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Nickel(II) and Palladium(II) Complexes with Tridentate [C,N,S] and [C,N,P] Ligands: Syntheses, Characterization, and Catalytic Norbornene Polymerization

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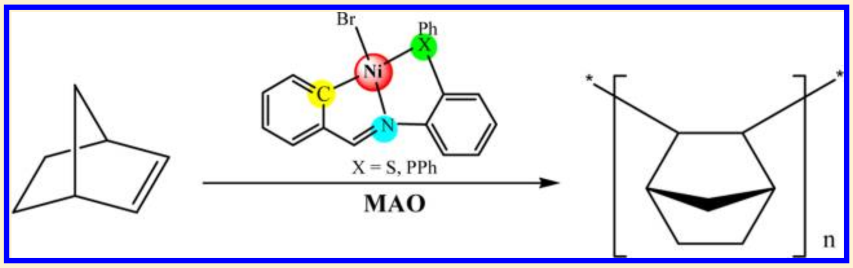
Supporting Information



ABSTRACT: A series of tridentate monoanionic [C$^-$,N,X] (X = S, P) nickel(II) complexes [(C$_6$H$_4$CH=NPh-2-XPh)NiBr] (X = S (**1a**), PPh (**1b**)) and palladium(II) complexes [(C$_6$H$_4$CH=NPh-2-XPh)PdCl] (X = S (**2a**), PPh (**2b**)) were synthesized from the reactions of **La** and **Lb** (**La** = BrC$_6$H$_4$CH=NPh-2-SPh, **Lb** = BrC$_6$H$_4$CH=NPh-2-PPh$_2$) with (DME)NiBr$_2$ and (COD)PdCl$_2$, respectively, in good yields. All complexes were fully characterized by IR, NMR, and elemental analyses. Single-crystal X-ray diffraction analysis of complex **2a** revealed an almost square-planar geometry of the metal center. After activation with methylaluminoxane (MAO), the title complexes **1a,b** and **2a,b** can be used as catalysts for norbornene polymerization to produce vinyl addition type polynorbornene (PNB) with good catalytic activities. The good catalytic activities of complexes **1b** and **2b** as procatalysts which contain a P atom as the third coordinated atom can be maintained even at high temperature, demonstrating their excellent thermal stability.

INTRODUCTION

Olefin polymerization based on late-transition-metal catalysts has been one of the most exciting developments in the area of catalysis, organometallic chemistry, and polymer science in recent years.[1] Norbornene (NB) polymerization has been widely used in industrial production, due to the special optical and mechanical properties of the polymers.[2] Up to now, catalytic systems based on titanium,[3] zirconium,[4] cobalt,[5] chromium,[6] nickel,[7] palladium,[8] and copper[9] have been mainly investigated for the addition polymerization of NB. Among these catalysts, nickel complexes bearing chelate [N,O] and [N,N] ligands exhibited especially high activity.[7]

The side-arm effect of an extra donor has a strong influence on catalytic polymerization.[10−13] Metal complexes coordinated by hard atoms (N, O) and soft atoms (P, S) in the side arm were mainly studied. In 2004, Gibson reported that catalysts which contain phenoxy-amide ligands bearing soft pendant donors showed higher ethylene polymerization activity than the counterparts containing hard donors or systems without a pendant donor.[11a] A series of titanium complexes reported by Tang's group having extra pendant S and P donors on salicylaldiminato ligands showed high activities toward ethylene polymerization and copolymerization with 1-hexene.[11b,c] Our group has also done some research in this field.[13] However, not many nickel and palladium complexes bearing these types of ligands were reported. Recently, a series of anilido-imine N$^-$NP and N$^-$NS tridentate nickel and palladium complexes were synthesized by our group.[13d] After activation with methylaluminoxane (MAO), the nickel(II) complexes can be used as catalysts for norbornene polymerization to produce vinyl addition type polynorbornene (PNB) with high catalytic activities: up to 5.82×10^7 g of PNB (mol of Ni)$^{-1}$ h^{-1}. Chelating anionic aryl carbon atom ligands have become an important class of ligands in homogeneous catalysis and materials chemistry.[14,15] However, most of them were the so-called ECE pincer ligands (ECE is [C$_6$H$_3$(CH$_2$E)$_2$-2,6]$^-$, in which E is NR$_2$, PR$_2$, SR, OMe).[14] Few complexes bearing different donor ligands with [C,X] (X = N, S, P) have been described, and their olefin polymerization was rarely developed.[16] As an ongoing project, we are interested in the design of nickel and palladium complexes with dissimilar donors including an anionic aryl carbon atom as catalysts for olefin polymerization. Herein, we report a series of nickel(II) and palladium(II) complexes with aryl carbon tridentate monoanionic ligands [C$^-$,N,X] (X = S, P) together with their catalytic activity for NB polymerization.

