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2-(1-Aryliminoethylidene)quinolylnickel(II) dibromides: Synthesis, characterization and ethylene dimerization capability

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ABSTRACT

A series of 2-(1-aryliminoethylidene)quinoline derivatives (**L1**–**L9**) and the nickel(II) dibromides (**C1**–**C9**) thereof, were synthesized and characterized. The molecular structures of **C2** (R^1 = Et, R^2 = H, R = Me) and **C9** (R^1 = ^{i}Pr, R^2 = H, R = ^{i}Pr) were confirmed as being distorted tetrahedral at nickel by single crystal X-ray diffraction. On treatment with diethylaluminium chloride (Et_2AlCl) or ethylaluminum sesquichloride (EASC), these nickel pre-catalysts exhibited high activity for selective ethylene dimerization ($0.89–3.29 \times 10^6$ g mol^{-1}(Ni) h^{-1}) at 20 °C under 10 atm of ethylene. The influence of the reaction parameters on the catalytic behaviour was investigated for these nickel systems, including variation of Al/Ni molar ratio and reaction temperature.

1. Introduction

The emergence of diimine-type nickel dichloride complexes [1–3] as highly active pre-catalysts together with the commercializing of the Shell Higher Olefin Process (SHOP) [4–6] resurrected research into nickel systems for ethylene reactivity. This, together with further successes with other late-transition metal systems, has stimulated extensive research activity in the area, much of which has been the focus of a number of recent reviews [6–13]. In the case of nickel-based pre-catalysts, much of the research has related to the variation of different ligand sets at the metal center, with bidentate chelate ligands of the type P^O [14,15], P^P [16], N^O [17–22], P^N [23–29], and N^N [30–47], and some tridentate ligands of N^N^O [48], N^P^N [49], P^N^N [44,50], and N^N^N [51–57], etc, proving to be popular. However, oligomers and polymers, both produced as a mixture in a catalytic system, can be considered as by-products of one another; such a catalytic system would be less important. With this in mind, pre-catalysts bearing N^N ligands were attractive targets to explore and more fully understand the scope for improving purification during the production process. Therefore a series of 2-(1-aryliminoethylidene) quinoline derivatives (**L1**–**L9**) were designed and used to form the nickel(II) dibromides complexes (**C1**–**C9**). Interestingly, the current nickel pre-catalysts were capable of selective dimerization with an optimum reaction temperature of 20 °C, more importantly, showing high activity and high selectivity for α-olefins. As a consequence, herein a series of 2-(1-aryliminoethylidene)quinoline derivatives have been synthesized, reacted with nickel dibromides, and the resultant pre-catalysts were investigated. Upon activation with Et_2AlCl or EASC, all the nickel pre-catalysts reported herein showed high activity towards ethylene dimerization, and the affects of reaction parameters on their catalytic performance has been investigated.

2. Results and discussion

2.1. Synthesis and characterization of complexes

A series of 2-(1-aryliminoethylidene)quinoline derivatives (**L1**–**L9**) were prepared by Scheme 1. All the ligands were characterized by FT–IR, ^1H and ^{13}C NMR spectroscopic measurements as well as by elemental analysis. Further reaction of the 2-(1-aryliminoethylidene)quinoline derivatives with an equivalent of 1,2-dimethoxyethane nickel(II) bromide [(DME)$NiBr_2$] in THF

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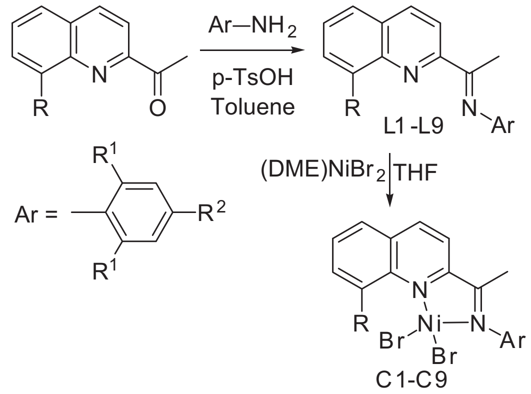

R	Me	Me	Me	Me	Me	Me	Me	Et	i-Pr
R^1	Me	Et	*i*-Pr	Me	Et	$CH(Ph)_2$	i-Pr	i-Pr	i-Pr
R^2	H	H	H	Me	Me	Me	NO_2	H	H
	L1	L2	L3	L4	L5	L6	L7	L8	L9
	C1	C2	C3	C4	C5	C6	C7	C8	C9

Scheme 1. Synthetic procedure of ligands (**L1**–**L9**) and their nickel bromide complexes (**C1**–**C9**).

afforded the title nickel complexes (Scheme 1: **C1**–**C9**) in high yields. All nickel complexes were characterized by FT–IR spectroscopic and elemental analyses, and were found to be highly stable both in the solid-state and in solution.

In the FT–IR spectra, the C=N stretching frequencies of the nickel complexes shifted to lower values with weaker intensity compared with those of the corresponding free ligand (1631–1646 cm^{-1}). Such changes are in line with the coordination between the imino-nitrogen and nickel. The molecular structures of the nickel complexes **C2** and **C9** were confirmed by single crystal X-ray diffraction studies.

2.2. Crystal structures

Single crystals of the nickel complexes **C2** and **C9** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into THF solutions. The molecular structures are shown in Figs. 1 and 2, respectively, with selected bond lengths and angles given in Table 1.

