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 [(C6H4CH=NHPh-2-XPh)NiBr] (X = S (1a), PPh (1b)) and palladium(II) complexes [(C6H4CH=NHPh-2-XPh)PdCl] (X = S (2a), PPh (2b)) were synthesized from the reactions of La and Lb (La = BrC6H4CH=NHPh-2-SPh, Lb = BrC6H4CH=NHPh-2-PPh2) with (DME)NiBr2 and (COD)PdCl2, 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

Olefins 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. Norbornene (NB) polymerization has been widely used in industrial production, due to the special optical and mechanical properties of the polymers. Up to now, catalytic systems based on titanium, zirconium, cobalt, chromium, nickel, palladium, and copper 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. The side-arm effect of an extra donor has a strong influence on catalytic polymerization. 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 phenoxo-amide ligands bearing soft pendant donors showed higher ethylene polymerization activity than the counterparts containing hard donors or systems without a pendant donor. 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. Our group has also done some research in this field. 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. 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 × 10⁷ 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. However, most of them were the so-called ECE pincer ligands (ECE is [C6H3(CH2E)2-2,6]−), in which E is NR2, PR2, SR, OMe). Few complexes bearing different donor ligands with [C,X] (X = N, S, P) have been described, and their olefin polymerization was rarely developed. 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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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 $\delta$ 8.77 ppm and that of Lb at $\delta$ 8.57 ppm, which can be ascribed to the proton CH=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.

The synthesis of ligands

[Scheme 1. Synthetic Procedure for La and Lb]

La + H2N,XPh + hexane → La

Lb + H2N,XPh + hexane → Lb

where X = S or PPh

Figure 1. Molecular structure of La 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).

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).

Treatments of the lithium salts of imino ligands with (DME)NiBr₂ and (COD)PdCl₂ in THF at room temperature afforded the desired nickel and palladium complexes 1a, 1b, 2a, and 2b, 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 single-crystal X-ray diffraction analyses was obtained from a CH₂Cl₂/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 Table 1, and the catalytic activities of complexes 1a, 1b toward norbornene polymerization at different temperatures are presented in Figure 4.

To investigate the reaction parameters affecting vinyl polymerization of norbornene, the catalyst precursors 1a, 1b 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 (M₅) 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 [C₅N=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
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 from 

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

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<thead>
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<th>entry</th>
<th>procat.</th>
<th>Al/M (ratio)</th>
<th>T (°C)</th>
<th>amt of polymer (g)</th>
<th>activity in 10⁶ g of PNB (mol of Ni)−1 h−1</th>
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<th>10⁻³Me₇</th>
<th>10⁻³Me₅</th>
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** Conditions: group VIII metal complex, 0.5 μmol; solvent, chlorobenzene (total volume 15 mL); norbornene, 1.68 g; reaction time, 20 min. **Activity in 10⁶ g of PNB (mol of Ni)⁻¹ h⁻¹, **M₉ measured by the Ubbelohde calibrated viscosimeter technique. **Undetermined.

![Scheme 2. Synthesis of Nickel and Palladium Complexes](image)

![Figure 3. Molecular structure of 2a with thermal ellipsoids drawn at the 30% level.](image)

![Figure 4. Catalytic activities of complexes 1a,b toward norbornene polymerization at different temperatures.](image)

![Figure 5. Molecular structure of 2a with thermal ellipsoids drawn at the 30% level.](image)
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 1H 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 1H 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 (Tg) 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 [C4N2X] (X = S, P) nickel(II) complexes [{(C5H4CH═N=Ph-2-XPh)NiBr2} (X = S (1a), PPh (1b)) and palladium(II) complexes [{(C5H4CH═N=Ph-2-XPh)PdCl2} (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 norbornene (PNB) with good catalytic activities: up to 8.78 × 10⁶ 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. Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium–benzophenone. Dichloromethane was distilled from calcium hydride. Commercial reagents, namely LiAlH₄, nBuLi, and CaH₂, were purchased from Acros Co. (DME)NiBr₂, (COD)PdCl₂, 2-(phenylthio)benzenamine, and 2-(diphenylphosphino)benzenamine from sodium borohydride. Commercial reagents, namely LiAlH₄, nBuLi, and CaH₂, were purchased from Acros Co. (DME)NiBr₂, (COD)PdCl₂, 2-(phenylthio)benzenamine, and 2-(diphenylphosphino)benzenamine from sodium borohydride.

