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Synthesis and characterization of novel neutral nickel complexes bearing fluorinated salicylaldiminato ligands and their catalytic behavior for vinylic polymerization of norbornene

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A series of salicylaldimine-based neutral Ni(II) complexes (3a–j) [$ArN=CH(C_6H_4O)$]$Ni(PPh_3)Ph$ [3a, $Ar = C_6H_5$; 3b, $Ar = C_6H_4F$(*o*); 3c, $Ar = C_6H_4F$(*m*); 3d, $Ar = C_6H_4F$(*p*); 3e, $Ar = C_6H_3F_2$(2,4); 3f, $Ar = C_6H_3F_2$(2,5); 3g, $Ar = C_6H_3F_2$(2,6); 3h, $Ar = C_6H_3F_2$(3,5); 3i, $Ar = C_6H_2F_3$(3,4,5); 3j, $Ar = C_6F_5$] have been synthesized in good yield, and the structures of complexes 3a and 3i have been confirmed by X-ray crystallographic analysis. Using modified methylaluminoxane as a cocatalyst, these neutral Ni(II) complexes exhibited high catalytic activities for the vinylic polymerization of norbornene. It was observed that the strong electron-withdrawing effect of the fluorinated salicylaldiminato ligand was able to significantly increase the catalyst activity for vinylic polymerization of norbornenes. In addition, catalyst activity, polymer yield and polymer molecular weight can also be controlled over a wide range by the variation of reaction parameters such as Al : Ni ratio, norbornene : catalyst ratio, monomer concentration, polymerization temperature and time.

Keywords: neutral nickel complexes; catalyst; electronic effect; norbornene; addition polymerization

Introduction

It is well known that strained norbornene can polymerize via ring-opening metathesis, cationic mechanism or coordination catalysis, which leads to their corresponding polymers with different structures and properties.[1] The coordination polymerization of norbornene yields 2,3-connected, rotationally strongly constrained vinyl-type polynorbornene, which results in unique physical properties, such as high chemical resistance, good UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, high refractive index, and low birefringence.[2,3]

Vinyl-type polynorbornenes can be prepared by transition metal catalysts based on nickel,[4–15] chromium,[16,17] titanium,[18,19] zirconium,[20,21] cobalt,[17,22,23] palladium[24–33] and copper complexes.[34,35] Zirconocenes and cationic palladium complexes are two important types of catalysts for vinylic polymerization of norbornene. Zirconocenes exhibit only low catalytic activity and afford high molecular weight polymers that decompose in air at high temperatures before melting, and are insoluble in organic solvents.[20,21] Cationic palladium complexes, such as $[Pd(CH_3CN)_4]-[BF4]_2$, display extremely high catalytic activity and produce high molecular weight polymers that are soluble in organic solvents, such as chlorobenzene and *o*-dichlorobenzene, and possess high glass transition temperatures ($T_g > 350\,^{\circ}C$). Recently, research in our group and in other groups indicate that well-defined neutral nickel(II) complexes are also efficient catalysts for vinylic polymerization of norbornene in the presence of methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), producing high molecular weight and amorphous polynorbornenes displaying good thermal stability.[36–44] We find little steric influence of salicylaldiminato ligand on catalytic behavior of the neutral nickel complex, activated with MAO or MMAO, towards norbornene vinylic polymerization.[36] Work from Sun and Carlini's groups indicates that introducing electron-withdrawing groups such as nitro and chlorine into the *O*-aryl moiety of salicylaldiminato ligands seems to enhance catalyst activity towards norbornene polymerization.[12,39]

The fact that variations of the ligand structures may lead to profound changes in the catalytic activity and the property of polymer prompted us to introduce strong electron-withdrawing fluorine atom(s) onto the *N*-aryl moiety of the salicylaldiminato ligand and to investigate fluorine-substituent effects. The results indicate that such strong electron-withdrawing groups can considerably increase catalyst activity. We report here the synthesis, characterization and catalytic behavior, towards norbornene polymerization, of neutral nickel catalysts bearing salicylaldiminato ligands with fluorinated *N*-aryl moieties.

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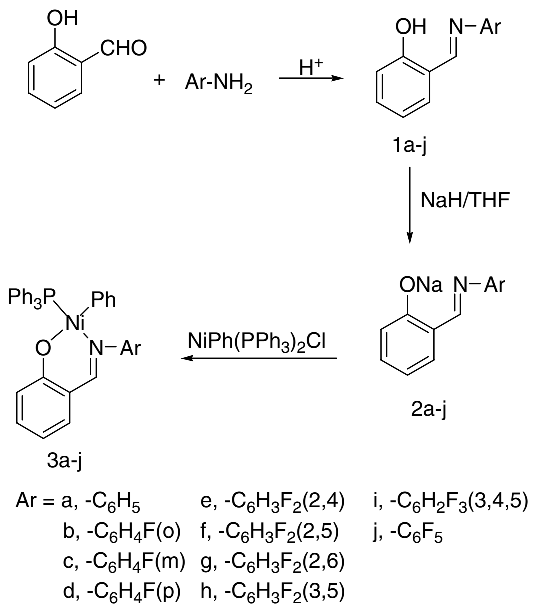


Scheme 1. Synthesis routes and structures of the neutral nickel complexes.