As shown in the Fig. 1, the geometry around the nickel center can be described as distorted tetrahedral, comprising one bidentate N^N ligand and two bromides. The Ni1–N1 bond length is 2.024(5) Å, which is longer than that of Ni1–N2 bond. The Ni1 atom deviates by 0.304 Å from the plane of the Br1–N1–Br2 atoms. The dihedral angle between the quinoline plane and the aryl ring is 86.83°.

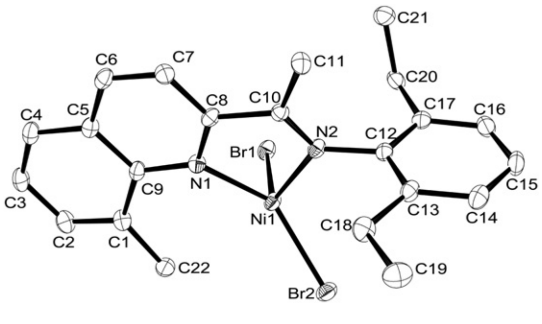

Fig. 1. ORTEP structure of **C2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

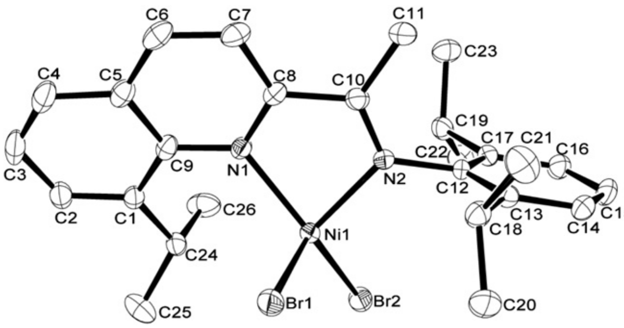

Fig. 2. ORTEP structure of **C9** with thermal ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

In the complex **C9** (Fig. 2), the geometry is slightly distorted tetrahedral geometry around each nickel, for example bond angles of N1–Ni1–N2 [81.62(15)°]. The distances of the Ni1–N1 [2.041(4) Å] and Ni1–N2 [1.987(4) Å] more closely resemble those of **C2**. Comparison of the corresponding bond lengths in complexes **C2**, reveals that the bond distances associated with the nickel atoms in complex **C9** are somewhat shorter, for example Ni1–Br1 [2.3797(8) Å] and Ni1–Br2 [2.3410(9) Å].

2.3. Ethylene dimerization

The catalytic behaviour of nickel (II) complexes towards ethylene was evaluated in the presence of various alkylaluminum reagents (Et_2AlCl, EASC, MAO and MMAO). The results are summarized in Table 2. Higher activities were obtained with Et_2AlCl and the selectivity for α-C_4 was more than 90%. The nickel (II) complex **C3** showed activities of up to 2.76 × 10^6 g mol^{-1} (Ni) h^{-1} upon activation with EASC. Based on catalytic activity, economic considerations (less co-catalyst) and the selectivity for α-C_4, both Et_2AlCl and EASC were selected for further investigation, and the catalytic system under 10 atm of ethylene was typically investigated, with variation of various reaction parameters (Table 3).

Ethylene activation in the presence of Et_2AlCl: According to Table 3, the reaction parameters have an influence on the ethylene dimerization activity. For example, upon changing the Al/Ni molar ratio or elevating the reaction temperature, the catalytic activity was greatly influenced. Such phenomena have been commonly observed in catalytic system of late-transition metal pre-catalysts [35,45,57]. Upon changing the Al/Ni molar ratio, the catalytic activities of **C3** initially increased and then decreased and the selectivity for α-olefins varied from 90.1% to 96.2%. Increasing the reaction temperature resulted in a considerable reduction in activity (entries 4 and 7–9 in Table 3), which might be caused by the instability of the active species or possibly a lower concentration of ethylene in the reaction solution at the elevated reaction temperature [40,55,57]. On increasing the temperature up to 50 °C, much lower activity resulted, indicating decomposition of the nickel active species, but with higher selectivity for the α-olefins.

To compare the influence of the ligand environment on the catalytic behaviour of the nickel pre-catalysts, the bromide pre-catalysts **C1**–**C9** were investigated under optimum reaction condition of molar ratio Et_2AlCl/Ni at 200:1, 20 °C at 10 atm ethylene, and the data is tabulated in Table 4. Different substituents on the quinoline (R) and on the phenyl group of the ligand (R^1, R^2) affected the catalytic behaviour of these nickel complexes. For complexes **C1**–**C3** containing 2,6-dialkyl substituents (entries 1–3 in Table 4), the bulkier the R^1 group used, the higher activity of dimerization observed, giving the activity order: **C1** (R^1 = Me) < **C2** (R^1 = Et) < **C3** (R^1 = ^{i}Pr). The greater bulkiness of the isopropyl

Table 1
Selected bond lengths (Å) and bond angles (°) for **C2** and **C9**.

