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New octahedral bis-α-diimine nickel(II) complexes containing chloro-substituted aryl groups: Synthesis, characterization and testing as ethylene polymerisation catalysts

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ABSTRACT

Three new 20-electron bis-α-diimine nickel (II) complexes containing chloro-substituted ligands, bis{bis[*N,N*′-(3-chloro-2-methylphenyl)imino]-1,2-dimethylethane}dibromonickel **2a**, bis{bis[*N,N*′-(3-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel **2b** and bis{bis[*N,N*′-(4-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel **2c**, were synthesized and characterized. The molecular structure of complex **2a** was determined by X-ray crystallography. In the solid state, complex **2a** has a pseudo-octahedral geometry about the nickel center, containing two α-diimine ligands in the pseudo-equatorial plane and two *trans* bromide ligands occupying the axial positions. These complexes, activated by diethylaluminum chloride (DEAC) were tested in the polymerization of ethylene under mild conditions. NMR analysis shows that highly branched polyethylenes are obtained using these bis-α-diimine nickel(II) complexes containing electron-withdrawing Cl groups in the aryl groups (*e.g.* 84 branches/1000 C, at 20 °C). The catalytic activity, polymer molecular weight and polymer degree of branching were significantly affected by the number of methyl substituents in the *ortho*-aryl position and the chlorine substituent position in the aryl rings of the coordinated α-diimine ligands.

1. Introduction

The discovery of Ni(II) and Pd(II) α-olefin polymerisation catalysts containing a bulky α-diimine ligand, [MX_2(α-diimine)] (M = Ni, Pd; X = halide), by Brookhart and co-workers [1–8], has stimulated renewed interest in the chemistry of 1,4-diazadiene ligands and their complexes. The coordination chemistry of α-diimine ligands of the type *N,N*′-diaryl-1,4-diaza-1,3-butadiene (Ar-DAB) or bis(arylimino)acenaphthene (Ar-BIAN) to late transition metals has attracted much interest due to their unusual electron donor and acceptor properties [9,10]. Organometallic compounds containing Ar-DAB or Ar-BIAN ligands have been extensively studied in recent years as catalysts for the oligomerisation and polymerisation of α-olefins [11–17].

The ligand structure has a dramatic effect on the reactivity of organometallic complexes. This has been especially evident in the recent development of late transition metal olefin polymerization catalysts. A variety of α-diimine ligands containing substituted *N*-aryl rings, including those with steric bulk and *ortho* and *para* substituted position modifications in the aryl rings [18–24], backbone effects on the α-diimine ligand structure [25–29], chiral α-diimine ligand systems [30,31], teraryl substituted-α-diimine ligands [32–35], cyclophane-based α-diimine ligands [36–39], were employed to study their influence on the catalytic activity of the 16-electron Ni(II) and Pd(II) [MX_2(α-diimine)] precatalysts. However, the effect of electron-withdrawing *N*-aryl rings substituents, especially of Cl atoms, on the catalytic behavior of α-diimine-Ni(II) complexes and the properties of the resulting polymers has only been reported in limited cases.

Conversely, the report of 20-electron complexes of NiX_2 bearing four coordinated nitrogen atoms that exhibit catalytic activity in the oligomerization or polymerization of olefins has also been scarce, being limited to the cases where the NiX_2 fragment is coordinated to *two* α-diimine ligands of the aryl-BIAN type ([$NiBr_2$(Ar-BIAN)$_2$]) [21] or to a tetradentate *N,N,N,N*-chelating α-diimine ligand ([$NiBr_2$(*N,N,N,N*-α-diimine)]) [40,41].

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In this paper, we report the synthesis and characterization of three new 20-electron octahedral bis-α-diimine Ni(II) complexes of the type [NiBr$_2$(Ar-DAB)$_2$] bearing electron-withdrawing substituents Cl in the *para*- or *meta*-aryl positions of the Ar-DAB ligand and their catalytic behaviors in the polymerization of ethylene when activated by diethylaluminum chloride (DEAC).

