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Vinyl Polymerization of Norbornene with Neutral Salicylaldiminato Nickel(II) Complexes

Wen-Hua Sun,[*,†] Haijian Yang,[†] Zilong Li,[‡] and Yan Li[†]

State Key Laboratory of Engineering Plastics and The Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China, and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

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A series of neutral salicylaldiminato Ni(II) complexes have been synthesized and characterized, and complexes **a** and **e** have been confirmed by X-ray single-crystal analyses. These compounds show highly catalytic activities for the vinyl polymerization of norbornene with MAO cocatalyst, which could be up to 2.86 × 10^8 g PNB/(mol Ni·h), and also lead to various activities, molecular weights, and distributions of polynorbornenes under different reaction conditions.

Introduction

Bicyclo[2.2.1]hept-2-ene, better known by its trivial name norbornene, can be homo-polymerized via three pathways, which lead to their corresponding polymers with different structures and properties.[1] The first report by Andersen and Merckling[2] in the 1950s, ring-opening metathesis polymerization (ROMP) of norbornene, was well investigated with a variety of catalysts containing transition metals (e.g., Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Re, Ru, Os, Co, or Ir in high oxidation state).[3] Those ROMP poly(norbornene)s containing double bonds in their backbones have been commercialized with further modification through vulcanization or hydrogenation.[4] The second type of poly(norbornene) is a cationic or free-radical polymerization product of norbornene through 2,7-linkage, which is, however, usually formed with low molecular weights (molecular weight <1000) and low yield because of the rearrangements and transfer reactions.[1a,b,e,5] Driven by industrial application, the vinyl polymerization of norbornene inspired the interest of chemists and chemical engineers.[6] V−PNB (vinylic polynorbornene), a special polymer with constrained rings in each unit, possesses interesting and unique properties such as high chemical resistance, good UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, large refractive index, and low birefringence.[1,7] Such a polymerization akin to the classical olefin polymerization is termed vinyl polymerization,[1a,e] in which the polymerization opens the double bond and leaves the bicyclic structural unit intact. V−PNB appeared with a $TiCl_4/Al^iBu_3$ catalyst back in the early 1960s.[1a,e,8] Subsequently various complexes of nickel, cobalt, chromium, titanium, zirconium, and palladium

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[*] To whom correspondence should be addressed. Fax: +86-10-62559373. E-mail: whsun@iccas.ac.cn.

[†] Institute of Chemistry.

[‡] Fujian Institute of Research on the Structure of Matter.

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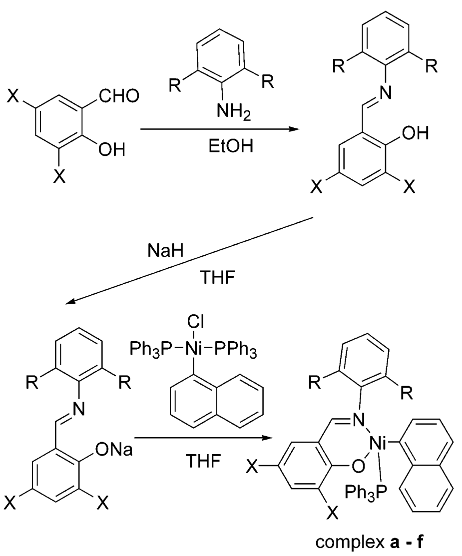
Scheme 1. Synthesis of Complexes



complex	a	b	c	d	e	f
X	I	Cl	I	Cl	I	Cl
R	i-Pr	i-Pr	Et	Et	Me	Me

have been used as catalysts for norbornene vinyl polymerization and strained cyclic olefins in general.[1,9] It was reported that the nickel(II) complexes bearing phosphoraniminato ligands had high catalytic activity for the vinyl polymerization of norbornene to produce high polymer.[9l] In addition, single-site neutral salicylaldiminato Ni(II) catalysts were used to copolymerize ethylene and norbornene derivatives.[9o] More recently, the neutral nickel complexes were reported for vinyl homopolymerization of norbornene.[9p] With those trailblazing studies of neutral nickel complexes as catalysts for vinyl polymerization of norbornene, their significant importance is further investigated to clarify catalytic activities of the nickel catalysts with their ligands for electronic and steric considerations as well as the reaction parameters. The scope of this contribution is designing a series of (1-naphthyl)(triphenylphosphine)-{*N*-[1-(2,6-dihalophenyl)]-(3,5-dialkylsalicylaldiminate)}-nickel(II) complexes and investigating their catalytic activities for vinyl polymerization of norbornene. Those complexes showed promising characteristics with good to extremely high activities up to 2.86 × 10^8 g PNB/(mol Ni·h) by varying their reaction conditions.

