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Synthesis and Characterization of Ni^{II} and Pd^{II} Complexes Bearing N,N,S Tridentate Ligands and Their Catalytic Properties for Norbornene Polymerization

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A series of new N,N,S tridentate nickel(II) complexes [(ArN = CHC_6H_4NPh-2-SPh)NiBr] (Ar = 2,6-diisopropylphenyl, **1**; Ar = 2,6-dimethylphenyl, **2**; Ar = Ph, **3**) and palladium(II) complexes [(ArN = CHC_6H_4NPh-2-SPh)$PdCH_3$] (Ar = 2,6-diisopropylphenyl, **4**; Ar = 2,6-dimethylphenyl, **5**; Ar = Ph, **6**) were synthesized and characterized. X-ray diffraction analyses of the single-crystal structures revealed that tridentate complexes **1**, **2**, **4**, **5**, and **6** featured a distorted square-planar coordination of the central metal. Compared to the bidentate metal complexes bearing anilido–imine ligands, the N,N,S tridentate metal complexes showed better stability. In the presence of methylaluminoxane (MAO), nickel complexes **1**–**3** showed moderate activity toward ethylene oligomerization at atmosphere pressure, but the palladium complexes were inactive. However, the nickel complexes exhibited high activity up to 8.20×10^6 g/(mol of Ni) h and palladium complexes showed very high activity up to 2.68×10^8 g/(mol of Pd) h toward norbornene polymerization with MAO as cocatalyst. The obtained polynorbornenes are vinylic addition polymers with high molecular weights.

Introduction

During the last decade, transition-metal catalysts for olefin polymerization have been extensively developed.[1] Brookhart et al. reported that bulky α-diimine nickel(II) and palladium(II) complexes exhibited high catalytic activity for olefin polymerization.[2] Iron or cobalt complexes bearing diimine–pyridine ligands were also reported as highly active catalyst precursors for ethylene polymerization.[3] (Salicylaldiminato)nickel complexes exhibited good tolerance to functional groups and even remained active for olefin polymerization in the presence of polar or protonic solvents.[4–6] Coates[7] and Fujita[8] reported that high performance olefin polymerization catalysts could be achieved by the moderate electron-donating properties of the ligands. For transition-metal olefin-polymerization catalysts, steric and electronic effects of ligands play important roles in determining the catalytic activity and polymer microstructure.[1,8,9] Therefore, the design and synthesis of transition-metal olefin-polymerization catalysts mainly came from two strategies: ligand sterics and electronic effects. Extensive research has been carried out to elucidate the influence of the sterics of the ligands and the electronic effects of the ligands on polymerization reactions.[1–14]

In addition, the sidearm approach had also proven to be an efficient strategy for the design of organometallic catalysts in olefin polymerization,[15–21] and the sidearm effect of the extra donor had a strong influence on catalytic polymerization. In particular, metal complexes with N, P, O, and S atoms in the sidearm were mainly reported. Chromium,[15] titanium,[16,17] and nickel[18] complexes containing salicylaldiminate ligands with pendant donors had higher catalytic activities than the corresponding complexes without sidearm donors. For the complexes containing relatively hard nitrogen- and oxygen-coordinated atoms, a sidearm containing the soft S or P donor atoms, for understandable reasons, was usually introduced into the ligand backbone.

During the past few years, our groups has focused our attention on nickel complexes bearing N,N ligands because they can be easily modified in terms of steric and electronic effects. Previously, from the ligand steric and electronic points of view, nickel complexes chelating β-diimine, β-diketiminate, fluorinated β-diketiminate, and anilido–imine ligands were prepared, and their catalytic properties for olefin polymerizations were studied.[22] Recently, interest in organometallic complexes chelating anilido–imine donor ligands has also increased dramatically. Yttrium,[23] nickel,[22a–22e,24] copper,[25] aluminium,[26] and zinc[27] complexes bearing anilido–imine ligands have also found appli-

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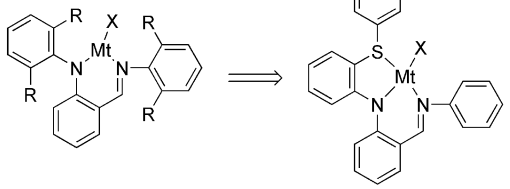
cation in many areas of inorganic and organometallic chemistry.

In this paper, modification of anilido–imine ligands by the sidearm approach and the synthesis of the corresponding N,N,S tridentate nickel(II) and palladium(II) complexes is reported. Molecular structures of the complexes were also characterized by X-ray single-crystal analyses. Additionally, ethylene oligomerizations and norbornene (NB) polymerizations catalyzed by these nickel and palladium complexes after activation with methylaluminoxane (MAO) were also investigated in detail.

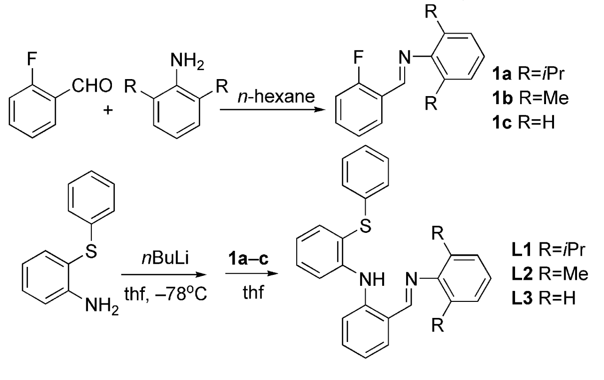
Results and Discussion

As described by the reported results, anilido–imino nickel complexes existed as four-coordinate dimers in the solid state, whereas they exist mainly as three-coordinate monomers in solution.[22a] The introduction of a sidearm group containing an S donor atom would lead to the formation of more stable four-coordinate complexes (Scheme 1). Therefore, nickel and palladium complexes with various sterically hindered substituents were selected for study.



Scheme 1.

Three N,N,S tridentate ligands with various sterically hindered substituents were synthesized. The synthetic route for these tridentate ligands is shown in Scheme 2. Condensation of 2-fluorobenzaldehyde with various anilines afforded imines **1a**–**c** in high yields. The corresponding N,N,S tridentate ligands were obtained by nucleophilic aromatic displacement of fluorine in the imines by using PhS-2-C_6H_4NHLi. Pure products were obtained as yellow crystals by recrystallization from ethanol in 44–57% yields. All of these ligands were proved by ^{1}H NMR and ^{13}C NMR spectroscopy and elemental analyses. A single crystal of L2 (Figure 1) growing in ethanol solution also assuredly confirmed the ligand structure.