	C2	**C9**		**C2**	**C9**
Bond lengths (Å)					
Ni(1)–N(1)	2.024(5)	2.041(4)	N(2)–C(10)	1.282(7)	1.283(6)
Ni(1)–N(2)	2.006(5)	1.987(4)	N(2)–C(12)	1.447(7)	1.445(5)
Ni(1)–Br(1)	2.3875(11)	2.3797(8)	N(1)–C(8)	1.333(7)	1.338(6)
Ni(1)–Br(2)	2.3455(11)	2.3410(9)	N(1)–C(9)	1.383(7)	1.375(6)
Bond angles (°)					
N(2)–Ni(1)–N(1)	82.0(2)	81.62(15)	N(1)–Ni(1)–Br(1)	96.43(14)	93.66(10)
N(2)–Ni(1)–Br(1)	109.01(14)	107.91(11)	N(1)–Ni(1)–Br(2)	139.24(15)	144.62(11)
N(2)–Ni(1)–Br(2)	103.99(14)	107.07(11)	Br(2)–Ni(1)–Br(1)	118.27(4)	114.79(3)

groups at the *ortho*-position of the imino-N aryl ring of complex **C3** may protect the active site from deactivation; moreover, bulkier alkyl substituents help to solubilize the nickel pre-catalysts thereby enhancing activity [58]. Regarding results observed by **C2** *versus* **C5** and **C1** *versus* **C4**, these pre-catalysts containing ligands with an additional methyl group showed better activity and gave the activity order **C4** > **C1** and **C5** > **C2**, presumably because they have a better solubility in solution, which can be helpful for activating the complex [39,40,56]. However, the catalytic activities slightly decreased in the presence of larger electron-donating groups [R^1 = CH(Ph)$_2$] on the phenyl ring. When the more electron-withdrawing nitro group (R^2 = NO$_2$) was present on the aryl, the activity order was **C3** > **C7**, which suggested that electron-withdrawing substituents in the R^2 position were not favourable for enhanced catalytic activities. Considering the groups at the 8-position of the quinoline (R^1 = ^{i}Pr and R^2 = H), the catalytic activity of **C3** was the highest, giving the order **C8** (R = Et) < **C9** (R = ^{i}Pr) < **C3** (R = Me) (entries 3, 8 and 9 in Table 4). Analogues of the 2-(1-aryliminomethylidene)quinolylnickel halide pre-catalysts, employing the same coordination environment, performed ethylene polymerization [59]; the current 2-(1-aryliminoethylidene)quinolylnickel(II) bromide pre-catalysts showed good activities in ethylene dimerization, but without the production of any observable polyethylene. Thus, substituents distant from the active metal center together with electronic effects changed the behaviour of the system, and in particular the nature of the ethylene reactivity; the influence of fine-tuning the ligands will be the focus of future studies. Moreover, nickel catalytic systems in ethylene oligomerization (including dimerization) commonly produced low portions of α-olefins due to β-H transfer processes [6,11]. It is noteworthy that the title nickel pre-catalysts showed higher activities in ethylene dimerization with high selectivity of α-olefin.

Ethylene activation in the presence of EACS: After variation of the ratio of EACS to nickel catalyst, high catalytic activity was observed with an Al/Ni molar ratio of 250 at 20 °C. Therefore, the catalytic behaviours of all the nickel complexes were investigated with a fixed Al/Ni molar ratio of 250, and the results are summarized in Table 5. On comparison with systems employing Et$_2$AlCl, all the complexes displayed higher catalytic activities for ethylene dimerization at 10 atm of ethylene pressure. The best performance of complex **C3** was observed at 20 °C (entry 4 in Table 5), with activities as high as 3.29×10^6 g mol^{-1} (Ni) h^{-1}. A similar trend for catalytic activities was displayed in regard to the nature of the ligands present. The dimerization activity, similar to that for the **C1**–**C9**/Et$_2$AlCl system, decreased in the order of **C3** > **C5** > **C2** > **C5** > **C4** > **C1**, **C3** > **C9** > **C8**, **C3** > **C6**, **C3** > **C7**. However, on comparison with the catalytic systems using the co-catalyst Et$_2$AlCl, the obtained dimerization with co-catalyst EASC afforded lower selectivity for α-olefins.

Table 2
Dimerization of ethylene with pre-catalyst **C3**.[a]

Entry	Co-catalyst	Al/Ni	Activity[b]	α-C$_4$[c]
1	MAO	1000	4.78	91.5
2	MMAO	1000	5.04	90.5
3	Et$_2$AlCl	200	24.0	92.5
4	EASC	200	27.6	82.4

[a] Conditions: 5 μmol Ni, 10 atm C$_2$H$_4$, 20 min, 20 °C, 100 mL toluene.
[b] Activity, 10^5 g mol^{-1} (Ni) h^{-1}.
[c] Determined by GC, $\sum$C denotes the total amount of oligomers, C$_4$/$\sum$C = 100%.

3. Conclusions

A series of nickel bromide complexes bearing 2-(1-aryliminopropylidene)quinoline ligands (**L1**–**L9**) were synthesized and characterized. Single crystal X-ray crystallographic studies for representative complexes were performed. The catalytic activities exhibited by these nickel pre-catalysts revealed clear activity trends. These nickel complexes exhibited high activities in ethylene dimerization, with α-C$_4$ as the main product. The catalytic activities decreased on elevating the reaction temperature. Further research efforts indicated that the ligand substituents present had a remarkable influence on the observed activities. However, the influence on selectivity for α-olefins was not obvious. The highest activity was obtained with the complexes having R as methyl, R^1 as isopropyl and R^2 as hydrogen. This implied that the less bulky R group was favourable for enhanced activity. It could also be observed that electron-withdrawing substituents at the R^2 position led to lower activities. Under optimum conditions, the activity was as high as 3.29×10^6 g mol^{-1} (Ni) h^{-1} with EASC.

