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Synthesis, Structure, and Olefin Polymerization Behavior of Nickel Complexes with Carborane [S,C] or [S,S] Ligands

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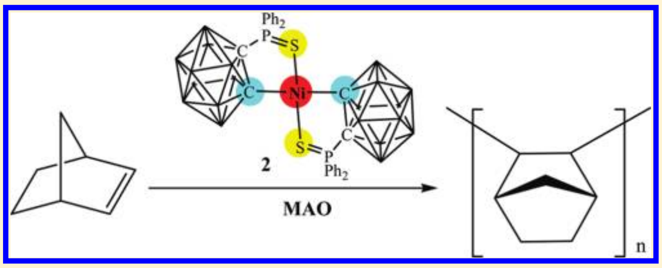
Supporting Information



ABSTRACT: The *o*-carborane [S,C] ligand **1** (1-(2′-(S)PPh$_2$)-*o*-carborane) was prepared by the reaction of a monophosphino *o*-carborane with elemental sulfur in the presence of Et$_3$N. Ligand **1** was lithiated with *n*-BuLi and then reacted with (Ph$_3$P)Ni(Ph)Cl$_2$, Ni(PPh$_3$)$_2$Cl$_2$, and (DME)NiBr$_2$, respectively, to give the same mononuclear Ni complex [1-(2′-(S)-PPh$_2$)-*o*-carborane]$_2$Ni (**2**). Additionally, the lithium salt of ligand **1** was treated with elemental sulfur and then reacted with (Ph$_3$P)Ni(Ph)Cl$_2$, affording the mononuclear Ni complex [1-S-(2′-(S)PPh$_2$)-*o*-carborane]$_2$Ni (**3**). Ni complexes **2** and **3** were characterized by IR, ^{1}H NMR, and ^{31}P NMR spectroscopy and elemental analysis. In addition, an X-ray structure analysis was performed on complex **2**, where the *o*-carborane [S,C] ligand **1** was found to coordinate in a bidentate mode. EXAFS spectroscopy was performed on complex **3** to confirm that the coordination geometry was similar to that for complex **2**. Two nickel complexes with carborane [S,C] or [S,S] ligands show good catalytic activities for the addition polymerization of norbornene in the presence of methylaluminoxane (MAO) as cocatalyst. Catalytic activities, molecular weights, and molecular weight distributions of polynorbornene (PNB) have been investigated under various reaction conditions.

INTRODUCTION

Norbornene polymerization has been widely used in industrial production, due to the special optical and mechanical properties of the polymers.[1] The norbornene addition polymerization product (PNB) displays a characteristic rigid random coil conformation, which shows restricted rotation about the main chain and exhibits high thermal stability (T_g > 350 °C). In addition, it has excellent dielectric properties, optical transparency, and unusual transport properties.[2] Therefore, it has been attractive to many chemists to study the NB (norbornene) addition−polymerization using organometallic complexes as catalysts. 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. Nickel complexes bearing [N,O] and [N,N] ligands employed for norbornene polymerization exhibited especially high activity.[7]

In the past two decades, transition-metal complexes with ligands containing dissimilar donor atoms have been widely studied, primarily for their applications in important homogeneous catalytic processes.[10] The coordinative labile donor atom in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle; at the same time, the strong donor moiety remains connected to the metal center. Therefore, the design of such ligand systems containing one functional group strongly bound to a late transition metal and another coordinative labile group has been of considerable interest.[11] In materials science or chemical research, rational design of new *o*-carborane-derived materials has attracted much attention.[12] Some reports on unusually stable C,N-,[13] C,P-,[14] N,S-,[15] N,P-,[16] and S,S-chelating[17] *o*-carboranyl metal complexes seem to imply that the rigid chelate conformation and the *o*-carboranyl ligand backbone might be ideal for the stabilization of possible metal intermediates in organometallic reactions. However, to the best of our knowledge, there are few reports on using carborane ligands to synthesize olefin polymerization catalysts.[18,19] It was therefore of interest to design a new family of nickel complexes containing dissimilar donor atoms as catalysts for olefin polymerization. In this paper, we describe the preparation, structures, and catalytic properties of norbornene addition polymerization of the nickel complexes with carborane [S,C] or [S,S] ligands.

