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Nickel complexes bearing *N*,*N*,*N*-tridentate quinolinyl anilido–imine ligands: Synthesis, characterization and catalysis on norbornene addition polymerization

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The *N*,*N*,*N*-tridentate quinolinyl anilido–imine ligands 2-(ArNC(H))C_6H_4–HNC_9H_6N (**L$_a$H**, Ar = 2,6-$Me_2C_6H_3$; **L$_b$H**, Ar = 2,6-$^iPr_2C_6H_3$) and 2-(C_9H_6N)NC(H)C_6H_4–HNAr (**L$_c$H**, Ar = 2,6-$Me_2C_6H_3$; **L$_d$H**, Ar = 2,6-$^iPr_2C_6H_3$) were synthesized and characterized. Reactions of these ligands with ^{n}BuLi and subsequent additions of $NiCl_2$(DME) afford the *N*,*N*,*N*-tridentate nickel complexes [2-(ArNC(H))C_6H_4–NC_9H_6N]NiCl (Ar = 2,6-$Me_2C_6H_3$ (**1a**), 2,6-$^iPr_2C_6H_3$ (**1b**)) and [2-(C_9H_6N)NC(H)C_6H_4–NAr]NiCl (Ar = 2,6-$Me_2C_6H_3$ (**2a**), 2,6-$^iPr_2C_6H_3$ (**2b**)). All the complexes were fully characterized by NMR and elemental analyses. X-ray diffraction analyses of **1b** and **2b** revealed an almost square-planar geometry around the metal center. When activated with MAO, these nickel complexes can be used as catalysts for the vinyl addition polymerization of norbornene affording high molecular weight polymer.

1. Introduction

In the past decades, late-transition metal catalysts for olefin polymerization have attracted considerable attention in both the academic and industrial fields due to their low electrophilicity and more heteroatom tolerance [1]. Since the discovery that the bulky α-diimine nickel(II) complexes can act as highly active catalysts in ethylene polymerization [2], a large amount of late-transition metal complexes were investigated, in which the nickel complexes [3–6] have drawn great attention for their high activities and good catalytic performance. Various bidentate ligands such as NN [7], NP [8], PO [9], and NO [5a,10] and tridentate NNN [4b–e,11], NPN [12] and NNO [13] were tested in supporting the nickel complexes for olefin polymerization. Recently the anilido-imine ligands, which feature easy preparation and modification of the steric and electronic demands, have been widely investigated in supporting rare-earth metal complexes and early transition metal complexes [14]. Some nickel complexes bearing anilido-imine ligands were investigated as catalysts for olefin polymerization. The cationic nickel complexes [15] and nickel(I) complexes [3e] bearing anilido–imine ligands show high activity in norbornene polymerization. Intrigued by these pioneering work, some modification on the anilido–imine ligands were made and some donor groups were introduced into the imine moieties forming the tridentate anilido–imine ligands. The modified anilido–imine tridentate ligands have been used to support various metal complexes. For example, the rare-earth metal alkyls bearing methoxyl-group decorated anilido-imine tridentate ligands can initiate the polymerization of lactide in single-site manner. The coordination of the methoxyl group to the metal center was believed to prevent the back-biting reaction in polymerization [16]. Jin group have incorporated the soft sulfur or phosphine groups into the anilido–imine ligands and the Ni and Pd complexes with these tridentate ligands show higher activity toward norbornene polymerization than those with the bidentate analogs [3f]. Recently we have introduced the quinolinyl group into the amine moieties giving the quinolinyl anilido–imine ligands and the rare-earth-metal complexes [17] and Al (Zn) complexes [18] bearing such ligands show high activity for ε-caprolactone or lactide polymerization and the polymerization were performed in living or immortal manner. The coordination of the quinolinyl group was believed to render the metal center more steric controllabilities and play an important role in the polymerization. In order to extend the investigation of the anilido–imine ligands in supporting the late transition metal complexes for olefin polymerization, we also introduce the quinolinyl group into the imino moieties. Herein we report a series of nickel(II) complexes bearing tridentate quinolinyl anilido-imino ligands, together with their catalytic activity for norbornene polymerization.