Results and Discussion

Synthesis and characterization of complexes

The synthetic routes for the new salicylaldiminato neutral nickel(II) complexes are shown in Scheme 1. Salicylaldimines **1a** and **1b–j** with fluorinated *N*-aryl moiety were synthesized in good yield (**1a**, 76; **1b**, 69; **1c**, 81; **1d**, 72; **1e**, 69; **1f**, 78; **1g**, 68; **1h**, 75; **1i**, 70; **1j**, 72%) via the condensation reaction of the corresponding aniline derivative with salicylaldehyde. Similar to previously procedures,[45–48] sodium salts of salicyldiminato **2a–j** were obtained by treatment of free salicylaldimines **1a–j** with NaH in THF at room temperature, and then reacted with *trans*-chloro-(1-phenyl)bis(triphenylphosphine)nickel(II) to give corresponding neutral nickel(II) complexes **3a–j** as red crystals (yields: **3a**, 65; **3b**, 53; **3c**, 75; **3d**, 64; **3e**, 60; **3f**, 61; **3g**, 73; **3h**, 60; **3i**, 70; **3j**, 78%). According to NMR data, these neutral nickel complexes with fluorinated salicylaldiminato ligands are also diamagnetic and adopt a square-planar geometry configuration like other neutral nickel.[37,40–42,44–49]

To further confirm the structure of these neutral nickel(II) complexes, crystals of complexes **3a** and **3i** suitable for X-ray crystallographic analysis were grown from a toluene–hexane solution. The data collection and refinement data are summarized in Table 1, and the ORTEP diagrams together with the selected bond lengths and angles for **3a** and **3i** are shown in Fig. 1 and 2, respectively. In the solid state, they crystallize in the orthorhombic form and the molecules adopt nearly ideal square-planar coordination geometries. In complexes **3a** and **3i**, the *N*-aryl moiety occupies a position *trans* to the triphenylphosphine ligand with N–Ni–P angles of 165.30(6) and 165.93(5)°, respectively. The phenyl group attached to Ni is located *trans* to O with O–Ni–C angles of 165.72(9) and 167.16(9)°, respectively. The O–Ni–N, C–Ni–N, C–Ni–P and O–Ni–P bond angles for **3a** are 93.27(7), 94.85(9), 88.01(7), and 87.09(5)°, respectively. Comparatively, the corresponding angles for **3i** are 92.70(7), 94.72(8), 88.34(6), and 86.98(5)°, respectively. The bond length of Ni–N [1.9491(17) Å] for complex **3i** is much longer than that [1.9372(18) Å] for complex **3a** due to the strong electron-withdrawing effect of fluorine atoms; the bond length of Ni–O [1.8843(14) Å] for complex **3i** is much shorter than that [1.8905(16) Å] for complex **3a**, and the bond

Table 1. Crystal data and structure refinement for complexes **3a** and **3i**

	3a	3i
Empirical formula	$C_{37}H_{30}NOPNi$	$C_{37}H_{27}NOF_3PNi$
Formula weight	594.30	648.28
Temperature	187(2) K	187(2) K
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.5604 (5)	9.5866 (8)
b (Å)	16.4789 (8)	16.6221 (13)
c (Å)	18.9825 (10)	19.2476 (15)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Z	4	4
V (Å^3)	2973.7 (3)	3067.1 (4)
ρ_{calcd} (mg/m^3)	1.327	1.404
Absorption coefficient (mm^{-1})	0.737	0.734
F(000)	1240	1336
θ range (deg)	1.64 to 25.38	1.62 to 26.05
Independent reflections	5454 ($R_{int} = 0.0277$)	6039 ($R_{int} = 0.0227$)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9033 and 0.7626	0.8991 and 0.7260
Parameters	−0.012 (10)	−0.009 (8)
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0303$, $wR_2 = 0.0716$	$R_1 = 0.0298$, $wR_2 = 0.0700$
Goodness-of-fit on F^2	1.020	1.037
Largest difference peak and hole (e Å^{-3})	0.321 and −0.185	0.555 and −0.194

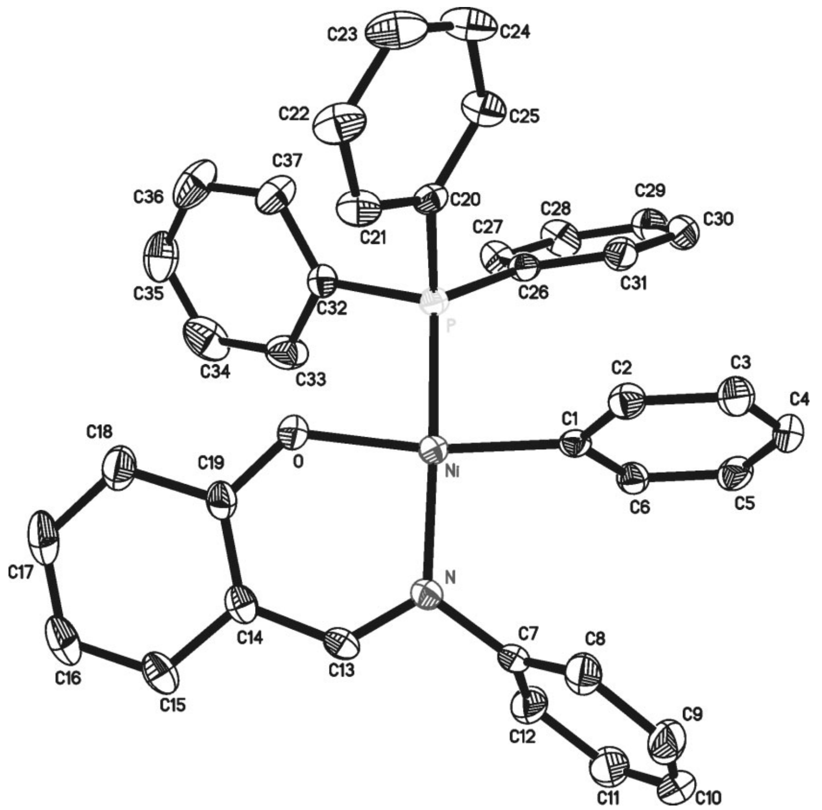


Figure 1. Molecular structure of complex **3a** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–C(1) = 1.887(2), Ni–N = 1.9372(18), Ni–P = 2.1816(6), Ni–O = 1.8905(16), N–C(7) = 1.438(3), N–C(13) = 1.304(3), P–C(32) = 1.830(2), P–C(20) = 1.828(2), P–C(26) = 1.831(2), O–Ni–C(1) = 165.72(9), O–Ni–N = 93.27(7), C(1)–Ni–N = 94.85(9), O–Ni–P = 87.09(5), C(1)–Ni–P = 88.01(7), N–Ni–P = 165.30(6).

