angles are comparably similar. The C═N bond lengths of organic compound **L1** are slightly shorter than those within the nickel complex **Ni2**, indicating the effective coordination of the nickel ions with all nitrogen atoms; the electronic donation from nitrogen to nickel ions causes weaker C═N bonds as well as corresponding C–N bonds.

The 4,5,9,10-tetra(arylimino) pyrenylidene derivatives provide tetradentate ligands to coordinate with two nickel ions, resembling two classical α-diiminonickel species. In comparison to its mono-analogs[10] and also rigid backbone dinickel complexes **D**,[9] the current organic compound **L1** and nickel complex **Ni2** exhibit similar geometrical data at the nitrogen and nickel atoms.

Ethylene polymerization

According to our previous work,[10] co-catalysts such as methylaluminoxane (MAO) or dimethylaluminium chloride (Me_2AlCl) are commonly employed with nickel complex pre-catalysts; therefore, **Ni1** was used to optimize the catalytic parameters with methylaluminoxane (MAO) or dimethyl(or diethyl)-aluminium chloride (Me_2AlCl/Et_2AlCl) as co-catalyst.

When the nickel pre-catalysts were activated with MAO, the activity reached a maximum at 30 °C, and then fell as the temperature increased to 40 and 50 °C. Comparison with the analogous mono-nuclear complex,[10] reveals that the temperature barely has any effect on the activity, presumably because the 'steric clash' is the same regardless of the addition of the other metal center. On changing the Al/Ni molar ratio, the best activity, namely 1.5 × 10^6 g (PE) mol^{-1} (Ni) h^{-1} was observed for Al/Ni at 500, *i.e.* less co-catalyst was required than for the mono-nuclear catalysts.[10] Regarding the stability of the complex pre-catalysts, the lifetime studies indicated that the activity increased slightly on prolonging the time from 15 to 30 min (entries 4, 9, Table 2), which indicated a period of induction. After this time, the activity does not decrease, but was maintained for over 60 min (entries 10–11, Table 2). The long lifetime of the pre-catalyst may be attributed to the presence of two metal centers in the complex, indicating that at least one of them is active in the catalytic system. The molecular weight and the polydispersity of the polymers decreased slightly as the temperature increased, and similarly as the Al/Ni ratio increased (shown in Fig. 3 and 4), which are consistent with the previous conclusion[12] that high temperature and high molar ratios of Al/Ni enhance chain transfer from the nickel species to aluminium, thereby resulting in lower molecular weight polymers.

Using Me_2AlCl as co-catalyst, the polymerization reaction parameters, including Al/Ni molar ratio, reaction time and

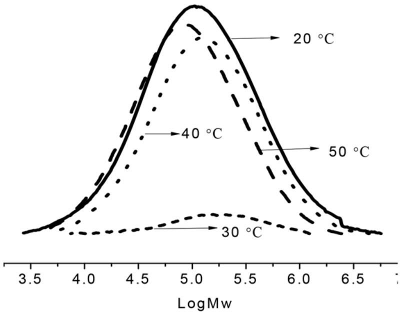


Fig. 3 The GPC curves of polyethylenes obtained by **Ni1** with MAO at different temperatures (entries 4, 6–8, Table 2).

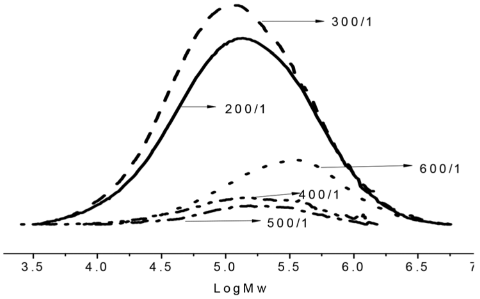


Fig. 4 The GPC curves of polyethylenes obtained by **Ni1** with MAO at different Al/Ni ratio (entries 1–5, Table 2).

