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Introduction

α-Diimino nickel type complex pre-catalysts have drawn much attention with respect to ethylene reactivity since their initial publication in 1995.¹ With the intention of enhancing their catalytic properties, different substituents have been used to modify such complex pre-catalysts.² Moreover, various nickel complexes bearing a variety of bi-dentate N^N³ and tri-dentate N^N^N⁴ ligand sets have been designed with subsequent ethylene reactivity studies in mind. The progress has been reviewed in a number of articles,⁵ which also indicate that there is ongoing research into tandem or bi-metallic catalytic systems.⁶ In the case of reported bi-nuclear nickel complex pre-catalysts,^{6–13} ligands of bridged coordination models have been favorably considered.^{7,13} In our previous work, we have synthesized

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Methylene-bridged bimetallic α-diimino nickel(II) complexes: synthesis and high efficiency in ethylene polymerization†

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A series of 1,2-bis(arylimino)acenaphthylidenes (L1–L5) and their corresponding 4,4'-methylenebis-(1-(2,6-diisopropylphenylimino)-2-(arylimino)acenaphthylene) derivatives (L6–L10) were synthesized and used to form mono-nuclear nickel bromides LnNiBr₂ (n = 1-5, Ni1–Ni5) and bi-nuclear nickel halides LnNi₂X₄ (n = 6-10: X = Br, Ni2-1–Ni2-5; n = 4, X = Cl, Ni2-6). All the organic compounds were fully characterized by FT-IR spectra, NMR measurements and elemental analysis. The nickel complexes were characterized by FT-IR spectra and elemental analysis and the molecular structures of the representative complexes Ni1, Ni2-1 and Ni2-3 were confirmed by single-crystal X-ray diffraction. Upon activation with either Et₂AlCl or MAO, all the nickel complex pre-catalysts exhibited high activity toward ethylene polymerization over the temperature range from ambient to 50 °C. In general, the bi-nuclear complexes showed a positive synergetic effect with higher activity than their mono nuclear analogs. The resultant polyethylene possessed higher molecular weight and a high degree of branching.

methylene-bridged bis(iminopyridyl) di-nickel(II) complexes (**A**, Scheme 1) derived from 2-iminopyridylnickel complexes¹⁴ and investigated their catalytic activity.¹⁰ Additionally, bi-nuclear nickel complexes bearing 2-methyl-2,4-bis-(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepine ligands (**B**, Scheme 1) were designed and used for ethylene oligomerization and polymerization.¹¹ 2,3,5,6-Tetramethylbenzene linked bis(iminopyridyl) bi-metallic nickel complexes (**C**, Scheme 1) were also reported to be capable of ethylene polymerization and oligomerization.¹² All these bi-metallic nickel pre-catalysts commonly produced both mixtures of oligomers and polyethylenes,¹⁰⁻¹³ however, they are also important sources of solely oligomeric products.

Recently, 1,2-bis(arylimino)acenaphthylidene nickel complex pre-catalysts have been extensively explored and shown to solely polymerize ethylene.¹⁵ With this in mind, bridged bi-nuclear nickel pre-catalysts based on such models would be worthy of revisiting. In the literature, methylene-bridged α -diimino bi-metallic nickel pre-catalysts (**D**, Scheme 1)¹³ were reported to be highly active in ethylene polymerization. In addition, the use of bulky anilines enhanced the catalytic performance, particularly the use of *i*-Pr substituents. Given this, 4,4'-methylenebis(2,6-diisopropylaniline) was chosen to target methylene-bridged 1,2-bis (arylimino)acenaphthylidenes and the nickel complexes (**E**, Scheme 1) thereof. For comparison, the catalytic performance of the 1-arylimino-2-(2,6-diisopropylphenylimino)acenaphthylenylidene-nickel complexes (**F**, Scheme 1) is also reported.

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E-mail: c.redshaw@hull.ac.uk; Fax: +44 (0) 1482 466410; Tel: +44 (0) 1482 465219 †CCDC 917315, 917316 and 917317 for **Ni1, Ni2-1** and **Ni2-3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00023k



Herein, the target bi-metallic and mono-nuclear nickel complexes (E and F, Scheme 1) were synthesized and fully characterized. All the nickel complex pre-catalysts revealed high activity in ethylene polymerization in the presence of either Et_2AlCl or MAO. All the bi-metallic nickel pre-catalysts exhibited a positive synergic activity compared to their corresponding mono-nuclear analogs. The bi-metallic nickel catalytic systems had higher activity for polyethylene and the obtained polyethylene possessed higher molecular weight but with a slightly broader molecular weight polydispersity.

Results and discussion

Synthesis and characterization of 1-arylimino-2-(2,6diisopropylphenylimino)acenaphthylenylidene (L1–L5), the methyl-bridged 1-arylimino-2-(2,6-diisopropylphenylimino)acenaphthylenylidene (L6–L10) and their corresponding nickel complexes (Ni1–Ni5 and Ni2-1–Ni2-5)

1-arylimino-2-(2,6-diisopropylphenylimino)acenaphthyl-The enylidenes (L1, L2, L4, and L5) were synthesized by the reaction of 1-(2,6-diisopropylphenylimino)acenaphthylen-2-one with various anilines (Scheme 2) according to the synthetic procedure for 1,2-bis(2,6-diisopropylphenylimino)acenaphthylenvlidene (L3),¹ following which the reaction of 1-arylimino-2-(2,6-diisopropylphenylimino)acenaphthylenylidenes with nickel bromide formed the corresponding nickel complexes (Ni1-Ni5). The nickel complex Ni3 has been previously reported.^{1,16} The reaction of acenaphthylene-1,2-dione with 4,4'-methylenebis (2,6-diisopropylaniline) formed a methylene-bridged 1-(2,6-diisopropylphenylimino)acenaphthylen-2-one, which was further reacted with various anilines to form the methylene-bridged bis(α -diimino)compounds (L6-L10) (Scheme 2). These methylene-bridged bis(α-diimino)compounds (L6-L10) were reacted with nickel halide to form the corresponding bi-nuclear nickel complexes Ni2-1-Ni2-6, as shown in Scheme 2.

It was necessary to add a slight excess (2.2 equivalents) of nickel halide to the methylene-bridged $bis(\alpha$ -diimino)compounds (L6–L10) in order to achieve a higher yield of the binuclear nickel complexes (Ni2-1–Ni2-6). All the complexes were

characterized by FT-IR spectroscopy and elemental analysis and the structures of the nickel complexes **Ni1**, **Ni2-1** and **Ni2-3** were confirmed by single-crystal X-ray diffraction analysis.

X-Ray crystallographic studies

Single crystals of Ni1 were obtained by the slow diffusion of diethyl ether into a saturated solution of dichloromethane, whilst single crystals of Ni2-1 and Ni2-3 were obtained by the slow diffusion of diethyl ether into a saturated mixture solution of dichloromethane and toluene at ambient temperature. The solid-state structures of Ni1, Ni2-1 and Ni2-3 are shown in Fig. 1-3 and selected bond lengths and bond angles are provided in Table 1. The molecular structures indicate the adoption of a distorted trigonal bipyramidal coordination at the nickel, consistent with the structures of the classical α -diimine nickel pre-catalysts.¹⁵ There are also free toluene molecules incorporated in the nickel complexes, however, these toluene molecules are somewhat disordered in the single crystals of Ni2-1 and Ni2-3. Therefore, the Platon Squeeze procedure was used to kill the free toluene molecules when refining Ni2-1 and Ni2-3.

The crystal structure of the nickel complex **Ni1** is shown in Fig. 1. The atoms N1, N2 and Ni form a basal plane, with the apical positions occupied by the Br1 and Br2 atoms with the Br1 atom placed 1.963 Å above the basal plane. The N1–C1 and N2–C12 C==N bonds are of equal length at 1.286(5) Å and the Ni–N bond lengths of 2.026(3) Å (Ni–N1) and 2.036(3) Å (Ni–N2) are similar. The planes of the two arenes linked to the imine-N atoms are nearly perpendicular with respect to the plane of the acenaphthylene with an angle of 80.90° for the arene at N1 and 89.39° for the arene at N2. These geometrical parameters reflect the different steric demands of the two aryl groups linked to the coordinating N atom and reveal that the bulkier *ortho* substituent resulted in a larger dihedral angle, as reflected in previous work.¹⁵

In the solid state of both of the bi-metallic nickel complexes **Ni2-1** and **Ni2-3**, the nickel centres possess similar coordination geometries to complex **Ni1**. Indeed, the corresponding bond lengths and angles, as shown in Table 1, for each structure are very similar. Fig. 2 depicts the bi-metallic nickel

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Scheme 2 Synthetic procedure for the organic compounds and nickel complexes.