Results and Discussion

The syntheses of the nickel complexes as catalytic precursors are shown in Scheme 1. The ligands of salicylaldimines were efficiently synthesized via the condensation reaction of substituted salicylaldehydes and anilines.[10] Similar to the procedure reported by Grubbs,[11e] the obtained salicylaldimines were treated with NaH in THF and then reacted with *trans*-chloro-(1-naphthyl)bis(triphenylphosphine)nickel(II) to give their corresponding complexes.

The structures of the salicylaldiminato complexes were confirmed by IR and ^{1}H NMR spectra. For further confirmation, crystals of complexes **a** and **e** suitable for X-ray structure determination were grown from diethyl ether solution. The data collection and refinement data of the analyses are summarized in Table 1, and the ORTEP diagrams are shown in Figure 1 and Figure 2. In the solid state, complex **a** is in the triclinic form and complex **e** is in the monoclinic geometry. Both molecules adopt a nearly ideal square-planar coordination geometry with the Ni approximately 0.0315 and 0.0611 Å, respectively, from the planes of the complexes.

Table 1. Summary of Crystallographic Data for Complexes a and e

	a	**e**
formula	$C_{51}H_{52}I_2NNiO_2P$	$C_{43}H_{34}I_2NNiOP$
fw	1054.42	924.19
temp (K)	293(2)	293(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/c$
a (Å)	11.4427(8)	15.599(2)
b (Å)	13.0579(7)	14.173(3)
c (Å)	18.0665(15)	17.799(3)
α (deg)	109.15(4)	90
β (deg)	96.460(2)	100.622(6)
γ (deg)	105.9380(10)	90
V, Å^3	2390.2(3)	3867.8(11)
Z	2	4
μ(Mo Kα), cm^{-1}	17.69	21.73
ρ_{calcd} (g cm^{-3})	1.465	1.587
cryst size (mm)	0.51 × 0.19 × 0.08	0.63 × 0.45 × 0.10
θ range (deg)	1.22−27.45	1.33−27.48
total no. of reflns	17 071	13 922
no. of unique data	10 555	8513
no. of params	507	392
F_{000}	1060	1824
R1	0.0355	0.0544
wR2	0.0880	0.1174
goodness of fit	0.944	0.758

In complex **a**, the bulky 2,6-diisopropylbenbzimine occupies the position *trans* to the triphenylphosphine ligand with a nearly linear N1−Ni1−P1 angle (176.88(9)°). The naphthyl group attached to Ni1 lies in a position *trans* to O1 with an O1−Ni1−C1 angle of 174.64(13)°. Moreover, the naphthalene unit swings out of the coordination mean plane defined by P1−N1−Ni1−O1−C1, forming an 84.3° angle. A similar structure is also obtained in its analogue complex **e**, in which the N1−Ni1−P1 angle of 174.60(17)° and the C16−Ni1−O1 angle of 173.6(3)° were observed. Compared to the angle in complex **a**, a wider angle of 94.5° was found between the naphthalene plane and the coordination plane defined by P1−N1−Ni1−O1−C16 in complex **e**. Additionally, the angle C16−Ni1−P1 (88.6(2)°) in complex **e** is wider than the C1−Ni1−P1 (86.77(11)°) angle of complex **a**; a plausible reason is the bulky isopropyl

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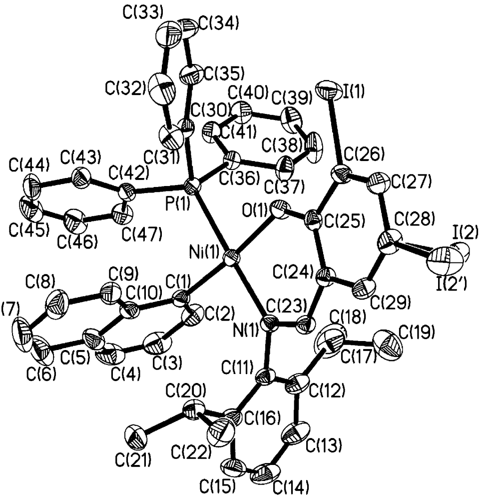

Figure 1. ORTEP of complex **a**. Selected bond distances (Å) and angles (deg): Ni(1)−C(1), 1.903(3); Ni(1)−O(1), 1.903(2); Ni(1)−N(1), 1.941(3); Ni(1)−P(1), 2.2002(10); C(1)−Ni(1)−O(1), 174.64(13); C(1)−Ni(1)−N(1), 93.01(13); O(1)−Ni(1)−N(1), 92.30(11); C(1)−Ni(1)−P(1), 86.77(11); O(1)−Ni(1)−P(1), 87.97(8); N(1)−Ni(1)−P(1), 176.88(9). One ethyl ether molecule was omitted for clarity.