4. Experimental section

4.1. General considerations

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and

Table 3
Dimerization of ethylene with **C3**/Et$_2$AlCl.[a]

Entry	T/°C	Al/Ni	Activity[b]	α-C$_4$[c]
1	20	50	4.95	94.1
2	20	100	10.5	93.5
3	20	150	10.6	92.9
4	20	200	24.0	92.5
5	20	250	13.0	90.7
6	20	300	5.72	96.2
7	30	200	5.03	90.1
8	40	200	3.91	92.2
9	50	200	2.81	93.1

[a] Conditions: 5 μmol Ni, Et$_2$AlCl as Co-catalyst, 10 atm C$_2$H$_4$, 20 min, 100 mL toluene.
[b] Activity, 10^5 g mol^{-1} (Ni) h^{-1}.
[c] Determined by GC, $\sum$C denotes the total amount of oligomers, C$_4$/$\sum$C = 100%.

Table 4
Dimerization of ethylene by nickel bromide pre-catalyst **C1**–**C9**.[a]

Entry	Pre-catalyst	Activity[b]	α-C_4[c]
1	**C1**	8.90	91.4
2	**C2**	14.1	92.6
3	**C3**	24.0	92.5
4	**C4**	9.10	93.6
5	**C5**	17.3	94.5
6	**C6**	16.3	93.3
7	**C7**	10.2	95.4
8	**C8**	21.9	91.7
9	**C9**	23.7	92.4

[a] Conditions: 5 μmol Ni, 200 equiv. Et_2AlCl, 20 °C, 10 atm C_2H_4, 20 min, 100 mL of toluene.

[b] Activity, 10^5 g mol^{-1} (Ni) h^{-1}.

[c] Determined by GC, $\sum C$ denotes the total amount of oligomers, $C_4/\sum C = 100\%$.

purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene was dried over sodium metal and distilled under nitrogen. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. Diethylaluminium chloride (Et_2AlCl, 1.70 M in toluene), ethylaluminum sesquichloride (EASC, 0.87 M in toluene) and other reagents were purchased from Aldrich or Acros Chemicals. (DME)$NiBr_2$ was synthesized by the reaction of 1,2-dimethoxyethane with anhydrous nickel(II) bromide. The ^1H and ^{13}C NMR spectra were recorded on Bruker DMX 400 MHz instruments 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 a Flash EA 1112 microanalyzer. GC analyses were performed with a Varian CP–3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) CP–Sil 5 CB column.

4.2. Syntheses and characterization

*4.2.1. 2-(1-(2,6-Dimethylphenylimino)ethylidene)-8-methylquinoline (**L1**)*

A reaction mixture of 1-(8-methylquinolin-2-yl)ethanone (1.85 g, 10.0 mmol), 2,6-dimethylaniline (1.21 g, 10.0 mmol), *p*-toluenesulfonic acid (0.20 g) and toluene (60 mL) was refluxed for 12 h. The solvent was rotary evaporated and the resulting solid was eluted with petroleum ether on an alumina column. The second eluting part was collected, concentrated to give a yellow solid and **L1** was obtained in 57% yield. Mp: 93–94 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.51 (1H, d, $J = 8.6$ Hz, quinoline), 8.20 (1H, d, $J = 8.6$ Hz, quinoline), 7.71 (1H, d, $J = 8.1$ Hz, quinoline), 7.60 (1H, d, $J = 6.9$ Hz, quinoline), 7.46 (1H, t, $J = 10.0$ Hz, quinoline), 7.09 (2H, d, $J = 7.5$ Hz, *m*-Ar), 6.96 (1H, t, $J = 10.0$ Hz, *p*-Ar), 2.87 (3H, s, $-CH_3$), 2.34 (3H, s, $-CH_3$), 2.07(6H, s, 2× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 168.1, 154.9, 149.4, 146.5, 138.2, 136.5, 130.1, 129.8, 128.9, 127.4, 125.8, 125.5, 123.4, 118.2, 18.32, 18.09, 16.55. Anal. Calcd for $C_{20}H_{20}N_2$ (288.16) C, 83.30; H, 6.99; N, 9.71. Found: C, 83.11; H, 7.02; N, 9.51. FT–IR (Diamond disk, cm^{-1}): 2962, 1639, 1599, 1567, 1494, 1449, 1361, 1310, 1193, 1138, 1101, 865, 762.

Table 5
Dimerization of ethylene with **C1**–**C9**/EASC.[a]

Entry	Pre-catalyst	*T*/°C	Al/Ni	Oligomer distribution[c] (%)	
				Activity[b]	α-C_4
1	**C3**	20	100	1.48	85.8
2	**C3**	20	150	1.76	83.5
3	**C3**	20	200	2.76	82.4
4	**C3**	20	250	3.29	74.6
5	**C3**	20	300	3.27	78.8
6	**C3**	20	400	2.44	81.4
7	**C3**	30	250	0.56	83.2
8	**C3**	40	250	0.32	80.9
9	**C1**	20	250	0.90	80.7
10	**C2**	20	250	2.19	76.4
11	**C4**	20	250	0.95	79.2
12	**C5**	20	250	2.40	84.7
13	**C6**	20	250	1.78	81.3
14	**C7**	20	250	1.45	78.9
15	**C8**	20	250	1.79	80.1
16	**C9**	20	250	2.23	82.1

[a] Conditions: 5 μmol Ni, Co-catalyst EASC, 10 atm C_2H_4, 20 min, 100 mL of toluene.