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 200 to 600, the catalytic activity first increased and then decreased; the best activity was observed with the Al/Ni molar ratio at 400/1. The increase of the Al/Ni molar ratio led to polyethylene of higher molecular weight (Fig. 5), which was not consistent of polyethylenes obtained with lower molecular weights at higher molar ratio of Al/Ni caused by the chain transfer from nickel species to aluminium.[12] This may be due to the large steric clash, the active nickel species were probably stabilized with more co-catalysts. So chain propagations generally surpassed both chain migrations and hydrogen-elimination, therefore, the obtained polyethylenes showed higher molecular weights as well as low branches. According to the entries 3 and 5–7 in Table 3, the optimum reaction temperature in the present study was found to be 30 °C; higher or lower temperatures led to a slight decrease of the catalytic activity, similar to the previously observed situation for reported α-diimine catalyst systems.[13] The temperature effect on the activity is more sensitive here than for the mono-nuclear catalyst,[10] which may relate to the quick responses of the two metal centers. In addition, when elevating the temperature from 20 to 50 °C, a remarkable decrease in the polymer molecular weight was observed (Fig. 6).

From the high temperature ^{13}C NMR spectrum of the polyethylene (entry 1 in Table 3) in Fig. 7, there are some branches of polyethylenes, also indicated by the results of the FT-IR spectra. In general, these obtained polyethylenes revealed less branches than those by the mono-analogs[10] and other dinickel pre-catalysts;[8,9] it is thought that the current ligands possibly protect the active sites thereby reducing hydrogen elimination. Lifetime studies indicated that higher activities were observed over shorter reaction time, the activities decreased on prolonging the period of polymerization (entries 8–10 in Table 3). This suggested that there was a rather short induction period, and

Table 3 Ethylene polymerization with Me_2AlCl[a]

Entry	Al/Ni	Temp (°C)	Act.[b]	M_w [c]	M_w [c]/M_n	T_m[d]/°C	Brs.[e]/ 1000C
1	300	30	2.00	1.32	2.84	123.9	13
2	400	30	2.25	1.41	3.24	122.3	12
3	500	30	1.45	1.47	3.53	124.5	10
4	600	30	0.65	1.59	4.58	126.7	11
5	400	20	1.65	1.55	4.30	122.3	8
6	400	40	1.35	0.79	3.10	121.1	12
7	400	50	0.25	0.60	3.00	108.6	13
8[f]	400	30	4.20	1.21	2.91	119.7	7
9[g]	400	30	1.60	1.44	3.70	121.2	8
10[h]	400	30	1.25	1.75	4.47	123.3	10
11	400	30	2.05	1.62	3.00	122.2	12
12[i]	400	30	0.50	1.17	3.46	120.6	10

[a] General conditions: 2 μmol **Ni1**; 100 mL toluene with 10 atm ethylene for entries 1–10 and 12 and 5 atm for entry 11. [b] 10^6 g (PE) mol^{-1} (Ni) h^{-1}. [c] Determined by GPC, 10^5 g mol^{-1}. [d] Determined by DSC. [e] Determined by FT-IR. [f] 15 min. [g] 45 min. [h] 60 min. [i] **Ni2**.

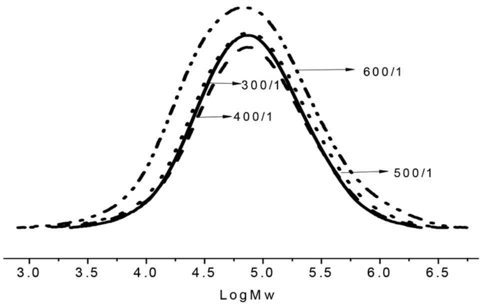


Fig. 5 The GPC curves of polyethylenes obtained at different Al/Ni ratio (entries 1–4, Table 3).

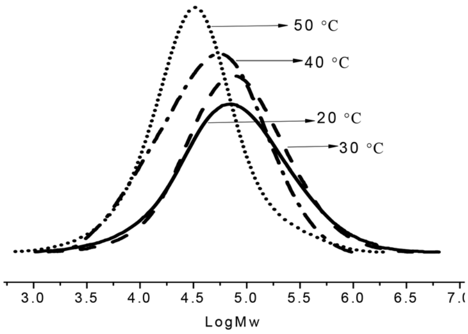


Fig. 6 The GPC curves of polyethylenes obtained at different temperatures (entries 2, 5–7, Table 3).