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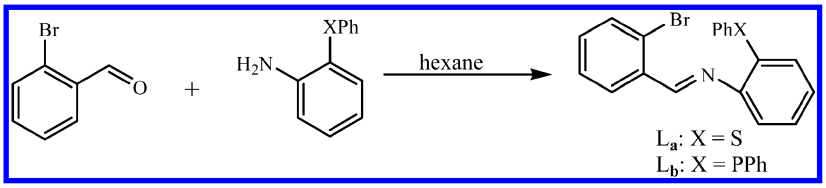
Scheme 1. Synthetic Procedure for La and Lb



■ RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands and Complexes. The synthesis of ligands **La** and **Lb** is outlined in Scheme 1. Condensation of 2-bromobenzaldehyde with 1 equiv of the corresponding substituent anilines in hexane gave **La** and **Lb**.

All ligands were characterized by elemental analysis and IR and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **La** showed a peak at δ 8.77 ppm and that of **Lb** at δ 8.57 ppm, which can be ascribed to the proton C*H*═N. The structures of **La** and **Lb** were further confirmed by single-crystal X-ray diffraction analysis (Figures 1 and 2). In **La**, the C7−N1 bond distance is 1.281(5) Å, while the distance in **Lb** is 1.265(7) Å, which is typical of a carbon−nitrogen double bond.

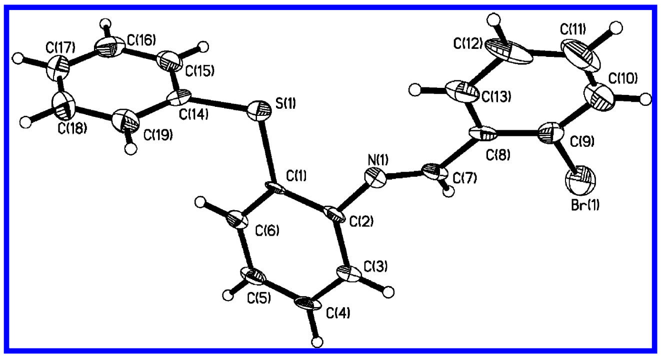


Figure 1. Molecular structure of **La** with thermal ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (deg): Br(1)−C(9) = 1.900(8), S(1)−C(1) = 1.768(6), S(1)−C(14) = 1.773(6), N(1)−C(7) = 1.265(7), N(1)−C(2) = 1.415(8); C(1)−S(1)−C(14) = 103.3(3), C(7)−N(1)−C(2) = 119.8(5), C(6)−C(1)−S(1) = 125.2(5), C(2)−C(1)−S(1) = 115.3(5), N(1)−C(7)−C(8) = 121.6(6), C(10)−C(9)−Br(1) = 116.5(6), C(8)−C(9)−Br(1) = 120.8(6), C(9)−C(8)−C(7) = 123.4(6).

Treatments of the lithium salts of imino ligands with (DME)$NiBr_2$ and (COD)$PdCl_2$ in THF at room temperature afforded the desired nickel and palladium complexes **1a**,**b** and **2a**,**b**, respectively (Scheme 2). In the solid state, all products were stable in dry air but the nickel complexes slowly decomposed in solution. These complexes were well characterized by ^{1}H NMR, IR spectra and elemental analyses. In comparison with the free ligands, the C*H*═N proton signals were shifted approximately 0.1 ppm in the ^{1}H NMR spectrum, indicating the formation of M−N (M = Ni, Pd) bonds. To further confirm the structures of these complexes, a single crystal suitable for X-ray diffraction analyses was obtained from a CH_2Cl_2/hexane solution of **2a** (Figure 3). The geometry at the palladium center can be described as a slightly distorted quadrilateral structure in which the five atoms Pd(1), N(1), S(1), C(1), and Cl(1) are nearly coplanar.

Norbornene Polymerization. With methylaluminoxane (MAO) as cocatalyst, these title complexes were not able to catalyze ethylene polymerization. However, they could be used for norbornene polymerization to afford vinyl addition type polynorbornene (PNB) with high activities after activation with MAO. The polymerization results are summarized in Table1, and the catalytic activities of complexes **1a**,**b** toward norbornene polymerization at different temperatures are presented in Figure 4.