length of Ni–P (2.1818(6) Å) for complex **3i** is slightly longer than that [2.1816(6) Å] for complex **3a**.

Catalysis for norbornene polymerization

Preliminary blank experiments were carried out with each fluorinated salicylaldiminato neutral nickel complex **3b–j**. No polymer was obtained in the absence of MAO or MMAO. Therefore, all other experiments were carried out with MMAO. MMAO's role is probably to extract the PPh_3 ligand from the nickel complex to create an empty binding site for initiating norbornene polymerization. All nickel complexes **3a–j** activated with MMAO exhibit high catalytic activity (24.9–42.9 kg/mmol$_{Ni}$•h) for vinylic polymerization of norbornene, to produce high molecular weight polynorbornene ($M_v = 6.1–8.5 \times 10^5$) under mild conditions. The typical polymerization results are summarized in Table 2. Complex (or precatalyst) **3a** without any substituent was chosen as the criterion to examine the influence of the fluorinated salicylaldiminato ligand on catalyst activity for norbornene polymerization. The data in Table 2 demonstrate that the introduction of fluorine atom(s) to the *N*-aryl moiety of the ligand considerably increases catalyst activity.

The addition-polymerization of norbornene by neutral nickel complexes was hypothesized as occurring via a 'coordination and insertion mechanism'.[50,51] Based on this point, the progress of vinylic polymerization of norbornene should include the coordination of norbornene to the center nickel atom (a) and insertion of norbornene to the 'Ni–C' bond (b), as shown in Scheme 2. The electrophilic characteristic of center nickel atom is one of the most important factors determining the rate of chain propagation. The more electrophilic the nickel center is the higher the rate of norbonene polymerization exhibits. In addition, the steric hindrance of the *ortho*-position substituent(s) of coordination nitrogen atom may also influence the rate of chain propagation and chain transfer. The introduction of fluorine atom(s) into the salicylaldimine ligand can weaken the electron releasing ability of the ligands and enhance the electrophilic characterstics of the center nickel atom, benefiting chain propagation. Indeed, we find that these modulations significantly improve catalyst activity. Precatalysts **3b–j** exhibit much higher activities for norbornene polymerization than unsubstituted complex **3a**.

We explored the effect of the position and amount of fluorine atom in salicylaldiminato ligands on the catalytic activity by **3b–h**. However, no significant difference was observed. For example, precatalysts **3b–d**, with fluorine atom in the *ortho*-, *meta*- and *para*-positions on the *N*-aryl moiety of the ligand, display similar catalytic activities (33.9, 34.8 and 35.7 kg PNB/mmol$_{Ni}$ · h). The analogs **3e–h** with two fluorine atoms in different positions on the *N*-aryl moiety of the ligands also display high catalytic activity for NBE polymerization (39.3, 42.9, 35.4 and 37.8 kg PNB/mmol$_{Ni}$ · h for **3e, 3f, 3g, 3h**, respectively), and the efficiency is at the same level as that of **3a–d**. No remarkable increase in catalytic activity can be seen by further increasing the amount of fluorine atoms in salicylaldiminato ligands (for **3i**, 42.3 kg PNB/mmol$_{Ni}$ · h; for **3j**, 41.7 kg PNB/mmol$_{Ni}$ · h).

Precatalyst **3h** was used investigated to study the effect of reaction conditions on vinyl polymerization of norbornene by