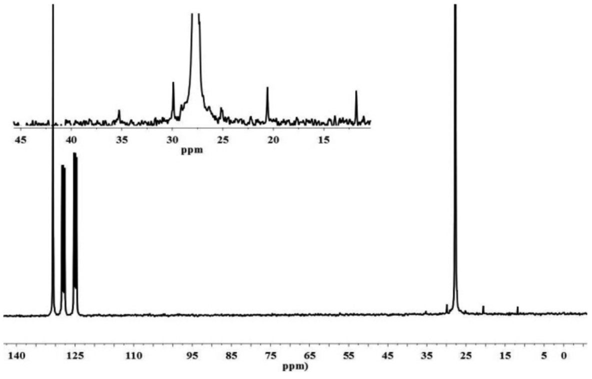


Fig. 7 The ^{13}C NMR spectra of the polyethylene (entry 1 in Table 3).

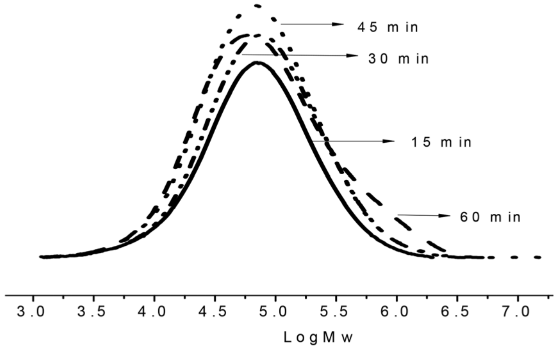


Fig. 8 The GPC curves of polyethylenes obtained over different times (entry 2, 8–10, Table 3).

that the active species did not live as long as that formed on activation with MAO. Moreover, both the M_w and M_w/M_n values of the obtained PEs increased slightly on extending the reaction time; the M_w changes are shown by GPC (Fig. 8). Given that the optimum conditions for the **Ni1**/Me_2AlCl system were found to be an Al/Ni ratio of 400 at 30 °C over 30 min (entry 2, Table 3), further investigations using the other pre-catalyst **Ni2** was conducted under such conditions (entry 12, Table 3). As shown in entries 2 and 12 of Table 3, results reveal the activity order **Ni1** > **Ni2**, which may result from electron donation or increased solubility. As illustrated by the above structural features for **Ni1**, efficient coordination to the nickel center in **Ni1** can stabilize the active species and thereby result in better activity, which is consistent with previous observations.[14]

Ni1 was also screened for ethylene polymerization under 1 atm pressure. The co-catalysts MAO and Et_2AlCl were chosen, and it was found that Et_2AlCl performed better than MAO (entries 1 and 2, Table 4). Parameters such as temperature and the Al/Ni ratio were varied. The activity decreased as the molar ratio of Al/Ni increased, and as the temperature increased, the activity decreased dramatically indicating here that the activity is much more sensitive to the temperature. The molecular weight of the polymers obtained at 1 atm also decreased as the temperature increased, as observed for the polymers at 10 atm. The degree of branching was greater at 1 atm, suggesting that this is beneficial to the chain transfer *cf.* 10 atm; contrastingly, the use of 10 atm is beneficial to chain growth.

Table 4 Ethylene polymerization by **Ni1** under 1 atm[a]

Entry	Al/Ni	Temp (°C)	Activity[b]	M_w[c]	M_w[c]/M_n	T_m[d]/°C	Brs./1000C[e]
1	1000	20	2.5	10.7	3.6	121.5	22
2	200	20	15	7.7	4.9	117.7	27
3	400	20	12	3.0	2.8	114.3	24
4	600	20	9.0	3.3	2.9	113.9	41
5	800	20	7.5	5.2	3.5	113.4	52
6	200	30	12.5	5.9	4.4	79.5	30
7	200	40	4.0	2.1	2.5	55.1	45
8	200	50	1.0	1.7	2.3	54.9	53

[a] General conditions: 2 μmol **Ni1**; Et_2AlCl as co-catalyst for entries 2–8, MAO as co-catalyst for entry 1; 30 mL toluene; 30 min. [b] 10^4 g (PE) mol^{-1} (Ni) h^{-1}. [c] Determined by GPC, 10^4 g mol^{-1}. [d] Determined by DSC. [e] Determined by FT-IR.