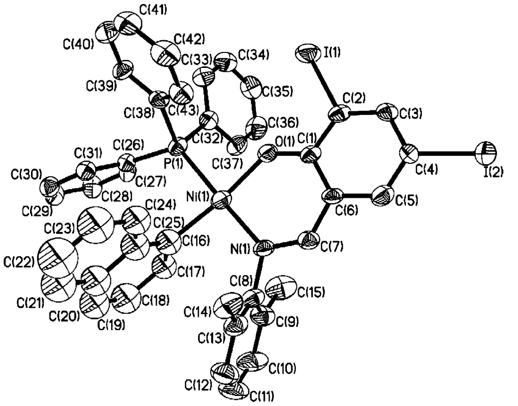

Figure 2. ORTEP of complex **e**. Selected bond distances (Å) and angles (deg): Ni(1)−O(1), 1.894(4); Ni(1)−N(1), 1.922(5); Ni(1)−C(16), 1.958(9); Ni(1)−P(1), 2.1979(17); O(1)−Ni(1)−C(16), 173.6(3); N(1)−Ni(1)−C(16), 92.9(3); O(1)−Ni(1)−N(1), 92.9(2); C(16)−Ni(1)−P(1), 88.6(2); O(1)−Ni(1)−P(1), 85.93(13); N(1)−Ni(1)−P(1), 174.60(17).

group of the 2,6-diisopropylbenzimine unit in complex **a** has a steric influence on the naphthalene and Ph_3P segments.

The Ni1−O1, Ni1−N1, Ni1−C1, and Ni1−C16 bond distances in complexes **a** and **e** are similar to those in known nickel complexes.[11] The Ni1−P bonds of complexes **a** and **e** (2.2002(10) Å for **a** and 2.1979(17) Å for **e**) are more than 0.02 Å longer than those in Grubbs' neutral nickel-based complex (2.172(2) Å) and in Cavell's [Ni(PPh_3)(*o*-tolyl)(N−O)] complexes with N−O bidentate pyridinecarboxylate ligands (d(Ni−P) = 2.1653(2) Å),[11d] which suggests that in the solid state there is steric interaction, although not significant, between the naphthalene moiety and the triphenylphosphine ligand.

The active catalysts were produced in situ in toluene solution by activating the catalytic precursors with the cocatalyst methylaluminoxane (MAO) in the presence of norbornene. Polymerization of norbornene in the presence of complexes and MAO resulted in the formation of vinyl-type PNB. It was realized that the catalytic activities greatly relied on the molar ratio of norbornene monomer to nickel catalytic precursor.[9m] In a combination of 20 000:1 norbornene monomer to nickel precursors (expressed as M/Ni) in toluene, 2000 equiv of MAO compared with the amount of the nickel precursors (Al/Ni = 2000) was added. The mixed solution resulted in a white solid mass that could no longer be stirred within 20 s. Therefore the resulting reaction mixture was quenched with acidic ethanol at 20 s, and the PNB was filtered and washed prior to drying to constant weight under vacuum at 100 °C. The norbornene polymerization results are collected in Table 2. Accordingly the complexes with more electron-withdrawing chloro substituents on the ligand segments showed a little higher activities than the ones with iodo substituents. The polymer molecular weight distribution exhibited a similar tendency as the activity, suggesting that the higher activity results in different chain growth and termination of polymerization. Unlike late-transition metal complexes as catalysts for ethylene polymerization,[12] the steric hindrance of individual ligands does not clearly affect their catalytic activities. The aryl group directly coordinated on the nickel center, however, made a significant difference in the catalytic activity. Compared to previous nickel phenyl complexes [with the highest activity as 7.08 × 10^7 g PNB/(mol Ni·h)],[9p] herein the nickel naphthyl complexes had higher activities. Plausible reasons could be attributed to the introduction of bigger naphthyl and the more electron-withdrawing substituents in the complexes. Furthermore, the volatile trimethylaluminum in MAO might affect the performance of this kind of catalyst.