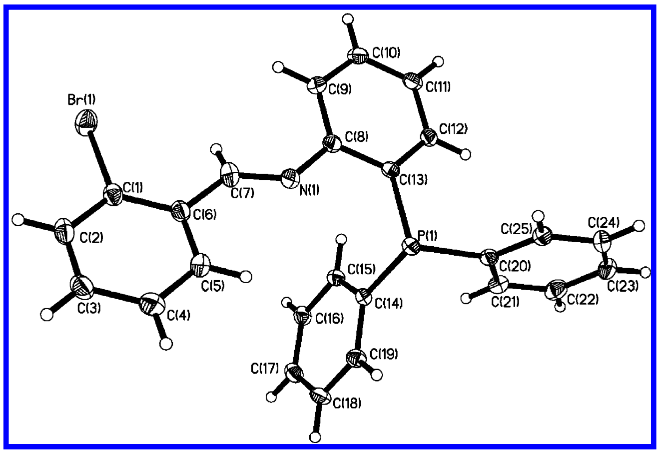
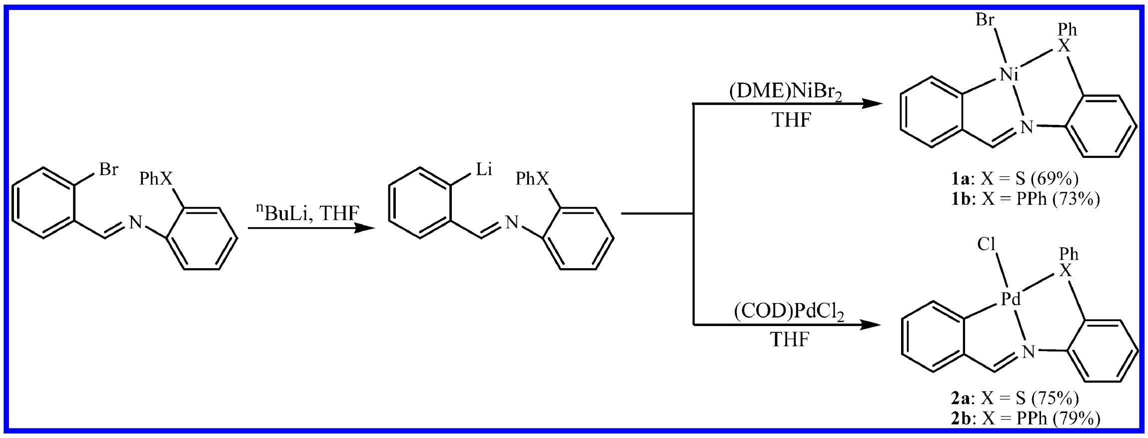


Figure 2. Molecular structure of **Lb** with thermal ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (deg): Br(1)−C(1) = 1.893(4), P(1)−C(14) = 1.825(3), P(1)−C(20) = 1.826(3), P(1)−C(13) = 1.830(3), N(1)−C(7) = 1.281(5), N(1)−C(8) = 1.408(4); C(14)−P(1)−C(20) = 102.86(14), C(14)−P(1)−C(13) = 102.37(14), C(20)−P(1)−C(13) = 101.69(14), C(7)−N(1)−C(8) = 119.6(3), C(2)−C(1)−Br(1) = 118.6(3), C(6)−C(1)−Br(1) = 120.6(3), N(1)−C(7)−C(6) = 121.2(3), C(9)−C(8)−N(1) = 122.5(3), C(13)−C(8)−N(1) = 117.6(3).

To investigate the reaction parameters affecting vinyl polymerization of norbornene, the catalyst precursors **1a**,**b** were typically investigated by changing the ratios of MAO and the reaction temperature. 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. The activity data in Table 1 showed that the optimal Al/Ni ratio was 6000 for the complex **1a**/MAO catalytic system and 8000 for the **1b** system. A lower molecular weight (M_v) of the polymer was observed as the Al/Ni molar ratio was increased (entries 1−3 and 8−10, Table 1). Additionally, the temperature was also investigated for the polymerization with the optimum Al/Ni ratio. We found that the the highest activities were obtained for the complex **1a**/MAO catalytic system at 50 °C and for the **1b**/MAO catalytic system at 100 °C, which indicates that the [C^-,N,P] ligand plays an important role in stabilizing the active species at high temperature. Nevertheless, as elevated temperature, the molecular weights of PNB decrease. This result is due to a faster chain transfer and termination at higher temperature. On comparison of the polymerization behavior of **1a** with that of **1b**, the results show that **1a**, which has an S atom on the side arm, has greater catalytic ability than the corresponding