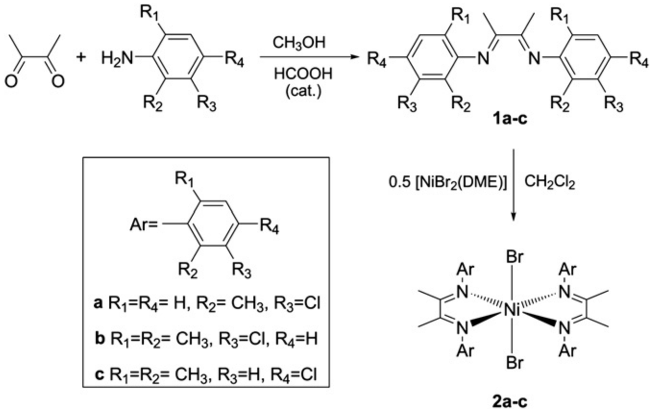
2. Results and discussion

2.1. Synthesis and characterization of ligands *1a–c* and complexes *2a–c*

The general synthetic route to three nickel(II) complexes **2a–c** is shown in Scheme 1. The free Ar-DAB ligands **1a–c** were prepared by the condensation of two equivalents of the appropriate aniline with one equivalent of 2,3-butanedione, usually in the presence of an acid catalyst. The compounds (**1a–c**) were characterized by ^{1}H NMR and ^{13}C NMR and were found elementally pure.

The reaction of 1 equivalent of [NiBr$_2$(DME)] and 2 equivalents of the α-diimine ligands **1a–c**, in CH$_2$Cl$_2$, led to the displacement of 1,2-dimethoxyethane and afforded the catalyst precursors **2a–c** as moderately air-stable light red microcrystalline solids in good yields. Due to the geometry around the nickel atom, these bis-α-diimine Ni(II) complexes are paramagnetic and their ^{1}H NMR is not assignable. The elemental analyses of complexes **2a–c** fit the stoichiometry Ni:α-diimine of 1:2 ([NiBr$_2$(Ar-DAB)$_2$]), which is further corroborated by the molecular structure obtained by X-ray structural studies. In fact, suitable crystals of **2a** for X-ray diffraction were obtained by double layering a solution of the complex in CH$_2$Cl$_2$ with *n*-hexane. The molecular structure of complex **2a** was determined and the corresponding ORTEP diagram is shown in Fig. 1, while selected bond distances and angles are summarized in Table 1.

In the solid state, the structure of complex **2a** shows two Ar-DAB and two bromide ligands featuring a six-coordinate distorted octahedral geometry around the nickel center, having a C$_2$ molecular symmetry. The nickel atom occupies a crystallographic inversion centre and only a half of the molecule is symmetry independent. The two α-diimine ligands coordinate the nickel atom in the equatorial plane, their corresponding DAB planes making a dihedral angle of 11.25°, whereas the two bromide ligands lie in the axial positions, their bonds to the nickel atom being perpendicular (89.98°) to the average plane defined by the nitrogens and the nickel atoms. Its structure is quite similar to that reported in the literature for the other [NiX$_2$(*N,N′*-diaryl-α-diimine)$_2$] compound characterized by X-ray, the bis[bis(*N,N′*-2,3-dichlorophenylimino) acenaphthene]dibromonickel [21], which contains two α-diimine ligands of the aryl-BIAN type. In fact, the Ni–N bond distances in complex **2a** (2.112–2.116 Å) are similar to that determined for that compound (2.144 Å), as well as the Ni–Br bond distances (2.5797–2.6128 Å for complex **2a** vs. 2.5354 Å) and the two bromine atoms are situated in the *trans*-position (Br–Ni–Br angle, 179° for complex **2a** vs. 180°), whereas the halide ligands display a *cis* geometry in the majority of the other nickel complexes containing two DAB-type ligands with non-aryl and non-bulky *N*-imine substituents [42–46]. The two imino C=N bonds have typical double bond character with C=N bond lengths of 1.272 Å. The aryl rings of each of the α-diimines lie nearly perpendicular to the plane formed by the nickel and coordinated nitrogen atoms, and face each others in a staggered conformation.



Scheme 1. Syntheses of α-diimine ligands **1a–1c** and their corresponding bis-α-diimine nickel(II) dibromide complexes **2a–2c**.

2.2. Polymerization of ethylene with nickel complexes *2a–c*

The three complexes **2a**, **2b** and **2c**, activated by diethylaluminum chloride (DEAC), were tested as catalyst precursors for the polymerization of ethylene, under the same reaction conditions. The results of the polymerization experiments are shown in Table 2. Noteworthy is the fact that blank experiments carried out with DEAC alone, under similar conditions, showed its inability to polymerize ethylene on its own.