Table 2. Activity of Complexes a−f for Norbornene Polymerization

cat.	yield (%)	activity[a]	M_w[b]	M_w/M_n	TGA (°C)
a	78	265.20	19.54	4.51	458
b	81	271.49	7.11	6.90	461
c	80	271.33	5.45	5.08	456
d	85	286.60	9.51	9.08	458
e	75	253.69	5.01	6.86	457
f	79	267.07	7.47	8.76	457

[a] (× 10^{-6} g PNB/(mol Ni·h)). [b] (× 10^{-5} g/mol). Conditions: solvent, toluene; total volume, 20 mL; temperature, 25 °C; reaction time, 20 s; M/Ni = 20 000; complex, 5 μmol; Al/Ni = 2000; MAO, 7.20 mL.

To investigate the reaction parameters affecting vinyl polymerization of norbornene, the catalyst precursor **a** was typically investigated by changing the ratios of MAO, the reaction temperature, and the molar ratios of norbornene monomer to the precursor (M/Ni). Although neutral salicylaldiminato nickel catalysts did not require activators in their ethylene polymerization,[9o,12c] the activator MAO was essential to the polymerization of norbornene here. The role of MAO is to initiate the polymerization and probably create an empty site for the insertion of the norbornene monomer. Moreover, it is necessary to use an excessive amount of MAO for good to high activities. In a combination of 5000:1 M/Ni, variation of the ratio of MAO:**a** (expressed as Al:Ni) showed considerable effects on polymer yield (Table 3). There is a remarkable difference from 500 to 1000 Al:

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Table 3. Influence of the MAO Amount on the Activity of Complex a

run no.	Al/Ni	yield (%)	activity[a]	M_w[b]	M_w/M_n	TGA (°C)
1	500	38	359.12	5.73	3.38	463
2	1000	71	671.20	2.72	3.20	459
3	1500	72	675.16	6.23	2.95	461
4	2000	81	761.60	8.40	3.81	456
5	2500	80	760.40	7.15	6.86	456

[a] ($\times 10^{-3}$ g PNB/(mol Ni·h)). [b] ($\times 10^{-5}$ g/mol). Conditions: temperature, 25 °C; solvent, toluene; total volume, 20 mL; reaction time, 30 min; complex **a**, 5 μmol; M/Ni = 5000.

Table 4. Influence of the Reaction Temperature (T) on the Activity of Complex a

run no.	T (°C)	yield (%)	activity[a]	M_w[b]	M_w/M_n	TGA (°C)
1	0	80	757.48	8.05	5.26	453
2	25	81	761.60	8.40	3.81	456
3	50	83	783.36	4.51	2.72	457
4	75	94	882.28	3.25	3.01	455
5	100	90	844.76	2.72	3.03	453

[a] ($\times 10^{-3}$ g PNB/(mol Ni·h)). [b] ($\times 10^{-5}$ g/mol). Conditions: solvent, toluene; total volume, 20 mL; reaction time, 30 min; M/Ni = 5000; complex **a**, 5 μmol; Al/Ni = 2000; MAO, 7.20 mL

Table 5. Influence of the Norbornene Concentration on the Activity of Complex a

run no.	M/Ni	yield (%)	activity[a]	M_w[b]	M_w/M_n	TGA (°C)
1	2500	98	0.47	2.92	5.17	458
2	5000	81	0.76	8.40	3.81	456
3	10 000	79	14.19	7.85	2.85	459
4	20 000	78	265.20	19.54	4.51	458

[a] ($\times 10^{-6}$ g PNB/(mol Ni·h)). [b] ($\times 10^{-5}$ g/mol). Conditions: temperature, 25 °C; solvent, toluene; total volume, 20 mL; complex **a**, 5 μmol; Al/Ni = 2000; MAO, 7.20 mL; reaction time, (1) 30 min; (2) 30 min; (3) 3 min; (4) 20 s.

Ni. However, the difference of yield for varying Al:Ni between 1000 and 2500 is not impressive. In addition, an Al:Ni ratio higher than 2000 will decrease the activity for the catalytic system.

Table 4 shows the results with respect to reaction temperature. The catalytic system shows good activity over a large range of reaction temperatures. The temperature was obtained with an external oil bath except for entry 1, in which 0 °C was maintained with an ice–water bath. Accordingly, the reaction showed better activity with increasing reaction temperature, but not higher than 75 °C. While the molecular weight dispersion varied with temperature, the molecular weight decreased with an increase in temperature.