Fig. 1 ORTEP drawing of Ni1. Thermal ellipsoids are shown at a 30% probability level. Hydrogen atoms have been omitted for clarity.

complex Ni2-1 and it can be seen that both nickel centres 'point' in the same direction with respect to the ligand framework and that the framework adopts a pinched structure with an angle at C4–C13–C14 of $109.7(9)^{\circ}$.

In the molecular structure of the bi-metallic complex Ni2-3 (Fig. 3), the two nickel atoms are coordinated to the methylene-bridged framework in more of a *trans*-like form with the angle at C4–C13–C14 = $108.0(6)^{\circ}$, *i.e.* rotation about the methylene-bridge has occurred. Generally though, the coordination geometry at each nickel is similar and related to that observed in Ni2-1 and the mono-nuclear nickel complex Ni1. In the framework derived solely from the aniline bearing bis (*ortho*-isopropyl)substituents, the dihedral angles of the arene



Fig. 2 ORTEP drawing of Ni2-1. Thermal ellipsoids are shown at a 30% probability level. Hydrogen atoms have been omitted for clarity and one toluene molecule has been killed by the Platon Squeeze procedure.

planes linked to the imine-N with the corresponding acenaphthylene plane are almost perpendicular at 87.37° for the arenes at N1 and 88.65° for the arenes at N2, respectively. However, these dihedral angles within **Ni2-1** have different angles of 86.03° and 89.86° due to the unsymmetrical substituents, each derived from 2,6-dimethylaniline and 2,6-diisopropylaniline. The use of these frameworks results in significant differences due to the folding of the two different ligands within **Ni2-1** and **Ni2-3**.

Ethylene polymerization

This primary focus of this work was to investigate for the presence of synergetic effects during the catalysis conducted by the bi-metallic complexes. Thus with this in mind, the catalytic behavior of complexes **Ni2-1–Ni2-6** have been explored. To ascertain the optimum catalytic conditions, various alkylaluminium reagents have been screened in conjunction with the nickel



Fig. 3 ORTEP drawing of **Ni2-3**. Thermal ellipsoids are shown at a 30% probability level. Hydrogen atoms have been omitted for clarity and two free toluene molecules has been killed by the Platon Squeeze procedure.

pre-catalyst **Ni2-4** under 10 atm of ethylene (Table 2) and in general, good activities with co-catalysts such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), diethylaluminium chloride (Et₂AlCl) and ethylaluminium sesquichloride (EASC) were observed, whereas low activity was found when employing triethylaluminium (TEA). Further investigations using either MAO or Et₂AlCl (entries 1 and 3 in Table 2) as a co-catalyst were conducted.

Ethylene polymerization employing the co-catalyst Et₂AlCl

The catalytic system Ni2-4/Et₂AlCl was investigated by varying the Al:Ni ratio from 400 to 700 (entries 1–4 in Table 3) at room temperature, which indicated that the optimum Al:Ni ratio was 500:1, achieving an activity of 5.60×10^6 g PE (mol Ni)⁻¹ h⁻¹ (entry 2 in Table 3). The resultant polyethylene

Table 2 Ethylene polymerization by pre-catalyst Ni2-4 with various co-catalysts

Entry	Co-cat.	PE/g	Activity ^a	$T_{\rm m}{}^b/^{\rm o}{\rm C}$	${M_{ m w}}^c/10^5$ g mol ⁻¹	$M_{\rm w}/M_{\rm n}^{\ c}$
1	MAO	2.85	3.80	129.9	3.15	2.50
2	MMAO	1.20	1.60	130.9	2.54	2.19
3	Et ₂ AlCl	4.12	5.49	126.9	3.50	2.50
4	EASC	2.26	3.01	125.0	3.19	2.57
5	TEA	Trace	_	_		_

Conditions: 1.5 µmol of [Ni]; Al/[Ni] = 600; 30 min; 20 °C; 10 atm of ethylene; total volume 100 mL.^{*a*} Activity:10⁶ g PE (mol Ni)⁻¹ h⁻¹. ^{*b*} Determined by DSC. ^{*c*} Determined by GPC.

 Table 1
 Selected bond lengths (Å) and angles (°) for complexes Ni1, Ni2-1 and Ni2-3

Ni1		Ni2-1		Ni2-3	
Bond lengths (Å)					
Ni-N(1)	2.026(4)	Ni(1)-N(1)	2.035(7)	Ni(1)-N(1)	2.020(6)
Ni-N(2)	2.036(4)	Ni(1)–N(2)	2.036(7)	Ni(1) - N(2)	2.031(6)
Ni-Br(2)	2.316(10)	Ni(1)-Br(2)	2.327(19)	Ni(1)-Br(2)	2.330(16)
Ni-Br(1)	2.336(9)	Ni(1)-Br(1)	2.348(19)	Ni(1)-Br(1)	2.327(17)
N(1) - C(1)	1.286(5)	N(1)-C(26)	1.306(10)	N(1) - C(26)	1.279(9)
N(1) - C(25)	1.451(5)	N(1)-C(38)	1.462(11)	N(1)-C(38)	1.477(9)
N(2)-C(13)	1.445(5)	N(2)-C(1)	1.478(11)	N(2)-C(1)	1.467(8)
N(2) - C(12)	1.286(5)	N(2) - C(37)	1.276(10)	N(2) - C(37)	1.292(9)
		Ni(2) - N(3)	2.025(8)	Ni(2) - N(3)	2.027(6)
		Ni(2) - N(4)	2.042(8)	Ni(2) - N(4)	2.035(6)
		Ni(2) - Br(3)	2.343(19)	Ni(2) - Br(3)	2.299(15)
		Ni(2) - Br(4)	2.327(2)	Ni(2) - Br(4)	2.331(15)
		N(3) - C(46)	1.283(10)	N(3) - C(50)	1.283(9)
		N(3)-C(58)	1.451(11)	N(3) - C(62)	1.420(4)
		N(4)-C(57)	1.303(11)	N(4) - C(61)	1.269(9)
		N(4) - C(17)	1.469(12)	N(4) - C(17)	1.468(9)
		$Ni(1) \cdots Ni(2)$	13.204	$Ni(1) \cdots Ni(2)$	10.641
Bond angles (°)					
N(2)-Ni-N(1)	83.33(14)	N(2)-Ni(1)-N(1)	84.0(3)	N(2)-Ni(1)-N(1)	82.2(2)
N(1)-Ni-Br(2)	116.29(11)	N(1) - Ni(1) - Br(2)	113.1(2)	N(1) - Ni(1) - Br(2)	111.70(19)
N(1)-Ni-Br(1)	104.82(11)	N(1)-Ni(1)-Br(1)	106.9(2)	N(1) - Ni(1) - Br(1)	110.84(18)
N(2)-Ni-Br(1)	111.46(10)	N(2) - Ni(1) - Br(1)	103.7(2)	N(2) - Ni(1) - Br(1)	113.14(19)
N(2)-Ni-Br(2)	108.25(11)	N(2) - Ni(1) - Br(2)	115.8(2)	N(2) - Ni(1) - Br(2)	110.04(19)
Br(1)-Ni-Br(2)	125.00(3)	Br(1)-Ni(1)-Br(2)	125.38(7)	Br(1)-Ni(1)-Br(2)	122.01(6)
		N(3) - Ni(2) - N(4)	82.7(3)	N(3) - Ni(2) - N(4)	82.1(2)
		N(3) - Ni(2) - Br(3)	107.3(2)	N(3) - Ni(2) - Br(3)	123.93(17)
		N(3) - Ni(2) - Br(4)	110.5(2)	N(3) - Ni(2) - Br(4)	103.32(17)
		N(4) - Ni(2) - Br(3)	108.7(2)	N(4) - Ni(2) - Br(3)	109.31(18)
		N(4)-Ni(2)-Br(4)	113.1(2)	N(4)-Ni(2)-Br(4)	115.35(18)
		Br(3)-Ni(2)-Br(4)	125.9(7)	Br(3)-Ni(2)-Br(4)	117.94(6)