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2. Results and discussion

2.1. Synthesis of the N,N,N-tridentate ligands

The ligands L_aH and L_bH were synthesized according to the literature and characterized with ^1H NMR and ^{13}C NMR spectroscopy [17]. The 2-(arylamino)benzaldehyde were prepared by coupling reactions of the 1,3-dioxolane protected 2-bromobenzaldehyde with 2,6-dimethylaniline or 2,6-diisopropylaniline in toluene using $Pd(OAC)_2$ as catalysts [18]. The ligands L_cH and L_dH were prepared by condensation of the 2-(arylamino)benzaldehyde with 8-amine-quinoline in hexane in the presence of catalytic amount of formic acid (Scheme 1). The ^1H NMR spectra of L_cH and L_dH show similar patterns in low field and the characteristic singlets for *H*C═N were found at 8.86–8.87 ppm, which shift to high field with respect to that in L_aH and L_bH. Additionally, the singlets of Ar–N*H* in L_cH and L_dH at 11.02–11.10 ppm are slightly shifted to low field compared with those in L_aH and L_bH. It is worth to note that, in the high field, L_dH shows two sets of doublets for $CH(CH_3)_2$ suggesting that the two *ortho* groups are in different environments. This may attribute to that the N_{amino} atom is sp^2 hybridized and the empty *p* orbitals interact with the π systems of the attached phenyl ring. The *p*–π interaction inhibits the free rotations of Ar–N bonds, leaving the two *ortho* isopropyl groups in different chemical environments.

2.2. Synthesis and characterization of the N,N,N-tridentate nickel complexes

The *N,N,N*-tridentate nickel complexes **1a** and **1b** were synthesized *via* a conventional lithium-salt metathesis reaction. The lithium salts of L_aH and L_bH were prepared *in-situ* by addition of the ^{n}BuLi to the solution of ligands in THF at low temperature. After stirring at low temperature for 30 min, the $NiCl_2(DME)$ was added in one portion and the resulted mixtures were allowed to warm to room temperature. Evaporation of the solvent and re-crystallization the residues with toluene/hexane mixed solvent afford the nickel complexes **1a** and **1b** as red powder (Scheme 2). The nickel complexes were characterized by elemental analyses, ^1H NMR, and ^{13}C NMR spectroscopy. For both complexes, the signals of –N*H* disappeared and the singlets resonance for *H*C═N were observed at 7.14–7.16 ppm, which were shifted upfield when compared to those in the free ligands (L_aH and L_bH). The signals of *ortho* substituents in the high field are shifted to low field. In **1b** two separated doublets for the $CH(CH_3)_2$ were found ($\Delta\delta = 0.41$ ppm), which suggested that the methyls in isopropyl groups are in different chemical environments. As can be seen from the molecular structure of **2b** (*vide infra*), the coordination of imine groups to the nickel inhibits the free rotation of the N-aryl bond and the two ^{i}Pr groups are therefore in different environments. Crystals of **1b** suitable for single crystal X-ray diffraction analysis were grown from CH_2Cl_2/hexane mixed solvent. The molecular structure is depicted in Fig. 1. The nickel atom in **1b** is in distorted square planar environment ligated by the *N,N,N* ligand and one chlorine atom. The N_{imine} atom and $N_{quinolinyl}$ atom are located in *trans* position and the N-aryl ring disposes the vertical position against the parent plane. The whole molecule is twisted with the dihedral angle between the quinolinyl ring and the parent ring being 40.70(6)°.

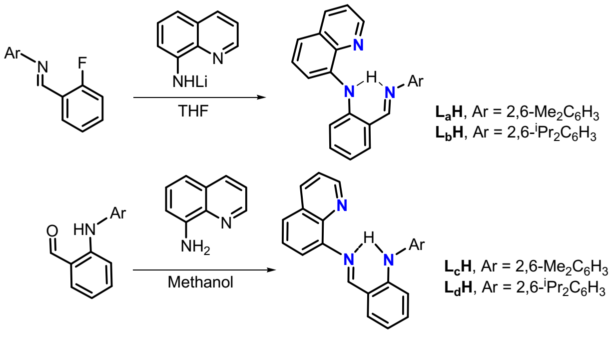
The nickel atom is almost coplanar with the plane defined by N1, N2, N3, Cl1 with the max deviation of 0.0365(8) Å. The Ni–N1 bond distance of 1.879(2) Å is slightly shorter than that of Ni–N3 (1.906(2) Å). While the Ni–N2 bond distance of 1.930(2) Å is much longer than those in the Ni–N1 and Ni–N3, and is also longer than those in NNP nickel complex [3f].

Complexes **2a** and **2b** were prepared in a similar procedure to that for preparation of **1a** and **1b** as shown in Scheme 3. Treatment of the ligands (L_cH and L_dH) with ^{n}BuLi at low temperature and subsequent addition of $NiCl_2(DME)$ gave complexes **2a** and **2b** as purple powder in moderate yields. Complexes **2a** and **2b** were fully characterized with elemental analysis and NMR spectroscopy. The ^1H NMR spectra of **2a** and **2b** show similar patterns in aromatic region and the singlets for *H*C═N groups are shifted upfield with respect to that in L_cH and L_dH. In the aliphatic area the resonances for *ortho* groups are shifted slightly to low field when compared to those in corresponding free ligands. Moreover, in **2b** two widely separated doublets for the $CH(CH_3)_2$ were found ($\Delta\delta = 0.60$ ppm). We reasoned that the coordination of the imino group to the nickel as well as the repulsions of the bulky *ortho* groups with the adjacent parent ring inhibit the free rotations of C–N bond in amino moieties and the methyls in two isopropyl group are in different environments.