RESULTS AND DISCUSSION

The *o*-carborane [S,C] ligand **1** was obtained in good yield by the reaction of a monophosphino *o*-carborane[20] with 1 equiv of

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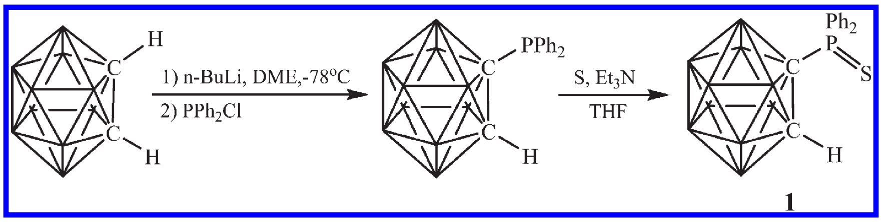
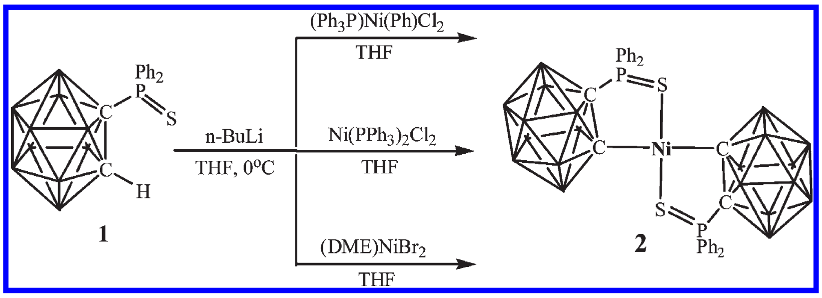
Scheme 1. Synthesis of Ligand 1



Scheme 2. Synthesis of Complex 2



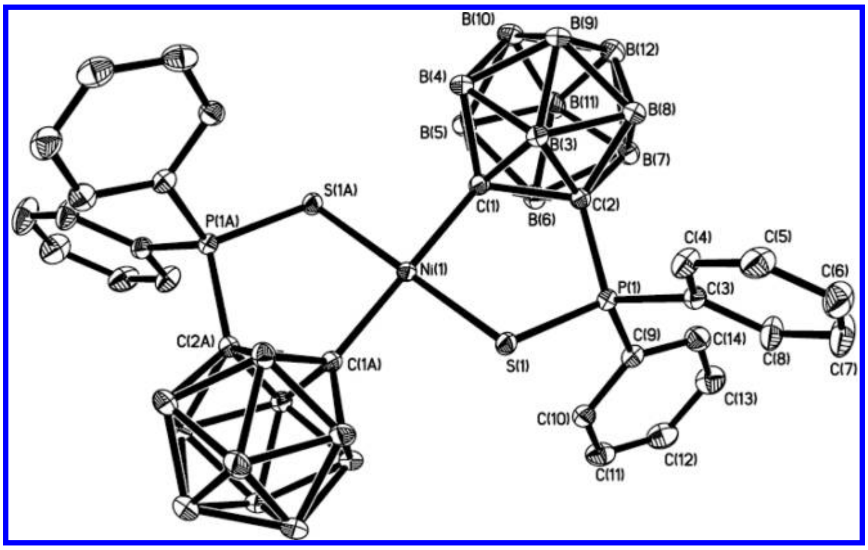


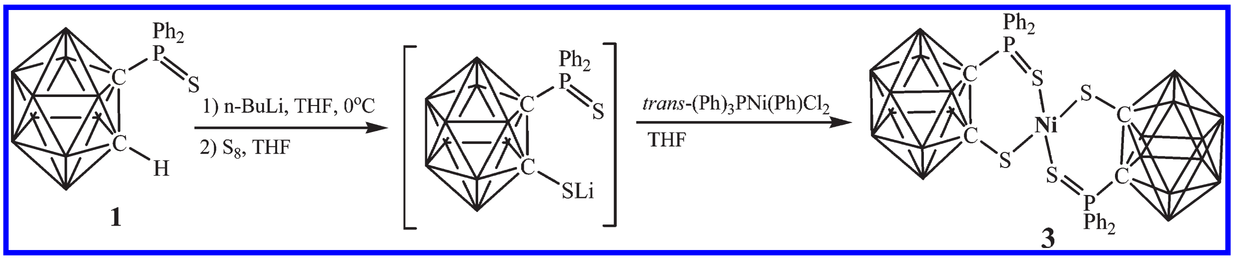
Figure 1. ORTEP drawing of the molecular structure of complex **2**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)−C(1) = 1.989(3), Ni(1)−S(1) = 2.2039(7), C(1)−C(2) = 1.711(4), S(1)−P(1) = 2.0024(11); C(1)−Ni(1)−C(1A) = 180.00(16), S(1A)−Ni(1)−S(1) = 179.998(1), C(1)−Ni(1)−S(1) = 93.26(9), C(1A)−Ni(1)−S(1) = 86.74(9), C(2)−P(1)−S(1) = 105.12(10).

elemental sulfur in the presence of Et$_3$N in refluxing THF (Scheme 1). The ligand **1** was characterized by IR, ^{1}H NMR, and ^{31}P NMR spectroscopy.