Conclusion

The newly synthesized 4,5,9,10-tetra(arylimino)pyrenylidenes were successfully complexed with nickel halide. The resulting nickel complex pre-catalysts showed high activities for ethylene polymerization with various co-catalysts, such as Me_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. Comparison with the analogous mono-nuclear complexes revealed that although there was no significant improvement in activity for the binuclear nickel complexes, there was a significant increase in the lifetime when activated with MAO. The polyethylene products were found to be moderately branched when the activators MAO, Me_2AlCl or Et_2AlCl were employed herein.

Experimental

General considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene), dimethylaluminium chloride (Me_2AlCl, 1.0 M solution in toluene) and diethylaluminium chloride (Et_2AlCl, 1.0 M in heptane) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. MALDI-TOF spectra were detected on autoflex III Bruker, using CCA as the substrate. Molecular weights (M_w) and molecular weight distribution (M_w/M_n) of polyethylenes were determined by a PL-GPC220 at 150 °C with three PLgel 10 μm MIXED-B columns, with 1,2,4-trichlorobenzene as the solvent. Melting points of polyethylenes were obtained from the second scanning run on Q2000 DSC-7 at a heating rate of 10 °C per minute to 150 °C; branches of the polymers were tested and calculated by FT-IR spectra.

Pyrene-4,5,9,10-tetraone

Pyrene was used as the starting material for synthesizing the pyrene-4,5,9,10-tetraone. To a solution of 20.2 g pyrene (0.1 mol) in CH_2Cl_2 (400 mL) and CH_3CN (400 mL) were added water (1000 mL), 175 g (0.8 mol) sodium periodate and 2.5 g (12 mmol) $RuCl_3$. The dark brown suspension was heated at

30–40 °C overnight. The next day, 3.5 L water was added to the mixture with intensive mixing and the aqueous phase was extracted by 2 L CH_2Cl_2 for 5 times, then the organic phase was combined together and washed by saturated NaCl solution, the CH_2Cl_2 solution was condensed, which resulted in 4.45 g of a dark yellow solid, yield 17.0%. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.52 (d, *J* = 7.6 Hz, 2H, Ph-*H*), 7.72 (t, *J* = 7.6, 1H, Ph-*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 180.5, 138.9, 136.5, 131.2, 128.3. FT-IR (KBr, cm^{-1}): 3066 (m), 2164 (m), 1668 ($\nu_{C=O}$, s), 1553 (m), 1416 (m), 1332 (w), 1271 (m), 1168 (m), 1050 (m), 903 (s), 803 (m), 706 (s).

4,5,9,10-Tetra(2,6-dimethylphenylimino)pyrenylidene (L1)

3.60 g (30 mmol) 2,6-dimethylaniline and 9.08 g (90 mmol) Et_3N was dissolved in 100 mL toluene and heated to 90 °C, then 3.2 mL $TiCl_4$ was added into the solution, some white fog appeared and then 1.33 g (5 mmol) pyrene-4,5,9,10-tetraone was added to the mixture, and the solution darkened. The reaction was stirred for 30 min, then the mixture was separated by column chromatography and 1.94 g red solid was collected, yield 57%. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.37 (d, *J* = 8.0 Hz, 2H, Ph-*H*), 7.13 (t, *J* = 7.6, 2H, Ph-*H*), 7.02 (d, *J* = 7.6 Hz, 4H, Ph-*H*), 6.92 (t, *J* = 7.6, 2H, Ph-*H*), 6.82–6.86 (m, 8H, Ph-*H*), 2.09 (s, 12H,4 × C*H*$_{3)}$, 1.44 (s, 12H, 4 × C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 130.4, 129.1, 128.5, 128.0, 127.7, 123.6, 122.9, 18.5, 17.1. FT-IR (cm^{-1}): 2938 (w), 1645 ($\nu_{C=N}$, m), 1619 (s), 1589 (m), 1464 (s), 1373 (w), 1320 (w), 1261 (m), 1199 (s), 1090 (m), 935.5 (m), 765 (s), 722 (s). Anal. Calcd for $C_{48}H_{42}N_4$ (673): C, 85.43; H, 6.27; N, 8.30. Found: C, 85.35; H, 6.50; N, 8.11. Ms (MALDI-TOF, *m*/*z*): 674.34. Found: 674.4.