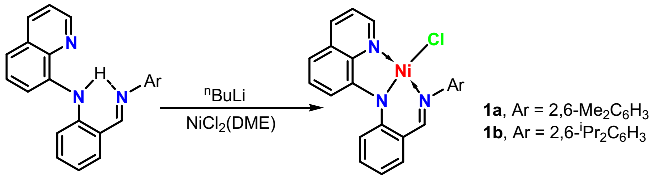
The molecular structure of **2b** was determined by X-ray diffraction analysis (Fig. 2). The unit cell of **2b** contains two crystallographically-independent molecules which possess similar connectivity. The nickel atoms in **2b** were ligated by the *N,N,N* tridentated ligand and a chlorine group, and the geometries around them can be best described as a distorted square planar. It is worth to note that in one molecule the quinolinyl moiety is essentially coplanar with the parent phenyl ring with the little dihedral angle (5.03(9)°). While in the other molecule the two rings are twisted slightly with the dihedral angle being 18.46(9)°. The bond distances of $Ni–N_{amino}$ (1.897(3) Å and 1.901(3) Å), $Ni–N_{imino}$ (1.937(3) Å, and 1.941(3) Å), and $Ni–N_{quinolinyl}$ (1.876(3) Å and 1.906(3) Å) are all comparable to those in **1b** and those in other anilido–imino nickel complexes [3e,3f,15].

2.3. Norbornene polymerization with nickel complexes

The nickel complexes were tested to initiate the norbornene polymerization. The selective data were summarized in Table 1. The results showed that, activated with MAO, the nickel complexes show moderate activities in norbornene polymerization at room temperature and the activities of 0.68×10^5–1.06×10^5 g PNB (mol of Ni)$^{-1}$ h^{-1} were obtained (entry 1–4). It is worth to note that in the catalytic system involving **1a** and **1b** the *ortho* substituents of the ligands shows strong influences on the activities. Complex **1b**



Scheme 1. Synthesis route of the *N,N,N*-tridentate ligands.



Scheme 2. Synthesis route of **1a** and **1b**.

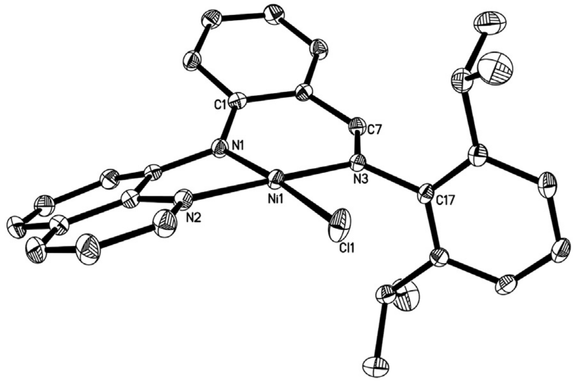
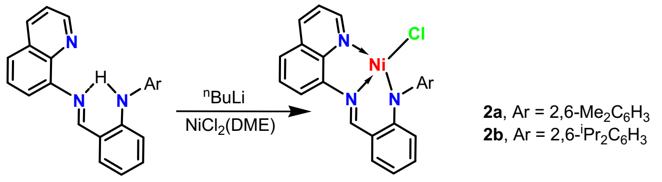


Fig. 1. Perspective view of complex **1b** with thermal ellipsoids drawn at 30% probability level. Uncoordinated solvents and hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Ni(1)–N(1) 1.879(2), Ni(1)–N(2) 1.930(2), Ni(1)–N(3) 1.906(2), Ni(1)–Cl(1) 2.187(1), C(1)–N(1) 1.378(2), C(7)–N(3) 1.301(3); N(1)–Ni(1)–Cl(1) 174.96(5), N(3)–Ni(1)–N(2) 175.49(7), N(1)–Ni(1)–N(3) 92.36(7).