Ligand **1** was lithiated with *n*-BuLi and then reacted with (Ph)$_3$PNi(Ph)Cl$_2$, Ni(PPh$_3$)$_2$Cl$_2$, and (DME)NiBr$_2$, respectively, to give a product with the same structure (Scheme 2). The nickel complex **2** is resolvable in common organic solvents, such as THF, CH$_2$Cl$_2$, and toluene. The complex **2** is stable for a short time in air due to the formation of a five-membered chelate ring.

Complex **2** has been fully characterized by IR, ^{1}H NMR, and ^{31}P NMR spectra and elemental analysis (see the Experimental Section). The molecular structure of complex **2** was determined by single-crystal X-ray diffraction studies. Dark red crystals of complex **2** suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of hexane into its CH$_2$Cl$_2$ solution. The molecular structure and selected bond distances and angles are depicted in Figure 1. The molecular structure reveals that the geometry at the nickel atom is distorted square planar, two chelates [S,C] adopt a trans arrangement around the nickel atom, and there is C_2 symmetry. The C(2)−P(1)−S(1) angle within the five-membered ring is smaller (105.12(10)°) than the expected 108°. The C(1)−Ni(1)−S(1) angle is slightly larger (93.26(9)°) than a right angle. The angles C(1)−Ni(1)−C(1A) (180.00(16)°) and S(1A)−Ni(1)−S(1) (179.998(1)°) are close to a straight angle, confirming that atoms C(1), Ni(1), C(1A) and S(1A), Ni(1), S(1) are in a line, respectively. The

Scheme 3. Synthesis of Complex 3



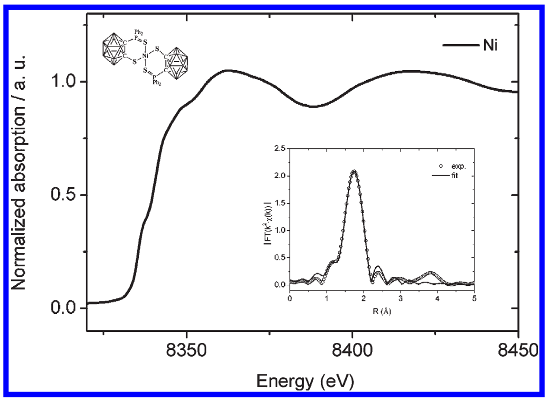


Figure 2. Ni K-edge XANES spectrum of **3**. The inset gives the Fourier transform of experimental data and fit for **3**.

Table 1. Fit Parameters of Ni EXAFS Spectra for Complex 3

shell	N^a	R^b	σ^2 (10^{-3} Å^2) ^{c}	ΔE_0 (eV) ^{d}
Ni−S	3.2 ± 0.2	2.19 ± 0.01	3.1 ± 0.8	5.9 ± 0.7

[a] Coordination number. [b] Distance between absorber and backscatterer atoms. [c] Debye−Waller factor. [d] Inner potential correction.

Table 2. Addition Polymerization of Norbornene with 2 and 3 Activated by MAO[a]

entry	complex	Al/Ni ratio	temp/°C	activity[b]	M_v[c]	M_w[d]	M_w/M_n[d]
1	**2**	4000	30	0.98	7.5		
2	**2**	6000	30	1.77	8.0	9.8	2.1
3	**2**	8000	30	1.43	8.3		
4	**2**	10000	30	1.10	8.7		
5	**2**	6000	0	0.50	8.2		
6	**2**	6000	50	1.55	7.0	8.8	2.0
7	**2**	6000	80	1.15	5.6		
8	**3**	4000	30	0.58	4.9		
9	**3**	6000	30	1.13	6.0		
10	**3**	8000	30	1.37	7.7	8.6	2.0
11	**3**	10000	30	0.95	8.1		
12	**3**	8000	0	0.38	8.3		
13	**3**	8000	50	1.25	7.1		
14	**3**	8000	80	0.92	5.4		

[a] Conditions: nickel complex, 0.8 μmol; solvent, chlorobenzene (total volume 15 mL); norbornene, 1.88 g; reaction time, 30 min. [b] In units of 10^6 g of PNB (mol of Ni)$^{1-}$ h^{-1}. [c] M_v (10^{-5} g mol^{-1}) values were measured by the Ubbelohde calibrated viscosimeter technique. [d] M_w (10^{-5} g mol^{-1}) and M_w/M_n values were determined by GPC.