Scheme 2. Synthesis of ligands L1–L3.

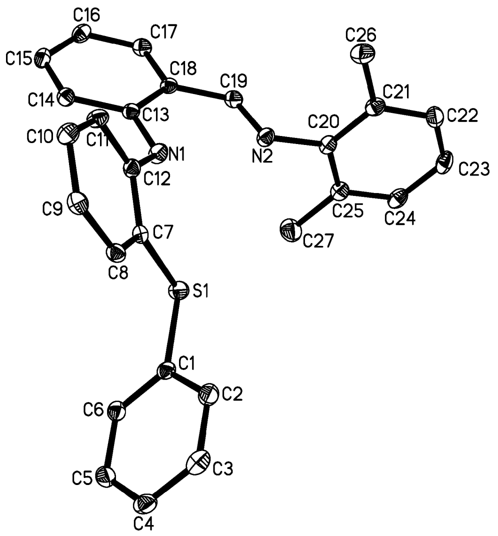
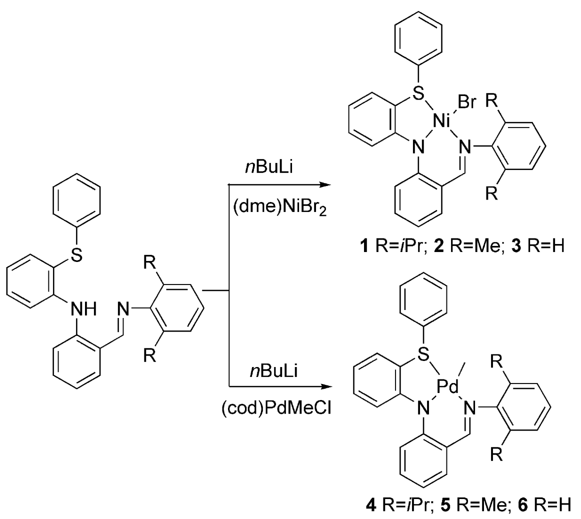


Figure 1. Molecular structure of L2. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–C1 1.782(2), S1–C7 1.785(2), C13–N1 1.383(3), N1–C12 1.410(2), C19–C18 1.460(3), N2–C19 1.273(3), N2–C20 1.436(2), C1–S1–C7 102.03(9), C13–N1–C12 124.81(17), C19–N2–C20 117.25(17), N2–C19–C18 125.04(18).

The synthetic route for these tridentate complexes is shown in Scheme 3. After the ligands were deprotonated with *n*-butyllithium (1.0 equiv.) in toluene, (1,2-dimethoxyethane)nickel(II) bromide [(dme)$NiBr_2$; 1.0 equiv.] was added to the solution, and nickel complexes **1**–**3** were obtained as dark-red solids in high yields. Similarly, when (1,5-cyclooctadiene)methylpalladium chloride [(cod)PdMeCl; 1.0 equiv.] was added, palladium complexes **4**–**6** were obtained as red solids in moderate yields. Nickel and palladium complexes **1**–**6** were fully characterized by ^{1}H NMR and IR spectroscopy, MS, and elemental analyses. The ^{1}H NMR spectra of complexes **4**–**6** exhibited methyl proton signals at high field (δ = –0.420, –0.490 and –0.236 ppm, respectively), which proved the existence of the Pd–Me bonds.

Crystals of nickel complexes **1** and **2** suitable for X-ray crystallography were grown from hexane/toluene solutions. Each of the crystal structures bears two crystallographically independent molecules, but there are no significant differences in the bond lengths and small deviations in the angles of the two molecules. Therefore, only one molecule of each of complexes **1** and **2** is discussed as a representative example. Crystals of palladium complexes **4**, **5**, and **6** suitable for X-ray crystallography were also grown from hexane/toluene solutions. ORTEP diagrams are given in Figures 2, 3, 4, 5, and 6 along with selected bond lengths and bond angles, respectively.

Unlike the tetrahedral geometries of the anilido–imino nickel complexes,[22a] all of these tridentate complexes feature a distorted square-planar coordination of the central



1 R=*i*Pr; **2** R=Me; **3** R=H

4 R=*i*Pr; **5** R=Me; **6** R=H

Scheme 3. Synthesis of complexes **1**–**6**.

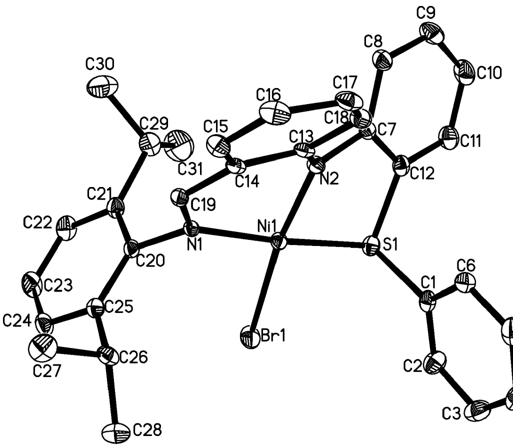


Figure 2. Molecular structure of complex **1**. One of two crystallographically independent molecules. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–N1 1.915(3), Ni1–N2 1.869(3), Ni1–S1 2.2013(11), Br1–Ni1 2.3241(6), N1–C19 1.291(4), N2–C13 1.363(5), N2–Ni1–N1 91.09(13), N2–Ni1–S1 87.27(10), N1–Ni1–S1 174.10(9), N2–Ni1–Br1 171.68(9), N1–Ni1–Br1 95.34(9), S1–Ni1–Br1 86.85(3), C1–S1–Ni1 106.18(14), C12–S1–Ni1 97.62(14), C12–S1–C1 104.45(18).