Scheme 3. Synthesis route of the **2a** and **2b**.

with bulky *ortho* substituents is more active than **1a** under same conditions. This might be ascribed to the differences in the stabilities of the resulted active species during the polymerization. Complexes with bulky substituents at the axial position may be more stable and can survive for long time. Interestingly, complex **2a** and complex **2b** show almost the same activities under the same conditions. It is more possible that in the systems with **2a** and **2b** the electronic effects rather than the steric effects play the key roles in the polymerization. In order to investigated the reaction parameters affecting the polymerization of norbornene complex **1b** was studied under different reaction conditions such as different Al/Ni molar ratios, and different temperature. Variations of the ratio of MAO to **1b** show significant effect on catalytic activity and the molecular-weight of the obtained polymers. As shown in Table 1, catalytic activity of **1b** increased rapidly firstly with increases in Al/Ni ratios, and then remained steady after the Al/Ni reached about 1500:1. Correspondingly molecular weights of the polymers gradually decrease from 8.61 × 10^5 to 0.83 × 10^5. This is may ascribe to the more efficient chain transfer at high Al/Ni ratios. Catalyst activity and molecular weights of the resultant polymers were also dramatically influenced by the polymerization temperature. When the polymerization temperature increased from 20 °C to 60 °C, the activities gradually decreased from 3.32 × 10^5 g PNB (mol of Ni)$^{-1}$ h^{-1} to 0.38 × 10^5 g PNB (mol of Ni)$^{-1}$ h^{-1}. This is perhaps due the deactivation of the active species at high temperature. The molecular-weight of the polymer also decreases with the increase of the polymerization temperature. This may probably due to the higher chain transfer rates at high temperature. The FT-IR spectra of the resulted polymer show the characteristic peak of polynorbornene in the range of 940 cm^{-1} to 943 cm^{-1} which can be assigned to the vinyl addition polymer. No detectable absorption peaks at 960 cm^{-1} was found suggesting that the norbornene polymerization initiated by the nickel complexes and MAO were performed in vinyl addition manner [19].

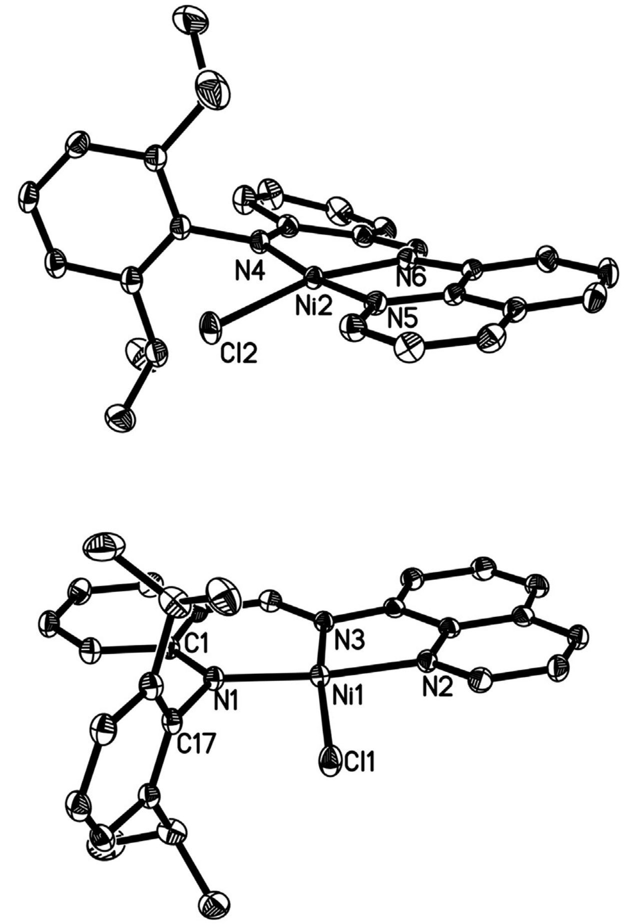


Fig. 2. Perspective view of complex **2b** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Ni(1)–N(1) 1.901(3), Ni(1)–N(2) 1.941(3), Ni(1)–N(3) 1.882(3), Ni(2)–N(4) 1.897(3), Ni(2)–N(5) 1.937(3), Ni(2)–N(6) 1.876(3), Ni(1)–Cl(1) 2.1965(10), Ni(2)–Cl(2) 2.1858(9); N(1)–Ni(1)–N(3) 93.81(12), N(3)–Ni(1)–Cl(1) 167.63(9), N(1)–Ni(1)–N(2) 173.58(12), N(4)–Ni(2)–N(6) 93.69(12), N(6)–Ni(2)–Cl(2) 166.62(9), N(4)–Ni(2)–N(5) 172.88(12).