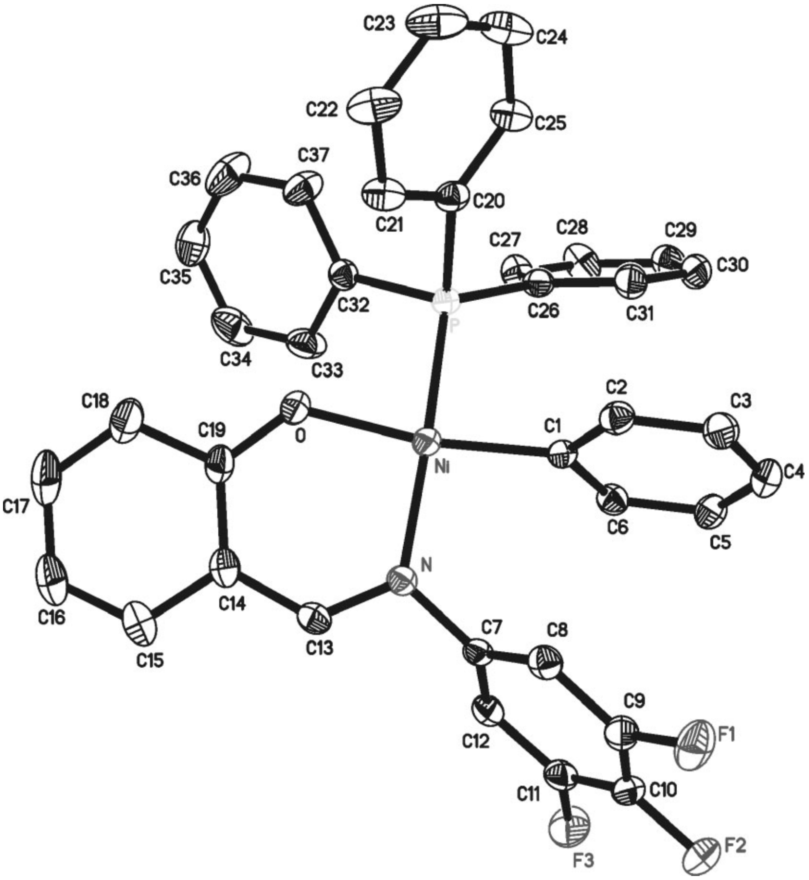
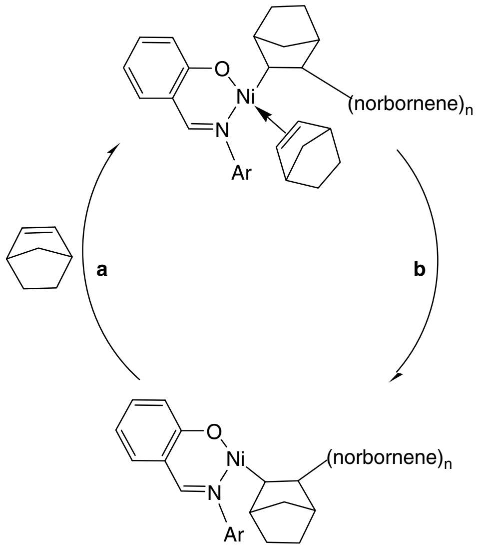


Figure 2. Molecular structure of complex **3i** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–C(1) = 1.888(2), Ni–N = 1.9491(17), Ni–P = 2.1818(6), Ni–O = 1.8843(14), N–C(7) = 1.432(2), N–C(13) = 1.311(3), P–C (20) = 1.826(2), P–C (26) = 1.828(2), P–C(32) = 1.824(2); O–Ni–C(1) = 167.16(9), O–Ni–N = 92.70(7), C(1)–Ni–N = 94.72(8), O–Ni–P = 86.98(5), C(1)–Ni–P = 88.34(6), N–Ni–P = 165.93(5).

Table 2. Polymerization of norbornene in C_6H_5Cl with different precatalysts[a]

Complex	Norbornene (g)	Polymer (g)	Yield (%)	Activity (kg/ $\text{mmol}_{\text{Ni}}{\bullet}\text{h}$)	M_v[c] (kg/mol)	T_g (°C)
3a	1.83	0.83	45	24.9	702	366
3b	1.83	1.13	62	33.9	697	416
3c	1.83	1.16	63	34.8	848	417
3d	1.83	1.19	65	35.7	611	413
3e	1.83	1.31	72	39.3	778	410
3f	1.83	1.43	78	42.9	611	–
3g	1.83	1.18	64	35.4	708	410
3h	1.83	1.26	69	37.8	720	–
3i	1.83	1.41	77	42.3	646	–
3j	1.83	1.39	76	41.7	653	–

[a] Polymerization conditions: [Ni] : [Al] : [NBE] = 1 : 2000 : 100 000 (molar ratio), $C_{\text{Ni}} = 1.33 \times 10^{-5}$ mol/l, $C_{\text{NBE}} = 1.30$ mol/l, $V_{\text{total}} = 15$ mL, polymerization at 20 °C for 10 min.



Scheme 2. Progress of the norbornene polymerization.

changing the Al : Ni molar ratios, reaction temperature and the molar ratios of norbornene monomer to the precursor (M–Ni). Variation of the ratio of MMAO:**3h**, which is expressed here as the Al : Ni molar ratio, displayed significant effects on catalyst activity and the molecular weight of the resultant polymers. As shown in Fig. 3, the catalytic activity of precatalyst **3h** increased rapidly first with increases in Al : Ni ratios, and then remained steady after the Al : Ni molar ratio reached about 2500 : 1. In contrast,

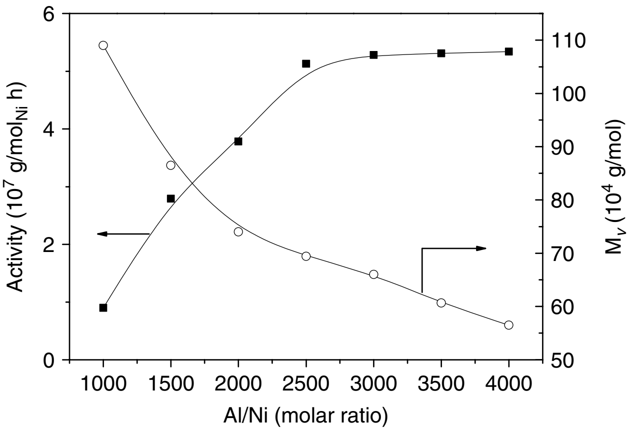


Figure 3. Plot of catalyst activity (■) and polymer M_v (○) vs Al : Ni (molar ratio); 0.2 µmol precatalyst **3h**, 1.83 g of norbornene feed, V_{total} = 15 ml, polymerization at 20 °C for 10 min.