Table 3 Ethylene polymerization by all the pre-catalysts activated with Et₂AlCl

Entry	Pre-cat.	Al/Ni	T/°C	Activity ^a	$T_{\rm m}^{\ \ b}/^{\rm o}{\rm C}$	${M_{ m w}}^c/10^5$ g mol ⁻¹	$M_{\rm w}/M_{\rm n}^{\ c}$
1	Ni2-4	400	20	3.03	128.2	3.87	2.80
2	Ni2-4	500	20	5.60	125.3	3.58	2.48
3	Ni2-4	600	20	5.49	126.9	3.50	2.50
4	Ni2-4	700	20	4.70	126.7	3.38	3.24
5	Ni2-4	500	30	5.89	120.9	3.48	2.84
6	Ni2-4	500	40	7.30	111.3	2.79	2.89
7	Ni2-4	500	50	7.86	106.7	2.05	2.83
8	Ni2-4	500	60	7.67	125.2	1.01	2.61
9	Ni2-4	500	70	5.92	65.9	0.93	2.33
10	Ni2-1	500	50	6.73	83.7	1.41	2.18
11	Ni2-2	500	50	5.62	76.3	2.08	2.24
12	Ni2-3	500	50	5.42	72.9	2.93	2.31
13	Ni2-5	500	50	5.69	90.6	2.11	2.36
14	Ni2-6	500	50	7.29	97.5	1.51	2.35
15	Ni1	500	50	3.85	96.5	1.01	2.09
16	Ni2	500	50	3.84	78.3	1.58	2.04
17	Ni3	500	50	2.05	86.1	1.40	2.14
18	Ni4	500	50	5.43	81.2	1.02	1.95
19	Ni5	500	50	4.68	83.2	1.32	1.95

Conditions: 1.5 μ mol of [**Ni**]; 10 atm of ethylene; 30 min; total volume 100 mL;^{*a*} Activity: 10⁶ g PE (mol Ni)⁻¹ h⁻¹; ^{*b*} Determined by DSC. ^{*c*} Determined by GPC.

had a slightly decreased molecular weight on increasing the ratio of Al: Ni, which was attributed to the faster chain transfer at higher Al concentrations.^{15b} The lowest molecular weight polydispersity was observed for the polyethylene obtained at the Al: Ni ratio of 500:1, suggesting a single active species under such conditions.

Regarding the thermal stability of the catalytic system, the reaction temperature was varied from 20 to 70 °C (entries 2, 5-9 in Table 3) using an Al: Ni ratio of 500:1 and revealed the highest catalytic activity of 7.86×10^6 g PE (mol Ni)⁻¹ h⁻¹ at 50 °C (entry 7 in Table 3). In addition, very close activities have been observed over the range of 40 to 60 °C (entries 6-8 in Table 3). The classical mono-metallic α -diimino nickel precatalysts displayed their highest activities between at 0 to 20 °C.^{1,2} At elevated temperatures, the resultant polyethylene gradually revealed lower molecular weights due to higher chain termination at elevated temperatures.¹⁵ According to the data in entries 2, 5-9 in Table 3, a slight increase of the PDI values was observed on going from 20 °C to 40 °C (entries 2, 5 and 6), whilst a decrease in the PDI values was observed over 40 °C to 70 °C (entries 6-9). In view of the structures of Ni2-1 and Ni2-3, the bi-metallic nickel complex Ni2-4 could yield two nickel-based active species possessing slightly different coordination environments. Such differing coordination means that the two active species could individually polymerize ethylene (*i.e.* multi-active species) at elevated temperatures, thereby producing polyethylene with a wider PDI. However, on further increasing the reaction temperature, it is possible that the different active centres exhibit different thermal stabilities and on increasing the temperature beyond 40 °C, one of the active centres no longer operates. Alternatively, an internal rearrangement may occur at elevated temperatures, which results in many of the coordination sites/active centres being nearly

identical, thereby affording the narrower observed PDIs. The optimum reaction temperature was shown to be 50 °C and higher temperatures led to lower activities due to deactivation of the activated species, consistent with other mono- α -diimino nickel pre-catalysts.^{1,15a}

Under such optimized conditions (10 atm of ethylene, 50 °C and Et₂AlCl/Ni = 500), all the nickel complex pre-catalysts were investigated and the results are tabulated in Table 3. According to the data performed by pre-catalysts Ni2-1-Ni2-6 (entries 2, 10-14 in Table 3), the substituents present significantly affected the catalytic activities and an order of Ni2-4 (with 2,4,6-tri(Me)) > Ni2-1 (with 2,6-di(Me)) > Ni2-5 (with 2,6-di(di(Et)-4-Me > Ni2-2 (with 2,6-di(Et) > Ni2-3 (with 2,6-(i-Pr)) was observed. These results are consistent with previous observations in the literature^{15c,17} and confirmed that the catalytic activities could be enhanced by either using less bulky ortho substituents or having an additional para-methyl substituent present. The chloride complex Ni2-6 exhibited a slightly lower activity than its analog Ni2-4. For comparison, the mononuclear nickel pre-catalysts (Ni1-Ni5) were investigated under the same conditions (entries 15-19 in Table 3). The catalytic influence exerted by the substituents on their mono-nuclear nickel pre-catalysts followed a similar trend to the bi-metallic nickel pre-catalysts. However, significantly better catalytic activities were achieved by the bi-metallic nickel complex precatalysts. Moreover, the resultant polyethylene obtained using the bi-metallic pre-catalysts showed a higher molecular weight and broader PDI. These results suggest a positive synergetic effect for these systems (bi- versus mono-metallic) under such conditions.

Ethylene polymerization using MAO as a co-catalyst

In a similar manner, MAO was also explored with nickel precatalyst **Ni2-4** for the optimum condition (Table 4). Based on a temperature of 50 °C for the catalytic system with Et₂AlCl, different ratios of MAO : Ni were explored at this temperature (entries 1–5 in Table 4), which indicated an optimum ratio of 2000 : 1 (entry 3 in Table 4). The obtained polyethylene showed gradually lower molecular weights on increasing the amount of MAO. This suggested that there was increased chain transfer to the aluminium in the MAO-activated catalytic process.

With the molar ratio of Al : Ni (2000) fixed, the influence of the polymerization temperature was surveyed (entries 3, 6–9 in Table 4). Different from the Ni2-4/Et₂AlCl system, on elevating the reaction temperature from 20 °C to 60 °C, the highest activity was found at 20 °C (up to 1.41×10^7 g PE (mol Ni)⁻¹ h⁻¹). On increasing the polymerization temperature, the molecular weights of the obtained polymer decreased, which was attributed to a much faster β -hydride elimination/chain transfer rate at elevated polymerization temperatures.^{5b} Compared to the above Ni2-4/Et₂AlCl system, the Ni2-4/MAO system exhibited a lower thermo-stability and required more co-catalyst. These observations suggest that different active species were operating in the Ni2-4/MAO and Ni2-4/Et₂AlCl systems.