Increasing the monomer concentration, with fixed amount of nickel precursor (5 μmol) and the same solution volume, resulted in a dramatic increase of activity with a higher ratio of M:Ni. High catalytic activity of complex **a** up to 2.65×10^8 g PNB/(mol Ni·h) was observed with the M:Ni ratio of 20000:1 compared to the activity [4.70×10^5 g PNB/(mol Ni·h)] with the M:Ni ratio of 2500:1. In addition, the higher concentration of norbornene produced a higher molecular weight and a wider molecular weight distribution of PNB. These results are listed in Table 5. That could be easily explained like the regular olefin polymerization: a higher pressure of monomer gives a higher catalytic activity and high-order polyolefins. However, since the reaction became very exothermic under these conditions, the control of reaction temperature became critical. Therefore the reaction was quenched in different reaction periods; shorter reaction periods were chosen for higher concentrations of norbornene. So the transformation of norbornene (yield) was not comparable in Table 5.

All the polymers obtained showed very similar IR and ^{1}H NMR spectra. The IR spectra proved the absence of a double bond, which often appear at 1620–1680 cm^{-1}, ensuring the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization (ROMP).[9j] ^{1}H NMR spectra also proved no trace of any double bond, which is typical for ROMP polynorbornene. TGA investigation for all obtained polymers showed that all of the polymer samples were very stable up to 450 °C. The determination of the glass transition temperature (T_g) of vinyl homo-polynorbornene has been described as being difficult, since it is apparently located close to the temperature where decomposition tends to set in.[8b,9m] Our attempts to determine the T_g of the obtained vinyl polymers also failed, and the DSC studies did not show an endothermic signal upon heating to the decomposition temperature. All the polymer samples obtained here are soluble in chlorobenzene at room temperature. No indication of stereoregularity was observed, which was verified by the amorphous morphology of the products.

Conclusion

In summary, the nickel complexes **a**–**f** and MAO systems showed extremely high activities in the vinyl-type polymerization of norbornene. The complexes with more electron-withdrawing chloro substituents on the ligands exhibited higher activity than those with less electron-withdrawing iodo substituents. The polymers obtained here are amorphous and soluble in halobenzene and stable up to 450 °C. Catalytic activity, conversion yield, polymer molecular weight, and molecular weight dispersion could be controlled over a wide range.

Experimental Section

General Considerations. All procedures were carried out by using standard Schlenk techniques. Toluene and THF were dried over sodium metal and distilled under nitrogen. Methylaluminoxane (MAO) was purchased from Albemarle as a 1.4 M toluene solution and used without further treating. 3,5-Dichlorosalicylaldehyde, 3,5-diiodosalicylaldehyde, 2,6-diisopropylaniline, 2,6-diethylaniline, and 2,6-dimethylaniline were bought from Aldrich Chem. Co. and used without further purification. NaH obtained from Beijing Chemical Regents Company was treated with petroleum ether to get rid of the outside wrapped oil before use. *trans*-Chloro(1-naphthyl)bis(triphenylphosphine)nickel was synthesized according to the procedure reported in the literature.[13] Norbornene (bicyclo[2.2.1]hept-2-ene; Acros) was purified by distillation over potassium and used as a solution in toluene.

Measurement. NMR spectra were recorded on a JEOL AL-300 or a Bruker BMX-300 MHz instrument at ambient temperature using TMS as internal standard, and NMR data for polynorbornene were obtained on a JEOL AL-300 instrument using *o*-dichlorobenzene-d_4 as solvent. The ^{31}P NMR spectra were obtained on a Varian-200 MHz with phosphoric acid as internal standard. The melting points (mp) of ligands and complexes were measured with an electrical apparatus.

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[13] Soolingen, J. V.; Verkruijsse, H. D.; Keegstra, M. A.; Brandsma, L. *Synth. Commun.* **1990**, *20*, 3153–3156.

IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Elemental analyses were carried out using a HP-MOD 1106 microanalyzer. Molecular weights of polymers were determined by a Waters Alliance GPCV 2000 system at 135 °C in 1,2,4-trichlorobenzene with polystyrene narrow distribution standards. TGA data were measured with a Perkin-Elmer 7 Series thermal analysis system instrument.

Syntheses of Ligands and Complexes. Dihalosalicylaldehyde and aniline were refluxed in ethanol for 5−10 h to afford the corresponding yellow or orange phenoxyimine products via a Schiff-base condensation reaction. The crude products were purified by recrystallization in ethanol, except for 4,6-dichloro-2-[[(4,6-diethylphenyl)imino]methyl]phenol, which was purified by column chromatography on silica gel using Et_2O−petroleum (volume ratio = 1:10) as eluent. All the ligands are known compounds,[14] and their structures were confirmed with ^1H NMR.