**Synthesis of Complexes.** 

- **N-[2-(Bromophenyl)allyl]-2-(diphenylphosphino)benzenamine (1a).** Buli (1.6 M, 0.13 mL, 0.2 mmol) was added by syringe to a solution of La (74 mg, 0.2 mmol) and (DME)NiBr₂ (0.062 g, 0.2 mmol). Workup afforded 1a as a light yellow powder. Pure products were obtained as light yellow crystals by recrystallization from ethanol in a yield of 69%.
- **N-[2-(Bromophenyl)allyl]-2-(diphenylphosphino)benzenamine (1b).** Buli (1.6 M, 0.13 mL, 0.2 mmol) was added by syringe to a solution of La (74 mg, 0.2 mmol) and (DME)NiBr₂ (0.062 g, 0.2 mmol). Workup afforded 1b as a light brown powder in a yield of 70%.
- **N-[2-(Bromophenyl)allyl]-2-(diphenylphosphino)benzenamine (2a).** Buli (1.6 M, 0.13 mL, 0.2 mmol), La (74 mg, 0.2 mmol), and (COD)PdCl₂ (60 mg, 0.2 mmol) were used as a chlorobenzene solution. Other commercially available reagents were purchased and used without purification.
- **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 MgSO₄ in n-hexane (20 mL) was stirred for 12 h at room temperature. The mixture was then filtered and washed with CH₂Cl₂. 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): 3436 (s), 2902 (w), 2854 (w), 1632 (s), 1505 (s), 1478 (s), 1381 (s), 1305 (s), 1243 (m), 1147 (m), 1105 (m), 1026 (m), 712 (s), 691 (s) cm⁻¹. 1H NMR (400 MHz, CDCl₃): δ 8.57 (s, 1H, CH=N-Ar), 7.62 (m, 6H, Ar-H), 7.40 (m, 3H, Ar-H), 7.21 (m, 6H, Ar-H). Anal. Calcd for C₂₃H₁₇BrNNiP: C, 59.70; H, 3.81; N, 2.70.
- IR (KBr): 3436 (s), 2902 (w), 2854 (w), 1632 (s), 1505 (s), 1478 (s), 1381 (s), 1305 (s), 1243 (m), 1147 (m), 1105 (m), 1026 (m), 712 (s), 691 (s) cm⁻¹. 1H NMR (400 MHz, CDCl₃): δ 8.57 (s, 1H, CH=N-Ar), 7.62 (m, 6H, Ar-H), 7.40 (m, 3H, Ar-H), 7.21 (m, 6H, Ar-H). Anal. Calcd for C₂₃H₁₇BrNNiP: C, 59.70; H, 3.81; N, 2.70.
X-ray Crystallography. Single crystals of complexes La, Lb, and 2a suitable for X-ray analysis were obtained from CH2Cl2/n-hexane solutions. The intensity data of the single crystals 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 = 0.71073 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 F² 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: C30H40BrN4, Mw = 603.09, T = 296(2) K, monoclinic, space group C2/c, a = 20.50(3) Å, b = 16.400(4) Å, c = 12.00(3) Å, β = 112.0(3)°, V = 3529(11) Å³, Z = 4, Rone = 0.0435. The structure was refined to final R1 = 0.0476 (I > 2σ(I)), wR2 = 0.1011 (all data), GOF = 1.065, and maximum/minimum residual electron density 0.98/−0.94 e Å⁻³.

Crystal data for Lb: C26H30N2, Mw = 364.50, T = 273(2) K, monoclinic, space group P2₁/a, a = 10.739(5) Å, b = 17.724(7) Å, c = 11.279(2) Å, β = 106.456(3)°, V = 2036.0(7) Å³, Z = 4, Rone = 0.1447. The structure was refined to final R1 = 0.0739 (I > 2σ(I)), wR2 = 0.1211 (all data), GOF = 0.943, and maximum/minimum residual electron density 0.689/−0.582 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. For all polymerization procedures, the total reaction volume was filtration, washed with ethanol, and dried at 80 °C.

Polymerization of Norbornene.

The authors declare no competing financial interest.

REFERENCES