Scheme 2. Synthesis of Nickel and Palladium Complexes



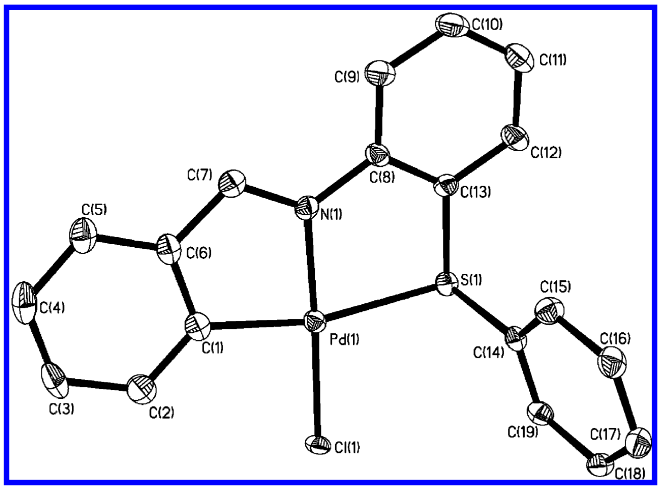


Figure 3. Molecular structure of **2a** with thermal ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 1.994(6), Pd(1)−N(1) = 2.005(5), Pd(1)−Cl(1) = 2.3453(13), Pd(1)−S(1) = 2.3922(15), S(1)−C(13) = 1.785(6), S(1)−C(14) = 1.788(5), N(1)−C(7) = 1.300(7), N(1)−C(8) = 1.430(7); C(1)−Pd(1)−N(1) = 81.3(2), C(1)−Pd(1)−Cl(1) = 96.87(17), N(1)−Pd(1)−Cl(1) = 177.21(13), C(1)−Pd(1)−S(1) = 165.93(17), N(1)−Pd(1)−S(1) = 84.63(14), Cl(1)−Pd(1)−S(1) = 97.16(5), C(13)−S(1)−C(14) = 102.3(2), C(13)−S(1)−Pd(1) = 96.24(19), C(14)−S(1)−Pd(1) = 104.09(18), C(7)−N(1)−C(8) = 123.5(5), C(7)−N(1)−Pd(1) = 115.9(4), C(8)−N(1)−Pd(1) =120.6(4), C(2)−C(1)−Pd(1) = 131.1(5), C(6)−C(1)−Pd(1) = 111.9(4).

analogous complex **1b**, which contains a P atom as the third coordinated atom. The reason for this might be that the structure of complex **1a** could provide more space in the axial direction for the coordination and insertion of norbornene in the polymerization process.[13d,17]

The nature of the metal has a significant influence on the activation process. With the same optimum conditions as for the corresponding nickel complexes, the effects of different metal centers on the polymerization were explored (entries 17 and 18, Table 1). On comparison of Pd complexes **2a**,**b** with Ni complexes **1a**,**b**, higher catalytic activities were observed for Pd, which can probably be attributed to the larger atom semidiameter. The polymers obtained by palladium(II) complexes **2a**,**b** are insoluble in chloroform, benzene, chlorobenzene, 1,2-dichlorobenzene, and *N*,*N*-dimethylformamide, which is different from the case for polymers obtained

Table 1. Results of Norbornene Polymerization Initiated by Complexes 1a,b/MAO and 2a,b/MAO[a]

entry	procat.	Al/M (ratio)	*T* (°C)	amt of polymer (g)	activity[b]	$10^{-4}M_v$[c]
1	**1a**	4000	15	0.586	3.52	8.38
2	**1a**	6000	15	0.850	5.10	7.71
3	**1a**	8000	15	0.642	3.85	5.28
4	**1a**	6000	0	0.653	3.92	3.95
5	**1a**	6000	30	0.885	5.31	3.35
6	**1a**	6000	50	1.10	6.58	2.26
7	**1a**	6000	80	0.855	5.13	1.37
8	**1b**	6000	15	0.079	0.47	5.28
9	**1b**	8000	15	0.149	0.89	3.95
10	**1b**	10000	15	0.129	0.77	3.35
11	**1b**	8000	0	0.105	0.63	4.62
12	**1b**	8000	30	0.137	0.82	2.27
13	**1b**	8000	50	0.151	0.91	1.79
14	**1b**	8000	80	0.385	2.31	1.52
15	**1b**	8000	100	0.656	3.94	1.36
16	**1b**	8000	120	0.612	3.67	1.36
17	**2a**	6000	50	1.421	8.52	d
18	**2b**	8000	100	1.464	8.78	