Table 1
Addition polymerization of norbornene with nickel complexes activated by methylaluminoxane (MAO).[a]

Entry	Cat	Al/Ni	M/I	Time, (min)	Temp, (°C)	Yield,[b] (g)	Activity[c]	M_v,[d] × 10^5
1	**1a**	500	2000	60	20	0.34	0.68	4.79
2	**1b**	500	2000	60	20	0.53	1.06	8.61
3	**2a**	500	2000	60	20	0.51	1.01	15.72
4	**2b**	500	2000	60	20	0.50	1.00	12.17
5	**1b**	500	1000	60	20	0.26	0.53	n.d.
6	**1b**	500	1500	60	20	0.26	0.53	3.63
7	**1b**	500	3000	30	20	0.92	1.85	2.55
8	**1b**	500	4000	90	20	1.28	2.57	8.60
9	**1b**	500	5000	120	20	1.65	3.32	8.28
10	**1b**	500	2000	60	40	0.22	0.46	1.85
11	**1b**	500	2000	60	60	0.18	0.38	0.67
12	**1b**	1000	2000	60	20	0.63	1.27	2.37
13	**1b**	1500	2000	60	20	0.72	1.45	1.12
14	**1b**	2000	2000	60	20	0.73	1.47	0.83

[a] Polymerization conditions: toluene 15 mL; catalyst, 5 μmol; M/I = monomer/initiator in mole ratio.

[b] Isolated yield.

[c] In units of 10^5 g (mol of Ni)$^{-1}$ h^{-1}.

[d] Obtained by capillary viscosimetry using the Mark–Houwink coefficients $a = 0.56$, $K = 7.78 \times 10^{-4}$ dl/g.

3. Conclusions

Four nickel complexes bearing *N*,*N*,*N*-tridentated quinolinyl anilido-imine ligands have been synthesized and characterized. The nickel complexes exhibit square planar coordination around the metal center. When activated with MAO, these nickel complexes show moderate activities in vinyl-addition polymerization of norbornene.

4. Experimental section

4.1. General methods

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk or dry box techniques. Toluene and hexane were dried over sodium/benzophenone and distilled under nitrogen prior to use. Elemental analyses were performed on a Varian EL microanalyzer. NMR spectra were recorded on a Varian Mercury-300 NMR spectrometer at room temperature in $CDCl_3$. 2,6-dimethylaniline and 2,6-diisopropylaniline were purchased from Aldrich.

4.2. Synthesis of (2-(2,6-dimethylphenylamino)benzaldehyde)

2,6-Dimethylaniline (3.00 g, 24.8 mmol), $Pd(OAc)_2$ (43.6 mg, 0.194 mmol), NaO^{t}Bu (2.86 g, 29.7 mmol), bis[2-(diphenylphosphino)phenyl]ether (DPEphos) (160.5 mg, 0.298 mmol), 1,3-dioxolane protected 2-bromobenzaldehyde (6.27 g, 27.3 mmol) and degassed toluene (50 mL) were added into a flask. After stirring at 100 °C for 10 h, water (40 mL) and toluene (100 mL) were added and the toluene phase was collected. *p*-TsOH (2.08 g) was added and the solution was stirred for 2 h and washed with concentrated aqueous $NaHCO_3$ (30 mL). The organic solution was dried with anhydrous $MgSO_4$ and the solvent was removed by rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with ethyl acetate and petroleum ether (v/v, 1:30). Yield (3.91 g, 70%). Anal. Calcd for $C_{15}H_{15}NO$ (%): C, 79.97; H, 6.71; N, 6.22. Found: C, 79.81; H, 6.67; N, 6.28. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.19 (s, 6H, C*H*$_3$), 6.21 (d, ^3J = 8.4 Hz, 1H, Ar–*H*), 6.76 (m, 1H, Ar–*H*), 7.16 (s, 3H, Ar–*H*), 7.29–7.22 (m, 1H, Ar–*H*), 7.56 (dd, ^3J = 7.8 Hz, J = 1.6 Hz, 1H, Ar–*H*), 9.55 (s, 1H, Ar–C*H*O), 9.96 (s, 1H, Ar–N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.3 (s, 2C, Ar*C*H$_3$), 116.0, 118.4, 112.3, 127.0, 128.6, 135.8, 136.4, 136.7, 149.6, 194.3 (s, 1C, *C*H=N) ppm.