Ni−S bond lengths of 2.2039(7) Å are typical for Ni−S bonds.[21] The Ni−C distances (1.989(3) Å) in **2** are similar to those observed in other crystallographically characterized nickel(II) complexes.[22]

Additionally, the lithium salt of ligand **1** was treated with 1 equiv of elemental sulfur and then reacted with $(Ph_3P)Ni(Ph)Cl_2$, affording the mononuclear Ni complex $[1\text{-S-}(2'\text{-}(S)PPh_2)\text{-}o\text{-carborane}]_2Ni$ (**3**) (Scheme 3).

Complex **3** has been characterized by IR, ^{1}H NMR, and ^{31}P NMR spectra and elemental analysis. The local atomic environment and charge state of the metal center in complex **3** was further confirmed by X-ray absorption spectroscopy, including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) (Figure 2). The Fourier transform of the EXAFS spectrum (inset of Figure 2, bottom) only comprises one main peak, which corresponds to the sulfur donor atoms in the first coordination sphere of the metal ion. The fitting results are summarized in Table 1. The fitting analysis for the first shell confirms that the nickel ions in this complex have the coordination number 3.2 ± 0.2, which is in the typical range of a four-coordinate NiS_4 environment. The average Ni−S distance is 2.19 Å. This bond lengths for **3** are similar to those observed in other crystallographically characterized nickel(II) complexes (average value of 2.10 Å).[21]

Preliminary experiments indicated that nickel complexes **2** and **3** can be used as catalysts for norbornene polymerization in the presence of MAO as a cocatalyst. The polymerization results are summarized in Table 2. It was revealed that MAO was essential for the polymerization. In the complex **2**/MAO catalytic system, the optimal Al/Ni ratio was 6000. Increasing the Al/Ni molar ratio from 4000 to 6000 led to higher activity in norbornene polymerization and molecular weight (M_v) of the polymer (entries 1−3, Table 2). However, when the Al/Ni ratio was increased to 8000 or 10 000, the catalytic activity slightly decreased (entries 4 and 5, Table 2). Additionally, the temperature was also crucial for the polymerization. We found that the complex **2**/MAO catalytic system showed the highest activity at room temperature (30 °C). The complex **3**/MAO catalytic system can also polymerize norbornene with moderate activity (entries 8−14, Table 2). The highest activity appears at 30 °C in the optimal Al/Ni molar ratio (entry 10, Table 2). The drop in activity at higher temperature seems to be indicative of complex decomposition. The molecular weights (M_v) of the resulting polymer are in the range of 490 000−870 000 with moderate molecular weight distributions (M_w/M_n = 2).

The norbornene polymerization catalyzed by complexes **2** and **3** was the typical addition-vinyl type as confirmed by IR, ^{1}H and ^{13}C NMR, and GPC analyses of the obtained PNB. The resonances of PNB appear at 0.9−3.03 ppm (m, maxima at 1.52, 1.87, 2.23, 2.59 ppm) in the ^{1}H NMR, and the absence of bands in the range 1680−1620 cm^{-1} in the IR spectra indicated no double bonds, which was different from the case for the polymers of norbornene ring-opening metathesis polymerization.[23] The ^{13}C NMR spectrum of PNB shows the main resonances at δ 30.0−48.8 ppm (m, maxima at 32.43, 39.12, 48.39, 48.77 ppm), attributed to the vinyl-addition polymer structure of polynorbornene, bridge carbon, bridgehead carbon, and the backbone carbon.[24] All of the obtained PNB are soluble in chlorobenzene, *o*-dichlorobenzene, and cyclohexane solvents, which indicates low stereoregularity.[25] Attempts to determine the glass transition temperatre (T_g) of PNB failed, and DSC studies did not give an endothermic signal upon heating to the decomposition temperature (above 450 °C).