[b] Activity, 10^6 g mol^{-1} (Ni) h^{-1}.

[c] Determined by GC, $\sum C$ denotes the total amount of oligomers.

*4.2.2. 2-(1-(2,6-Diethylphenylimino)ethylidene)-8-methylquinoline (**L2**)*

In a manner similar to that described for **L1**, **L2** was prepared as a yellow solid in 74% yield. Mp: 102–104 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.51 (1H, d, $J = 8.5$ Hz, quinoline), 8.20 (1H, d, $J = 8.6$ Hz, quinoline), 7.71 (1H, d, $J = 8.0$ Hz, quinoline), 7.60 (1H, d, $J = 6.7$ Hz, quinoline), 7.49 (1H, t, $J = 10.0$ Hz, quinoline), 7.14 (2H, d, $J = 7.6$ Hz, *m*-Ar), 7.04 (1H, t, $J = 10.0$ Hz, *p*-Ar), 2.87 (3H, s, $-CH_3$), 2.52–2.36 (7H, m, 2× $-CH_2-$, $-CH_3$), 1.16 (6H, s, 2× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 167.8, 154.8, 148.2, 146.3, 138.2, 136.4, 131.2, 129.7, 128.8, 127.3, 126.0, 125.6, 123.3, 118.3, 24.75, 17.88, 16.75, 13.83. Anal. Calcd for $C_{22}H_{24}N_2$ (316.19) C, 83.50; H, 7.64; N, 8.85. Found: C, 83.56; H, 7.69; N, 8.75. FT–IR (Diamond disk, cm^{-1}): 2964, 1637, 1589, 1569, 1496, 1445, 1363, 1322, 1196, 1138, 1101, 855, 763, 690.

*4.2.3. 2-(1-(2,6-Diisopropylphenylimino)ethylidene)-8-methylquinoline (**L3**)*

In a manner similar to that described for **L1**, **L3** was prepared as a yellow solid in 78% yield. Mp: 182–184 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.52 (1H, d, $J = 8.5$ Hz, quinoline), 8.21 (1H, d, $J = 8.5$ Hz, quinoline), 7.71 (1H, d, $J = 8.0$ Hz, quinoline), 7.60 (1H, d, $J = 8.6$ Hz, quinoline), 7.49 (1H, t, $J = 9.8$ Hz, quinoline), 7.20(2H, s, *m*-Ar), 7.11 (1H, t, $J = 10.0$ Hz, *p*-Ar), 2.88 (3H, s, $-CH_3$), 2.80 (2H, m, 2× $-CH-$), 2.39 (3H, s, $-CH_3$), 1.19 (12H, s, 4× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 167.8, 154.9, 146.9, 146.4, 138.2, 136.4, 135.8, 129.7, 128.8, 127.3, 125.6, 123.6, 123.1, 118.4, 28.45, 23.35, 23.00, 17.87, 17.08. Anal. Calcd for $C_{24}H_{28}N_2$ (344.23) C, 83.68; H, 8.19; N, 8.13. Found: C, 83.58; H, 8.33; N, 8.09. FT–IR (Diamond disk, cm^{-1}): 2958, 1643, 1591, 1567, 1456, 1430, 1361, 1321, 1193, 1135, 1098, 852, 756, 689.

*4.2.4. 2-(1-(2,4,6-Trimethylphenylimino)ethylidene)-8-methylquinoline (**L4**)*

In a manner similar to that described for **L1**, **L4** was prepared as a yellow solid in 58% yield. Mp: 95–96 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.51 (1H, d, $J = 8.6$ Hz, quinoline), 8.20 (1H, d, $J = 8.9$ Hz, quinoline), 7.71 (1H, d, $J = 8.1$ Hz, quinoline), 7.60 (1H, d, $J = 6.9$ Hz, quinoline), 7.48 (1H, t, $J = 10.0$ Hz, quinoline), 6.92 (2H, s, *m*-Ar), 2.88 (3H, s, $-CH_3$), 2.34–2.31 (6H, 2× $-CH_3$), 2.03 (6H, s, 2× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 168.3, 154.9, 146.7, 146.4, 138.2, 136.4, 132.3, 129.7, 128.8, 128.7, 127.3, 125.6, 125.3, 118.4, 20.93, 18.08, 17.93, 16.40. Anal. Calcd for $C_{21}H_{22}N_2$ (302.18) C, 83.40; H, 7.33; N, 9.26 Found: C, 83.30; H, 8.48; N, 7.21. FT–IR (Diamond disk, cm^{-1}): 2908, 1638, 1567, 1494, 1470, 1361, 1318, 1284, 1209, 1096, 1037, 856, 842, 764, 681.