4.3. Synthesis of 2-(8-(C_9H_6N)NC(H)C_6H_4–HN(2,6-$Me_2C_6H_3$)) (**L$_c$H**)

To a solution of 2-(2,6-dimethylphenylamino)benzaldehyde (2.25 g, 10.0 mmol) in hexane (30 mL) quinolin-8-amine (1.6 g, 11.0 mmol) and few drops of formic acid were added. After refluxing for 12 h, the resulted mixture was evaporated to dryness. Treatment of the residue with methanol affords the L$_c$H as yellow powder. Yield 2.28 g (65%). Anal. Calcd for $C_{24}H_{21}N_3$ (%): C, 82.02; H, 6.02; N, 11.96. Found: C, 82.12; H, 6.07; N, 11.91. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.36 (s, 6H, C*H*$_3$), 6.33 (d, ^3J = 6.0 Hz, 1H, Ar–*H*), 6.72 (m, 1H, Ar–*H*), 7.07–7.20 (m, 4H, Ar–*H*), 7.37–7.41 (m, 2H, Ar–*H*), 7.45–7.48 (m, 1H, Ar–*H*), 7.54 (t, ^3J = 9.0 Hz, 1H, Ar–H), 7.62–7.65 (m, 1H, Ar–*H*), 8.13 (dd, ^3J = 9.0 Hz, J = 1.7 Hz, 1H, Ar–*H*), 8.86 (s, 1H, Ar–C*H*=N), 8.88 (dd, ^3J = 4.1 Hz, J = 1.6 Hz, 1H, Ar–*H*), 11.10 (s, 1H, Ar–N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.77 (s, 2C, Ar*C*H$_3$), 112.17, 115.64, 117.88, 118.17, 121.59, 125.00, 126.17, 128.45, 129.24, 132.36, 134.97, 135.92, 136.78, 138.25, 142.85, 148.62, 149.19, 150.08, 164.57 (s, 1C, *C*H=N) ppm.

4.4. Synthesis of 2-(8-(C_9H_6N)NC(H)C_6H_4–HN(2,6-$Me_2C_6H_3$)) (**L$_d$H**)

To a solution of 2-(2,6-diisopropylphenylamino)benzaldehyde (2.81 g, 10.0 mmol) in hexane (30 mL), quinolin-8-amine (1.60 g, 11.0 mmol) and few drops of formic acid were added. After refluxing for 12 h, the hexane was removed under reduced pressure. Treatment of the residue with methanol affords the L$_d$H as yellow powder. Yield 2.72 g (67%). Anal. Calcd for $C_{28}H_{29}N_3$ (%): C, 82.52; H, 7.17; N, 10.31. Found: C, 82.61; H, 7.20; N, 10.28. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.16 (d, ^3J = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, ^3J = 9.0 Hz, 6H, CH(C*H*$_3$)$_2$), 3.29–3.38 (m, 2H, C*H*(CH$_3$)$_2$), 6.29 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 6.69 (m, 1H, Ar–*H*), 7.11–7.16 (m, 2H, Ar–*H*), 7.24–7.27 (m, 3H, Ar–*H*), 7.35–7.41 (m, 2H, Ar–*H*), 7.44–7.47 (m, 1H, Ar–*H*), 7.55 (t, ^3J = 9.0 Hz, 1H, Ar–H), 7.63–7.65 (m, 1H, Ar–*H*), 8.13 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 8.84–8.86 (m, ^3J = 4.1 Hz, J = 1.6 Hz, 1H, Ar–*H*), 8.87 (s, 1H, Ar–C*H*=N), 11.02 (s, 1H, Ar–N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 23.27 (s, 2C, ArC(*C*H$_3$)$_2$), 25.02 (s, 2C, ArC(*C*H$_3$)$_2$), 28.71 (s, 2C, Ar*C*(CH$_3$)$_2$), 112.36, 115.31, 117.43, 118.26, 121.57, 123.87, 124.89, 126.91, 129.25, 132.23, 134.86, 135.42, 135.87, 142.80, 147.90, 149.38, 150.06, 150.38, 164.76 (s, 1C, *C*H=N) ppm.

4.5. Synthesis of [2-(2,6-$Me_2C_6H_3$NC(H)C_6H_4–NC_9H_6N)]NiCl (**1a**)

A hexane solution of ^{n}BuLi (0.66 mL, 1.05 mmol) was added dropwise to a THF (20 ml) solution of L$_a$H (0.35 g, 1.00 mmol) at −78 °C. The mixture was stirred for 1 h and then $NiCl_2$(DME) (0.22 g, 1.00 mmol) was added. The reaction mixture was allowed to warm gradually to room temperature and stirred overnight. The solvent was removed under reduce pressure and the residue was treated with toluene, after evaporation of the toluene to dryness, the product was obtained as purple powder. Yield, 0.37 g (85%). Anal. Calcd for $C_{24}H_{20}ClN_3Ni$ (%): C, 64.84; H, 4.53; N, 9.45. Found: C, 64.75; H, 4.61; N, 9.60. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.82 (s, 6H, C*H*$_3$), 6.69 (t, ^3J = 6.0 Hz, 1H, Ar–*H*), 7.07 (s, 1H, *H*C=N), 7.12 (d, ^3J = 9.0 Hz, 1H Ar–H), 7.23–7.30 (m, 5H Ar–H), 7.40 (t, ^3J = 9.0 Hz, 1H, Ar–H), 7.67 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 7.95 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 8.17 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 8.67 (d, ^3J = 6.0 Hz, 1H, Ar–*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 20.03 (s, 2C, Ar*C*H$_3$), 116.45, 116.94, 117.41, 118.03, 121.47, 126.13, 128.01, 128.23, 133.68, 134.07, 138.66, 151.36, 164.37 (s, 1C, *C*H=N) ppm.