For a ratio [Al]/[Ni] = 600, an increase in the reaction temperature in the range 0–40 °C increases the activity of precatalysts **2b** and **2c** (containing two methyl substituents in both *ortho* aryl positions) activated by DEAC, (**2b**: entries 6–8; **2c**: entries 11–13), while precatalyst **2a** (containing a single methyl substituent in one of the *ortho* aryl positions) revealed to be inactive (entries 1–3). An increase of the [Al]/[Ni] ratio in the range 600–1500 increases the activity of all the precatalysts, at 20 °C, which seem to go through a maximum around [Al]/[Ni] = 1000 (**2a**: entries 2, 4 and 5; **2b**: entries 7, 9 and 10; **2c**: entries 12, 14 and 15). The molecular weight of the polyethylenes (PE) produced under these conditions were found to slightly increase, in the case of **2b**, or decrease, in the cases of **2a** and **2c**, with an increasing [Al]/[Ni] ratio.

The performances of the nickel precatalysts are significantly affected by the position of the chlorine substituent on the aryl rings of the the bis-α-diimine Ni(II) complexes **2a–c** (Table 2). Complex **2b**, bearing a Cl substituent in the *meta*-aryl position of the ligand (two methyl groups in the *ortho*-aryl positions), displays the highest catalytic activity, of 7.08×10^5 g PE/(mol Ni·h·bar), and produces one of the highest molecular weights ($M_n = 53600$, entry 9, 20 °C, [Al]/[Ni] = 1000) among our three complexes. Complex **2c**, bearing a Cl substituent in the *para*-aryl position of the ligand (also with two methyl groups in the *ortho*-aryl positions), exhibits a slightly lower catalytic activity of 6.81×10^5 g PE/(mol Ni·h·bar) and yields polyethylene with substantially lower molecular weight ($M_n = 39\,800$, entry 14, 20 °C, [Al]/[Ni] = 1000). This shows that a Cl substituent in the *meta*-aryl position (**2b**) increases the rate of chain propagation (migratory insertion of coordinated ethylene into the Ni-chain alkyl bond) and decreases the rate of chain transfer (β-hydrogen transfer to the metal or to the monomer) in comparison with that in the *para*-aryl position (**2c**). For the same ratio [Al]/[Ni] = 1000, complex **2a**, bearing Cl substituent in the *meta*-aryl position in the ligand (only one methyl group in the *ortho*-aryl position), shows the lowest catalytic activity (1.90×10^5 g PE/(mol Ni·h·bar)) and produces the lowest molecular weight ($M_n = 15\,200$, Entry 4, 20 °C) of the three precatalysts. These results indicate that the rate of chain propagation is greatly promoted by the bulkiness of the ligand's aryl rings. As a result, the following activity trend can be summarized for our Cl substituted precatalysts under low ethylene pressure (1.2 bar), in the range 0–40 °C: **2b** > **2c** > **2a**.

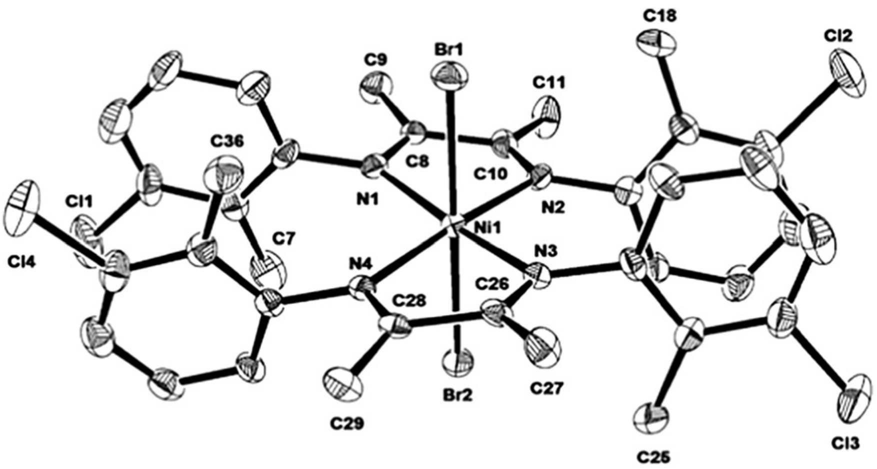


Fig. 1. ORTEP drawing of complex **2a** with 30% probability displacement ellipsoid. The hydrogen atoms are omitted for clarity.