(1-Naphthyl)(triphenylphosphine){*N*-[1-(2,6-diisopropylphenyl)]-(3,5-diiodosalicylaldiminate)}nickel(II) (complex a). To a stirred solution of 4,6-diiodo-2-[[(2,6-diisopropylphenyl)imino]methyl]phenol (5.0 mmol) in THF (100 mL) at room temperature was added NaH (5.0 mmol) at once. The reaction was allowed to stir for 1 h. Then *trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel (5.0 mmol) was added quickly. After being stirred at room temperature for 10 h, the mixture was filtered through a glass filter, and the filtrate was evaporated in vacuo to yield a dark brown solid. The brown solid was again dissolved in diethyl ether and concentrated to 1/5 volume. After filtration and drying in vacuo, complex **a** was obtained as a reddish brown powder (75%). Mp: 209−211 °C. IR (KBr pellet): 3050.98 (m), 2959.88 (s), 2927.76 (w), 2867.43 (w), 1893.46 (w), 1732.38(w), 1583.11 (vs), 1546.96 (w), 1487.02 (m), 1437.40 (vs), 1372.23 (m), 1323.53 (m), 1245.03 (w), 1223.68(m), 1151.26 (s), 1094.70 (m), 1026.96 (w), 954.59(w), 871.48 (w), 841.86 (w), 746.05 (m), 694.12 (s), 620.06 (w), 542.13 (m), 527.71 (s), 509.86 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ −0.38 (d, J = 6.6 Hz, 3H, CH_3), 0.82 (d, J = 6.9 Hz, 3H, CH_3), 1.08 (d, J = 6.6 Hz, 3H, CH_3), 1.70 (d, J = 6.9 Hz, 3H, CH_3), 2.50−2.59 (m, 1H, CH), 4.71−4.81 (m, 1H, CH), 6.04−7.96 (m, 27H, aromatic-H), 10.01 (d, J = 8.4 Hz, 1H, CH=N, Hz). ^{31}P NMR ($CDCl_3$, 300 MHz): δ. 24.41. Anal. Calcd for $C_{47}H_{42}I_2NNiOP{\cdot}Et_2O$: C, 58.09; H, 4.97; N, 1.33. Found: C, 58.10; H, 4.91; N, 1.31.

(1-Naphthyl)(triphenylphosphine){*N*-[1-(2,6-diisopropylphenyl)]-(3,5-dichlorosalicylaldiminate)}nickel(II) (complex b). A dark brown powder was obtained in a manner similar to that for complex **a** in good yield (68%). Red crystals were obtained from CH_3CN. Mp: 174−176 °C. IR (KBr pellet): 3054.36 (s), 2961.20 (vs), 2926.83 (m), 2867.28 (w), 1956.70 (w), 1895.09 (w), 1816.82 (w), 1602.27 (vs), 1545.94 (w), 1512.31 (m), 1479.56 (w), 1449.76 (vs), 1437.20 (vs), 1373.57 (m), 1328.16 (s), 1260.53 (m), 1212.92 (w), 1166.03 (vs), 1118.92 (m), 1095.45 (s), 1071.22 (w), 1026.84 (m), 999.24 (w), 954.21 (w), 933.68 (w), 862.76 (m), 755.03 (s), 745.46 (s), 722.32 (m), 694.68 (vs), 630.54 (w), 541.77 (vs), 509.92 (s), 454.97 (w), 422.10 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ −0.33 (d, J = 6.6 Hz, 3H, CH_3), 0.86 (d, J = 6.6 Hz, 3H, CH_3), 1.11 (d, J = 6.6 Hz, 3H, CH_3), 1.74 (d, J = 6.6 Hz, 3H, CH_3), 2.59−2.68 (m, 1H, CH), 4.70−4.79 (m, 1H, CH), 6.19−7.92 (m, 27H, aromatic-H), 10.12 (d, J = 8.2 Hz, 1H, CH=N). ^{31}P NMR ($CDCl_3$, 300 MHz): δ 24.24. Anal. Calcd for $C_{47}H_{42}Cl_2NNiOP{\cdot}CH_3CN$: C, 70.19; H, 5.41; N, 3.34. Found: C, 70.03; H, 5.50; N, 3.38.