4.6. Synthesis of [2-(2,6-^{i}Pr$_2$$C_6H_3$NC(H)$C_6H_4$–N$C_9H_6$N)]NiCl (**1b**)

Complex **1b** was synthesized in the same procedure as that for **1a** with L$_b$H (0.41 g, 1.00 mmol) and $NiCl_2$(DME) (0.22 g, 1.00 mmol) as starting materials or reagents. Pure **1b** was obtained as purple powder. Yield: 0.44 g (88%). Single crystals for X-ray diffraction analysis were obtained from hexane/THF mixed solution. Anal. Calcd for $C_{28}H_{28}ClN_3Ni$ (%): C, 67.17; H, 5.64; N, 8.39. Found: C, 67.25; H, 5.60; N, 8.48. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.17 (d, J_{H-H} = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.59 (d, ^3J = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 4.27 (sept, ^3J = 6.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.69 (t, ^3J = 6.0 Hz, 1H, Ar–*H*), 7.11 (s, 1H, *H*C=N), 7.12 (d, ^3J = 9.0 Hz, 1H Ar–H), 7.23–7.30 (m, 5H Ar–H), 7.41 (t, ^3J = 9.0 Hz, 1H, Ar–H), 7.69 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 7.96 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 8.16 (d, ^3J = 9.0 Hz, 1H, Ar–*H*), 8.69 (d, ^3J = 6.0 Hz, 1H, Ar–*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 23.89 (s, 2C, ArCH(*C*H$_3$)$_2$), 24.79 (s, 2C, ArCH(*C*H$_3$)$_2$), 29.31 (s, 2C, Ar*C*H(CH$_3$)$_2$), 116.41, 116.91, 117.43, 117.08, 121.47, 123.37, 123.91, 126.84, 128.18, 129.17, 133.63, 134.11, 138.58, 141.51, 145.58, 148.07, 149.32, 149.38, 151.51, 164.32 (s, 1C, *C*H=N) ppm.

4.7. Synthesis of [2-(8-(C_9H_6N)NC(H)C_6H_4–N(2,6-$Me_2C_6H_3$))]NiCl (**2a**)

Complex **2a** was synthesized in the same manner as **1a** with L_cH (0.35 g, 1.00 mmol) and $NiCl_2$(DME) (0.22 g, 1.00 mmol) as starting materials or reagents. Pure **2a** was obtained as purple powder. Yield: 0.35 g (79%). Anal. Calcd for $C_{24}H_{20}ClN_3Ni$ (%): C, 64.84; H, 4.53; N, 9.45. Found: C, 64.97; H, 4.66; N, 9.51. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.55 (s, 6H, CH_3), 6.04 (d, $^3J = 9.0$ Hz, 1H, Ar–*H*), 6.34 (t, $^3J = 6.0$ Hz, 1H, Ar–*H*), 6.80 (m, 1H, Ar-*H*), 7.00–7.09 (m, 3H, Ar-*H*), 7.26 (dd, $^3J = 6.0$ Hz, $J = 1.6$ Hz, 1H, Ar–*H*), 7.35–7.40 (m, 1H, Ar–H), 7.54–7.62 (m, 2H, Ar–*H*), 7.84 (dd, $^3J = 6.0$ Hz, $J = 1.2$ Hz, 1H, Ar–*H*), 8.14 (s, 1H, Ar–C*H*=N), 8.20 (dd, $^3J = 6.0$ Hz, $J = 1.1$ Hz, 1H, Ar–*H*), 9.19 (dd, $^3J = 6.0$ Hz, $J = 1.2$ Hz, 1H, Ar–*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 19.46 (s, 2C, CH_3), 114.63, 114.69, 118.31, 118.80, 122.69, 123.86, 124.72, 127.99, 128.42, 134.21, 134.28, 134.60, 138.30, 143.25, 147.32, 151.03, 152.66, 154.26 ppm.