In general, all the three catalysts exhibited high activities toward ethylene polymerization ($10^6 \geq$ activities $\geq 10^5$ g PE/(mol Ni·h·bar)) under low ethylene pressure, which are comparable to those of metallocene catalysts [47]. The polymerization activities obtained in this work (**2b**: 7.08 × 10^5 g PE/(mol Ni·h·bar); **2c**: 6.81 × 10^5 g PE/(mol Ni·h·bar), when activated by DEAC) showed to be of the same order of magnitude of those observed for 16-electron [$NiBr_2$(Ar-DAB)] catalyst precursors such as the {bis[*N,N′*-(2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel, which activity reported by Brookhart et al. is *ca*. 9.00 × 10^5 g PE/(mol Ni·h·bar) [1], although the experimental conditions (reaction time, 10 min; temperature, 0 °C; pressure, 2 bar; co-catalyst, MAO; [Al]/[Ni] = 1000) are not exactly the same as those used in the present work. These high activities may indicate that the active species operating in the case of our 20-electron precatalysts **2a**–**c** ([$NiBr_2(Ar\text{-}DAB)_2$]) is the same as that admitted for the corresponding 16-electron species [$NiBr_2$(Ar-DAB)] [4]. In fact, similar to what was proposed by other authors [21], the bis-α-diimine nickel(II) used in the present work may be involved in an equilibrium where one of the Ar-DAB ligands dissociates, giving rise to a 16-electron complex [$NiBr_2$(Ar-DAB)], which can also be originated by the coordination/abstraction from the precatalysts of one of such donor chelating ligands to the Lewis acidic co-catalyst ($AlEt_2Cl$) (Scheme 2, route a). The 16-electron [$NiBr_2$(Ar-DAB)] precatalyst can then follow the classical polymerization mechanism put forward by Brookhart and co-workers [4]. Alternatively, the hemilabile α-diimine ligands may partially dissociate giving rise to 16-electron complexes containing unidentate α-diimine ligands, as proposed for the recently reported tetradentate *N,N,N,N*-chelated α-diimine nickel complexes [41], which, upon reaction with $AlEt_2Cl$, could give rise to the corresponding cationic alkyl unsaturated active species (Scheme 2, route b).

Table 1
Selected bond lengths (Å) and angles (°) for complex **2a**.

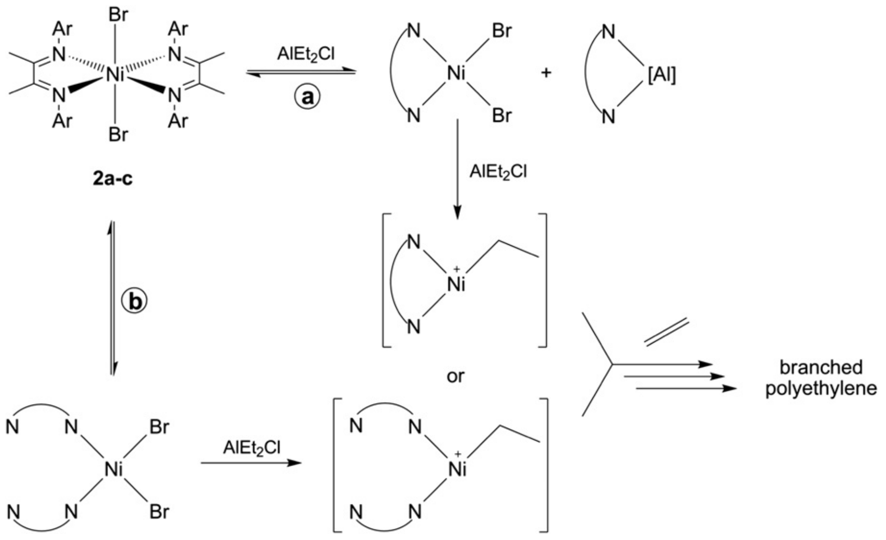
Bond lengths	(Å)	Bond angles	(°)
Ni(1)–N(3)	2.112(4)	N(3)–Ni(1)–N(4)	77.37(16)
Ni(1)–N(4)	2.112(4)	N(3)–Ni(1)–N(2)	103.20(17)
Ni(1)–N(2)	2.113(4)	N(4)–Ni(1)–N(2)	174.66(13)
Ni(1)–N(1)	2.116(4)	N(3)–Ni(1)–N(1)	173.65(14)
Ni(1)–Br(2)	2.5797(18)	N(4)-Ni(1)–N(1)	102.40(16)
Ni(1)–Br(1)	2.6128(18)	N(2)–Ni(1)–N(1)	77.63(16)
C(1)–C(6)	1.383(7)	C(6)–C(1)–C(2)	122.2(5)
C(1)–N(1)	1.433(6)	C(2)–C(1)–N(1)	120.4(4)
C(2)–C(3)	1.405(7)	C(1)-C(2)–C(7)	122.0(5)
C(2)–C(7)	1.484(7)	N(3)–Ni(1)-Br(1)	86.62(10)
C(3)–C(4)	1.346(8)	N(4)–Ni(1)–Br(1)	92.45(9)
C(3)–Cl(1)	1.743(6)	N(2)–Ni(1)–Br(1)	92.89(10)
C(4)–C(5)	1.351(8)	N(1)-Ni(1)-Br(1)	87.05(10)
C(5)–C(6)	1.402(8)	Br(2)–Ni(1)–Br(1)	179.00(3)