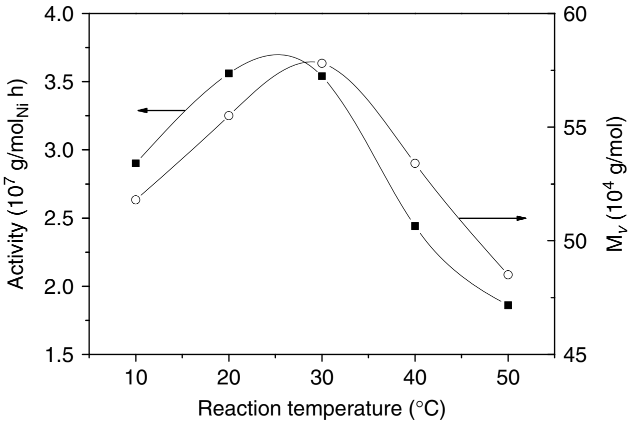


Figure 4. Plot of catalyst activity (■) and polymer M_v (○) vs reaction temperature; 0.2 µmol precatalyst **3h**, 1.83 g of norbornene feed, Al : Ni = 2000 : 1 (molar ratio), V_{total} = 15 ml, polymerization for 15 min.

Table 3. Influence of norbornene : Ni ratio on polymerization with precatalyst **3h**[a]

[NBE]: [Ni]	Norbornene (g)	Polymer (g)	Yield (%)	Activity (kg PNB/ mmol$_{Ni}$ · h)	M_v (kg/mol)
100000 : 1	1.83	1.78	97	53.4	590
150000 : 1	1.83	1.65	90	75.0	678
200000 : 1	1.83	1.28	70	76.8	834
400000 : 1	1.83	trace	–	–	–

[a] Polymerization conditions: Al : Ni = 4000 : 1 (molar ratio), 1.83 g of norbornene feeds, V_{total} = 15 ml, polymerization at 20 °C for 10 min.

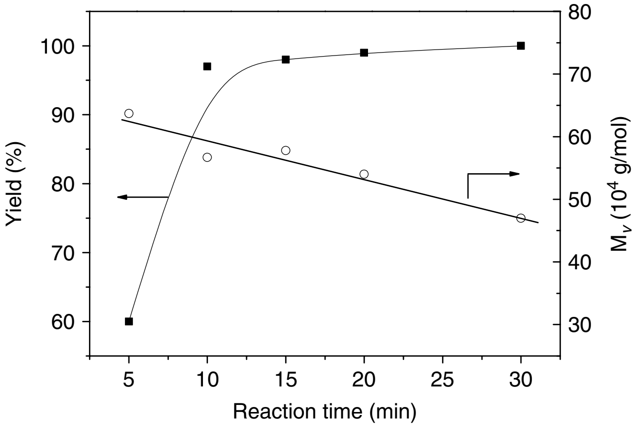


Figure 5. Plot of polymer yield (■) and M_v (○) vs polymerization time: 0.2 µmol precatalyst **3h**, 1.83 g of norbornene feed, Al : Ni = 4000 : 1 (molar ratio), V_{total} = 15 ml, polymerization at 30 °C.

the viscosity-average molecular weights (M_v) of the polymers gradually decreased with increasing Al : Ni ratios.

As shown in Fig. 4, catalyst activity and molecular weights for the resultant polymers were also considerably influenced by reaction temperature. With increases in the reaction temperature, both catalyst activity and the molecular weights of the polymer first increased; as the temperature rose to 25 and 30 °C, catalyst activity and the molecular weight reached their maximum values (37.8 kg PNB/mmol$_{Ni}$ · h and 575 kg/mol), respectively, and then gradually decreased.

The data in Table 3 indicate that decreasing the catalyst concentration, with a fixed amount of norbornene (1.83g) and the same solution volume, led to a dramatic increase in activity with a higher monomer : Ni molar ratio. With the monomer : Ni ratio at 200 000 : 1, a high activity for precatalyst **3h** of up to 76.8 kg PNB/mmol$_{Ni}$ · h was observed compared with an activity of 53.4 PNB/mmol$_{Ni}$ · h with a monomer : Ni ratio of 100 000 : 1. Variation of the monomer : Ni ratio also leads to an enhancement of the molecular weight of the polymers.

As shown in Fig. 5, the polymer yield increased with increased reaction time. No induction period was observed in the polymerization process, indicating that the active species can be formed rapidly at the initial stage of the reaction. In contrast, the molecular weight of the polymers decreased with longer reaction times since the polymerization rate gradually slowed down with the monomer consumed.

Vinyl addition polymerization yielded a completely saturated polynorbornene. As shown in Table 2, all polymers displayed high molecular weights (M_vs up to 840 kg/mol) and polynorbornenes produced by **3b–e** and **3g** containing fluorinated salicylaldiminato ligands provided higher glass transition temperatures up to 410 °C, compared with the *ca* 366 °C of polynorbornene created by **3a.** However, our attempts to determine the T_g of the obtained vinyl polymers produced by **3f** and **3h-j** failed, and the DSC studies did not show an endothermic signal upon heating to the decomposition temperature.

Conclusions

A series of novel neutral Ni(II) complexes bearing fluorinated salicylaldiminato ligands were synthesized and characterized. With MMAO as cocatalyst, these well-defined complexes are more active towards vinylic polymerization of norbornene than unsubstituted complex **3a** under the same conditions. The electronic effect of the fluorine atom(s), as electron-withdrawing groups, in the *N*-aryl moiety of the salicylaldiminato ligand, significantly increases catalyst activity. Catalyst activity, polymer yield and polymer molecular weight can be controlled by variation of the reaction parameters such as reaction temperature, Al : Ni molar ratio and monomer concentration.