4,5,9,10-Tetra(mesitylimino)pyrenylidene (L2)

4.00 g (30 mmol) mesitylamine and 9.08 g (90 mmol) Et_3N was dissolved in 100 mL toluene and heated to 90 °C, then 3.2 mL $TiCl_4$ was added into the solution, and some white fog appeared and then 1.33 g (5 mmol) pyrene-4,5,9,10-tetraone was added into the mixture, and the solution darkened. The reaction was stirred for 30 min, then the mixture was separated by column chromatography and 1.69 g red solid was collected, yield 45.6%. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.29 (d, *J* = 7.6 Hz, 2H, Ph-*H*), 7.12 (t, *J* = 7.6 Hz, 2H, Ph-*H*), 6.88 (t, *J* = 7.6 Hz, 2H, Ph-*H*), 6.84 (s, 4H, Ph-*H*), 6.63 (s, 4H, Ph-*H*), 2.34 (s, 6H, 2 × C*H*$_3$), 2.27 (s, 6H, 2 × C*H*$_3$), 2.18 (s, 12H, 4 × C*H*$_3$), 1.31 (s, 12H, 4 × C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 158.6, 157.3, 146.2, 144.8, 133.3, 133.0, 132.1, 131.2, 130.4, 129.0, 128.7, 128.8, 128.5, 128.4, 125.1, 124.7, 20.8, 18.5, 17.0. FT-IR (cm^{-1}): 2911 (m), 1738 (w), 1632 ($\nu_{C=N}$, m), 1606 (s), 1472 (s), 1374 (w), 1319 (m), 1265 (m), 1211 (s), 1089 (m), 937 (m), 788 (s), 721 (s). Anal. Calcd for $C_{52}H_{50}N_4$ (730): C, 85.44; H, 6.89; N, 7.66. Found: C, 85.42; H, 7.26; N, 7.42.

4,5,9,10-Tetra(2,6-diethylphenylimino)pyrenylidene (L3)

4.47 g (30 mmol) 2,6-diethylaniline and 9.08 g (90 mmol) Et_3N was dissolved in 100 mL toluene and heated to 90 °C, then 3.2 mL $TiCl_4$ was added into the solution, some white fog appeared and then 1.33 g (5 mmol) pyrene-4,5,9,10-tetraone was added to the mixture, and the solution darkened. The reaction was stirred for 30 min, then the mixture was separated by column chromatography and 1.62 g red solid was collected, yield 41.5%. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.36 (d, *J* = 8.0 Hz, 2H, Ph-*H*), 7.11–7.04 (m, 10H, Ph-*H*), 6.96–6.83 (m, 6H, Ph-*H*), 2.52–2.46 (m, 4H, 2 × C*H*$_2$), 2.39–2.34 (m, 4H, 2 × C*H*$_2$), 1.69–1.62 (m, 8H, 4 × C*H*$_2$), 0.87 (t, *J* = 7.6 Hz, 12H, 4 × C*H*$_3$), 0.73 (t, *J* = 7.6 Hz, 12H, 4 × C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.2, 156.6, 147.7, 146.3, 133.2, 131.2, 130.8, 130.7, 130.5, 130.2, 130.1, 129.4, 128.5, 125.9, 125.4, 125.2, 124.0, 123.2, 24.8, 23.5, 13.5, 13.4. FT-IR (cm^{-1}): 2908 (m), 1686 (w), 1641 ($\nu_{C=N}$, m), 1614 (s), 1440 (s), 1371 (w), 1320 (m), 1288 (m), 1194 (m), 1080 (m), 848 (s), 801 (m), 709 (s). Anal. Calcd for $C_{56}H_{58}N_4$ (787): C, 85.45; H, 7.43; N, 7.12. Found: C, 85.66; H, 7.21; N, 7.32.