The type and amount of branches formed in the polymerization of ethylene promoted by typical α-diimine nickel precatalysts depends on reaction parameters such as the reaction temperature, ethylene pressure and ligand bulkiness/structure [4]. As shown in Table 3, the catalyst systems **2b**/DEAC and **2c**/DEAC, containing an electron-withdrawing Cl group, generated polyethylene with high degrees of branching at 20 °C. The total branching degrees of the polymer samples prepared with **2b**/DEAC (entries 9 and 10: 84 and 76 branches/1000 C, respectively) and **2c**/DEAC (entries 14 and 15: 82 and 84 branches/1000 C, respectively) are much higher than those observed for similar non-chlorinated precatalyst/DEAC systems such as {bis[*N,N′*-(4-tert-butyl-diphenylsilyl-2,6-diisopropylphenyl)imino]acenaphthene}dibromonickel (45 branches/1000 C, at 20 °C) [1,4] or precatalyst/MAO systems such as {bis[*N,N′*-(2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel (20 branches/1000 C, at 0 °C) [4], {bis[*N,N′*-(2,6-diisopropylphenyl)imino]-1,2-dimethylethane}dibromonickel (48, 30, 67, 80 and 90 branches/1000 C, at 0, 25, 50, 65 and 80 °C, respectively) [4], {bis[*N,N′*-(2,6-diisopropylphenyl)imino]acenaphthene}dibromonickel (65 branches/1000 C, at 25 °C) [4], although the reaction conditions are not exactly the same as in the present work. Therefore, the precatalysts containing *ortho*-dialkyl substituted aryl rings and an

Table 2
Ethylene polymerizations using nickel precatalysts **2a**, **2b** and **2c** activated by DEAC.[a]

Entry	Precatalyst	[Al]/[Ni]	T_p (°C)	Yield (g)	Activity × 10^{-5} (g PE/(mol Ni·h·bar))	M_n[b] × 10^{-4} (g/mol)	M_w/M_n [b]
1	**2a**	600	0	Traces	–	–	–
2	**2a**	600	20	Traces	–	–	–
3	**2a**	600	40	Traces	–	–	–
4	**2a**	1000	20	0.41	1.90	1.52	1.85
5	**2a**	1500	20	0.40	1.85	1.45	1.79
6	**2b**	600	0	0.32	1.48	2.93	1.61
7	**2b**	600	20	0.39	1.81	2.55	1.75
8	**2b**	600	40	0.84	3.89	3.31	1.82
9	**2b**	1000	20	1.53	7.08	5.36	1.76
10	**2b**	1500	20	1.45	6.71	5.39	1.73
11	**2c**	600	0	0.25	1.16	4.94	1.56
12	**2c**	600	20	0.33	1.53	4.53	1.59
13	**2c**	600	40	0.82	3.80	3.47	1.68
14	**2c**	1000	20	1.47	6.81	3.98	1.60
15	**2c**	1500	20	1.43	6.62	3.41	1.61

[a] Polymerization conditions: n(Ni) = 3.6 μmol; pressure of C_2H_4 = 1.2 bar (absolute); Polymerization time t_p = 0.5 h; solvent = toluene (50 ml); T_p = polymerization temperature.
[b] Determined by GPC/SEC.



Scheme 2. Possible dissociative equilibria involving **2a**–**2c** and initiation of the polymerization of ethylene.

additional electron-withdrawing Cl substituent favor the Chain-Walking mechanism [4].