Regarding the lifetime of the Ni2-4/MAO system (entries 6, 10 and 11 in Table 4), the polymerization activity was

Table 4 Ethylene polymerization by the pre-catalyst activated with MAO

Entry	Pre-cat.	Al/Ni	T/°C	t/min	Activity ^a	$T_{\rm m}^{\ \ b}$ /°C	$M_{\rm w}^{\ \ c}/10^5 {\rm \ g \ mol}^{-1}$	$M_{\rm w}/M_{\rm n}^{\ c}$
1	Ni2-4	1500	50	30	6.36	101.6	1.63	2.57
2	Ni2-4	1750	50	30	7.40	102.7	_	
3	Ni2-4	2000	50	30	9.35	105.1	1.57	2.32
4	Ni2-4	2250	50	30	8.71	107.2	1.11	2.15
5	Ni2-4	2500	50	30	7.29	118.6	1.08	2.37
6	Ni2-4	2000	20	30	14.05	124.5	3.03	3.06
7	Ni2-4	2000	30	30	10.45	119.3	2.67	2.80
8	Ni2-4	2000	40	30	9.52	108.5	1.90	2.86
9	Ni2-4	2000	60	30	8.95	100.4	0.89	2.37
10	Ni2-4	2000	20	15	15.86	126.9	2.62	2.86
11	Ni2-4	2000	20	45	10.41	124.7	3.09	2.94
12^d	Ni2-4	2000	20	30	0.92	110.9	3.59	2.20
13^e	Ni2-4	2000	20	30	2.00	126.9	2.57	2.15
14	Ni2-1	2000	20	30	12.71	123.6	2.96	2.54
15	Ni2-2	2000	20	30	10.94	118.8	4.24	2.71
16	Ni2-3	2000	20	30	9.07	116.8	3.79	2.60
17	Ni2-5	2000	20	30	12.50	126.6	4.84	2.28
18	Ni2-6	2000	20	30	15.99	121.6	3.15	2.66
19	Ni1	2000	20	30	7.13	120.1	2.35	2.53
20	Ni2	2000	20	30	5.35	118.6	2.88	2.25
21	Ni3	2000	20	30	3.84	107.7	2.72	2.34
22	Ni4	2000	20	30	7.15	123.5	2.82	2.40
23	Ni5	2000	20	30	5.67	123.6	3.49	2.19

Conditions: 1.5 µmol of [Ni]; 10 atm of ethylene; total volume 100 mL.^{*a*} Activity: 10^6 g PE (mol Ni)⁻¹ h⁻¹. ^{*b*} Determined by DSC. ^{*c*} Determined by GPC. ^{*d*} 1 atm of ethylene.

monitored at different time intervals. On prolonging the reaction time from 15 to 45 min, more polymer was obtained, whilst the overall activity declined. The highest activity of 1.59×10^7 g PE (mol Ni)^{-1} h^{-1} was observed within 15 min (entry 10 in Table 4). Compared to many classical mono-metallic α -diimino pre-catalysts,^{15} the bi-metallic Ni2-4/MAO system achieved higher catalytic activities over a much longer polymerization period. This observation is tentatively ascribed to the synergetic effect arising from the two metal sites. The Ni2-4/MAO system was also studied under increased ethylene pressure (from 1 to 10 atm: entries 6, 12 and 13 in Table 4) and it was found that the activity rapidly rose from 0.92×10^6 to 14.1×10^6 g PE (mol Ni)^{-1} h^{-1} on increasing the ethylene pressure.

On employing the optimum conditions (Al: Ni of 2000: 1 at 20 °C over 30 min), all the nickel/MAO catalytic systems were evaluated for ethylene polymerization (entries 6, 14-23 in Table 4). In contrast to the mono-metallic nickel/E2tAlCl systems (entries 19-23 in Table 3), the methylene-bridged bimetallic Ni2-1-Ni2-5 pre-catalysts (entries 2, 10-14 in Table 3) exhibited more than double the activity (most up to 1×10^7 g PE (mol Ni)⁻¹ h⁻¹), whilst the polyethylene produced possessed a higher molecular weight and broader PDIs. In general, the Ni/MAO systems (entries 6, 14-23 in Table 4) performed with higher activities than the Ni/E2tAlCl systems (entries 2, 10-14 in Table 3) but the optimum reaction temperature was lower: 20 °C for the Ni/MAO systems versus 50 °C for the Ni/E2tAlCl systems. This was attributed to a different degree of ion-pair formation between the cationic active nickel center and the weakly coordinating aluminium-based anion.¹⁸ In both systems, all the bi-metallic nickel pre-catalysts showed

higher activities than their analogous mono-metallic pre-catalysts. Given that positive synergic effects can be achieved in such nickel model pre-catalysts, these bi-metallic complex precatalysts are promising candidates in ethylene polymerization. At the same time, it is noted that the anion (bromide or chloride) did not markedly change the catalytic activity or the properties of the resultant polyethylene (entries 6 and 18 in Table 4). The observed M_w values for the polyethylene obtained *via* the bi-metallic complex pre-catalysts were higher than those obtained using their mono-nuclear analogues. This observation is consistent with the 'rule' that bi-metallic complex pre-catalysts enhance chain propagation and result in polyethylene with a higher molecular weight.^{6a} We note, however, that multi-active species of bi-metallic pre-catalysts would result in polyethylene with a broader PDI.

To assess for any branching in the obtained PE samples, representative polyethylene prepared with pre-catalyst Ni2-4/ MAO at 60 °C (entry 9 in Table 4) was measured by ¹³C NMR spectroscopy (Fig. 4). The signals were interpreted (Table 5) according to the literature,¹⁹ which indicated that the main branches were methyl (41%) and ethyl (21%) as well as some longer chains, which is consistent with previous observations.¹⁵

Experimental details

General procedures

All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were distilled from sodium wire prior to use and chemicals were obtained



Fig. 4 $^{13}\mathrm{C}$ NMR spectrum of polyethylene by Ni2-4/MAO at 60 °C (entry 9 in Table 4).

 $\ensuremath{\text{Table 5}}$ Experimental integrals and percentage of branching over the total branching of Fig. 4

Entry	Chem. shift/ppm	Integral exp.	Peak no.	Branch content		Percentage over total branching
1	11.16	1.00	1	Nm	5.13	41.07%
2	14.10	2.71	2	$N_{m(1,4)}$	1.23	9.85%
3	14.43	0.62	3	$N_{m(1,5)}$	0.00	0.00%
4	19.96	10.04	5	$N_{m(1,5)}$	0.94	7.53%
5	22.88	1.67	8	N _o	2.57	20.58%
6	26.65	0.95	10	N _n	0.00	0.00%
7	27.27	7.41	11	N _b	0.84	6.73%
8	27.44	14.59	12	N _a	0.00	0.00%
9	27.81	1.87	13	N	1.78	14.25%
10	29.58	1.78	15	$N_{I(1,4)}$	0.00	0.00%
11	30.00	141.92	16	CH_2	140.26	
12	30.37	16.18	17	[E]	70.13	
13	30.46	11.26	18	[R]	12.49	100.00%
14	32.19	1.66	20	Branchir	ng = 151 I	Branches/
				1000C	0	
15	33.20	6.50	22			
16	33.57	2.51	23			
17	33.99	2.77	24			
18	34.48	6.43	26			
19	34.81	2.42	27			
20	37.52	15.73	29			
21	38.11	2.42	31			

from commercial suppliers. MAO (1.46 M solution in toluene) and MMAO (1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Et₂AlCl (0.79 M in toluene) and EASC (0.87 M in toluene) were purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yanshan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. δ values are given in ppm and *J* values in Hz. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. The molecular weights of polyethylene were determined by PL-GPC220 at 150 °C with 1,2,4-trichlorobenzene as the solvent. The

melting points of polyethylene were measured from the second scanning run on a Perkin-Elmer TA-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere. In the procedure, a sample of about 2.0–4.0 mg was heated to 140 °C at a rate of 20 °C min⁻¹ and kept for 5 min at 140 °C to remove the thermal history and then cooled at a rate of 10 °C min⁻¹ to 0 °C. ¹³C NMR spectra of the polyethylene were recorded on a Bruker DMX-300 MHz instrument at 115 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

Syntheses and characterization

Synthesis of 1-(2,6-diisopropylphenylimino)-2-aryliminoacenaphthylenylidenes (L1–L5). The 1-(2,6-diisopropylphenylimino)-2-aryliminoacenaphthylenylidene series (L1–L5) was synthesized by the reaction of various anilines and 1-(2,6-diisopropylphenylimino)acenaphthylen-2-one according to the literature procedure.^{1,16} The 1,2-bis(2,6-diisopropylphenylimino)acenaphthylenylidene (L3) and its nickel bromide (Ni3) were previously synthesized.^{1,16}