*4.2.5. 2-(1-(2,6-Diethyl-4-methylphenylimino)ethylidene)-8-methylquinoline (**L5**)*

In a manner similar to that described for **L1**, **L5** was prepared as a yellow solid in 73% yield. Mp: 105–106 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.50 (1H, d, $J = 8.6$ Hz, quinoline), 8.19 (1H, d, $J = 8.6$ Hz, quinoline), 7.70 (1H, d, $J = 8.0$ Hz, quinoline), 7.59 (1H, d, $J = 6.9$ Hz, quinoline), 7.48 (1H, t, J = 10.1 Hz, quinoline), 6.95 (2H, s, *m*-Ar), 2.87 (3H, s, $-CH_3$), 2.45−2.29 (10H, m, 2× $-CH_2-$, 2× $-CH_3$), 1.15 (6H, s, 2× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 168.0, 155.0, 146.4, 145.7, 138.2, 136.4, 132.5, 131.1, 129.7, 128.8, 127.3, 126.8, 125.6, 118.4, 24.80, 21.18, 17.91, 16.73, 14.01. Anal. Calcd for $C_{23}H_{26}N_2$ (330.21) C, 83.59; H, 7.93; N, 8.48. Found: C, 83.39; H, 8.10; N, 8.34. FT−IR (Diamond disk, cm^{-1}): 2967, 1646, 1570, 1456, 1362, 1253, 1099, 868, 842, 803, 760, 689.

4.2.6. 2-(1-(2,6-Dibenzhydryl-4-methylphenylimino)ethylidene)-8-methylquinoline (*L6*)

In a manner similar to that described for **L1**, **L6** was prepared as a yellow solid in 71% yield. Mp: 189−190 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.12 (2H, d, J = 8.3 Hz), 7.70 (1H, d, J = 8.0 Hz, quinoline), 7.59 (1H, d, J = 6.9 Hz, quinoline), 7.47 (1H, t, J = 10.1 Hz, quinoline), 7.23−7.00 (20H, m), 6.70 (2H, s, *m*-Ar), 5.31 (2H, s, 2× $-CH-$), 2.75 (3H, s, $-CH_3$), 2.19 (3H, s, $-CH_3$), 1.21 (3H, s, $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 170.9, 154.8, 146.5, 146.3, 143.9, 142.8, 138.3, 136.1, 132.3, 131.6, 130.0, 129.6, 129.4, 128.8, 128.6, 128.4, 128.1, 127.1, 126.2, 126.1, 125.5, 118.6, 52.24, 31.74, 22.97, 22.81, 21.49, 17.86, 16.83, 14.28. Anal. Calcd for $C_{45}H_{38}N_2$ (606.3) C, 89.07; H, 6.31; N, 4.62. Found: C, 89.00; H, 6.42; N, 4.46. FT−IR (Diamond disk, cm^{-1}): 2955, 1645, 1597, 1569, 1493, 1447, 1363, 1321, 1240, 1103, 1030, 851, 765, 682.

4.2.7. 2-(1-(2,6-Isopropyl-4-nitrolphenylimino)ethylidene)-8-methylquinoline (*L7*)

In a manner similar to that described for **L1**, **L7** was prepared as a yellow solid in 65% yield. Mp: 206−207 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.45 (1H, d, J = 8.6 Hz, quinoline), 8.24 (1H, d, J = 8.6 Hz, quinoline), 8.04 (2H, s, *m*-Ar), 7.74 (1H, d, J = 8.1 Hz, quinoline), 7.63 (1H, d, J = 6.9 Hz, quinoline), 7.50 (1H, t, J = 10.1 Hz, quinoline), 3.03 (3H, s, $-CH_3$), 2.87−2.80 (2H, m, 2× $-CH-$), 2.40 (3H, s, $-CH_3$), 1.24−1.19 (12H, s, 4× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 168.2, 153.6, 153.0, 146.4, 144.6, 138.2, 137.3, 136.8, 130.0, 128.9, 127.8, 125.6, 119.4, 118.1, 28.74, 22.90, 22.52, 17.85, 17.62. Anal. Calcd for $C_{24}H_{27}N_3O_2$ (389.21) C, 74.01; H, 6.99; N, 10.79. Found: C, 73.92; H, 7.14; N, 10.69. FT−IR (Diamond disk, cm^{-1}): 2962, 1645, 1576, 1509, 1459, 1363, 1312, 1245, 1096, 900, 846, 766, 680.

4.2.8. 2-(1-(2,6-Diisopropylphenylimino)ethylidene)-8-ethylquinoline (*L8*)

In a manner similar to that described for **L1**, **L8** was prepared as a yellow solid in 73% yield. Mp: 126−127 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.50 (1H, d, J = 8.5 Hz, quinoline), 8.20 (1H, d, J = 8.5 Hz, quinoline), 7.71 (1H, d, J = 8.0 Hz, quinoline), 7.60 (1H, d, J = 8.6 Hz, quinoline), 7.51 (1H, t, J = 9.9 Hz, quinoline), 7.18(2H, d, *m*-Ar), 7.10 (1H, t, J = 10.0 Hz, *p*-Ar), 3.38 (2H, m, $-CH_2-$), 2.81 (2H, m, 2× $-CH-$), 2.34 (3H, s, $-CH_3$), 1.47 (3H, s, $-CH_3$), 1.17 (12H, s, 4× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 167.8, 154.9, 146.9, 145.8, 144.0, 136.5, 135.8, 128.9, 128.2, 127.5, 125.6, 123.7, 123.2, 118.4, 28.47, 24.91, 23.37, 23.02, 17.12, 15.31. Anal. Calcd for $C_{25}H_{30}N_2$ (358.24) C, 83.75; H, 8.43; N, 7.81. Found: C, 83.59; H, 8.56; N, 7.21. FT−IR (Diamond disk, cm^{-1}): 2959, 1642, 1591, 1569, 1458, 1432, 1361, 1312, 1191, 1135, 1099, 851, 765, 692.