Experimental

General procedures and materials

All work involving air and moisture-sensitive compounds were carried out using standard Schlenk techniques. NMR analyses of polymers were performed on a Varian Unity 400 MHz spectrometer at 135 °C, using o-$C_6D_4Cl_2$ as solvent. NMR data of ligands and complexes were obtained on a Varian Unity 300 MHz spectrometer at ambient temperature, using $CDCl_3$ as solvent. Differential scanning calorimetric (DSC) measurements were performed with a PerkinElmer Pyris 1 DSC. Viscosity-average molecular weights were calculated from the intrinsic viscosity by using the Mark–Houwink coefficients: $a = 0.56, K = 7.78 \times 10^{-4}$ dl/g.[49]

All the fluorinated anilines were obtained from Acros and used without any purification. Chlorobenzene was dried over CaH_2 and distilled. Norbornene was purchased from Aldrich and purified by sublimation under reduced pressure before use. MMAO (7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc.

Synthesis of ligands1a–j

Salicylal and aniline or fluorinated aniline were added in methanol (15 ml) with formic acid (0.5 ml) as catalyst and stirred for 24 h to afford the corresponding yellow or orange phenoxyimine products via a Schiff-base condensation reaction. The crude products were purified by recrystallization in methanol, except for **2a**, which was purified by column chromatography on silica gel using ethyl acrtate–petroleum mixture (1 : 4) as an eluent. $C_6H_5N{=}CH(C_6H_4OH)$, **1a** (76%): ^1H NMR ($CDCl_3$): δ 13.23 (w, 1H, O–H), 8.56 (s, 1H, N=C–H), 7.39 (m, 4H, Ar–H), 7.27 (m, 2H, Ar–H), 7.02 (d, J = 8.1 Hz, 1H, Ar–H), 6.95 (t, J = 7.5 Hz, 3H, Ar–H). Anal. calcd for $C_{13}H_{10}NOF$: C, 72.55%; H, 4.68%; 6.51%. Found: C, 72.23%; H, 4.63%; 6.54%.

o–$C_6H_4FN{=}CH(C_6H_4OH)$, 1b (69%): ^1H NMR ($CDCl_3$): δ 13.1 (s, 1H, O–H), 8.7 (s, 1H), 7.4 (m, 2H, Ar–H), 7.2 (m, 5H, Ar–H), 7.1 (d, J = 8.7 Hz, 1H, Ar–H), 6.9 (t, J = 7.5 Hz, 1H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 164.97, 161.72, 157.78, 154.45, 136.69, 133.96, 132.88, 128.27, 125.06, 121.83, 119.53, 117.84, 116.99. Anal. calcd for $C_{13}H_{10}NOF$: C, 72.55%; H, 4.68%; N, 6.51%. Found: C, 72.23%; H, 4.63%; N, 6.54%.

m–$C_6H_4FN{=}CH(C_6H_4OH)$, 1c (81%): ^1H NMR ($CDCl_3$): 12.95(s, 1H, O–H), 8.63 (s, 1H, N=C–H), 7.42 (m, 5H, Ar–H), 7.04 (m, 3H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 164.98, 163.63, 161.70, 161.13, 150.30, 133.59, 132.53, 130.59, 119.23, 118.92, 117.23, 113.64, 108.35. Anal. calcd for $C_{13}H_{10}NOF$: C, 72.55%; H, 4.68%; N, 6.51%. Found: C, 72.19%; H, 4.63%; N, 6.48%.

p–$C_6H_4FN{=}CH(C_6H_4OH)$, 1d (72%): ^1H NMR ($CDCl_3$): δ 13.11, (s, 1H, O–H), 8.61 (s, 1H, N=C–H), 7.41 (m, 2H, Ar–H), 7.28 (m, 2H, Ar–H), 7.05 (d, 2H, Ar–H), 7.00 (t, 2H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 163.69, 162.84, 161.44, 160.42, 145.03, 133.63, 132.70, 123.02, 119.56, 117.67, 116.77, 116.47. Anal. calcd for $C_{13}H_{10}NOF$: C, 72.55%; H, 4.68%; N, 6.51%. Found: C, 73.08%; H, 4.65%; N, 6.46%.

2, 4–$C_6H_3F_2N{=}CH(C_6H_4OH)$, 1e (69%): ^1H NMR ($CDCl_3$): δ 12.97 (s, 1H, O–H), 8.70 (s, 1H, N=C–H), 7.41 (m, 2H, Ar–H), 7.28 (m, 1H, Ar–H), 7.06 (d, J = 9.3 Hz, 1H, Ar–H), 6.95 (m, 3H, Ar–H).^{13}C NMR ($CDCl_3$): δ 164.61, 161.61, 161.56, 156.18, 134.01, 132.90, 122.21, 119.52, 117.81, 112.07, 105.36. Anal. calcd for $C_{13}H_9NOF_2$: C, 66.95%; H, 3.89%; N, 6.01%. Found: C, 66.73%; H, 3.86%; N, 6.05%.

2, 5–$C_6H_3F_2N{=}CH(C_6H_4OH)$, 1f (78%): ^1H NMR ($CDCl_3$): δ 12.81 (s, 1H, O–H), 8.68 (s, 1H, N=C–H), 7.42 (m, 2H, Ar–H), 7.15 (m, 1H, Ar–H), 7.00 (m, 4H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 165.73, 161.79, 159.25, 152.36, 137.46, 134.40, 119.66, 119.30, 117.90, 117.57, 114.30, 108.54. Anal. calcd for $C_{13}H_9NOF_2$: C, 66.95%; H, 3.89%; N, 6.01%. Found: C, 66.78%; H, 3.87%; N, 5.97%.