CONCLUSION

We have synthesized two nickel complexes containing an *o*-carboranyl S,C or S,S chelating ligand. The combination of X-ray crystallographic and X-ray absorption spectroscopy confirms the structures of these mononuclear nickel complexes. A preliminary study shows that the new complexes **2** and **3** can be used as catalysts for the addition polymerization of norbornene and exhibited high activities in the presence of excess methylaluminoxane (MAO). Further investigations of the olefin polymerization of such complexes and of the polymerization mechanism are ongoing.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed using standard Schlenk techniques. Dichloromethane was distilled from calcium hydride. Commercial reagents, namely ^{n}BuLi (1.6 M in hexene), Et$_3$N, sulfur, methylaluminoxane (MAO, 1.46 M in toluene), *trans*-(Ph$_3$P)Ni-(Ph)Cl$_2$ and norbornene, were purchased from Acros Co. (DME)NiBr$_2$,[26] Ni(PPh$_3$)$_2$Cl$_2$,[27] and 1-(PPh$_2$)-1,2-C$_2$B$_{10}$H$_{11}$[20] were prepared according to the literature. Other solvents were used as received as technical grade solvents. IR (KBr) spectra were recorded on a Nicolet FT-IR spectrophotometer. ^{1}H NMR measurements were obtained on a Bruker AC 400 spectrometer in CDCl$_3$ solution. ^{31}P NMR (162 MHz) spectra were measured with a VAVCE DMX-400 spectrometer. Elemental analyses for C and H were carried out on an Elementar III Vario EI analyzer.

Synthesis of 1. Sulfur (32 mg, 0.5 mmol) and 2 mL of triethylamine were added to a solution of 1-(PPh$_2$)-1,2-C$_2$B$_{10}$H$_{11}$ (164.2 mg, 0.5 mmol) in THF (10 mL). The reaction mixture was stirred at reflux temperature for 2 h and cooled to room temperature. Purification by column chromatography used 1/3 ethyl acetate/petroleum ether. The product was obtained as white needles in 85% yield. IR (KBr, cm^{-1}): 3052 m, 3023 s (carborane C−H), 2571 s (BH), 1642 w, 1584 m, 1436 s (Ph), 690 s (P═S). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.25−8.19 (m, 5H, Ph H), δ 7.56−7.54 (m, 5H, Ph H), 4.66(s, 1H, carborane CH), 2.78−2.05 (br, 10H, carborane BH). ^{31}P NMR (162 MHz, CDCl$_3$, H$_3$PO$_4$, 25 °C): δ 51.33 (s, P═S) ppm.

Synthesis of 2. *Method 1.* To a stirred solution of **1** (90 mg, 0.25 mmol) in 15 mL of THF, which was cooled to −78 °C, was added 1.6 M of *n*-BuLi (0.16 mL, 0.25 mmol) via a syringe. The resulting pale yellow solution was stirred at −78 °C for 1 h and then transferred through a cannula to a solution of *trans*-(Ph)$_3$PNi(Ph)Cl (87 mg, 0.125 mmol) in 15 mL of THF. The resulting dark red solution was warmed to room temperature and stirred overnight. The solvent was removed under vacuum, leaving a dark red powder. Recrystallization of the product from CH$_2$Cl$_2$/hexane afforded **2** as dark red crystals in a yield of 71%. IR (KBr, cm^{-1}): 2567 m (BH), 1631 m, 1576 m, 1436 s (Ph), 693 s (P═S). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.23−7.46 (m, 20 H, Ph H), 2.9−1.8 (br, 20H, carborane BH). ^{31}P NMR (162 MHz, CDCl$_3$, H$_3$PO$_4$, 25 °C): δ 68.26 (s, P═S) ppm. Anal. Calcd for C$_{28}$H$_{40}$B$_{20}$NiP$_2$S$_2$: C, 43.25; H, 5.18. Found: C, 43.29; H, 5.21.

Method 2. To a stirred solution of **1** (90 mg, 0.25 mmol) in 15 mL of THF, which was cooled to −78 °C, was added 1.6 M *n*-BuLi (0.16 mL, 0.25 mmol) via a syringe. The resulting pale yellow solution was stirred at −78 °C for 1 h and then transferred through a cannula to a solution of Ni(PPh$_3$)$_2$Cl$_2$ (81.7 mg, 0.125 mmol) in 15 mL of THF. The resulting dark red solution was warmed to room temperature and stirred overnight. The solvent was removed under vacuum, leaving a dark red powder. Recrystallization of the product from CH$_2$Cl$_2$/hexane afforded **2** as dark red crystals in a yield of 63%.