4.2.9. 2-(1-(2,6-Diisopropylphenylimino)ethylidene)-8-isopropylquinoline (*L9*)

In a manner similar to that described for **L1**, **L9** was prepared as a yellow solid in 73% yield. Mp: 100−102 °C. δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.49 (1H, d, J = 8.6 Hz, quinoline), 8.21 (1H, d, J = 8.6 Hz, quinoline), 7.70 (1H, d, J = 7.9 Hz, quinoline), 7.63 (1H, d, J = 6.8 Hz, quinoline), 7.55 (1H, t, J = 10.1 Hz, quinoline), 7.19 (2H, d, *m*-Ar), 7.12 (1H, t, J = 10.1 Hz, *p*-Ar), 4.42−4.36 (1H, m, $-CH-$), 2.82−2.76 (2H, m, 2× $-CH-$), 2.35 (3H, s, $-CH_3$), 1.44 (6H, s, 2× $-CH_3$), 1.17 (12H, s, 4× $-CH_3$). δ_C (100 MHz; $CDCl_3$; Me_4Si) 167.9, 154.7, 148.1, 146.9, 145.2, 136.7, 135.9, 128.9, 127.6, 125.5, 125.4, 123.7, 123.1, 118.3, 28.48, 28.07, 23.56, 23.38, 23.07, 17.23. Anal. Calcd for $C_{26}H_{32}N_2$ (372.26) C, 83.82; H, 8.66; N, 7.52. Found: C, 83.72; H, 8.70; N, 7.42. FT−IR (Diamond disk, cm^{-1}): 2962, 1631, 1594, 1566, 1461, 1434, 1364, 1191, 1104, 847, 791, 764, 695.

Preparation of **C1**. To a solution of the ligand 2,6-dimethyl-*N*-(1-(quinolin-2-yl)ethylidene)benzenamine (**L1**, 0.288, 1.0 mmol) in THF (10 mL), (DME)$NiBr_2$ (0.308 g, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for 12 h to afford a yellow precipitate from the reaction mixture (**C1**, 0.491 g, 88% yield). Anal. Calcd for $C_{20}H_{20}Br_2N_2Ni$ (503.93) C, 47.39; H, 3.98; N, 5.53. Found: C, 47.28; H, 4.03; N, 5.41. FT−IR (Diamond disk, cm^{-1}): 2965, 1624, 1513, 1447, 1366, 1311, 1231, 854, 764.

Preparation of **C2**. Using the same procedure as for the synthesis of **C1**, **L2** was used in the reaction with (DME)$NiBr_2$ to form **C2** (yellow powder, 91% yield). Anal. Calcd for $C_{22}H_{24}Br_2N_2Ni$ (531.97) C, 49.40; H, 4.52; N, 5.24. Found: C, 49.20; H, 4.56; N, 5.14. FT−IR (Diamond; cm^{-1}): 2968, 1625, 1510, 1448, 1369, 1311, 1221, 854, 774.

Preparation of **C3**. Using the same procedure as for the synthesis of **C1**, **L3** was used in the reaction with (DME)$NiBr_2$ to form **C3** (yellow powder, 92% yield). Anal. Calcd for $C_{24}H_{28}Br_2N_2Ni$ (560.00) C, 51.20; H, 5.01; N, 4.98. Found: C, 51.00; H, 5.13; N, 4.73. FT−IR (Diamond; cm^{-1}): 2967, 1625, 1589, 1513, 1446, 1370, 1307, 1257, 1216, 1059, 836, 805, 763.

Preparation of **C4**. Using the same procedure as for the synthesis of **C1**, **L4** was used in the reaction with (DME)$NiBr_2$ to form **C4** (yellow powder, 90% yield). Anal. Calcd for $C_{21}H_{22}Br_2N_2Ni$ (517.95) C, 48.42; H, 4.26; N, 5.38. Found: C, 48.16; H, 4.43; N, 5.19. FT−IR (Diamond; cm^{-1}): 2966, 1625, 1509, 1462, 1441, 1370, 1301, 1219, 1153, 1031, 844, 776.

Preparation of **C5**. Using the same procedure as for the synthesis of **C1**, **L5** was used in the reaction with (DME)$NiBr_2$ to form **C5** (yellow powder, 91% yield). Anal. Calcd for $C_{23}H_{26}Br_2N_2Ni$ (545.98) C, 50.32; H, 4.77; N, 5.10. Found: C, 50.14; H, 4.89; N, 4.88. FT−IR (Diamond; cm^{-1}): 2967, 1619, 1510, 1447, 1367, 1313, 1220, 854, 775.