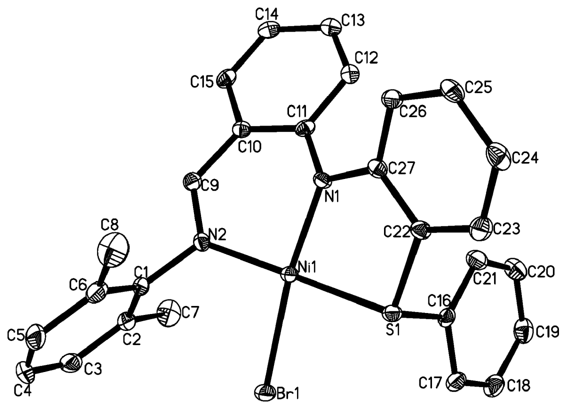


Figure 3. Molecular structure of complex **2**. One of two crystallographically independent molecules. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–N1 1.888(3), Ni1–N2 1.906(3), Ni1–S1 2.1783(10), Br1–Ni1 2.3364(5), N1–C11 1.369(4), N2–C9 1.298(4), N2–Ni1–N1 92.30(12), N2–Ni1–S1 175.81(8), N1–Ni1–S1 87.65(9), N2–Ni1–Br1 94.79(8), N1–Ni1–Br1 172.34(9), S1–Ni1–Br1 85.49(3), C16–S1–Ni1 105.99(11), C22–S1–Ni1 97.30(12), C22–S1–C16 104.31(16).

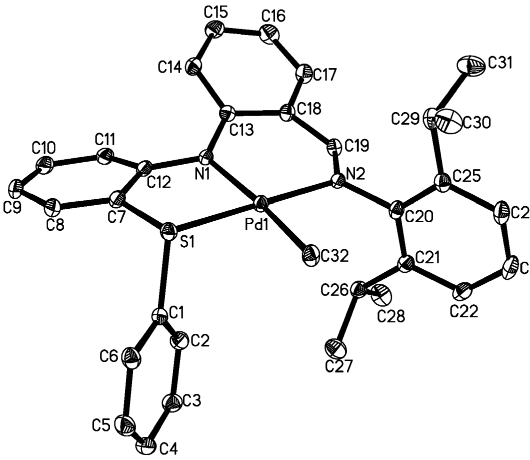


Figure 4. Molecular structure of complex **4**. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.099(2), Pd1–N2 2.046(2), Pd1–S1 2.2433(7), Pd1–C32 2.056(3), N1–C13 1.370(4), N2–C19 1.294(3), N2–Pd1–N1 92.46(9), N2–Pd1–S1 178.38(6), N1–Pd1–S1 86.49(6), N2–Pd1–C32 93.21(10), N1–Pd1–C32 174.33(10), S1–Pd1–C32 87.85(8), C7–S1–Pd1 98.93(10), C1–S1–Pd1 106.34(9), C7–S1–C1 101.51(13).

metal due to the coordination of the S-donor sidearm. Each nickel atom is surrounded by N, N, and S atoms and a terminal Br ligand, whereas each palladium atom is surrounded by N, N, and S atoms, and a terminal methyl ligand.

Compared to ligand L2, imine bond (C=N) length of complex **2** becomes long, whereas the amine bond (C–N) length becomes short due to the coordination of the N, N, and S donor atoms to metal. The bond angles of Mt–S–C and C–S–C (ca. 100°) of all complexes suggest that the S atom is sp^3 hybridized.[17] The five-membered S,N chelate ring is coplanar, and the metal atom lies out of the SCCN plane 0.5029 Å for **1**, 0.5404 Å for **2**, 0.2255 Å for **4**, 0.2839 Å for **5**, 0.5755 Å for **6**. The six-membered N,N chelate ring has a boat conformation with the metal atom lying out of the NCCCN plane (slightly twisted coplanar). Previously, we reported that the anilido–imino nickel complexes are localized and have two nitrogen atoms bound to nickel with different bond lengths.[22a] In a comparison of the N–Ni bond lengths of the anilido–imino nickel complexes with those of the N,N,S nickel complexes, the N(amine)–Ni bond lengths are nearly the same (ca. 1.88 Å), whereas the N(imine)–Ni bond lengths of the anilido–imino nickel complexes are slightly longer than those of the N,N,S nickel complexes. In addition, the Br–Ni bond lengths of the anilido–imino nickel complexes (ca. 2.45 Å) are also longer than those of the N,N,S nickel complexes (ca. 2.33 Å). These results indicate that the N,N,S nickel complexes are more stable than the anilido–imino nickel com-

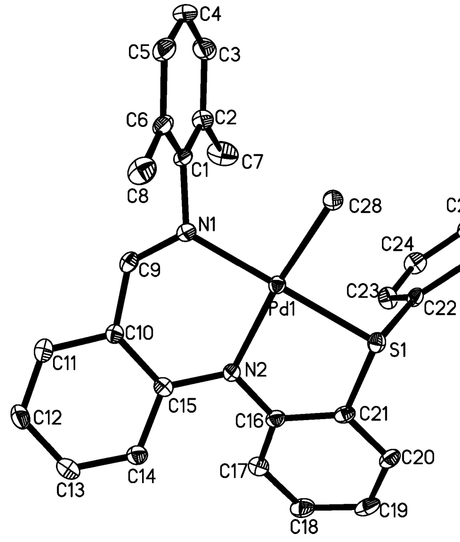


Figure 5. Molecular structure of complex **5**. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.040(3), Pd1–N2 2.090(3), Pd1–S1 2.2466(11), Pd1–C28 2.066(4), N1–C9 1.290(5), N2–C15 1.379(5), N2–Pd1–N1 92.30(13), N2–Pd1–S1 86.38(9), N1–Pd1–S1 175.96(9), N2–Pd1–C28 174.48(14), N1–Pd1–C28 93.20(15), S1–Pd1–C28 88.16(12), C22–S1–Pd1 102.41(12), C21–S1–Pd1 98.83(13), C21–S1–C22 101.90(18).