1-(2,6-Diisopropylphenylimino)-2-(2,6-dimethylphenylimino)acenaphthylenylidene (L1). A catalytic amount of p-toluenesulfonic acid (0.03 g) was added to a stirred mixture of 0.20 g (0.58 mmol) of 1-(2,6-diisopropylphenylimino)acenaphthylen-2-one and 0.08 g (0.70 mmol) of 2,6-dimethylaniline in 30 mL of toluene. The mixture was stirred at 110 °C for 9 h and the solvent was evaporated to dryness. The resultant residue was dissolved in dichloromethane, filtered and the resulting solution was reduced in volume to saturation point when 10 mL ethyl acetate was added and the solution was cooled overnight. Yield 0.13 g (51%) of orange solid L1. ¹H NMR (400 Hz, CDCl₃, TMS): 7.88 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.35 (m, 3H), 7.29–7.23 (m, 3H), 6.98 (s, 1H), 6.78 (d, J = 7.2 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H), 2.84 (m, 2H), 2.21 (s, 6H), 1.17 (d, J = 6.8 Hz, 6H), 0.90 (d, J = 6.8 Hz, 6H). ¹³C NMR (100 Hz, CDCl₃, TMS): 161.13, 160.93, 148.78, 147.62, 140.91, 135.58, 131.25, 130.89, 129.75, 129.64, 129.07, 128.27, 128.05, 126.64, 124.49, 124.17, 123.64, 123.49, 123.12, 28.77, 24.93, 23.54, 23.32, 14.07. IR (KBr; cm^{-1}): 2960(s), 2926(m), 2867(w), 1674(s), 1593(s), 1464(s), 1428(s), 1326(m), 1228(s), 1159(w), 1085(s), 925(s), 867(s), 786(vs), 747(s), 655(m). Anal. Calcd for C₃₂H₃₂N₂ (444.61): C, 86.44; H, 7.25; N, 6.30%. Found: C, 86.35; H, 7.30; N, 6.30%.

1-(2,6-Diisopropylphenylimino)-2-(2,6-diethylphenylimino)acenaphthylenylidene (L2). Using the same procedure as for the synthesis of L1, except that 2,6-diethylaniline (0.10 g, 0.70 mmol) was used in place of 2,6-dimethylaniline, L2 was obtained as a yellow powder in 65% (0.18 g). ¹H NMR (400 Hz, CDCl₃, TMS): 7.88 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.39–7.34 (m, 2H), 7.25–7.29 (m, 3H), 7.23–7.44 (m, 3H), 6.69 (d, J = 7.2 Hz, 1H), 6.64 (d, J = 7.2 Hz, 1H), 3.02 (m, 2H), 2.58 (m, 2H), 2.46 (m, 2H), 1.23 (d, J = 6.8 Hz, 6H), 1.11 (t, J =7.6 Hz, 6H), 0.97 (d, J = 6.8 Hz, 6H). ¹³C NMR (100 Hz, CDCl₃, TMS): 161.13, 160.93, 148.78, 147.62, 140.91, 135.58, 131.25, 130.89, 129.75, 129.07, 128.27, 128.05, 126.64, 124.49, 124.17, 123.64, 123.49, 123.12, 28.77, 24.93, 23.54, 14.07. IR (KBr; cm⁻¹): 2962(s), 2929(m), 2867(m), 1673(s), 1650(s), 1592(s), 1456(s), 1430(s), 1362(w), 1326(m), 1255(s), 1088(m), 1039(m), 925(s), 835(s), 810(vs), 747(vs), 656(w). Anal. Calcd for $C_{34}H_{36}N_2$ (472.66): C, 86.40; H, 7.68; N, 5.93%. Found: C, 86.25; H, 7.57; N, 5.80%.

1-(2,6-Diisopropylphenylimino)-2-(2,4,6-trimethylphenylimino)acenaphthylenylidene (L4). The synthetic procedure for L4 was analogous to that for L1, except that 2,4,6-trimethylaniline (0.09 g, 0.70 mmol) was used in place of 2,6-dimethylaniline. A yellow solid of L4 was collected in a yield of 60% (0.16 g). 1 H NMR (400 Hz, CDCl₃, TMS): 7.88 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.29-7.23 (m, 3H), 6.98 (s, 1H), 6.78 (d, J = 7.2 Hz, 1H), 6.64 (d, J = 7.2 Hz, 1H), 3.00 (m, 2H), 2.39 (s, 3H), 2.10 (s, 6H), 1.23 (d, J = 7.2 Hz, 6H), 0.98 (d, J = 7.2 Hz, 6H). ¹³C NMR (100 Hz, CDCl₃, TMS): 161.1, 161.0, 147.5, 146.9, 140.8, 135.5, 132.9, 131.1, 129.7, 129.6, 129.1, 128.9, 128.3, 127.9, 124.6, 124.4, 124.1, 123.5, 123.3, 122.6, 28.7, 23.4, 23.2, 21.0, 17.8. IR (KBr; cm⁻¹): 2961(s), 2925(m), 2864(w), 1675(s), 1655(s), 1594(m), 1471(s), 1429(s), 1361(w), 1326(w), 1237(s), 1153(m), 1037(m), 934(s), 836(vs), 786(vs), 657(w). Anal. Calcd for C₃₃H₃₄N₂ (458.64): C, 86.42; H, 7.47; N, 6.11%. Found: C, 86.25; H, 7.50; N, 5.98%.

1-(2,6-Diisopropylphenylimino)-2-(2,6-diethyl-4-methylphenylimino)acenaphthylenylidene (L5). Using the same procedure as for the synthesis of L1, except that 2,6-diethyl-4-methylaniline (0.11 g, 0.70 mmol) was used in place of 2,6-dimethylaniline, L5 was obtained as a yellow powder in a 58% (0.17 g) yield. ¹H NMR (400 Hz, CDCl₃, TMS): 7.88 (d, *J* = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.40–7.33 (m, 2H), 7.23–7.28 (m, 3H), 7.01 (s, 2H), 6.75 (d, J = 7.2 Hz, 1H), 6.62 (d, J = 6.8 Hz, 1H), 3.02 (m, 2H), 2.47-2.38 (m, 5H), 1.22 (d, J = 6.8 Hz, 6H), 1.09 (t, J = 7.6 Hz, 6H), 0.96 (d, J = 6.8 Hz, 6H). ¹³C NMR (100 Hz, CDCl₃, TMS): 161.1, 147.6, 146.2, 140.8, 135.6, 133.3, 131.2, 130.7, 129.8, 129.7, 128.9, 128.8, 128.2, 128.0, 127.4, 124.4, 123.6, 123.4, 123.1, 28.7, 24.8, 23.5, 23.3, 21.3, 14.1. IR (KBr; cm⁻¹): 2960(s), 2926(m), 2865(w), 1675(s), 1654(s), 1594(w), 1461(s), 1431(w), 1325(w), 1255(s), 1224(m), 1090(s), 1038(s), 924(s), 785(vs), 756(vs), 657(w). Anal. Calcd for $C_{35}H_{38}N_2$ (486.69): C, 86.37; H, 7.87; N, 5.76%. Found: C, 86.31; H, 7.95; N, 5.65%.

Synthesis of 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)acenaphthylen-2-one). A solution of 4,4'-methylenebis (2,6-diisopropylaniline) (1.83 g, 5.0 mmol), acenaphthylene-1,2-dione (1.82 g, 10.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid in dichloromethane (150 mL) were stirred for 24 h under atmospheric temperature. The solvent was then removed by vacuum evaporation and the residue was further purified by silica column chromatography (40:1 petroleum ether: ethyl acetate) to afford 1.91 g of 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)-acenaphthylen-2-one)

(yellow, 55% yield). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.20 (d, J = 7.6 Hz, 2H), 8.18 (d, J = 8.8, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.83 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.16 (s, 4H), 6.73 (d, J = 7.2 Hz, 2H), 4.18 (s, 2H), 2.85 (m, 4H), 1.18 (d, J = 6.8 Hz, 12H), 0.90 (d, J = 6.8 Hz, 12H). ¹³C NMR (100 Hz, CDCl₃, TMS): 189.7, 160.8, 144.5, 143.1, 138.1, 135.3, 132.3, 131.1, 131.0, 129.5, 128.4, 128.1, 127.8, 124.3, 123.3, 122.3,

41.7, 28.4, 23.6. IR (KBr; cm⁻¹): 2959(s), 2928(m), 2868(m), 1728(vs), 1651(s), 1595(s), 1461(s), 1437(s), 1360(m), 1300(w), 1273(s), 1216(s), 1170(s), 1120(m), 1071(s), 1027(s), 957(m), 908(s), 827(s), 777(vs), 732(s), 701(s). Anal. Calcd for $C_{49}H_{46}N_2O_2$ (694.90): C, 84.69; H, 6.67; N, 4.03%. Found: C, 84.39; H, 6.75; N, 4.10%.