[a] Conditions: group VIII metal complex, 0.5 μmol; solvent, chlorobenzene (total volume 15 mL); norbornene, 1.68 g; reaction time, 20 min. [b] Activity in 10^6 g of PNB (mol of Ni) $^{-1}$ h^{-1}. [c] M_v measured by the Ubbelohde calibrated viscosimeter technique. [d] Undetermined.

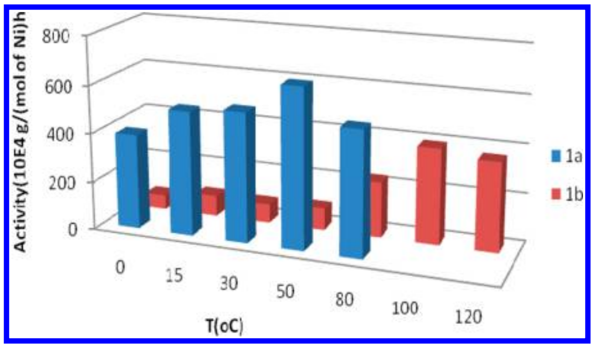


Figure 4. Catalytic activities of complexes **1a**,**b** toward norbornene polymerization at different temperatures. Conditions: complexes, 0.5 μmol; solvent, chlorobenzene, total volume 15 mL; norbornene, 1.68 g; Al/Ni (**1a**, 6000; **1b**, 8000); reaction time, 20 min. The activity is given in units of 10^4 g of PNB (mol of Ni)$^{-1}$ h^{-1}.

with nickel catalysts. The molecular weights of the polymers obtained could not be determined because of their insolubility, which is similar to the results reported.[18]

All polymers showed similar IR and ^{1}H NMR spectra. The absence of signals at 1620−1680, 966, and 735 cm^{-1} in the IR spectra revealed that there were no traces of double bonds, and signals only in the 0.9−3.0 ppm range observed in the ^{1}H NMR spectra supplied the same information.[19] These data indicated that the polymers were vinyl addition type products. Attempts to determine the glass transition temperature (T_g) of PNB failed, and the DSC studies did not give an endothermic signal upon heating to the decomposition temperature (above 450 °C).

■ CONCLUSION

In summary, a series of tridentate monoanionic [C$^-$,N,X] (X = S, P) nickel(II) complexes [($C_6H_4CH{=}NPh$-2-XPh)NiBr] (X = S (**1a**), PPh (**1b**)) and palladium(II) complexes [($C_6H_4CH{=}NPh$-2-XPh)PdCl] (X = S (**2a**), PPh (**2b**)) were synthesized and characterized. With methylaluminoxane (MAO) as cocatalyst, these title complexes were not able to catalyze ethylene polymerization, but norbornene polymerization was possible to afford vinyl addition type polynorbornene (PNB) with good catalytic activities: up to 8.78 × 10^6 g of PNB (mol of Pd)$^{-1}$ h^{-1}. The molecular weights of the polymers obtained by palladium(II) complexes **2a**,**b** could not be determined because of their insolubility.

■ EXPERIMENTAL SECTION

General Data. All manipulations of air- and/or water-sensitive compounds were carried out under dry argon using standard Schlenk techniques. Tetrahydrofran (THF), hexane, and toluene were distilled from sodium−benzophenone. Dichloromethane was distilled from calcium hydride. Commercial reagents, namely $LiAlH_4$, ^{n}BuLi, methylaluminoxane (MAO, 1.46 M in toluene), and 2-bromobenzaldehyde, were purchased from Acros Co. (DME)$NiBr_2$,[20] (COD)$PdCl_2$,[19b] 2-(phenylthio)benzenamine,[11c] and 2-(diphenylphosphino)benzenamine[11c] were synthesized according to the literature procedures. Norbornene was purified by distillation over sodium and used as a chlorobenzene solution. Other commercially available reagents were purchased and used without purification.

IR spectra were measured on a Nicolet Avatar-360 spectrophotometer. NMR measurements were obtained on a Bruker AC 400 spectrometer in $CDCl_3$ solution. The NMR spectra of all the compounds and complexes were recorded at ambient temperature. Elemental analyses for C, N, and H were carried out on an Elementar III Vario EI analyzer.