The total branching degree of the polymer sample obtained with **2a** (entry 4: 31 branches/1000 C) is much lower than those of **2b** and **2c**. This difference is a consequence of the fact that **2a** has less bulky aryl groups (only one methyl substituent in the *ortho* positions) than **2b** and **2c** (two methyl substituents in the *ortho* positions). As can be seen in Table 3, precatalysts **2b** and **2c** give rise to polyethylenes with lower crystallinities, and thus lower melting points, than that produced by **2a**, which supports their higher degree of branching.

3. Conclusions

Three new 20-electron octahedral bis-α-diimine dibromonickel(II) complexes containing different chloro-substituted aryl groups (**2a**–**c**) have been prepared and characterized. These compounds show a pseudo-octahedral geometry around the nickel atom. Complexes **2a**–**c**, when activated by diethylaluminum (DEAC), behave as catalysts for the polymerization of ethylene, showing high activities of the order of those presented by classical 16-electron Brookhart's α-diimine nickel(II) catalysts. The influence of a chlorine substitution in the ligand's aryl rings *meta* and *para* positions was studied, being the higher branching degrees of the polyethylenes synthesized the most important difference in relation to non-chlorinated α-diimine nickel precatalysts. Additionally, the precatalyst **2b**, bearing a Cl substituent in the *meta* position of the ligand's 2,6-dimethylarylimine rings, showed the highest catalytic activity and produced the higher molecular weight polyethylenes, whereas **2c**, bearing a Cl substituents in the *para* position, produces lower molecular weights with similar catalyst activities. Complex **2a**, containing only one methyl substituent in the *ortho* positions and a *meta*-aryl Cl substituent, shows considerably lower activities, branching degrees and molecular weights in relation to those of **2b** and **2c**.

Table 3
Thermal analysis and branching degrees of selected polyethylene samples.

Entry	Precatalyst	T_p (°C)	T_m[a] (°C)	T_d[a] (°C)	χ_c[a] (%)	Branches /1000C[b]
4	**2a**	20	113	383	50.7	31
9	**2b**	20	89	381	24.3	84
10	**2b**	20	94	380	23.1	76
14	**2c**	20	76	382	16.6	82
15	**2c**	20	78	381	0.12	84

[a] Determined by DSC. T_p = polymerization temperature; T_m = melting temperature; T_d = decomposition temperature; χ_c = crystallinity [48].
[b] Estimated by ^{1}H NMR [7].

4. Experimental

4.1. General considerations

All manipulations involving air and/or water sensitive compounds were carried out with standard Schlenk techniques under nitrogen. Methylene chloride and *o*-dichlorobenzene were pre-dried with 4 Å molecular sieves and distilled from CaH_2 under dry nitrogen. Toluene, diethyl ether, and 1, 2-dimethoxyethane (DME) were distilled from sodium/benzophenone under N_2 atmosphere. Anhydrous $NiBr_2$ (99%), Diethylaluminum chloride (DEAC, 0.9 M solution in toluene) were obtained from Acros. 2,3-Butanedione (98%), 3-chloro-2-methylaniline (98%), 3-chloro-2,6-dimethylaniline (98%) and 4-chloro-2,6-dimethylaniline (98%), were purchased from Alfa Aesar, and used without further purification. [$NiBr_2$(DME)] was synthesized according to the literature [49].

NMR spectra were recorded at 400 (^{13}C) and 100 (^{1}H) MHz, respectively, on a Varian Mercury plus-400 instrument, using TMS as internal standard. FTIR spectra were recorded on a Digilab Merlin FTS 3000 FTIR spectrophotometer on KBr pellets. Differential Scanning Calorimetry (DSC) analyses of the polymers were performed on a Perkin–Elmer 7 Series thermal analysis system in the range of 25–250 °C, at a heating rate of 10 °C/min. The molecular weights and molecular weight distributions (MWD) of the polymers were determined by Gel Permeation Chromatography/Size-Exclusion Chromatography (GPC/SEC) via a Waters Alliance GPCV2000 chromatograph, using 1, 2, 4-trichlorobenzene as the eluent, at a flow rate of 1.0 ml/min and operated at 140 °C.

4.2. X-ray structure determinations

Single crystals of complex **2a** suitable for X-ray analysis were obtained at −30 °C by dissolving the nickel complex in CH_2Cl_2, following by slow layering of the subsequent solution with *n*-hexane. Data collections were performed at 296(2) K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo*Kα* radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and refinement parameters are listed in Table 4.

4.3. Syntheses and characterizations of ligands and complexes

The syntheses of ligands **1a**–**c** and the corresponding complexes **2a**–**c** were adapted from the literature [50,51].