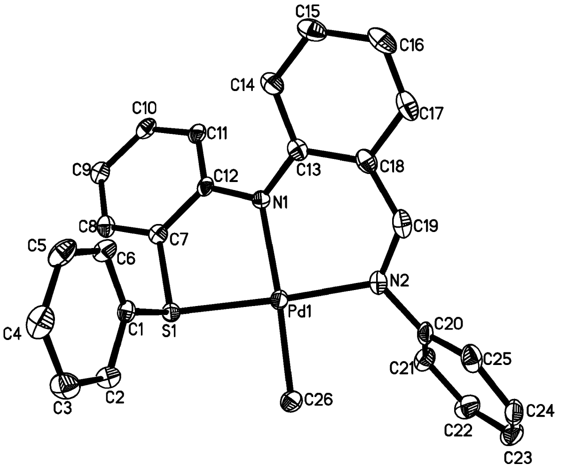


Figure 6. Molecular structure of complex **6**. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.076(4), Pd1–N2 2.031(4), Pd1–S1 2.2503(13), Pd1–C26 2.055(5), N1–C13 1.362(5), N2–C19 1.306(6), N2–Pd1–N1 91.10(14), N2–Pd1–S1 175.53(10), N1–Pd1–S1 85.61(10), N2–Pd1–C26 92.29(17), N1–Pd1–C26 176.28(15), S1–Pd1–C26 91.08(14), C1–S1–Pd1 105.58(13), C7–S1–Pd1 97.41(15), C7–S1–C1 104.4(2).

plexes due to the coordination of the S sidearm to the metal atom. In contrast to the nickel complexes, the N(amine)–Pd bond lengths of the palladium complexes are slightly longer than the N(imine)–Pd bond lengths, and the Pd–CH_3 bond lengths (ca. 2.06 Å) are shorter than Br–Ni bond lengths of the nickel complexes. Despite the different metal atoms and different steric effects of the *N*-aryl groups, the two bite angles (N–Mt–N and N–Mt–S) of all the complexes are nearly same. The bite angles (N–Mt–N) are slightly more than 90° (<93°), whereas the bite angles (N–Mt–S) are slightly less than 90° (>85°).

Ethylene oligomerizations were carried out with the nickel and palladium complexes in the presence of MAO. When nickel complexes **1**–**3** catalyzed ethylene oligomerization at atmospheric pressure, no solid polymer was obtained, and an amount of oligomeric products were formed [activity: ca. 10^4 g/(mol of Ni) h atm)]. However, palladium complexes **4**–**6** were inactive toward ethylene polymerization or oligomerization. GC–MS analyses confirmed that the oligomers obtained by the nickel catalysts mainly contained dimers (C4) and trimers (C6); only a few tetramers (C8) and higher oligomers were detected, which may be a result of the lower steric hindrance of the complexes.

The nickel and palladium complexes bearing N,N,S ligands showed very high catalytic activities for norbornene polymerization after activation with MAO. The polymerization results are collected in Table 1. In general, the type of metal had an important influence on the catalytic activity for norbornene polymerization. For palladium catalysts, the norbornene polymerization reaction was so rapid that the polynorbornene with high molecular weight precipitated and the stirring was stopped within less than 10 s under the reaction conditions (Table 1, Run 4).[28a] Decreasing the monomer concentration still resulted in precipitation of the great amount of polymer within less than 30 s (Table 1, Run 5). Therefore, at fixed MAO concentration, norbornene polymerizations were carried out on the condition of low norbornene and complex concentration (Table 1, Run 6–8), and a high monomer conversion (66.5%) with palladium catalysts was still obtained in 3 min. Under the same conditions of low norbornene and complex concentration (Table 1, Run 9), a low conversion (16.0%) with **1**/MAO was obtained in 1 h. This result suggests that the palladium complex exhibits a markedly higher catalytic activity than the nickel analogues. The obtained polynorbornenes catalyzed by nickel catalysts can dissolve in common organic solvents, but those obtained catalyzed by palladium catalysts are insoluble in any solvents, which has been noted before by Janiak and other groups.[21,28] Moreover, steric hindrance of the aryl substituent of the complexes also affects their catalytic activities and the molecular weights of the polynorbornene. The nickel and palladium complexes with bulky aryl substituents showed higher activity toward norbornene polymerization and produced higher molecular weight polymers. For example, under the same polymerization conditions, **1** with 2,6-diisopropyl on *N*-aryl groups produced a polynorbornene with a molecular weight of 112.2×10^4 g/mol in the highest activity 6.80×10^6 g/(mol of Ni) h, whereas **3** without substituents on the aryl groups produced a polynorbornene with a molecular weight of 72.5×10^4 g/mol in the relatively low activity 4.60×10^6 g/(mol of Ni) h, which is in accord with the steric hindrance order of the three nickel complexes (**1** > **2** > **3**). These results indicate that the bulky steric hindrance could stabilize the active species and suppress the chain transfer reaction during the polymerization process. Similar results were obtained with the palladium catalysts.

Table 1. Results of norbornene polymerization with Ni or Pd catalysts.[a]

Run	Complex	Al/Ni(Pd)	% Yield	Activity[f]	M_w[g]	M_w/M_n
1	**1** (1 μmol)	2000	42.5	6.80	112.2	2.48
2	**2** (1 μmol)	2000	36.5	5.84	104.6	2.49
3	**3** (1 μmol)	2000	28.8	4.60	72.5	2.59
4[b]	**4** (1 μmol)	2000	70.0	–	–	–
5[c]	**4** (1 μmol)	2000	84.0	201	–	–
6[d]	**4** (0.1 μmol)	20000	66.5	266	–	–
7[d]	**5** (0.1 μmol)	20000	59.0	236	–	–
8[d]	**6** (0.1 μmol)	20000	56.5	226	–	–
9[e]	**1** (0.1 μmol)	20000	16.0	3.2	–	–
10	AI-Pr (1 μmol)	2000	13.0	2.08	–	–
11	AI-Me (1 μmol)	2000	12.1	1.94	–	–

[a] Polymerization conditions: 50 °C, NB (4 g), 15 min, toluene (20 mL). [b] NB (4 g), <10 s. [c] NB (2 g), 30 s. [d] NB (2 g), 3 min. [e] NB (2 g), 60 min. [f] In units of 10^6 g PNB/(mol of cat) h. [g] In units of 10^4 g/mol.

Table 2. Results of norbornene polymerization with **2**/MAO.[a]

Run	Al/Ni	T_p [°C]	NB [g]	% Yield	Activity[b]	M_w[c]	M_w/M_n
1	2000	0	4	39.0	6.24	168.4	3.01
2	2000	25	4	40.8	6.52	141.5	2.68
3	2000	50	4	36.5	5.84	104.6	2.49
4	2000	75	4	29.8	4.76	93.6	2.47
5	0	25	4	0	0	–	–
6	1000	25	4	34.5	5.52	141.8	3.55
7	3000	25	4	38.3	6.12	–	–
8	4000	25	4	35.5	5.68	131.9	3.09
9	2000	25	2	20.8	1.68	–	–
10	2000	25	3	32.4	3.88	–	–
11[d]	2000	25	5	40.8	8.20	–	–

[a] Polymerization conditions: complex (1 μmol), NB (4 g), toluene (20 mL), 15 min. [b] In units of 10^6 g PNB/(mol of Ni) h. [c] In units of 10^4 g/mol. [d] 10 min.