Synthesis of 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)-2-(arylimino)acenaphthylene) derivatives (L6–L10)

4,4'-Methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,6-dimethylphenylimino)acenaphthylene) (L6). A solution of 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)-acenaphthylen-2-one) (0.19 g, 0.27 mmol), 2,6-dimethylaniline (0.080 g, 0.66 mmol) and a catalytic amount of p-toluenesulfonic acid in 70 mL of toluene at 110 °C were stirred for 9 h and then the solvent was removed by vacuum evaporation. The residue was further purified by silica column chromatography (40:1 petroleum ether:ethyl acetate) to afford 0.15 g of L6 (yellow, 62% yield). ¹H NMR (400 MHz, $CDCl_3$, TMS): δ 7.89 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 7.19-7.16 (m, 8H), 7.09 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.76 (d, J = 7.2 Hz, 2H), 6.71 (d, J = 7.2 Hz, 2H), 4.20 (s, 2H), 3.02 (m, 4H), 2.15 (s, 12H), 1.25 (d, J = 6.8 Hz, 12H), 0.98 (d, J = 6.8 Hz, 12H). ¹³C NMR (100 Hz, CDCl₃, TMS): 161.4, 160.9, 149.5, 145.4, 140.9, 137.6, 135.4, 131.3, 129.8, 129.7, 129.1, 128.9, 128.4, 128.0, 124.9, 124.4, 123.8, 123.3, 122.6, 41.9, 28.8, 23.6, 23.4, 17.9. IR (KBr; cm⁻¹): 2958(s), 2867(m), 1665(s), 1635(s), 1592(s), 1462(s), 1434(s), 1379(m), 1361(m), 1272(m), 1228(s), 1203(s), 1171(s), 1086(s), 1029(s), 921(s), 827(s), 773(vs), 703(s). Anal. Calcd for C₆₅H₆₄N₄ (901.23): C, 86.63; H, 7.16; N, 6.22%. Found: C, 86.45; H, 7.23; N, 6.15%.

4,4'-Methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,6-diethylphenylimino)acenaphthylene) (L7). The synthetic procedure of L7 was similar to that for L6, except that 2,6-diethylaniline (0.098 g, 0.66 mmol) was used in place of 2,6-dimethylaniline. A yellow solid of L7 was collected in a yield of 60% (0.16 g). ¹H NMR (400 MHz, CDC1₃, TMS): 7.87 (d, *J* = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.35-7.39 (m, 2H), 7.29-7.33 (m, 2H), 7.21–7.19 (m, 10H), 6.76 (d, J = 7.2 Hz, 2H), 6.69 (d, J = 7.2 Hz, 2H), 4.20 (s, 2H), 3.04 (m, 4H), 2.63-2.57 (m, 4H), 2.45-2.50 (m, 4H), 1.25 (d, J = 6.8 Hz, 12H), 1.12 (t, J = 7.4 Hz, 12H), 0.98 (d, J = 6.4 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃, TMS): 161.4, 161.1, 146.3, 145.6, 140.9, 137.6, 135.4, 133.2, 131.2, 130.9, 130.7, 129.9, 128.9, 128.2, 127.9, 127.39, 126.6, 124.4, 124.1, 123.3, 123.1, 42.0, 28.8, 24.9, 23.7, 23.4, 21.3, 14.2, 14.1. IR (KBr; cm⁻¹): 2961(s), 2928(m), 2867(m), 1663(s), 1641(s), 1594 (s), 1459(s), 1437(s), 1362(m), 1334(w), 1271(m), 1228(m), 1205 (m), 1172(m), 1089(s), 1037(s), 955(w), 921(s), 857(m), 830(s), 780(vs), 702(m). Anal. Calcd for C₆₉H₇₂N₄ (957.34): C, 86.57; H, 7.58; N, 5.85%. Found: C, 86.35; H, 7.45; N, 5.72%.

4,4'-Methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,6-diisopropylphenylimino)acenaphthylene) (**L8**). Using the same procedure as for the synthesis of **L6**, except that 2,6-diisopropylaniline (0.12 g, 0.66 mmol) was used in place of 2,6-dimethylaniline, **L8** was obtained as a yellow powder in 53% (0.15 g). ¹H NMR (400 MHz, CDC1₃, TMS): 7.87 (d, J =

8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.36 (m, 2H), 7.33–7.26 (m, 8H), 7.19 (s, 4H), 6.75 (d, J = 6.8 Hz, 2H), 6.64 (d, J = 7.2 Hz, 2H), 4.20 (s, 2H), 3.04 (m, 8H), 1.25 (d, J = 6.4 Hz, 12H), 1.24 (d, J = 6.4 Hz, 12H), 0.97 (d, J = 6.8 Hz, 24H). ¹³C NMR (100 MHz, CDCl₃, TMS): 161.3, 161.1, 147.7, 145.5, 140.9, 137.6, 135.6, 135.4, 131.3, 129.7, 129.6, 129.0, 128.0, 127.9, 124.4, 124.3, 123.6, 123.5, 123.4, 41.9, 28.8, 23.7, 23.5, 23.4, 23.3. IR (KBr; cm⁻¹): 2960(s), 2928(m), 2868(m), 1978(w), 1650(s), 1592(s), 1460(s), 1431(s), 1382(m), 1361(m), 1272(m), 1249(s), 1175(s), 1107(m), 1038(m), 945(w), 921(w), 834(s), 782 (vs), 750(s), 702(w), 667(w). Anal. Calcd for C₇₃H₈₀N₄ (1013.44): C, 86.52; H, 7.96; N, 5.53%. Found: C, 86.45; H, 7.83; N, 5.44%.

4,4'-Methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,4,6-tri*methylphenylimino*)*acenaphthylene*) (L9). The synthetic procedure for L9 was analogous to that for L6, except that 2,4,6-trimethylaniline (0.089 g, 0.66 mmol) was used in place of 2,6-dimethylaniline. A yellow solid of L9 was collected in a yield of 57% (0.14 g). ¹H NMR (400 MHz, CDCl₃, TMS): 7.88 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.38–7.42 (m, 2H), 7.32-7.26 (m, 4H), 7.19 (s, 3H), 6.98 (s, 3H), 6.78 (d, J = 7.2 Hz, 2H), 6.75 (d, J = 7.2 Hz, 2H), 4.20 (s, 2H), 3.02 (m, 4H), 2.39 (s, 6H), 2.11 (s, 12H), 1.24 (d, J = 6.4 Hz, 12H), 0.98 (d, J = 6.8 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃, TMS): 161.3, 160.9, 149.5, 145.4, 140.9, 137.6, 131.2, 129.7, 129.7, 129.1, 128.9, 128.4, 127.5, 124.9, 124.3, 123.8, 123.3, 122.6, 41.9, 28.7, 23.5, 23.4, 17.9. IR (KBr; cm^{-1}): 2960(s), 2926(m), 2867(w), 1664(s), 1636(s), 1592(s), 1462(s), 1435(s), 1380(w), 1361(m), 1228(s), 1203(s), 1085(s), 1032(s), 905(s), 831(s), 774(vs), 726(vs). Anal. Calcd for C₆₇H₆₈N₄ (929.28): C, 86.60; H, 7.38; N, 6.03%. Found: C, 86.53; H, 7.42; N, 5.98%.