4,5,9,10-Tetra(2,6-diethyl-4-methyl-phenylimino)pyrenylidene (L4)

4.89 g (30 mmol) 2,6-diethyl-4-methylaniline and 9.08 g (90 mmol) Et_3N was dissolved in 100 mL toluene and heated to 90 °C, then 3.2 mL $TiCl_4$ was added into the solution, some white fog appeared and then 1.33 g (5 mmol) pyrene-4,5,9,10-tetraone was added into the mixture, and the solution darkened. The reaction was carried for 30 min, then the mixture was separated by column chromatography and 1.73 g red solid was collected, yield 41.1%. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.33 (d, *J* = 8.0 Hz, 2H, Ph-*H*), 7.10 (t, *J* = 8.0 Hz, 2H, Ph-*H*), 6.89–6.84 (m, 8H, Ph-*H*), 6.74 (s, 6H, Ph-*H*), 2.48–2.42 (m, 4H, 2 × C*H*$_2$), 2.36–2.25 (m, 10H, 5 × C*H*$_2$), 2.34 (s, 6H, 2 × C*H*$_3$), 2.23 (s, 6H, 2 × C*H*$_3$), 1.13 (t, *J* = 7.6 Hz, 12H, 4 × C*H*$_3$), 0.84 (t, *J* = 7.6 Hz, 12H, 4 × C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.7, 156.7, 145.2, 143.9, 133.2, 132.1, 130.8, 130.5, 130.1, 130.0, 129.8, 129.2, 128.7, 128.4, 126.8, 126.6, 126.2, 126.0, 24.8, 23.5, 23.2, 21.2, 21.1, 13.4. FT-IR (cm^{-1}): 2966 (s), 1745 (w), 1615 ($\nu_{C=N}$, s), 1453 (s), 1373 (w), 1321 (m), 1264 (m), 1207 (m), 1087 (m), 859 (s), 799 (m), 722 (s). Anal. Calcd for $C_{60}H_{66}N_4$ (843): C, 85.47; H, 7.89; N, 6.64. Found: C, 85.57; H, 8.04; N, 6.46.

Synthesis and characterization of binuclear nickel complexes

Ni1. A mixture of 0.67 g (1 mmol) 4,5,9,10-tetra(2,6-dimethylphenylimino)pyrenylidene (L1) and 0.60 g (2 mmol) (DME)$NiBr_2$ in CH_2Cl_2 (5 mL) was stirred for 12 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Ni1** as a brown solid (1.06 g, yield 96.3%). FT-IR (cm^{-1}): 3314 (s), 1608 ($\nu_{C=N}$, m), 1463 (m), 1381 (w), 1338 (s), 1284 (s), 1164 (w), 1091 (w), 1033 (w), 764 (s), 703 (s). Anal. Calcd for $C_{48}H_{42}Br_4N_4Ni_2$ (1111): C, 51.85; H, 3.81; N, 5.04. Found: C, 51.54; H, 3.67; N, 4.93.

Ni2. A mixture of 0.73 g (1 mmol) 4,5,9,10-tetra(mesitylimino)pyrenylidene (**L2**) and 0.60 g (2 mmol) (DME)$NiBr_2$ in CH_2Cl_2 (5 mL) was stirred for 12 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Ni2** as a brown solid (0.98 g, yield 83.9%). FT-IR (cm^{-1}): 3328 (s), 1608 ($\nu_{C=N}$, m), 1456 (m), 1380 (w), 1337 (s), 1286 (s), 1194 (w), 1111 (w), 1032 (w), 753 (m), 703 (s). Anal. Calcd for $C_{52}H_{50}Br_4N_4Ni_2$ (1167): C, 53.47; H, 4.31; N, 4.80. Found: C, 53.42; H, 4.26; N, 4.42.