For a comparison, the results of norbornene polymerizations with anilido–imino nickel complexes [(ArN = CHC_6H_4NAr)NiBr] (Ar = 2,6-diisopropylphenyl, AI-Pr; Ar = 2,6-dimethylphenyl, AI-Me) were also listed in Table 1 (Runs 10 and 11). The N,N,S tridentate nickel complexes were more active than the N,N bidentate nickel complexes in the norbornene polymerization. The coordination of S sidearm to nickel metal resulted in a more stable four-coordinate catalytic species, which would enhance the catalytic activity. In addition, palladium complexes **4**–**6** also showed much higher activity for norbornene polymerization than the dinuclear tridentate P,N,S palladium complexes reported by Kersting and coworkers with MAO as a cocatalyst [8.7×10^5 g/(mol of Pd) h].[21]

To further investigate the reaction parameters affecting norbornene polymerization, complex **2** was typically investigated by changing the polymerization temperature, Al/Ni ratio, and the monomer concentration (Table 2). The **2**/MAO catalytic system showed high activities over a large range of reaction temperature. With an increase in reaction temperature, the activity of complex **2** increased and reached a maximal value of 6.52×10^6 g/(mol of Ni) h at 25 °C, and then decreased gradually, whereas the molecular weights of the obtained polynorbornenes decreased uniformly. The activator MAO was essential to norbornene polymerization, but the effects of the Al/Ni ratio on catalytic activity and molecular weight of the obtained polynorbornenes were not obvious with an increase in Al/Ni from 1000 to 4000. Increasing the monomer concentration at fixed other reaction conditions resulted in dramatic increase in the polymerization rate and catalytic activity. Figure 7 shows the time dependence of the norbornene polymerization with **2**/MAO. Apparently, the polymer yield increased in this whole process with longer reaction time. No induction period was observed in the polymerization process. This observation suggests that the active species can be formed rapidly at the initial stage of the reaction and are then stabilized for a period of time.

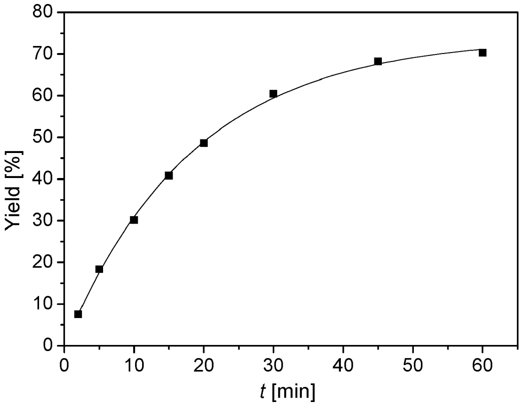


Figure 7. Influence of polymerization time on the polymerization yield with **2**/MAO. Polymerization conditions: Al/Ni ratio, 2000; complex (1 μmol); NB (4 g); toluene (20 mL); 25 °C.

The influences of the polymerization temperature and Al/Pd ratio for the **4**–**6**/MAO catalytic system were in a rough analogy to that in the cases of the **2**/MAO system. As shown in Figure 8, the polymerization temperature strongly influenced the catalytic activity. The catalytic activity increased obviously with increasing reaction temperature and reached a maximal value at 50 °C. Additionally, preliminary experiments indicated that these palladium complexes were not able to catalyze norbornene polymerization without cocatalysts. As we all know, MAO alone is also inactive for norbornene polymerization.[29] The role of MAO in the metal-catalyzed polymerization processes mainly are cleanup of the impurity, activation of metal complex, and stabilization of active species.[30] Therefore, it is necessary to use an excess amount of MAO for good to high activities. With an increase in the Al/Pd ratio from 10000 to 25000, the catalytic activities for norbornene polymerization increased markedly and then increased slowly (Figure 9). Similar results were obtained with other palladium catalysts.[31]

Additionally, under the conditions of very low monomer concentration (0.04 g/mL), the time dependence of the norbornene polymerization with **5**/MAO was investigated (Figure 10). Like that of the nickel catalyst, polymer yield increased with an increase in reaction time and no induction period was observed. Polymerization yield was up to 85%

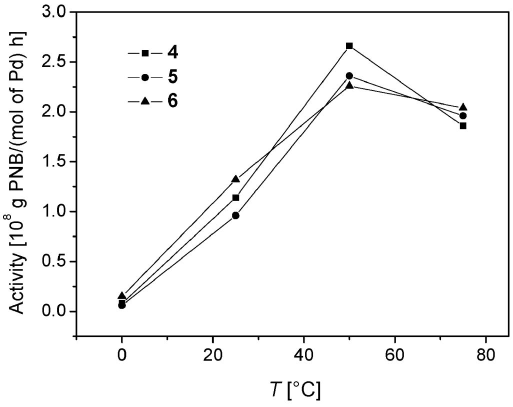


Figure 8. Influence of polymerization temperature on catalytic activity for norbornene polymerization with **4**, **5**, and **6**/MAO. Polymerization conditions: Al/Pd ratio, 20000; complex (0.1 µmol); NB (2 g); toluene (20 mL); 3 min.

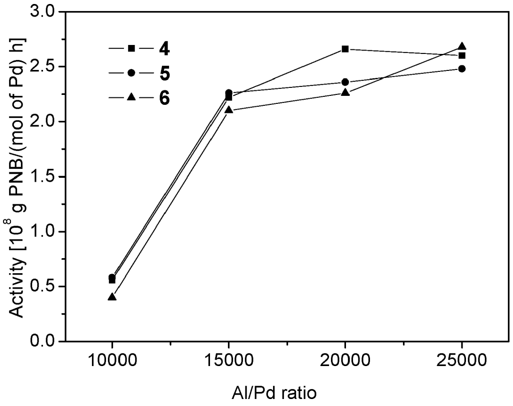


Figure 9. Influence of Al/Pd ratio on catalytic activity for the norbornene polymerization with **4**, **5**, and **6**/MAO. Polymerization conditions: 50 °C, complex (0.1 µmol), NB (2 g), toluene (20 mL), 3 min.

within 10 min. This observation suggests that the palladium active species can be formed rapidly at the initial stage of the reaction and is stabilized for a period of time until the majority of the monomer is consumed.