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) measurements were obtained on a Bruker AC500 spectrometer in $CDCl_3$ solution. Elemental analyses for C, H, and N were carried out on an Elementar III Vario EI analyzer. The intrinsic viscosity (η) was measured in chlorobenzene at 25 °C using an Ubbelohde viscometer. Viscosity average molecular weight (M_v) values of polymer were calculated by the following equation: $\eta = (5.97 \times 10^{-4})M_v^{0.56}$.[21]

Synthesis of Ligands. *(E)-N-(2-Bromobenzylidene)-2-(phenylthio)benzenamine (**La**).* A solution of 2-bromobenzaldehyde (0.93 g, 5 mmol), 2-(phenylthio)benzenamine (1.01 g, 5 mmol), and 0.07 g of $MgSO_4$ in *n*-hexane (20 mL) was stirred for 12 h at room temperature. The mixture was then filtered and washed with CH_2Cl_2. The combined bright yellow solution was concentrated to dryness to give a yellow powder. Pure products were obtained as yellow crystals by recrystallization from ethanol in a yield of 72%.

IR (KBr): 3542 (m), 3465 (s), 3414 (s), 3049 (w), 2952 (w), 2911 (s), 1616 (s), 1565 (m), 1469 (m), 1434 (m), 1355 (m), 1267 (m), 1191 (m), 1057 (m), 1022 (m), 754 (s), 728 (m), 689 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H, C*H*=N-Ar), 8.25 (t, 1H, Ar-*H*), 7.63 (d, 1H, Ar-*H*), 7.47 (d, 2H, Ar-*H*), 7.41 (t, 1H, Ar-*H*) 7.24−7.37 (m, 5H, Ar-*H*), 7.05−7.15 (m, 3H, Ar-*H*). Anal. Calcd for $C_{19}H_{14}BrNS$: C, 61.96; H, 3.83; N, 3.80. Found: C, 61.83; H, 3.95; N, 3.82.

*(E)-N-(2-Bromobenzylidene)-2-(diphenylphosphino)benzenamine (**Lb**).* A procedure similar to that for the preparation of **La** was used, starting from 2-bromobenzaldehyde (0.93 g, 5 mmol), 2-(diphenylphosphino)benzenamine (1.39 g, 5 mmol), and 0.07 g of $MgSO_4$ in *n*-hexane (20 mL). Workup afforded **Lb** as a light yellow powder. Pure products were obtained as light yellow crystals by recrystallization from ethanol in a yield of 55%.

IR (KBr): 3481 (m), 3416 (m), 3301 (m), 3044 (w), 2927 (w), 2920 (w), 1614 (s), 1594 (s),1562 (s), 1449 (m), 1434 (s), 1470 (m), 1324 (m), 1172 (m), 1105 (m), 1025 (m), 766 (s), 754 (s), 736 (s), 698 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H, C*H*=N-Ar), 7.92 (d, 1H, Ar−H), 7.71 (t, 3H, Ar-*H*), 7.49−7.62 (m, 6H, Ar-*H*), 7.32 (m, 3H, Ar-*H*), 7.08 (m, 3H, Ar-*H*), 6.86 (d, 1H, Ar-*H*), 6.58 (t, 1H, Ar-*H*). Anal. Calcd for $C_{25}H_{19}BrNP$: C, 67.58; H, 4.31; N, 3.15. Found: C, 67.35; H, 4.35; N, 3.20.

Synthesis of Complexes. *Ni[C$^-$NS]Br (**1a**).* ^{n}BuLi (1.6 M, 0.13 mL, 0.2 mmol) was added by syringe to a solution of **La** (74 mg, 0.2 mmol) in THF (15 mL) cooled to 0 °C. The resulting orange solution was stirred at room temperature for 2 h and then was transferred dropwise into a suspension of (DME)$NiBr_2$ (62 mg, 0.2 mmol) in dried THF (15 mL) at −78 °C, and the resulting mixture was slowly warmed to room temperature and stirred overnight at room temperature. The crude reaction mixture was filtered under nitrogen and concentrated under reduced pressure to ca. 2 mL, and then dry hexane (20 mL) was added. The solvent was filtered, and the residual brown solid was washed with *n*-hexane. Drying in vacuo produced the desired nickel complex in a yield of 69%.