Method 3. To a stirred solution of **1** (90 mg, 0.25 mmol) in 15 mL of THF, which was cooled to −78 °C, was added 1.6 M *n*-BuLi (0.16 mL, 0.25 mmol) via a syringe. The resulting pale yellow solution was stirred at −78 °C for 1 h and then transferred through a cannula to a solution of (DME)NiBr$_2$ (38.2 mg, 0.125 mmol) in 15 mL of THF. The resulting dark red solution was warmed to room temperature and stirred overnight. The solvent was removed under vacuum, leaving a dark red powder. Recrystallization of the product from CH$_2$Cl$_2$/hexane afforded **2** as dark red crystals in a yield of 80%.

Synthesis of 3. To a stirred solution of **1** (90 mg, 0.25 mmol) in 15 mL of THF, which was cooled to −78 °C, was added 1.6 M *n*-BuLi (0.16 mL, 0.25 mmol) via a syringe. The resulting pale yellow solution was stirred at −78 °C for 1 h. Sulfur (8 mg, 0.25 mmol) was added after the reaction mixture was warmed to room temperature. The resulting yellow solution was transferred through a cannula to a solution of *trans*-(Ph)$_3$PNi(Ph)Cl$_2$ (87 mg, 0.125 mmol) in 15 mL of THF. The resulting dark red solution was warmed to room temperature and stirred overnight. The solvent was removed under vacuum, leaving a dark red powder. Recrystallization of the product from CH$_2$Cl$_2$/hexane afforded **3** as a dark red powder in a yield of 66%. IR (KBr, cm^{-1}): 2573 m (BH), 1637 m, 1570 m, 1434 s (Ph), 691 s (P═S). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.71−7.45 (m, 20H, Ph H), 3.18−1.74 (br, 20H, carborane BH). ^{31}P NMR (162 MHz, CDCl$_3$, H$_3$PO$_4$, 25 °C): δ 43.99 (s, P═S) ppm. Anal. Calcd for C$_{28}$H$_{40}$B$_{20}$NiP$_2$S$_4$: C, 39.95; H, 4.79. Found: C, 39.91; H, 4.80.

Single-Crystal X-ray Structure Determination of Compound 2. Compound **2** did not show signs of decomposition during X-ray data collection, which was carried out at room temperature, and the intensity data of a single crystal were collected on a CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All data were collected at room temperature using the ω-scan technique. The structures was solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.[28] All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data and processing parameters are given in ref 29.

XAFS Data Collection and Analysis. The X-ray absorption data at the Ni K-edge of the sample were measured at room temperature in transmission mode using ion chambers at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), People's Republic of China. The station was operated with a Si (311) double-crystal monochromator. During the measurement, the synchrotron was operated at an energy of 3.5 GeV and a current between 150 and 210 mA. The photon energy was calibrated with Ni metal foil. Data processing was performed using the program ATHENA.[30] All fits to the EXAFS data were performed using the program ARTEMIS.[30]

Norbornene Polymerization. In a typical procedure, 0.8 μmol of nickel complex **2** or **3** in 2.0 mL of chlorobenzene, 1.88 g of norbornene, and 5 mL of fresh chlorobenzene were added into a special polymerization bottle (20 mL) with a strong stirrer under an Ar atmosphere. After the mixture was kept at the desired temperature for 10 min, the desired MAO (10%) was charged into the polymerization system via syringe, and the reaction was started. Thirty minutes later, acidic ethanol (20/1 v/v ethanol/concentrated HCl) was added to terminate the reaction. The PNB was isolated, washed with ethanol, and dried at 80 °C for 48 h under vacuum. For all the polymerization procedures, the total reaction volume was 15.0 mL, which can be achieved by variation of chlorobenzene when necessary. IR (KBr, cm^{-1}): 2947 vs, 2869 vs, 1476 m, 1450 s, 1375 m, 1295 m, 1258 m, 1222 m, 1148 m, 1108 m, 1040 w, 943 w, 893 m, 805 m. ^{1}H NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ 0.9−3.03 ppm (m, maxima at 1.52, 1.87, 2.23, 2.59). ^{13}C NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ 30.0−48.8 ppm (m, maxima at 32.43, 39.12, 48.39, 48.77).