The obtained polymers catalyzed by **1**–**3**/MAO could be characterized by ^{1}H NMR and IR spectroscopy and GPC analyses, whereas those catalyzed by **4**–**6**/MAO were characterized by IR spectroscopy because of their insolubility. All of the obtained polymers showed very similar IR spectra (Figure 11), which prove the absence of a double bond at 1620–1680 cm^{-1}, and the ^{1}H NMR spectrum (Figure 12) of the obtained polynorbornenes catalyzed by **2**/MAO also prove no any traces of double bond, ensuring all of the obtained polymers catalyzed by nickel or palladium catalysts are vinylic addition polynorbornenes.[22b,28,29] TGA studies indicated that the obtained polymers were stable up to 450 °C under an atmosphere of nitrogen. The determination of the glass transition temperature (T_g) of vinyl polynorbornenes is difficult, because the T_g of vinyl homopolymers is apparently close to the temperature.[22b] Attempts to measure T_g of polynorbornene from DSC curves was

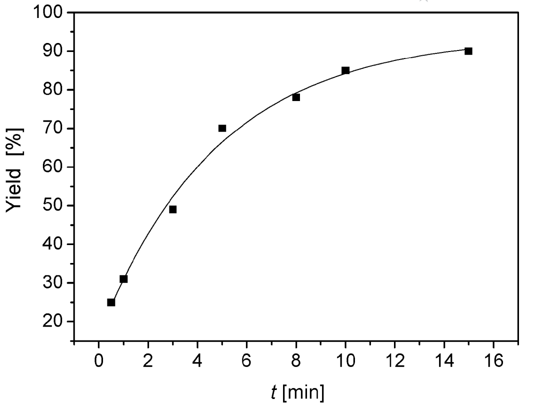


Figure 10. Influence of polymerization time on polymerization yield with **5**/MAO. Polymerization conditions: 50 °C; Al/Pd ratio, 20000; complex (0.1 µmol); NB (0.8 g); toluene (20 mL).

unsuccessful, and the DSC curves did not show an endothermic signal upon heating the polymers up to the decomposition temperature.

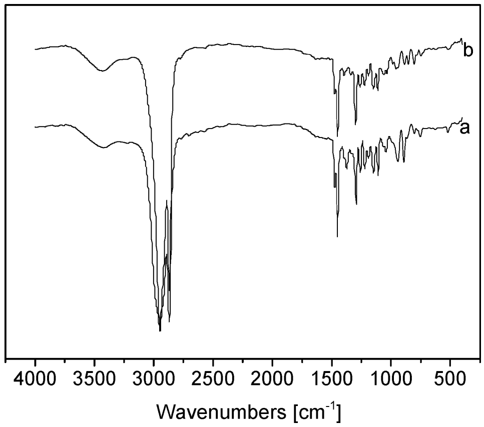


Figure 11. FTIR spectra of polynorbornenes catalyzed by **2**/MAO (a) and **5**/MAO (b).

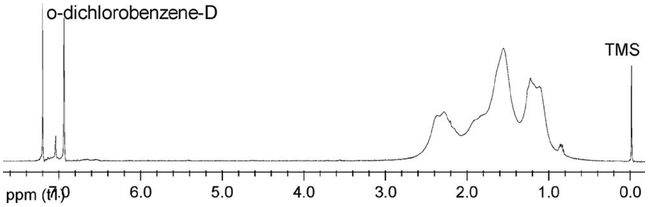


Figure 12. ^{1}H NMR spectrum of polynorbornene catalyzed by **2**/MAO.

Conclusions

We successfully synthesized and characterized N,N,S tridentate ligands and the corresponding nickel and palladium complexes by modifying an anilido–imine ligand from a sidearm approach. These complexes have a distorted square-planar coordination of the central metal. In the presence of MAO, nickel complexes **1**–**3** show moderate activity for ethylene oligomerization, but the palladium complexes are inactive. The obtained oligomers consist of dimers (C4) and trimers (C6) and a few tetramers (C8) and higher oligomers. All of the nickel and palladium complexes exhibit very high activity up to 8.20×10^6 g/(mol of Ni) h for nickel complexes and 2.68×10^8 g/(mol of Pd) h for palladium complexes toward norbornene polymerizations. The coordination of the S sidearm to nickel metal results in a more stable four-coordinate catalytic species; thus, the N,N,S tridentate nickel complexes have higher catalytic activity than N,N bidentate anilido–imino nickel complexes. All of the obtained polynorbornenes are vinylic addition polymers with high molecular weights.

Experimental Section

General: All manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of nitrogen by using standard Schlenk and vacuum-line techniques. Toluene, hexane, and tetrahydrofuran (thf) were dried with sodium metal and distilled under nitrogen. [D]Chloroform was dried with CaH_2. 2-Fluorobenzaldenyde (97%), 2,6-diisopropylaniline (92%), 2,6-dimethylniline(95%), 2-(phenoxythio)aniline (98%) and *n*-butyllithium solution (2.86 M in hexane) were bought from Aldrich Chemical Co. and used without further purification. Norbornene (NB, Acros) was purified by distillation over potassium and used as a solution (0.4 g/mL) in toluene. The (dme)$NiBr_2$[32] and (cod)-PdMeCl[33] complexes were synthesized according to the literature. Methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminium (TMA) in toluene at 0–60 °C with $Al_2(SO_4)_3 \cdot 18H_2O$ as the water source. The initial H_2O/Al molar ratio was 1.3. Other commercially available reagents were purchased and used without purification. Elemental analyses were performed with a Vario EL micro analyzer. Mass spectra were measured with an LC–MS instrument by using electro spray ionization (ESI). ^1H NMR and ^{13}C NMR spectra were recorded with an INOVA 300 MHz instrument at room temperature in $CDCl_3$ or C_6D_6 solution for ligands and complexes (with TMS as internal standard), and *o*-dichlorobenzene solution for polymers (by using solvent as internal standard). IR spectra were recorded with a Nicolet NEXUS-670 spectrometer. M_n, M_w, and M_w/M_n values of obtained polymers were determined by using a Waters Alliance GPC 2000 series at 135 °C (by using polystyrene calibration, 1,2,4-trichlorobenzene as the solvent at a flow rate of 1.0 mL/min). The GC–MS data were recorded with a Finnigan Voyager GC-8000 TOP series GC-MS system with DB-5MS GC column and the GC spectra were recorded with Varian CP3800 series GC system with a HP-5MS GC column. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin–Elmer DCS-7 system. The DSC curves were recorded at a heating rate of 10 °C/min. The cooling rate was 10 °C/min. TGA data were collected with a TG-290C thermal analysis system instrument under a nitrogen atmosphere up to 600 °C at heating rate of 10 °C/min.