2, 6–$C_6H_3F_2N{=}CH(C_6H_4OH)$, 1g (68%): ^1H NMR ($CDCl_3$): δ 12.91 (s, 1H, O–H), 8.87 (s, 1H, N=C–H), 7.39 (t, J = 8.1 Hz, 2H, Ar–H), 7.12 (m, 1H, Ar–H), 7.02 (m, 4H, Ar–H).^{13}C NMR ($CDCl_3$): δ 169.12, 161.85, 156.46, 134.31, 133.22, 126.83, 125.73, 119.55, 117.92, 112.48. Anal. calcd for $C_{13}H_9NOF_2$: C, 66.95%; H, 3.89%; N, 6.01%. Found: C, 67.18%; H, 3.92%; N, 5.96%.

3, 5–$C_6H_3F_2N{=}CH(C_6H_4OH)$, 1h (75%): ^1H NMR ($CDCl_3$): δ 12.64 (s, 1H, O–H), 8.60 (s, 1H, N=C–H), 7.44 (t, J = 4.5 Hz, 2H, Ar–H), 7.06 (d, J = 8.4 Hz, 1H, Ar–H), 6.99 (t, J = 7.5 Hz, 1H, Ar–H), 6.84, (m, 3H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 164.52, 163.49, 161.22, 151.21, 134.05, 132.80, 119.40, 118.69, 117.44, 104.67, 102.00. Anal. calcd for $C_{13}H_9NOF_2$: C, 66.95%; H, 3.89%; N, 6.01%. Found: C, 67.11%; H, 3.86%; N, 5.95%.

3, 4, 5–$C_6H_2F_3N{=}CH(C_6H_4OH)$, 1i (70%): ^1H NMR ($CDCl_3$): δ 12.52 (s, 1H, O–H), 8.56 (s, 1H, N=C–H), 7.46 (t, J = 8.4 Hz, 2H, Ar–H), 6.98 (m, 4H, Ar–H).^{13}C NMR ($CDCl_3$): δ 164.69, 161.49, 151.96, 144.56, 139.08, 134.48, 133.18, 119.85, 118.99, 117.80, 106.10. Anal. calcd for $C_{13}H_8NOF_3$: C, 62.16%; H, 3.21%; N, 5.58%. Found: C, 62.32%; H, 3.17%; N, 5.61%.

$C_6F_5N{=}CH(C_6H_4OH)$, 1j (72%): ^1H NMR ($CDCl_3$): δ 12.26 (s, 1H, O–H), 8.85 (s, 1H, N=C–H), 7.46 (m, 2H, Ar–H), 7.04 (m, 2H, Ar–H).^{13}C NMR ($CDCl_3$): δ 170.64, 161.56, 142.63, 140.74, 139.64, 137.20, 136.43, 135.01, 133.34, 123.44, 119.60, 118.78, 117.81. Anal. calcd for $C_{13}H_6NOF_5$: C, 54.37%; H, 2.11%; N, 4.88%. Found: C, 54.32%; H, 2.07%; N, 4.83%.

Synthesis of neutral nickel complexes3a–j

A solution of **1a** (0.26 g, 1.30 mmol) in THF (15 ml) was added to sodium hydride (62 mg, 2.60 mmol). The resultant mixture was stirred at room temperature for 4 h, then filtered and evaporated. The resultant solid residue and *trans*-$[Ni(PPh_3)_2PhCl]$ (0.91 g, 1.30 mmol) were dissolved in anhydrous benzene (30 ml) in an Schlenk flask and stirred at room temperature for 14 h. The resultant mixture was filtered, and the filtrate was removed by vacuum to obtain yellow solid powder which was then recrystallized from toluene and hexane to yield 0.35g (65%) of **3a**. The complexes **3b–j** were prepared by the same procedure with similar yields.

$[C_6H_5N{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3a: ^1H NMR ($CDCl_3$): δ 7.90 (w, 1H, N=C–H), 6.65–7.80 (m, 29H, Ar–H). Anal. calcd for $C_{37}H_{30}NNiOP$: C, 74.78%; H, 5.09%; N, 2.36%. Found: C, 74.54%; H, 5.13%; N, 2.31%.

[o–$C_6H_4FN{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3b (53%): ^1H NMR ($CDCl_3$): δ 8.06 (d, J = 8.7 Hz, 1H, N=C–H), 7.00–7.92 (m, 28H, Ar–H). Anal. calcd for $C_{37}H_{29}NOFPNi$: C, 72.58%; H, 4.77%; N, 2.29%. Found: C, 74.44%; H, 4.73%; N, 2.23%.

[m–$C_6H_4FN{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3c (75%): ^1H NMR ($CDCl_3$): δ 8.06 (d, J = 6.0 Hz, 1H, N=C–H), 6.98–7.95 (m, 28H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 166.57, 166.17, 155.62, 153.19, 148.89, 148.39, 142.17, 138.12, 134.33, 133.90, 131.32, 130.88, 129.43, 127.66, 126.24, 125.85, 124.83, 122.78, 120.96, 119.18, 114.95, 113.85. Anal. calcd for $C_{37}H_{29}NOFPNi$: C, 72.58%; H, 4.77%; N, 2.29%. Found: C, 74.63%; H, 4.82%; N, 2.25%.

[o–$C_6H_4FN{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3d (64%): ^1H NMR ($CDCl_3$): δ 8.05 (s, 1H, N=C–H), 6.80–7.98 (m, 28H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 165.74, 165.46, 160.70, 158.29, 150.52, 149.09, 148.58, 138.55, 134.25, 134.03, 133.75, 131.99, 131.77, 131.26, 130.82, 129.42, 128.41, 127.62, 125.10, 122.52, 120.87, 119.13, 113.75. Anal. calcd for $C_{37}H_{29}NOFPNi$: C, 72.58%; H, 4.77%; N, 2.29%. Found: C, 74.47%; H, 4.74%; N, 2.34%.