4,4'-Methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,6-diethyl-4-methylphenylimino)acenaphthylene) (L10). Using the same procedure as for the synthesis of L6, except that 2,6-diethyl-4-methylaniline (0.11 g, 0.66 mmol) was used in place of 2,6dimethylaniline, L10 was obtained as a yellow powder in a 64% yield (0.17 g). ¹H NMR (400 MHz, CDC1₃, TMS): 7.87 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.39 (m, 2H), 7.31–7.26 (m, 2H), 7.19 (s, 4H), 7.01 (s, 4H), 6.76-6.73 (m, 4H), 4.19 (s, 2H), 3.03 (m, 4H), 2.56 (m, 4H), 2.48-2.38 (m, 10H), 1.24 (d, J = 6.8 Hz, 12H), 1.09 (t, J = 7.6 Hz, 12H), 0.98 (d, J = 6.4 Hz, 12H), ¹³C NMR (100 MHz, CDCl₃, TMS): 161.4, 161.1, 146.3, 145.6, 140.9, 137.6, 135.4, 133.2, 131.2, 130.7, 129.9, 129.8, 128.9, 128.2, 127.9, 127.4, 124.3, 123.3, 123.1, 41.9, 28.7, 24.9, 23.7, 23.4, 21.3, 14.1 IR (KBr; cm⁻¹): 2959(s), 2927(m), 2866(m), 1663(s), 1641(s), 1595(m), 1460(s), 1438(s), 1362(w), 1273(m), 1228(s), 1088(s), 1038(s), 921(s), 834(vs), 782(vs), 702(w). Anal. Calcd for C71H76N4 (985.39): C, 86.54; H, 7.77; N, 5.69%. Found: C, 86.45; H, 7.78; N, 5.55%.

Preparation of nickel halides bearing 1-(2,6-diisopropylphenylimino)-2-aryliminoacenaphthylenylidene (Ni1–Ni5) and the bimetallic nickel halides bearing 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)-2-(arylimino)-acenaphthylene) derivatives (Ni2-1–Ni2-6)

Nickel dibromide bearing 1-(2,6-diisopropylphenylimino)-2-(2,6dimethylphenylimino)acenaphthylenylidene (Ni1). A mixture of 1-(2,6-diisopropylphenylimino)-2-(2,6-dimethyl-phenylimino)acenaphthylenylidene (L1) (0.09 g, 0.20 mmol) and (DME) NiBr₂ (0.06 g, 0.20 mmol) in dried dichloromethane (10 mL) was stirred for 24 h at room temperature in a Schlenk tube. The majority of the solvent was then removed and cyclohexane (10 mL) was added to precipitate the complex. The residue was washed with cyclohexane and dried under vacuum to obtain a red powder of **Ni1** in an 80% yield (0.11 g). IR (KBr; cm⁻¹): 2960(s), 2926(m), 2866(w), 1649(s), 1622(s), 1590(s), 1463(s), 1419(s), 1382(w), 1290(m), 1085(s), 1043(s), 926(m), 770(vs). Anal. Calcd for $C_{32}H_{32}Br_2N_2Ni$ (663.11): C, 57.96; H, 4.86; N, 4.22%. Found: C, 57.88; H, 4.88; N, 4.19%.

Nickel dibromide bearing 1-(2,6-*diisopropylphenylimino*)-2-(2,6*diethylphenylimino*)*acenaphthylenylidene* (*Ni2*). Using the same procedure as for the synthesis of **Ni1**, except that 1-(2,6-diisopropylphenylimino)-2-(2,6-diethylphenylimino)acenaphthylenylidene (L2) (0.09 g, 0.20 mmol) was in place of L1, **Ni2** was obtained as a red powder in an 85% (0.12 g) yield. IR (KBr; cm⁻¹): 2961(s), 2929(m), 2867(m), 1644(s), 1593(s), 1456(s), 1430(s), 1363(w), 1326(w), 1254(m), 1189(s), 1089(s), 1038(s), 924(s), 874(m), 835(m), 845(s), 784(vs), 747(vs). Anal. Calcd for $C_{34}H_{36}Br_2N_2Ni$ (691.16): C, 59.08; H, 5.25; N, 4.05%. Found: C, 59.14; H, 5.23; N, 4.10%.

Nickel dibromide bearing 1-(2,6-diisopropylphenylimino)-2-(2,4,6-trimethylphenylimino)acenaphthylenylidene (Ni4). The synthetic procedure of Ni4 was similar to that for Ni1, except that 1-(2,6-diisopropylphenylimino)-2-(2,4,6-trimethylphenylimino)acenaphthylenylidene (L4) (0.09 g, 0.20 mmol) was used in place of L1. Red powdered Ni4 was collected in a yield of 86% (0.12 g). IR (KBr; cm⁻¹): 2960(s), 2925(m), 2865(w), 1622(s), 1646(s), 1581(s), 1461(m), 1431(s), 1324(w), 1255(m), 1039(m), 924(s), 886(w), 835(s), 784(vs), 756(vs). Anal. Calcd for $C_{33}H_{34}Br_2N_2Ni$ (677.14): C, 58.53; H, 5.06; N, 4.14%. Found: C, 58.34; H, 5.10; N, 4.20%.

Nickel dibromide bearing 1-(2,6-diisopropylphenylimino)-2-(2,6diethyl-4-methylphenylimino)acenaphthylenylidene (Ni5). Using the same procedure as for the synthesis of Ni1, except that 1-(2,6-diisopropylphenylimino)-2-(2,6-diethyl-4-methylphenylimino)acenaphthylenylidene (L5) (0.10 g, 0.20 mmol) was used in place of L1, Ni5 was obtained as a red powder in a 90% (0.13 g) yield. IR (KBr; cm⁻¹): 2960(s), 2925(m), 2865(w), 1646(s), 1622(s), 1581(s), 1428(s), 1326(w), 1291(m), 1224(s), 1131(s), 1045(s), 929(m), 832(s), 773(vs), 737(vs). Anal. Calcd for $C_{35}H_{38}Br_2N_2Ni$ (705.19): C, 59.61; H, 5.43; N, 3.97%. Found: C, 59.49; H, 5.40; N, 3.89%.

Bimetallic nickel tetrabromide bearing 4,4'-methylenebis(1-(2,6diisopropylphenylimino)-2-(2,6-dimethylphenylimino)-acenaphthylene) (Ni2-1). A mixture of 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,6-dimethylphenylimino)acenaphthylene) (L6) (0.09 g, 0.10 mmol) and (DME)NiBr₂ (0.07 g, 0.22 mmol) in dried dichloromethane (10 mL) was stirred for 24 h at room temperature in a Schlenk tube and then the solvent was evaporated to dryness. The resultant residue was dissolved in dichloromethane and filtered and the dichloromethane was evaporated. Then diethyl ether (10 mL) was added to precipitate the complex. The deposit was washed with diethyl ether and dried under vacuum to obtain a crimson powder of **Ni2-1** in 69% yield (0.08 g). IR (KBr; cm⁻¹): 2960(m), 2924(m), 2867(w), 1622(s), 1581(s), 1462(s), 1435(s), 1382(m), 1291(s), 1189(s), 1129(m), 1045(s), 953(s), 832(s), 773(vs), 656(s). Anal. Calcd for $C_{65}H_{64}Br_4N_4Ni_2$ (1338.23): C, 58.34; H, 4.82; N, 4.19%. Found: C, 58.22; H, 4.80; N, 4.10%.

Bimetallic nickel tetrabromide bearing 4,4'-methylenebis(1-(2,6diisopropylphenylimino)-2-(2,6-diethylphenylimino)-acenaphthylene) (Ni2-2). Using the same procedure as for the synthesis of Ni2-1, except that 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,6-diethylphenylimino)acenaphthylene) (L7) (0.09 g, 0.10 mmol) was used in place of L6, Ni2-2 was obtained as a crimson powder in a 76% (0.11 g) yield. IR (KBr; cm⁻¹): 2962(s), 2928(s), 2868(m), 1621((s), 1580(s), 1458(s), 1437(s), 1381(w), 1291(s), 1225(m), 1128(m), 1046(m), 931(s), 776(vs), 659(w). Anal. Calcd for $C_{69}H_{72}Br_4N_4Ni_2$ (1394.34): C, 59.44; H, 5.20; N, 4.02%. Found: C, 59.35; H, 5.15; N, 4.08%.

Bimetallic nickel tetrabromide bearing 4,4'-methylenebis(1-(2,6diisopropylphenylimino)-2-(2,6-diisopropylphenylimino)acenaphthylene) (Ni2-3). The synthetic procedure for Ni2-3 was analogous to that for Ni2-1, except that 4,4'-methylenebis(1-(2,6-diisopropylphenylimino)-2-(2,6-diisopropylphenylimino)acenaphthylene) (L8) (0.10 g, 0.10 mmol) was used in place of L6. A crimson solid of Ni2-3 was collected in a yield of 74% (0.11 g). IR (KBr; cm⁻¹): 2961(s), 2928(s), 2867(m), 1648(m), 1622(s), 1585(s), 1462(m), 1436(s), 1383(w), 1290(w), 1182(w), 1047(w), 954(w), 832(m), 776(vs), 706(m). Anal. Calcd for $C_{73}H_{80}Br_4N_4Ni_2$ (1450.45): C, 60.45; H, 5.56; N, 3.86%. Found: C, 60.36; H, 5.59; N, 3.78%.