2-C_6H_4F(CH=NC_6H_3*i*Pr_2-2,6) (1a): A solution of 2-fluorobenzaldehyde (11.7 g, 94.4 mmol) and 2,6-diisopropylaniline (17.6 g, 99.4 mmol) in *n*-hexane (40 mL) was stirred for 2 h before $MgSO_4$ was added. The mixture was then filtered and washed with *n*-hexane. The bright-yellow solution was concentrated to ca. 30 mL and then cooled to –10 °C overnight to give large yellow crystals (13.5 g). The filtrate was condensed to lower volume and cooled to –10 °C to give additional pure crystals (4.2 g). Total yield: 17.7 g (66%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H, CH=NAr), 8.24 (dt, 1 H, ph), 7.52 (q, 1 H, ph), 7.30 (t, 1 H, ph), 7.24–7.09 (m, 4 H, ph), 2.99 (sp, 2 H, CH of *i*Pr), 1.23 (d, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3 (d, C–F), 155.5 (CH=N), 149.2, 137.4, 132.9, 127.6, 124.5, 124.2, 123.7, 123.0, 116.0, 28.0, 23.6 ppm. $C_{19}H_{22}FN$ (283.38): calcd. C 80.53, H 7.82, N 4.94; found C 80.54, H 7.67, N 4.73.

2-C_6H_4F(CH=N$C_6H_3Me_2$-2,6) (1b): A solution of 2-fluorobenzaldehyde (9.4 g, 75.8 mmol) and 2,6-diimethylaniline (10.0 g, 82.5 mmol) in *n*-hexane (40 mL) was stirred for 2 h before $MgSO_4$ was added. The mixture was then filtered, and the bright-yellow solution was evaporated to dryness in vacuo to give a yellow oil. The oil was distilled under reduced pressure, and a light-yellow distillate at 170 °C/5 Torr was collected. Yield: 13.4 g (78%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H, CH=NAr), 8.29 (dt, 1 H, ph), 7.52 (q, 1 H, ph), 7.30 (t, 1 H, ph), 7.24–7.06 (m, 3 H, ph), 7.00 (t, 1 H, ph), 2.12 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3 (d, C–F), 156.1 (CH=N), 151.0, 132.9, 127.9, 127.5, 126.9, 124.3, 123.8, 116.0, 18.4 ppm. $C_{15}H_{14}FN$ (227.28): calcd. C 79.27, H 6.21, N 6.16; found C 79.37, H 6.22, N 6.13.

2-C_6H_4F(CH=NC_6H_5) (1c): A solution of 2-fluorobenzaldehyde (9.4 g, 75.8 mmol) and aniline (8.0 g, 85.9 mmol) in *n*-hexane (40 mL) was stirred for 2 h before $MgSO_4$ was added. The mixture was then filtered, and the bright-yellow solution was evaporated to dryness in vacuo to give a yellow oil. The oil was distilled under reduced pressure, and the light-yellow distillate at 120 °C/5 Torr was collected. Yield: 11.5 g (76%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.84 (s, 1 H, CH=NAr), 8.26 (dt, 1 H, ph), 7.54–7.12 (m, 8 H, ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3 (d, C–F), 153.2 (CH=N) ppm. $C_{13}H_{10}FN$ (199.22): calcd. C 78.37, H 5.06, N 7.03; found C 78.16, H 5.15, N 7.03.

Ligand L1: A solution of *n*-butyllithium (2.86 M in hexane, 9.3 mL, 26.6 mmol) was added slowly to a solution of 2-(phenylthio)aniline (5.33 g, 26.5 mmol) in thf (40 mL) at –78 °C, and the reaction mixture was warmed to room temperature and stirred overnight. This pale suspension was added to a solution of **1a** [2-C_6H_4F(CH=NC_6H_3*i*Pr_2-2,6); 7.51 g, 26.5 mmol) in thf (20 mL) at room temperature. After stirring for 12 h, the reaction was quenched with H_2O (20 mL) and extracted with *n*-hexane. The organic phase was evaporated to dryness in vacuo to give the crude product as a yellow oil. Pure product was obtained as yellow crystals by recrystallization from ethanol. Yield: 6.33 g (51%). ^1H NMR (300 MHz, $CDCl_3$): δ = 11.06 (s, 1 H, N–H), 8.25 (s, 1 H, CH=N), 7.58 (d, 1 H, Ar–H), 7.35 (d, 1 H, Ar–H), 7.30–7.05 (m, 12 H, Ar–H), 6.98 (t, 1 H, Ar–H), 6.82 (t, 1 H, Ar–H), 3.05 (sp, 2 H, CH of *i*Pr), 1.13 (d, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 148.6, 145.8, 141.0, 138.1, 135.0, 134.5, 133.4, 131.6, 130.5, 128.8, 128.6, 128.0, 126.6, 124.2, 123.8, 122.8, 122.4, 119.0, 117.6, 113.4, 28.0, 23.7 ppm. $C_{31}H_{32}N_2S$ (464.66): calcd. C 80.13, H 6.94, N 6.03; found C 80.30, H 7.18, N 6.00.

Ligand L2: A similar procedure to that used for the preparation of L1 was employed. 2-(Phenoxythio)aniline (4.20 g, 20.9 mmol), *n*-butyllithium (2.86 M in hexane, 7.3 mL, 20.9 mmol), and **1b** (4.75 g, 20.9 mmol). Yield: 4.86 g (57%). ^1H NMR (300 MHz, $CDCl_3$): δ = 11.17 (s, 1 H, N–H), 8.25 (s, 1 H, CH=N), 7.68, (d, 1 H, Ar–H), 7.25–7.44 (m, 5 H, Ar–H), 6.96–7.10 (m, 9 H, Ar–H), 6.86 (t, 1 H, Ar–H), 2.12 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.9, 150.4, 145.3, 142.0, 135.5, 135.0, 134.4, 131.5, 128.7, 127.8, 127.6, 126.3, 125.9, 123.6, 123.4, 1216, 119.3, 117.7, 113.6, 18.6 ppm. $C_{27}H_{24}N_2S$ (408.56): calcd. C 79.37, H 5.92, N 6.86; found C 79.21, H 6.15, N 6.64.