*4.3.1. Synthesis of bis[N,N′-(3-chloro-2-methylphenyl)imino]-1,2-dimethylethane (**1a**)*

Formic acid (0.5 ml) was added to a stirred solution of 2,3-butanedione (0.260 g, 3 mmol) and 3-chloro-2-methylaniline (0.850 g, 6 mmol) in methanol (20 ml). The mixture was refluxed for 24 h, then cooled and the precipitate was separated by filtration. The solid was recrystallized from EtOH/CH_2Cl_2 ($v/v = 8:1$), washed with cold ethanol and dried under vacuum. Yield: 0.91 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.11 (s, 6H, Ar–*o*–C*H*$_3$), 2.16 (s, 6H, C–C*H*$_3$), 6.57 (d, 2H, Ar–*H*, $J = 7.2$ Hz), 7.14 (t, 4H, Ar–*H*, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.71 (C–*C*H$_3$) 15.71 (Ar–*C*H$_3$), 116.16 (Ar–*o*-*C*), 124.63 (Ar–*C*–CH$_3$), 125.08 (Ar–*p*-*C*), 126.86 (Ar–*m*–*C*), 135.26 (Ar–*C*–Cl), 150.56 (Ar–*C*–N), 168.25 (*C*=N). FTIR (KBr, cm^{-1}): 1644 ($\nu_{C=N}$). Anal. Calcd. For $C_{18}H_{18}N_2Cl_2$: C, 64.87; H, 5.44; N, 8.41. Found: C, 64.88; H, 5.44; N, 8.40.

*4.3.2. Synthesis of bis[N,N′-(3-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane (**1b**)*

Formic acid (0.5 ml) was added to a stirred solution of 2,3-butanedione (0.260 g, 3 mmol) and 3-chloro-2,6-dimethylaniline (0.934 g, 6 mmol) in methanol (20 ml). The mixture was refluxed for 24 h, then cooled and the precipitate was separated by filtration. The solid was recrystallized from EtOH/CH_2Cl_2 ($v/v = 10:1$), washed with cold ethanol and dried under vacuum. Yield: 0.94 g (88.5%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.93 (d, 6H, Ar–*o*–C*H*$_3$), 1.96 (s, 6H, C–C*H*$_3$), 2.01 (d, 6H, Ar–*o*–C*H*$_3$) 6.93–7.19 (m, 4H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.73 (C–*C*H$_3$), 16.01 (Ar–*o*–*C*H$_3$ near Cl), 17.65 (Ar–*o*–*C*H$_3$), 122.78 (Ar–*C*–*o*–CH$_3$ near Cl), 123.32 (Ar–*C*–*o*–CH$_3$), 123.87 (Ar–*p*–*C*), 128.44 (Ar–*m*–*C*), 132.44 (Ar–*C*–Cl), 149.27 (Ar–*C*–N), 168.63 (*C*=N). FTIR (KBr, cm^{-1}): 1642 ($\nu_{C=N}$). Anal. Calcd. For $C_{20}H_{22}N_2Cl_2$: C, 66.48; H, 6.14; N, 7.75. Found: C, 66.46; H, 6.15; N, 7.76.

Table 4
Crystal data and structure refinements of complex **2a.**

Empirical Formula	$C_{36}H_{36}Br_2Cl_4N_4Ni$
Formula mass	885.02
Temperature (K)	296(2) K
Wavelength (Å)	0.71073
Crystal size (mm^3)	0.38 × 0.36 × 0.35
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	15.260(10)
b (Å)	12.417(8)
c (Å)	23.979(15)
V (Å^3)	4364(5)
Z	4
Density (calcd.) (mg/cm^3)	1.347
Absorption coefficient (mm^{-1})	2.548
F(000)	1784
Theta range for data collec. (°)	2.15 to 25.20
Limiting indices	$-16 \le h \le 18$, $-14 \le k \le 14$, $-28 \le l \le 28$
Reflections collected	28 326
Independent reflections	7829
R_{int}	0.0514
Completeness to $\theta = 25.20°$	99.6%
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0549$, $wR_2 = 0.1229$
R indices (all data)	$R_1 = 0.1026$, $wR_2 = 0.1354$
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.011
Max. and min. transmission	0.4692 and 0.4444
Largest diff. peak and hole (e.Å^{-3})	0.787 and −0.614

*4.3.3. Synthesis of bis[N,N′-(4-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane (**1c**)*