X-ray crystallographic studies

Single crystals of ligand **L1** and complex **Ni2** suitable for X-ray diffraction analysis were obtained by laying ethyl ether on their respective dichloromethane solutions at room temperature. With graphite-monochromated Mo-Kα radiation (k = 0.71073 Å), single-crystal X-ray diffraction for ligand **L1** and complex **Ni2** was performed on a Rigaku Saturn724+ CCD at 100(2) K. 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 SHELXTL-97 package.[15] Crystal data is given in Table 5 and refinement details are given in the ESI.†

General procedure for ethylene polymerization

Ethylene polymerization at ambient pressure. The pre-catalyst was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under ethylene atmosphere (1 atm) with a steam bath for controlling the desired temperature. Finally, the required amount of co-catalyst (MAO, Me_2AlCl or Et_2AlCl) was added by a syringe. After the reaction was carried out for the required period, a small amount of the reaction solution was collected and terminated by the addition of 10% aqueous hydrogen chloride immediately. The organic layer was analyzed by gas chromatography (GC) for monitoring the oligomers formed; the precipitated polymer was collected, washed with water and ethanol, and finally dried.

Table 5 Crystal data and structure refinement details for **L1** and **Ni2**

	L1	**Ni2**
Crystal color	Red	Black
Empirical formula	$C_{48}H_{46}N_4$	$C_{53}H_{52}N_4Br_4Ni_2Cl_2$
F_W	678.89	1252.95
T (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	*Cc*	*P*2(1)2(1)2(1)
a (Å)	28.504(6)	13.286(3)
b (Å)	10.357(2)	14.439(3)
c (Å)	12.460(3)	29.687(6)
α (°)	90.00	90.00
β (°)	90.05(3)	90.00
γ (°)	90.00	90.00
V (Å^3)	3678.3(13)	5695(2)
Z	4	4
D_{calcd} (mg m^{-3})	1.226	1.461
μ (mm^{-1})	0.072	3.597
F(000)	1448	2512
Cryst size (mm)	0.33 × 0.16 × 0.13	0.28 × 0.17 × 0.05
θ range (°)	1.43–27.47	1.37–27.47
Limiting indices	$-36 \le h \le 36$ $-13 \le k \le 13$ $-16 \le l \le 16$	$-17 \le h \le 17$ $-18 \le k \le 18$ $-37 \le l \le 38$
No. of rflns collected	12 077	12 792
No. unique rflns [R(int)]	7140 (0.0315)	7195
Completeness to θ (%)	99.0%	99.9%
Goodness of fit on F^2	1.071	1.416
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.066$ w$R_2 = 0.1802$	$R_1 = 0.1172$ w$R_2 = 0.3006$
R induces (all data)	$R_1 = 0.0695$ w$R_2 = 0.1855$	$R_1 = 0.1399$ w$R_2 = 0.3230$
Largest diff. peak and hole (Å^{-3})	0.35 and −0.74	3.96 and −1.17

Ethylene polymerization at elevated pressure (10 atm). A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, 50 mL toluene (freshly distilled) was injected to the clave which is full of ethylene. When the temperature required was reached, another 30 mL toluene which dissolved the complex (2.0 mol of metal) before, the required amount of co-catalyst (MAO or Me_2AlCl), the residual toluene were added by syringe successively. The reaction mixture was intensively stirred for the desired time under corresponding pressure of ethylene through the entire experiment. The reaction was terminated and analyzed using the same procedure as above for ethylene polymerization.

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Notes and references

1 (*a*) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (*b*) C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664.

2 (*a*) C. Popeney and Z.-B. Guan, *Organometallics*, 2005, **24**, 1145; (*b*) D. H. Leung, J. W. Ziller and Z.-B. Guan, *J. Am. Chem. Soc.*, 2008, **130**, 7538; (*c*) C. Popeney and Z.-B. Guan, *J. Am. Chem. Soc.*, 2009, **131**, 12384; (*d*) 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; (*e*) W.-H. Sun, K. Wang, K. Wedeking, D. Zhang and S. Zhang, *Organometallics*, 2007, **26**, 4781; (*f*) S. Zhang, W.-H. Sun, X. Kuang, I. Vystorop, J. Yi, J. Cai and Y. J. Li, *J. Organomet. Chem.*, 2007, **692**, 5307.

3 (*a*) Z. Guan and C. S. Popeney, *J. Am. Chem. Soc.*, 2009, **131**, 12384; (*b*) R. Gao, W.-H. Sun and C. Redshaw, *Catal. Sci. Technol.*, 2013, **3**, 1172; (*c*) S. Wang, W.-H. Sun and C. Redshaw, *J. Organomet. Chem.*, 2014, **751**, 717–741.