■ ASSOCIATED CONTENT

Supporting Information. A CIF file giving crystallographic data for complex **2**, an ORTEP diagram of complex **2**, and a ^{13}C NMR spectrum of the norbornene polymers formed by the complex **2**/MAO system. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

Dedicated to Herr Professor Dr. Max Herberhold on the occasion of his 75th birthday

■ REFERENCES

(1) (a) Janiak, C. *Coord. Chem. Rev.* **2006**, *250*, 66–94. (b) Janiak, C.; Lassahn, P. G. *J. Mol. Cata. A: Chem* **2001**, *166*, 193–209. (c) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565–1604. (d) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252. (e) Blank, F; Janiak, C. *Coord. Chem. Rev.* **2009**, *253*, 827–861. (f) Janiak, C.; Lassahn, P.-G.; Lozan, V. *Macromol. Symp.* **2006**, *236*, 88–99.

(2) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315.

(3) Tritto, I.; Boggioni, L.; Sacchi, M. C.; Locatelli, P. *J. Mol. Catal. A: Chem.* **1998**, *133*, 139–150.

(4) Kaminsky, W.; Bark, A.; Arndt, M. *Makromol. Chem. Macromol. Symp.* **1991**, *47*, 83–93.

(5) (a) Goodall, B. L.; McIntosh, L. H., III; Rhodes, L. F. *Makromol. Chem. Macromol. Symp.* **1995**, *89*, 421–432. (b) Yasuda, H.; Nakayama, Y.; Sato, Y. *J. Organomet. Chem.* **2004**, *689*, 744–750.

(6) Peuckert, U.; Heitz, W. *Macromol. Rapid Commun.* **1998**, *19*, 159–162.

(7) (a) Gao, H.; Guo, W.; Bao, F.; Gui, G.; Zhang, J.; Zhu, F.; Wu, Q. *Organometallics* **2004**, *23*, 6273–6280. (b) Wang, X.; Liu, S.; Jin, G.-X. *Organometallics* **2004**, *23*, 6002–6007. (c) Huang, Y.-B.; Tang, G.-R.; Jin, G.-X. *Organometallics* **2008**, *27*, 259–269. (d) Chen, F.-T.; Tang, G.-R.; Jin, G.-X. *J. Organomet. Chem.* **2007**, *692*, 3435–3442.

(8) (a) Carlini, C.; Giaiacopi, S.; Marchetti, F.; Pinzino, C.; Galletti, A. M. R.; Sbrana, G. *Organometallics* **2006**, *25*, 3659–3664. (b) Tang, G.-R.; Lin, Y.-J.; Jin, G.-X. *J. Organomet. Chem.* **2007**, *692*, 4106–4112. (c) Blank, F.; Scherer, H.; Ruiz, J.; Rodriguez, V.; Janiak, C. *Dalton Trans.* **2010**, *39*, 3609–3619. (d) Blank, F.; Vieth, J.; Ruiz, J.; Rodriguez, V.; Janiak, C. *J. Organomet. Chem.* **2011**, *696*, 473–487. (e) Blank, F.; Scherer, H.; Janiak, C. *J. Mol. Catal. A: Chem.* **2010**, *330*, 1–9.

(9) (a) Lassahn, P.-G.; Lozan, V.; Janiak, C. *Dalton Trans.* **2003**, 927–935. (b) Berchtold, B.; Lozan, V.; Lassahn, P.-G.; Janiak, C. *J. Polym. Sci. A: Polym. Chem.* **2002**, *40*, 3604–3614.

(10) (a) Takei, I.; Nishibayashi, Y.; Arikawa, Y.; Uemura, S.; Hidai, M. *Organometallics* **1999**, *18*, 2271–2274. (b) Yang, H.; Alvarez-Gressier, M.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 1401–1409. (c) Yang, H.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 2089–2095.

(11) (a) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741. (b) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741–748. (c) Chen, J. C. C.; Lin, I. J. B. *Organometallics* **2000**, *19*, 5113–5121. (d) Gandelman, M.; Milstein, D. *Chem. Commun.* **2000**, 1603–1604.

(12) (a) Hawthorne, M. F.; Zink, J. I.; Skelton, J. M.; Bayer, M. J.; Liu, C.; Livshits, E.; Baer, R.; Neuhauser, D. *Science* **2004**, *303*, 1849–1851. (b) Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352–5355.

(13) Lee, J. D.; Kim, S. J.; Yoo, D.; Ko, J.; Cho, S.; Kong, S. O. *Organometallics* **2000**, *19*, 1695–1703.