4.8. Synthesis of [2-(8-(C_9H_6N)NC(H)C_6H_4–N(2,6-$^iPr_2C_6H_3$))]NiCl (**2b**)

Complex **2b** was synthesized in the same manner as **1a** with L_dH (0.41 g, 1.00 mmol) and $NiCl_2$(DME) (0.22 g, 1.00 mmol) as starting materials or reagents. Pure **2b** was obtained as purple powder. Yield: 0.41 g (82%). Single crystals for X-ray diffraction analysis were obtained from CH_2Cl_2/hexane mixed solution. Anal. Calcd for $C_{28}H_{28}ClN_3Ni$ (%): C, 67.17; H, 5.64; N, 8.39. Found: C, 67.28; H, 5.74; N, 8.53. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.01 (d, $^3J = 6.0$ Hz, 6H, CH(CH_3)$_2$), 1.61 (d, $^3J = 6.0$ Hz, 6H, CH(CH_3)$_2$), 3.95 (sept, 2H, C*H*(CH_3)$_2$), 6.01 (d, $^3J = 9.0$ Hz, 1H, Ar–*H*), 6.32 (t, $^3J = 9.0$ Hz, 1H, Ar–*H*), 6.71–6.77 (m, 2H, Ar–*H*), 7.12–7.14 (m, 2H, Ar–*H*), 7.20–7.25 (m, 3H, Ar–*H*), 7.33–7.37 (m, 1H, Ar–*H*), 7.57 (t, $^3J = 9.0$ Hz, 1H, Ar–*H*), 7.57 (d, $^3J = 12.0$ Hz, 1H, Ar–*H*), 7.87 (d, $^3J = 9.0$ Hz, 1H, Ar–*H*), 8.18 (m, 1H, Ar–*H*), 8.19 (s, 1H, Ar–C*H*=N), 9.20 (d, 1H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 24.57 (s, 2C, ArC(CH_3)$_2$), 24.73 (s, 2C, ArC(CH_3)$_2$), 28.84 (s, 2C, Ar*C*(CH_3)$_2$), 114.51, 114.66, 117.47, 120.90, 122.59, 123.48, 125.44, 128.35, 133.08, 134.50, 138.22, 142.90, 143.59, 147.13, 147.21, 148.42, 151.00, 153.70, 154.43 ppm.

4.9. General procedure for norbornene polymerization

A 0.5 ml aliquot of a fresh catalyst solution (toluene, 5 μmol catalyst), 4.0 ml of a solution of norbornene (20 mmol) in toluene and 10.5 ml toluene were added under inert gas atmosphere into a Schlenk flask with a mechanical stirrer. The reaction was started by the addition of 5 ml of a MAO solution (5 mmol MAO in toluene). The total reaction volume was 20 ml, which was achieved by variation of the amount of toluene if necessary. After desired period of time, acidic ethanol was injected into the Schlenk flask to end the reaction and the reaction mixture was poured into 200 ml of acidic ethanol. The polymer was isolated by filtration, washed with acetone and dried under vacuum at 80 °C for 24 h.

4.10. Crystal structure determination

The crystals were mounted on a glass fiber using the oil drop. Data obtained with the $\omega - 2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, and refined with full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages.

4.10.1. Crystal data for **1b**

$C_{31}H_{35}ClN_3Ni$, M = 543.78, monoclinic, $P2_1/n$, $a = 14.2122(9)$, $b = 13.7132(9)$, $c = 15.0734(10)$ Å, $\beta = 109.9600(10)°$, $V = 2761.3(3)$ Å^3, $Z = 4$, $D_{calc} = 1.308$ g cm^{-3}, 16,720 measured intensities ($1.70° \le \theta \le 26.05°$), 5442 independent ($R_{int} = 0.0277$) diffraction data, $R = 0.0349$, $wR = 0.0820$ for data ($I \ge 2\sigma(I)$), $R_{all} = 0.0457$, $wR_{all} = 0.0875$ for all data. CCDC (949273).

4.10.2. Crystal data for **2b**

$C_{28.5}H_{29}Cl_{1.5}N_3Ni$, $M = 522.43$, triclinic, P-1, $a = 10.8383(5)$, $b = 14.2146(7)$, $c = 17.0475(8)$ Å, $\alpha = 103.3220(10)°$, $\beta = 97.7830(10)°$, $\gamma = 100.4710(10)$, $V = 2469.6(2)$ Å^3, $Z = 4$, $D_{calc} = 0.971$ g cm^{-3}, 14,613 measured intensities ($1.51° \le \theta \le 26.05°$), 9492 independent ($R_{int} = 0.0166$) diffraction data, $R = 0.0525$, $wR = 0.1341$ for data ($I \ge 2\sigma(I)$), $R_{all} = 0.0653$, $wR_{all} = 0.1431$ for all data. CCDC (949274).

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