Bimetallic nickel tetrabromide bearing 4,4'-methylenebis(1-(2,6diisopropylphenylimino)-2-(2,4,6-trimethylphenylimino)acenaphthylene) (Ni2-4). The synthetic procedure for Ni2-4 was analogous to that for Ni2-1, except that 4,4'-methylenebis (1-(2,6-diisopropylphenylimino)-2-(2,4,6-trimethylphenylimino)acenaphthylene) (L9) (0.09 g, 0.10 mmol) was used in place of L6. Crimson powdered Ni2-4 was collected in a yield of 70% (0.10 g). IR (KBr; cm⁻¹): 2959(s), 2923(s), 2865(m), 1622(s), 1581(vs), 1460(s), 1435(s), 1359(m), 1291(s), 1240(m), 1129(m), Anal. 1043(s), 831(vs), 777(vs), 658(w). Calcd for C₆₇H₆₈Br₄N₄Ni₂ (1366.29): C, 58.90; H, 5.02; N, 4.10%. Found: C, 58.77; H, 5.00; N, 4.01%.

Bimetallic nickel tetrabromide bearing 4,4'-methylenebis(1-(2,6diisopropylphenylimino)-2-(2,6-diethyl-4-methylphenylimino)acenaphthylene) (Ni2-5). Using the same procedure as for the synthesis of Ni2-1, except that 4,4'-methylenebis(1-(2,6diisopropylphenylimino)-2-(2,6-diethyl-4-methylphenylimino) acenaphthylene) (L10) (0.10 g, 0.10 mmol) was used in place of L6 (0.09 g, 0.10 mmol), Ni2-5 was obtained as a crimson powder in a yield of 77% (0.11 g). IR (KBr; cm⁻¹): 2962(s), 2929(s), 2868(m), 1622(s), 1581(s), 1458(s), 1437(s), 1382(w), 1291(s), 1128(m), 1045(m), 953(w), 831(s), 776(vs), 658(w). Anal. Calcd for $C_{71}H_{76}Br_4N_4Ni_2$ (1422.39): C, 59.95; H, 5.39; N, 3.94%. Found: C, 60.14; H, 5.45; N, 4.01%.

Bimetallic nickel tetrachloride bearing 4,4'-methylenebis(1-(2,6diisopropylphenylimino)-2-(2,4,6-trimethylphenylimino)acenaphthylene) (Ni2-6). Using the same procedure as for the synthesis of **Ni2-4**, except that (DME)NiCl₂ (0.05 g, 0.22 mmol) was used in place of (DME)NiBr₂ (0.07 g, 0.22 mmol), **Ni2-6** was obtained as a red powder in a yield of 60% (0.07 g). IR (KBr; cm⁻¹): 2961(s), 2925(s), 2868(m), 1625(s), 1584(s), 1463(m), 1438(m), 1291(m), 1224(w), 1194(w), 1081(w), 1041(w), 732(w), 775(vs), 656(w). Anal. Calcd for $C_{67}H_{68}Cl_4N_4Ni_2$ (1188.48): C, 67.71; H, 5.77; N, 4.71%. Found: C, 67.58; H, 5.69; N, 4.57%.

X-Ray crystallographic studies

Single-crystal X-ray diffraction studies for Ni1, Ni2-1 and Ni2-3 were carried out on a Rigaku RAXIS Rapid IP diffractometer graphite-monochromatic Mo-K α radiation (λ with 0.71073 Å). Cell parameters were obtained by a global refinement of the positions of all the collected reflections. The intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. The structure solution and refinement were performed using the SHELXL-97 package.²⁰ Crystal data and processing parameters for Ni1, Ni2-1 and Ni2-3 are summarized in Table 6. Using the Platon Squeeze procedure,²¹ the free solvent was killed off (one toluene molecule for Ni2-1 and two toluene molecules for Ni2-3).

General procedure for ethylene polymerization

Ethylene polymerization under 10/5 atm of ethylene. Equipped with a mechanical stirrer and temperature controller, a 300 mL stainless steel autoclave was employed for the polymerization reaction. First of all, 20 mL of freshly distilled toluene was injected into the autoclave which was full of ethylene. When the temperature was stabilized, another 40 mL of toluene which dissolved the complex (1.5 µmol [Ni]), the required amount of the co-catalyst (MAO, MMAO, EASC, Et₂AlCl) and the residual toluene were added by syringe successively. The reaction mixture was intensively stirred for the desired time under the corresponding pressure of ethylene (10/5 atm) throughout the entire experiment. The reaction was quenched with acidic ethanol containing 30% hydrochloric acid and then the precipitated polymer was collected by filtration, adequately washed with ethanol and water and dried in a vacuum until of constant weight.

Ethylene polymerization under 1 atm of ethylene. The precatalyst **Ni2-4** was dissolved in toluene using standard Schlenk techniques and the reaction solution was stirred with a magnetic stirrer under an ambient ethylene atmosphere. The required amount of the co-catalyst (MAO) was added by a syringe. After the reaction was carried out for the required period, the reaction was terminated and analyzed using the same procedure shown above for ethylene polymerization at an elevated pressure.

Table 6 Crystal data and structure refinement for Ni1, Ni2-1 and Ni2-3

Paper

Identification code	Ni1	Ni2-1	Ni2-3
CCDC	917315	917316	917317
Empirical formula	C ₃₂ H ₃₂ Br ₂ N ₂ Ni	$C_{65}H_{64}Br_4N_4Ni_2$	C73H80Br4N4Ni2
Fw	663.13	1338.26	1450.47
$T(\mathbf{K})$	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/n	$P\bar{1}$	P2(1)/n
a (Å)	10.642(2)	10.690(6)	20.688(4)
b (Å)	20.891(4)	15.864(8)	19.271(4)
c (Å)	13.085(3)	21.146(9)	21.750(4)
α (°)	90	73.54(19)	90
β (°)	97.26(3)	80.11(2)	112.01(3)
γ (°)	90	86.03(17)	90
$V(A^3)$	2885.9(10)	3387(3)	8039(3)
Z	4	2	4
$D_{\text{calcd}} (\text{mg m}^{-3})$	1.526	1.312	1.198
$\mu ({\rm mm^{-1}})$	3.465	2.953	2.493
F(000)	1344	1356	2968
Cryst size (mm)	0.56 imes 0.38 imes 0.10	0.28 imes 0.26 imes 0.22	0.28 imes 0.26 imes 0.22
θ range (°)	2.16-27.46	1.02-27.32	1.16-25.00
Limiting indices	$-13 \le h \le 8$	$-12 \le h \le 12$	$-24 \le h \le 24$
	$-25 \le k \le 26$	$-18 \le k \le 18$	$-22 \le k \le 13$
	$-16 \le l \le 16$	$-19 \le l \le 25$	$-24 \le l \le 25$
No. of rflns collected	19 252	24 233	34 573
No. unique rflns [<i>R</i> (int)]	6546 (0.0743)	12 812 (0.0635)	$14119\ (0.0769)$
Completeness to θ (%)	$99.3(\theta = 27.46)$	99.0 $(\theta = 25.00)$	$99.7(\theta = 25.00)$
Goodness of fit on F^2	1.113	1.042	1.073
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0666$	$R_1 = 0.0995$	$R_1 = 0.0915$
	$wR_2 = 0.1456$	$wR_2 = 0.2458$	$wR_2 = 0.2304$
R induces (all data)	$R_1 = 0.0811$	$R_1 = 0.1455$	$R_1 = 0.1376$
• •	$wR_2 = 0.1553$	$wR_2 = 0.2782$	$wR_2 = 0.2579$
Largest diff. peak and hole $(Å^{-3})$	0.673 and -0.678	0.948 and -0.785	0.617 and -0.688

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