Formic acid (0.5 ml) was added to a stirred solution of 2,3-butanedione (0.260 g, 3 mmol) and 4-chloro-2,6-dimethylaniline (0.934 g, 6 mmol) in methanol (20 ml). The mixture was refluxed for 24 h, then cooled and the precipitate was separated by filtration. The solid was recrystallized from EtOH/CH_2Cl_2 ($v/v = 10:1$), washed with cold ethanol and dried under vacuum. Yield: 1.00 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.00 (s, 12H, Ar–*o*–C*H*$_3$), 2.01 (s, 6H, C–C*H*$_3$), 7.07 (s, 4H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 15.90 (C–*C*H$_3$), 17.69 (Ar–*C*H$_3$), 126.49(Ar–*p*–*C*), 127.68 (Ar–*C*–*o*–CH$_3$), 128.06 (Ar–*C*–Cl), 146.71 (Ar–*C*–N), 168.63 (*C*=N). FTIR (KBr, cm^{-1}): 1640 ($\nu_{C=N}$). Anal. Calcd. For $C_{20}H_{22}N_2Cl_2$: C, 66.48; H, 6.14; N, 7.75. Found: C, 66.46; H, 6.15; N, 7.76.

*4.3.4. Synthesis of bis{bis[N,N′-(3-chloro-2-methylphenyl)imino]-1,2-dimethylethane}dibromonickel (**2a**)*

[$NiBr_2$(DME)] (0.310 g, 1.0 mmol), ligand **1a** (0.733 g, 2.2 mmol) and dichloromethane (40 ml) were mixed in a Schlenk flask and stirred at room temperature for 16 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 16 ml), and then dried under vacuum at room temperature to give catalyst **2a** (0.73 g, 82% yield). FTIR (KBr, cm^{-1}): 1635 ($\nu_{C=N}$). Anal. Calcd. For $C_{36}H_{36}N_4Cl_4NiBr_2$: C, 48.86; H, 4.10; N, 6.33. Found: C, 48.80; H, 4.12; N, 6.34.

*4.3.5. Synthesis of bis{bis[N,N′-(3-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel (**2b**)*

[$NiBr_2$(DME)] (0.310 g, 1.0 mmol), ligand **1b** (0.795 g, 2.2 mmol) and dichloromethane (40 ml) were mixed in a Schlenk flask and stirred at room temperature for 16 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 16 ml), and then dried under vacuum at room temperature to give catalyst **2b** (0.75 g, 79.6% yield). FTIR (KBr, cm^{-1}): 1627 ($\nu_{C=N}$). Anal. Calcd. For $C_{40}H_{44}N_4Cl_4NiBr_2$: C, 51.05; H, 4.71; N, 5.95. Found: C, 51.02; H, 4.77; N, 5.91.

*4.3.6. Synthesis of bis{bis[N,N′-(4-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel (**2c**)*

[$NiBr_2$(DME)] (0.310 g, 1.0 mmol), ligand **1c** (0.795 g, 2.2 mmol) and dichloromethane (40 ml) were mixed in a Schlenk flask and stirred at room temperature for 16 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 16 ml), and then dried under vacuum at room temperature to give catalyst **2c** (0.84 g, 89.3% yield). FTIR (KBr, cm^{-1}): 1629 ($\nu_{C=N}$). Anal. Calcd. For $C_{40}H_{44}N_4Cl_4NiBr_2$: C, 51.05; H, 4.71; N, 5.95. Found: C, 51.01; H, 4.79; N, 5.93.

4.4. Procedure for the polymerization of ethylene

The polymerization of ethylene was carried out in a flame dried 250 ml crown capped pressure bottle sealed with neoprene septa. After drying the polymerization bottle under N_2 atmosphere, 50 ml of dry toluene was added to the polymerization bottle. The resulting solvent was then saturated with a prescribed ethylene pressure. The co-catalyst (MAO) was then added in Al/Ni molar ratios in the range of 600–1500 to the polymerization bottle via a syringe. At this time, the solutions were thermostated to the desired temperature and allowed to equilibrate for 15 min. Subsequently, an *o*-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. The polymerization, conducted under a dynamic pressure of ethylene (absolute pressure = 1.2 bar), was terminated by quenching the reaction mixtures with 100 ml of a 2% HCl–MeOH solution. The precipitated polymer was filtered, washed with methanol and dried under vacuum at 60 °C to a constant weight.

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Appendix A. Supplementary material

CCDC 809390 contains the supplementary crystallographic data for complex **2a**. 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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