(1-Naphthyl)(triphenylphosphine){*N*-[1-(2,6-diethylphenyl)]-(3,5-diiodosalicylaldiminate)}nickel(II) (complex c). A reddish brown powder was obtained in a manner similar to that for complex **a** in a yield of 37%. Mp: 187−189 °C. IR (KBr pellet): 3049.55 (m), 2967.43 (m), 2930.36 (w), 2873.81 (w), 1897.82 (w), 1581.45 (vs), 1545.59 (w), 1484.63 (m), 1438.66 (vs), 1393.77 (w), 1372.57 (m), 1323.50 (s), 1242.40 (w), 1222.16 (m), 1178.51 (w), 1150.08 (s), 1096.25 (s), 1028.26 (w), 999.84 (w), 954.45 (w), 892.39 (w), 863.88 (w), 843.45 (w), 810.53 (w), 784.86 (w), 772.36 (w), 748.28 (m), 722.96 (w), 693.05 (s), 620.01 (w), 543.49 (w), 527.27 (w), 510.74 (m), 493.10 (w), 422.56 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.62 (t, J = 7.4 Hz, 3H, CH_3), 1.19 (t, J = 7.4 Hz, 3H, CH_3), 1.89−1.98 (m, H, CH_2), 2.36−2.45 (m, H, CH_2), 3.01−3.21 (m, 2H, CH_2), 6.20−7.96 (m, 27H, aromatic-H), 9.46 (d, J = 7.5 Hz, 1H, CH=N). ^{31}P NMR ($CDCl_3$, 300 MHz): δ. 24.56. Anal. Calcd for $C_{45}H_{38}I_2NNiOP{\cdot}Et_2O$: C, 57.34; H, 4.71; N, 1.36. Found: C, 57.18; H, 4.66; N, 1.41.

(1-Naphthyl)(triphenylphosphine){*N*-[1-(2,6-diethylphenyl)]-(3,5-dichlorosalicylaldiminate)}nickel(II) (complex d). A dark brown powder was obtained in a manner similar to that for complex **a** in a yield of 54%. Mp: 167−169 °C. IR (KBr pellet): 3052.06 (m), 2956.12 (w), 2914.21 (m), 2876.52 (w), 1897.45 (w), 1585.88 (s), 1544.53 (m), 1482.37 (s), 1434.78 (vs), 1371.27 (m), 1311.37 (m), 1243.65 (m), 1188.14 (m), 1158.47 (m), 1094.65 (s), 1028.03 (w), 999.58 (w), 954.01 (w), 848.97 (w), 785.67 (m), 744.19 (s), 693.88 (vs), 645.69 (w), 540.36 (m), 513.19 (vs), 494.54 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.07 (t, J = 7.5 Hz, 3H, CH_3), 1.69 (t, J = 7.5 Hz, 3H, CH_3), 2.38 (m, H, CH_2), 2.84 (m, H, CH_2), 4.58−4.72 (m, 2H, CH_2), 7.71−9.30 (m, 27H, aromatic-H), 10.06 (d, J = 8.0 Hz, 1H, CH=N). ^{31}P NMR ($CDCl_3$, 300 MHz): δ 22.08. Anal. Calcd for $C_{45}H_{38}Cl_2NNiOP{\cdot}Et_2O$: C, 69.77; H, 5.74; N, 1.66. Found: C, 70.01; H, 5.71; N, 1.63.

(1-Naphthyl)(triphenylphosphine){*N*-[1-(2,6-dimethylphenyl)]-(3,5-diiodosalicylaldiminate)}nickel(II) (complex e). A reddish brown powder was obtained in a manner similar to that for complex **a** in good yield (63%). Mp: 199−201 °C. IR (KBr pellet): 3050.34 (m), 2978.34 (w), 2914.97 (m), 2878.21 (w), 1897.36 (w), 1776.09 (w), 1581.82 (vs), 1545.39 (m), 1483.23 (s), 1439.23 (vs), 1372.73 (m), 1324.00 (s), 1241.68 (w), 1227.86 (w), 1181.07 (m), 1151.06 (s), 1096.12 (s), 1028.89 (w), 999.70 (w), 954.49 (w), 891.98 (w), 861.06 (w), 844.11 (w), 784.27 (m), 771.00 (m), 744.38 (m), 722.86 (w), 692.75 (s), 646.17 (w), 610.96 (w), 543.94 (m), 527.66 (w), 512.35 (s), 421.02 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 6.19−7.98 (m, 27H, aromatic-H), 9.56 (d, J = 6.9 Hz, 1H, CH=N). ^{31}P NMR ($CDCl_3$, 300 MHz): δ 24.51. Anal. Calcd for $C_{43}H_{34}I_2NNiOP{\cdot}Et_2O$: C, 56.54; H, 4.44; N, 1.40. Found: C, 56.61; H, 4.41; N, 1.39.