Preparation of **C6**. Using the same procedure as for the synthesis of **C1**, **L6** was used in the reaction with (DME)$NiBr_2$ to form **C6** (yellow powder, 89% yield). Anal. Calcd for $C_{45}H_{38}Br_2N_2Ni$ (822.08) C, 65.49; H, 4.64; N, 3.39. Found: C, 65.29; H, 4.89; N, 3.25. FT−IR (Diamond; cm^{-1}): 2917, 1601, 1494, 1446, 1370, 1304, 1255, 1214, 1073, 1031, 840, 751, 680.

Preparation of **C7**. Using the same procedure as for the synthesis of **C1**, **L7** was used in the reaction with (DME)$NiBr_2$ to form **C7** (yellow powder, 90% yield). Anal. Calcd for $C_{24}H_{27}Br_2N_3NiO_2$ (604.98) C, 47.41; H, 4.48; N, 6.91. Found: C, 47.21; H, 4.59; N, 4.26. FT−IR (Diamond; cm^{-1}): 3339, 2965, 1640, 1585, 1510, 1305, 1253, 1096, 1070, 905, 842.

Preparation of **C8**. Using the same procedure as for the synthesis of **C1**, **L8** was used in the reaction with (DME)$NiBr_2$ to form **C8** (yellow powder, 91% yield). Anal. Calcd for $C_{25}H_{30}Br_2N_2Ni$ (574.01) C, 52.04; H, 5.24; N, 4.85. Found: C, 51.99; H, 5.44; N, 4.65. FT−IR (Diamond; cm^{-1}): 2963, 1618, 1515, 1463, 1441, 1372, 1310, 1193, 1060, 856, 762.

Preparation of **C9**. Using the same procedure as for the synthesis of **C1**, **L9** was used in the reaction with (DME)$NiBr_2$ to form **C9** (yellow powder, 92% yield). Anal. Calcd for $C_{26}H_{32}Br_2N_2Ni$ (588.03) C, 52.83; H, 5.46; N, 4.74. Found: C, 52.67; H, 5.71; N, 4.51. FT−IR (Diamond; cm^{-1}): 2961, 1627, 1510, 1456, 1374, 1310, 1194, 841, 765.

4.3. General procedure for ethylene dimerization

Ethylene dimerization at 10 atm ethylene pressure was performed in a stainless steel autoclave (0.25 L capacity) equipped

Table 6
Crystal data and structure refinement for complexes **C2** and **C9**.

	C2	**C9**
Cryst colour	Yellow	Brown
Empirical formula	$C_{22}H_{24}Br_2N_2Ni$	$C_{26}H_{32}Br_2N_2Ni$
fw	534.96	591.07
T (K)	446(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Cryst syst	Monoclinic	Orthorhombic
Space group	P2(1)/c	Pbca
a (Å)	8.0242(16)	15.609(3)
b (Å)	19.652(4)	16.917(3)
c (Å)	13.681(3)	19.492(4)
α (°)	90	90
β (°)	102.08(3)	90
γ (°)	90	90
V (Å^3)	2109.6(7)	5146.9(18)
Z	4	8
Dcalcd. (m gm^{-3})	1.684	1.526
μ (mm^{-1})	4.717	3.875
F(000)	1072	2400
Cryst size (mm)	0.20 × 0.15 × 0.10	0.24 × 0.22 × 0.05
θ range (°)	1.84–27.49	2.06–27.48
Limiting indices	$-10 \le h \le 10$	$-20 \le h \le 20$
	$-25 \le k \le 20$	$-21 \le k \le 20$
	$-17 \le l \le 17$	$-21 \le l \le 25$
No. of rflns collected	17,033	44,073
No. unique rflns [R(int)]	4770 (0.0626)	5889(0.0950)
Completeness to θ (%)	98.4%	99.8%
Abs corr	None	None
Data/restranints/params	5770/0/244	5889/0/280
Goodness of fit on F^2	1.354	1.307
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0679$	$R1 = 0.0628$
	$wR2 = 0.1571$	$wR2 = 0.1542$
R indices (all data)	$R1 = 0.0803$	$R1 = 0.0702$
	$wR2 = 0.1688$	$wR2 = 0.1577$
Largest diff peak and hole (e Å^{-3})	0.642 and −0.549	0.853 and −0.908

with a mechanical stirrer, a temperature controller and gas ballast through a solenoid clave for continuous feeding of ethylene at constant pressure. The catalyst precursor was dissolved in 50 mL toluene in a Schlenk tube stirred with a magnetic stirrer and injected into the reactor under an ethylene flux. With $EtAlCl_2$, 50 mL toluene was also added. When the reaction temperature had been reached, ethylene with the desired pressure was introduced to start the reaction. After the reaction mixture had been stirred for the desired period of time, the reaction was stopped and about 1 mL of the reaction solution was collected, terminated by the addition of 10% aqueous hydrogen chloride. The organic layer was analyzed by gas chromatography (GC) for determining the composition and mass distribution of the oligomers obtained.

4.4. *Crystal structure determinations*

Single crystals of **C2** and **C9** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into its THF solution. Diffraction data of complexes **C2** and **C9** were collected on a Rigaku R–AXIS Rapid IP diffractometer with graphite monochromated Mo Kα radiation ($l = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. Data were collected using phi-scans and the structures were solved by direct methods (SIR97) using the SHELX97 software [60] and the refinement was by full–matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. Crystal data and processing parameters for **C9** are summarized in Table 6.

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Appendix A. Supplementary material

CCDC 831463 and 831464 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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