$[2,4\text{-}C_6H_3F_2N{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3e (60%): ^1H NMR ($CDCl_3$): δ 8.00 (w, 1H, N=C–H), 6.75–7.72 (m, 27H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 166.97, 166.27, 160.85, 158.41, 155.33, 152.90, 148.78, 138.52, 134.27, 133.86, 133.08, 131.98, 131.18, 130.73, 129.45, 128.43, 127.64, 126.57, 125.00, 122.74, 121.15, 119.00, 113.92, 109.55, 103.05. Anal. calcd for $C_{37}H_{28}NOF_2PNi$: C, 70.51%; H, 4.48%; N, 2.22%. Found: C, 70.68%; H, 4.44%; N, 2.16%.

$[2,5\text{-}C_6H_3F_2N{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3f (61%): ^1H NMR ($CDCl_3$): δ 8.04 (d, J = 7.5 Hz, 1H, N=C–H), 6.90–7.81 (m, 27H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 166.65, 166.41, 158.51, 156.11, 152.06, 149.67, 148.46, 142.69, 138.06, 134.97, 134.30, 133.95, 132.01, 131.15, 130.70, 129.50, 128.55, 127.67, 126.41, 125.02, 122.82, 121.28, 118.89, 115.50, 114.02, 113.51, 111.00. Anal. calcd for $C_{37}H_{28}NOF_2PNi$: C, 70.51%; H, 4.48%; N, 2.22%. Found: C, 70.37%; H, 4.43%; N, 2.27%.

$[2,6\text{-}C_6H_3F_2N{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3g (73%): ^1H NMR ($CDCl_3$): δ 8.02 (d, J = 7.8 Hz, 1H, N=C–H), 6.79–7.80 (m, 27H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 168.03, 166.65, 156.34, 153.89, 149.15, 148.65, 137.44, 134.57, 134.35, 134.02, 131.24, 130.08, 129.47, 127.69, 125.47, 124.87, 122.91, 121.33, 119.11, 113.95, 110.58. Anal. calcd for $C_{37}H_{28}NOF_2PNi$: C, 70.51%; H, 4.48%; N, 2.22%. Found: C, 70.33%; H, 4.53%; N, 2.17%.

$[3,5\text{-}C_6H_3F_2N{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3h (60%): ^1H NMR ($CDCl_3$): δ 8.06 (s, 1H, N=C–H), 6.96–7.80 (m, 27H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 166.18, 165.21, 162.99, 160.49, 156.46, 148.46, 147.96, 138.53, 134.48, 134.19, 133.91, 131.13, 130.68, 129.55, 128.45, 127.71, 125.17, 122.76, 121.31, 118.77, 114.12, 107.07, 99.66. Anal. calcd for $C_{37}H_{28}NOF_2PNi$: C, 70.51%; H, 4.48%; N, 2.22%. Found: C, 70.40%; H, 4.45%; N, 2.18%.

$[3,4,5\text{-}C_6H_2F_3N{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3i (70%): ^1H NMR ($CDCl_3$): δ 8.04 (d, J = 7.8 Hz, 1H, N=C–H), 6.92–7.83 (m, 26H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 166.75, 166.07, 151.67, 150.08, 149.29, 148.62, 138.97, 135.10, 134.74, 134.37, 131.58, 130.98, 130.07, 129.83, 128.19, 125.77, 123.29, 121.93, 119.10, 114.69, 109.48. Anal. calcd for $C_{37}H_{27}NOF_3PNi$: C, 68.55%; H, 4.20%; N, 2.16%. Found: C, 68.32%; H, 4.15%; N, 2.11%.

$[C_6F_5N{=}CH(C_6H_4O)]Ni(PPh_3)Ph$, 3j (78%): ^1H NMR ($CDCl_3$): δ 7.94 (d, J = 7.5 Hz, 1H, N=C–H), 6.90–7.90 (m, 24H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 168.48, 167.34, 149.75, 149.24, 137.17, 135.30, 134.30, 134.08, 133.64, 132.09, 131.89, 130.84, 130.39, 129.68, 128.41, 127.78, 125.22, 123.25, 121.98, 118.69, 114.43. Anal. calcd for $C_{37}H_{25}NOF_5PNi$: C, 64.95%; H, 3.68%; N, 2.05%. Found: C, 64.36%; H, 3.62%; N, 2.10%.

Typical polymerization procedure

A 0.5 ml aliquot of a fresh catalyst solution (chlorobenzene, 0.2 μmol catalyst), 3.7 ml of a solution of norbornene (19.5 mmol, 1.83 g) in chlorobenzene and 10.8 ml chlorobenzene were added under inert gas atmosphere into a Schlenk flask with a mechanical stirrer. The reaction was started by the addition of 0.2 ml of a MMAO solution (0.4 mmol in chlorobenzene) at 20 °C. The total reaction volume was 15 ml, which was achieved by variation of the amount of chlorobenzene if necessary. After 10 min, acidic ethanol was injected into the Schlenk flask to end the reaction and the reaction mixture was poured into 200 ml of acidic ethanol (ethanol : HCl_{conc} = 50 : 1). The polymer was isolated by filtration, washed with acetone and dried under vacuum at 80 °C for 24 h.

X-ray crystallography

The intensity data were collected with the ω scan mode (187 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo K_α radiation (λ = 0.71073 Å). Lorentz polarization factors were made for the intensity data and absorption corrections were performed using SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least squares. The position of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

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Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos 655730 and 655731 and for the complexes **3a** and **3i**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://ccdc.cam.ac.uk)

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