4 A. S. Ionkin and W. J. Marshall, *Organometallics*, 2004, **23**, 3276.

5 (*a*) H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang and W.-H. Sun, *Organometallics*, 2011, **30**, 2418; (*b*) H. Liu, W. Zhao, J. Yu, W. Yang, X. Hao, C. Redshaw, L. Chen and W.-H. Sun, *Catal. Sci. Technol.*, 2012, **2**, 415; (*c*) S. Kong,

C. Guo, W. Yang, L. Wang and W.-H. Sun, *J. Organomet. Chem.*, 2013, **725**, 37; (*d*) D. Jia, W. Zhang, W. Liu, L. Wang, C. Redshaw and W.-H. Sun, *Catal. Sci. Technol.*, 2013, **3**, 2737; (*e*) Q. Liu, W. Zhang, D. Jia, X. Hao, C. Redshaw and W.-H. Sun, *Appl. Catal., A*, 2014, **475**, 195.

6 (*a*) N. Guo, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 2246; (*b*) L. R. Gahan, S. J. Smith, A. Neves and G. Schenk, *Eur. J. Inorg. Chem.*, 2009, 2745; (*c*) Y. Guo, P. Ai, L. Han, L. Chen, B. Li and S. Jie, *J. Organomet. Chem.*, 2012, **716**, 222.

7 (*a*) A. L. Gavrilova and B. Bosnich, *Chem. Rev.*, 2004, **104**, 349; (*b*) E. Szuromi, H. Shen, B. L. Goodall and R. F. Jordan, *Organometallics*, 2008, **27**, 402; (*c*) P. M. Gurubasavaraj and K. Nomura, *Organometallics*, 2010, **29**, 3500; (*d*) M. R. Salata and T. J. Marks, *Macromolecules*, 2009, **42**, 1920; (*e*) Y. Cui, S. Zhang and W.-H. Sun, *Chin. J. Polym. Sci.*, 2008, **26**, 539; (*f*) W.-H. Sun, Q. Xing, J. Yu, E. Novikova, W. Zhao, X. Tang, T. Liang and C. Redshaw, *Organometallics*, 2013, **32**, 2309; (*g*) M. Delferro and T. Marks, *Chem. Rev.*, 2011, **111**, 2450.

8 (*a*) 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; (*b*) J. D. A. Pelletier, J. Fawcett, K. Singh and G. A. Solan, *J. Organomet. Chem.*, 2008, **693**, 2723; (*c*) S. Kong, K. Song, T. Liang, C.-Y. Guo, W.-H. Sun and C. Redshaw, *J. Chem. Soc., Dalton Trans.*, 2013, 9176; (*d*) T. V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Lofgren and M. Leskela, *Macromol. Rapid Commun.*, 1999, **20**, 487.

9 L. Zhu, Z.-S. Fu, H.-J. Pan, W. Feng, C. Chen and Z.-Q. Fan, *Dalton Trans.*, 2014, **43**, 2900–2906.

10 K. Song, W. Yang, B. Li, Q. Liu, C. Redshaw, Y. Li and W.-H. Sun, *Dalton Trans.*, 2013, **42**, 9166.

11 J. Hu, D. Zhang and F. W. Harris, *J. Organomet. Chem.*, 2005, **70**, 707.

12 (*a*) 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. Strolmberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728; (*b*) G. J. P. Britovsek, S. A. Cohen, V. C. Gibson and M. V. Meurs, *J. Am. Chem. Soc.*, 2004, **126**, 10701; (*c*) M. V. Meurs, G. J. P. Britovsek, V. C. Gibson and S. A. Cohen, *J. Am. Chem. Soc.*, 2005, **127**, 9913.

13 (*a*) R. J. Maldanis, J. S. Wood, A. Chandrasekaran, M. D. Rausch and J. C. W. Chien, *J. Organomet. Chem.*, 2002, **645**, 158; (*b*) D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, *Macromolecules*, 2000, **33**, 2320; (*c*) M. M. Wegner, A. K. Ott and B. Rieger, *Macromolecules*, 2010, **43**, 3624.

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

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