IR (KBr): 3436 (s), 2902 (w), 2854 (w), 1632 (s), 1505 (s), 1478 (m), 1437 (m), 1261 (m), 1099 (m), 1025 (m), 803 (s), 751 (m), 703 (m), 617 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H, C*H*=N-Ar), 7.82 (d, 1H, Ar-*H*), 7.73 (d, 1H, Ar-*H*), 7.69 (t, 1H, Ar-*H*), 7.48−7.62 (m, 4H, Ar-*H*), 7.41 (d, 1H, Ar-*H*), 7.29 (d, 3H, Ar-*H*), 7.17 (t, 1H, Ar-*H*), 7.11 (s, 1H, Ar-*H*). Anal. Calcd for $C_{19}H_{14}BrNNiS$: C, 53.45; H, 3.30; N, 3.28. Found: C, 53.43; H, 3.40; N, 3.25.

*Ni[C$^-$NP]Br (**1b**).* This complex was prepared as described above for **1a**, starting from ^{n}BuLi (1.6 M, 0.13 mL, 0.2 mmol), **Lb** (89 mg, 0.2 mmol), and (DME)$NiBr_2$ (0.062 g, 0.2 mmol). Workup afforded **1b** as a light brown powder in a yield of 73%.

IR (KBr): 3420 (s), 2957 (w), 1622 (s), 1560 (s), 1436 (m), 1252 (w), 1154 (w), 1120 (m), 1026 (w), 761 (m), 747 (m), 724 (m), 691 (s), 619 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H, C*H*=N-Ar), 8.02 (d, 1H, Ar-*H*), 7.79 (t, 3H, Ar-*H*), 7.52−7.70 (m, 6H, Ar-*H*), 7.40 (m, 3H, Ar-*H*), 7.12 (m, 3H, Ar-*H*), 6.98 (d, 1H, Ar-*H*), 6.63 (t, 1H, Ar-*H*). Anal. Calcd for $C_{25}H_{19}BrNNiP$: C, 59.70; H, 3.81; N, 2.78. Found: C, 59.73; H, 3.85; N, 2.70.

*Pd[C$^-$NS]Cl (**2a**).* This complex was prepared as described above for **1a**, starting from ^{n}BuLi (1.6 M, 0.13 mL, 0.2 mmol), **La** (74 mg, 0.2 mmol), and (COD)$PdCl_2$ (60 mg, 0.2 mmol). Workup afforded **2a** as a brown powder in a yield of 75%.

IR (KBr): 3433 (s), 2936 (w), 1637 (s), 1541 (m), 1475 (m), 1437 (w), 1380 (w), 1188 (w), 1072 (m), 1018 (m), 982 (m), 750 (s), 695 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H, C*H*=N-Ar), 7.90 (d, 1H, Ar-*H*), 7.79 (d, 1H, Ar-*H*), 7.71 (t, 1H, Ar-*H*), 7.49−7.61 (m, 4H, Ar-*H*), 7.43 (d, 1H, Ar-*H*), 7.33 (d, 3H, Ar-*H*), 7.15 (t, 1H, Ar-*H*), 7.01 (s, 1H, Ar-*H*). Anal. Calcd for $C_{19}H_{14}ClNPdS$: C, 53.04; H, 3.28; N, 3.26. Found: C, 52.98; H, 3.35; N, 3.30.

*Pd[C$^-$NP]Cl (**2b**).* This complex was prepared as described above for **1a**, starting from ^{n}BuLi (1.6M, 0.13 mL, 0.2 mmol), **Lb** (89 mg, 0.2 mmol), and (COD)$PdCl_2$ (60 mg, 0.2 mmol). Workup afforded **2b** as a brown powder in a yield of 79%.

IR (KBr): 3433 (s), 2957 (w), 2931(w), 1634 (s), 1591 (m), 1457 (m), 1436 (s), 1319 (m), 1257 (m), 1100 (m), 1021 (m), 802 (m), 747 (m), 691 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H, C*H*=N-Ar), 8.17 (d, 1H, Ar-*H*), 7.84 (t, 3H, Ar-*H*), 7.63−7.74 (m, 6H, Ar-*H*), 7.48 (m, 3H, Ar-*H*), 7.24 (m, 3H, Ar-*H*), 7.01 (d, 1H, Ar-

H), 6.77 (t, 1H, Ar-*H*). Anal. Calcd for $C_{25}H_{19}ClNPPd$: C, 59.31; H, 3.78; N, 2.77. Found: C, 59.28; H, 3.82; N, 2.74.