(14) Lee, T.; Lee, S. W.; Wang, H. G.; Ko, J.; Kang, S. O.; Ko, J. *Organometallics* **2001**, *20*, 741–748.

(15) Chung, S. W.; Ko, J.; Park, K.; Cho, S.; Kang, S. O. *Collect. Czech. Chem. Commun.* **1999**, *64*, 883–894.

(16) Lee, H. S.; Bae, J. Y.; Ko, J.; Kang, Y. S.; Kim, H. S.; Kim, S.-J.; Chung, J.-H.; Kang, S. O. *J. Organomet. Chem.* **2000**, *614−615*, 83–91.

(17) (a) Jin, G.-X. *Coord. Chem. Rev.* **2004**, *246*, 587–602. (b) Yu, X. Y.; Lu, S. X.; Jin, G.-X. *Inorg. Chim. Acta* **2004**, *357*, 361–366. (c) Yu, X. Y.; Jin, G.-X.; Hu, N. H.; Weng, L. H. *Organometallics* **2002**, *21*, 5540–5548. (d) Jin, G.-X.; Wang, J.-Q.; Zhang, C.; Weng, L. H.; Herberhold, M. *Angew. Chem.* **2005**, *44*, 259–262. (e) Wang, J.-Q.; Hou, X. F.; Weng, L. H.; Jin, G.-X. *Organometallics* **2005**, *24*, 826–830.

(18) (a) Zi, G. F.; Li, H.-W.; Xie., Z. W. *Organometallics* **2002**, *21*, 3850–3855. (b) Wang, H. P.; Wang, Y. R.; Li., H.-W.; Xie., Z. W. *Organometallics* **2001**, *20*, 5110–5118.

(19) (a) Wang, X.; Jin., G.-X. *Organometallics* **2004**, *23*, 6319–6322. (b) Wang, X.; Weng, L. H.; Jin, G.-X. *Chem. Eur. J.* **2005**, *11*, 5758–5764. (c) Wang, X.; Liu, S.; Jin., G.-X. *Organometallics* **2004**, *23*, 6002–6007.

(20) Clara, V.; Rajae, B.; Francesc, T.; Jaume, C. *Inorg. Chem.* **1995**, *34*, 3844–3845.

(21) Huang, Y.-B.; Jia, W.-G.; Jin, G.-X. *J. Organomet. Chem.* **2009**, *694*, 86.

(22) Wang, X.; Jin, G.-X. *Organometallics* **2004**, *23*, 6319–6322.

(23) (a) Sacchi, M. C.; Sonzogni, M.; Losio, S.; Forlin, F. *Macromol. Chem. Phys.* **2001**, *202*, 2052–2058. (b) Barnes, D. A.; Benedikt, G. M.; Goodall, B. L.; Huang, S. S. *Macromolecules* **2003**, *36*, 2623–2632.

(24) Huang, W. J.; Chang, F. C.; Chu, P. P. *J. Polym. Sci.* **2000**, *38*, 2554–2563. Mi, X.; Ma, Z.; Cui, N. *J. Appl. Polym. Sci.* **2003**, *88*, 3273–3278.

(25) Mast, C.; Krieger, M.; Dehnicke, K.; Greiner, A. *Macromol. Rapid Commun.* **1999**, *20*, 232–235.

(26) Kermagoret, A.; Braunstein, P. *Organometallics* **2008**, *27*, 88–99.

(27) Pei, L. X.; Liu, X. M.; Gao, H. Y.; Wu, Q. *Appl. Organomet. Chem.* **2009**, *23*, 455–459.

(28) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen, Göttingen, Germany, 1997.

(29) Crystal data for **2**: $C_{28}H_{40}B_{20}NiP_2S_2$, M_r = 777.57, monoclinic, space group *Pbca*, a = 9.9525(8) Å, b = 18.2899(15) Å, c = 24.3850(19)

Å, α = 90°, β = 90°, γ = 90°, V = 4438.8(6) Å^3, Z = 4, ρ_{calcd} = 1.164 g cm^{-3}, 30 302 total reflections, 5082 of which were independent (R_{int} = 0.0334). The structure was refined to final R1 = 0.0663 ($I > 2\sigma(I)$), wR2 = 0.1540 for all data, GOF = 1.240, and the maximum/minimum residual electron density was 0.8110/0.7620 e Å^{-3}.

(30) Ravel, B.; Newville, M. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.