(1-Naphthyl)(triphenylphosphine){*N*-[1-(2,6-dimethylphenyl)]-(3,5- dichlorosalicylaldiminate)}nickel(II) (complex f). A reddish brown powder was obtained in a manner similar to that for complex **a** in a yield of 52%. Mp: 178−180 °C. IR (KBr pellet): 3052.77 (m), 2974.14 (w), 2935.83 (w), 2969.51 (w), 1933.49 (w), 1736.71 (w), 1604.97 (vs), 1589.23 (w), 1518.79 (s), 1470.31 (w), 1444.29 (vs), 1372.84 (m), 1328.59 (w), 1315.46 (s), 1242.74 (w), 1221.25 (m), 1171.62 (vs), 1093.62 (m), 1030.10 (w), 998.40 (w), 970.76 (w), 862.65 (m), 779.69 (vs), 763.66 (w), 749.53 (w), 693.88 (s), 625.04 (m), 588.14 (w), 539.84 (w), 520.71 (s), 455.88 (w), 419.84 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.63 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 6.25−7.83 (m, 27H, aromatic-H), 9.69 (d, J = 7.9 Hz, 1H, CH=N). ^{31}P NMR ($CDCl_3$, 300 MHz): δ 22.15. Anal. Calcd for $C_{43}H_{34}Cl_2NNiOP{\cdot}Et_2O$: C, 69.23; H, 5.44; N, 1.72. Found: C, 69.31; H, 5.41; N, 1.75.

X-ray Crystallography. Indensity data of crystal **a** and **e** were collected on a Rigaku R-Axis Rapid IP CCD area detector at 293(2) K with graphite-monochromated Mo Kα radiation (λ = 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. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Each

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[14] Darensbourg, Donald J.; Rainey, P.; Yarbrough, J. *Inorg. Chem.* **2001**, *40*, 986−993; *Chem. Abstr.* **2001**, *134*, 260482r. (b) Ismail, M. M. *Indian J. Pharm. Sci.* **1986**, *48*, 121−124; *Chem. Abstr.* **1986**, *107*, 175589d.

H atom was placed in a calculated position and refined anisotropically. Structure solution and refinement were performed using the SHELXL-97 package. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as CCDC-199518 for complex **a** and CCDC-199519 for complex **e**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Polymerization of Norbornene. In a typical procedure (entry 4, Table 2), the catalyst (5 μmol) was dissolved in 9.50 mL of toluene under nitrogen, and 3.30 mL of a toluene solution of norbornene (7.80 M, 25 mmol of norbornene) was added via syringe. The polymerization was initiated by addition of methylaluminoxane (MAO) (7.2 mL, 10.00 mmol) in toluene via syringe. After 30 min, the polymerization was terminated by injecting 200 mL of acidic ethanol (ethanol−HCl_{conc}, 95:5). The polymer was isolated by filtration, washed with ethanol, and dried in a vacuum at 100 °C for 100 h. Unless otherwise stated, the total reaction volume was 20 mL, which was achieved by variation of the amount of toluene when necessary.

All the polymer samples exhibited similar IR and NMR spectral absorption. The following are the spectral data of the above-mentioned typical procedure. IR (KBr): 2947.55 (vs), 2869.30 (vs), 1473.45 (s), 1452.69 (s), 1374.89 (m), 1295.35 (m), 1258.08 (m), 1222.49 (m), 1147.57 (m), 1108.43 (m), 1041.40 (w), 942.69 (m), 892.91 (m), 756.45 (w) cm^{-1}. ^1H NMR (*o*-dichlorobenzene-d_4, 300 MHz): δ 0.86−2.30 (m, maxima at 0.86, 1.22, 1.58, 2.21). ^{13}C NMR (*o*-dichlorobenzene-d_4, 300 MHz): δ 29.65−50.18 (m, maxima at 29.65, 30.02, 31.79, 32.14, 37.31, 38.63, 47.47, 50.18).

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Supporting Information Available: Text giving experimental details and analysis data for the compounds prepared in this work, and tables of crystals and intensity collection data, positional and thermal parameters, and all bond distances and angles for complexes **a** and **e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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