X-ray Crystallography. Single crystals of complexes **La**, **Lb**, and **2a** suitable for X-ray analysis were obtained from CH_2Cl_2/*n*-hexane solutions. The intensity data of the single crystals were collected on the CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were collected at room temperature or −100 °C using the ω scan technique. These structures were solved by direct methods using Fourier techniques and refined on F^2 by full-matrix least-squares methods. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined.

*Crystal data for **La**:* $C_{19}H_{14}BrNS$, M_r = 368.28, T = 293(2) K, monoclinic, space group $C2/c$, a = 29.613(19) Å, b = 7.948 (5) Å, c = 17.260(11) Å, β = 123.962(8)°, V = 3369(4) Å^3, Z = 8, ρ_{calcd} = 1.452 g cm^{-3}, 6566 total reflections, 2951 of which were independent (R_{int} = 0.1447). The structure was refined to final R1 = 0.0739 ($I > 2\sigma(I)$), wR2 = 0.1211 (all data), GOF = 0.943, and maximum/minimum residual electron density 0.689/−0.582 e Å^{-3}.

*Crystal data for **Lb**:* $C_{25}H_{19}BrNP$, M_r = 444.29, T = 173(2) K, monoclinic, space group $P2_1/c$, a = 10.739(2) Å, b = 17.527(4) Å, c = 11.279(2) Å, β = 106.456(3)°, V = 2036.0(7) Å^3, Z = 4, ρ_{calcd} =1.449 g cm^{-3}, 14480 total reflections, 4669 of which were independent (R_{int} = 0.0435). The structure was refined to final R1 = 0.0476 ($I > 2\sigma(I)$), wR2 = 0.0541 for all data, GOF = 1.065, and maximum/minimum residual electron density 1.672/−0.528 e Å^{-3}.

*Crystal data for **2a**:* $C_{19}H_{14}ClNPdS$, M_r = 430.22, T = 173(2) K, monoclinic, space group $P2_1/c$, a = 12.2201(12) Å, b = 15.1340(16) Å, c = 9.0568(10) Å, β = 106.708(2)°, V = 1604.2(3) Å^3, Z = 4, ρ_{calcd} =1.781 g cm^{-3}, 11974 total reflections, 3779 of which were independent (R_{int} = 0.0625). The structure was refined to final R1 = 0.0447 ($I > 2\sigma(I)$), wR2 = 0.1505 for all data, GOF = 0.858, and maximum/minimum residual electron density 1.359/−0.584 e Å^{-3}.

Polymerization of Ethylene. A 100 mL flask was equipped with an ethylene inlet and a magnetic stirrer and attached to a vacuum line. The flask was filled with 30 mL of freshly distilled toluene, MAO (10 wt % in toluene) was added, and the flask was placed in a bath at the desired polymerization temperature for 10 min. The polymerization reaction was started by adding a toluene solution of the catalyst precursor (2 μmol) with a syringe. Then the solvent toluene was added to make the total volume of the solution 50 mL. The polymerization was terminated by addition of acidic ethanol ($V_{ethanol}/V_{concd\ HCl}$ = 20/1).

Polymerization of Norbornene. In a typical procedure (entry 5, Table 1), 0.5 μmol of nickel complex **1a** in 0.5 mL of chlorobenzene, 1.68 g of norbornene in 3.0 mL of chlorobenzene, and another 9.5 mL of fresh chlorobenzene were placed in a special polymerization bottle (50 mL) with a strong stirring under a nitrogen atmosphere. After the mixture was kept at 30 °C for 10 min, 2.0 mL of MAO was charged into the polymerization system via syringe and the reaction was initiated. Twenty minutes later, acidic ethanol ($V_{ethanol}/V_{concd\ HCl}$ = 20/1) was added to terminate the reaction. The PNB was isolated by filtration, washed with ethanol, and dried at 80 °C for 48 h under vacuum. For all polymerization procedures, the total reaction volume was 15.0 mL, which can be achieved by varying the amount of chlorobenzene when necessary. IR (KBr, cm^{-1}): 2945 vs, 2867 vs, 1476 m, 1450 s, 1375 m, 1296 m, 1257 m, 1222 m, 1148 m, 1106 m, 1040 w, 941 w, 893 m, 805 m. ^{1}H NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ 0.9−3.05 ppm (m, maxima at 1.50, 1.88, 2.21, 2.59). ^{13}C NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ 30.2−48.9 ppm (m, maxima at 32.45, 39.11, 48.42, 48.67).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for **La**, **Lb**, and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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