Ligand L3: A similar procedure to that used for the preparation of L1 was employed. 2-(Phenoxythio)aniline (7.71 g, 38.3 mmol), *n*-

butyllithium (2.86 M in hexane, 13.4 mL, 38.3 mmol), and **1c** (7.63 g, 38.3 mmol). Yield: 6.36 g (44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.395 (s, 1 H, N–H), 8.52 (s, 1 H, CH=N), 7.60 (d, 1 H, Ar–H), 7.28–6.85 (m, 16 H, Ar–H), 6.81 (t, 1 H, Ar–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5, 153.2, 150.6, 145.0, 142.0, 134.6, 132.3, 131.4, 130.9, 129.3, 128.8, 126.4, 126.1, 125.7, 123.2, 121.2, 121.0, 119.7, 117.8, 113.4 ppm. $C_{25}H_{20}N_2S$ (380.50): calcd. C 78.91, H 5.30, N 7.36; found C 78.82, H 5.63, N 7.46.

Complex 1: To a solution of compound L1 (1.05 g, 2.3 mmol) in dried toluene (30 mL) at –78 °C was added *n*-butyllithium (2.86 M in hexane, 0.8 mL, 2.3 mmol) dropwise over a 10 min period. The mixture was warmed to room temperature and stirred overnight. (dme)$NiBr_2$ (0.75 g) was added at room temperature, and the resulting mixture was stirred overnight and filtered. The solid was washed with toluene (3 × 10 mL). The combined organic filtrates were concentrated under reduce pressure to ca. 3 mL, and then dry hexane (50 mL) was added. After the mixture was stirred for 30 min, filtration of the mixture gave complex **1** as a dark-red solid in 89% yield (1.23 g). MS (ESI): *m*/*z* = 521, 522, 523, 524, 525 (isotope, $[M - Br]^+$). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.82–7.68 (m, 2 H, CH=N, Ar–H overlap), 7.63 (d, 1 H, Ar–H), 7.23–7.05 (m, 3 H, Ar–H), 6.99–6.78 (m, 7 H, Ar–H), 6.73 (t, 1 H, Ar–H), 6.50 (t, 1 H, Ar–H), 6.30 (t, 1 H, Ar–H), 2.62–0.64 [m, 14 H, $CH(CH_3)_2$, overlap] ppm. IR (KBr): $\tilde{\nu}$ = 1606, 1579, 1533, 1437, 1322, 1214, 1159, 1124, 1039, 745, 685 cm^{-1}. $C_{31}H_{31}BrN_2NiS$ (602.25): calcd. C 61.82, H 5.19, N 4.65; found C 61.59, H 5.45, N 4.60.

Complex 2: A similar procedure to that used for the preparation of complex **1** was employed. L2 (0.82 g, 2.0 mmol), *n*-butyllithium (2.86 M in hexane, 0.7 mL, 2.0 mmol), (dme)$NiBr_2$ (0.69 g). Yield: 1.03 g (91%). MS (ESI): *m*/*z* = 465, 466, 467, 468, 469, 470 (isotope, $[M - Br]^+$). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.75–7.62 (m, 2 H, CH=N, Ar–H overlap), 7.55 (d, 1 H, Ar–H), 7.23 (d, 1 H, Ar–H), 7.04–6.60 (m, 10 H, Ar–H), 6.53–6.36 (m, 2 H, Ar–H), 6.26 (t, 1 H, Ar–H), 3.75–1.64 (m, 6 H, CH_3, overlap) ppm. IR (KBr): $\tilde{\nu}$ = 1602, 1579, 1522, 1449, 1317, 1212, 1090, 1031, 752, 690 cm^{-1}. $C_{27}H_{23}BrN_2NiS$ (546.15): calcd. C 59.38, H 4.24, N 5.13; found C 59.65, H 4.39, N 4.80.

Complex 3: A similar procedure to that used for the preparation of complex **1** was employed. L3 (0.97 g, 2.5 mmol), *n*-butyllithium (2.86 M in hexane, 0.89 mL, 2.55 mmol), and (dme)$NiBr_2$ (0.86 g). Yield: 0.87 g (65.9%). MS (ESI): *m*/*z* = 437, 438, 439, 440, 441, 442 (isotope, $[M - Br]^+$). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.80–7.51 (m, 3 H, CH=N, Ar–H overlap); 7.50–6.46 (m, 16 H, Ar–H) ppm. IR (KBr): $\tilde{\nu}$ = 1612, 1579, 1523, 1448, 1318, 1219, 1181, 1158, 1123, 1027, 746, 691 cm^{-1}. $C_{25}H_{19}BrN_2NiS$ (518.09): calcd. C 57.96, H 3.70, N 5.41; found C 57.56, H 3.98, N 5.30.

Complex 4: To a solution of compound L1 (0.52 g, 1.12 mmol) in dried toluene (30 mL) at –78 °C was added a *n*-butyllithium (2.86 M in hexane, 0.4 mL, 1.14 mmol) dropwise over a 10 min period. The mixture was warmed to room temperature and stirred overnight. (cod)PdMeCl (0.30 g) in dichloromethane (10 mL) was added at room temperature. The resulting mixture was stirred overnight and filtered. The solid was washed with toluene (3 × 10 mL). The combined organic filtrates were concentrated under reduce pressure, and then dry hexane (5 mL) was added. After the mixture was stirred for 30 min, the filtration of the mixture gave complex **4** as a red powder in 62% yield (0.41 g). MS (ESI): *m*/*z* = 583, 584, 585, 586, 587, 588, 589, 590 [isotope, M^+]; 566, 567, 568, 569, 570, 571, 572, 573, 574 [isotope, $(M - CH_3)^+$]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.71 (m, 3 H, CH=N, Ar–H overlap), 7.61–7.51 (m, 2 H, Ar–H), 7.29–7.23 (m, 3 H, Ar–H), 7.21–7.07 (m, 7 H, Ar–H), 6.59 (t, 1 H, Ar–H), 6.50 (t, 1 H, Ar–H), 3.36 (sp, 2 H, CH of *i*Pr), 1.22–1.05 (m, 12 H, CH_3), –0.42 (s, 3 H, Pd–CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1602, 1582, 1525, 1473, 1447, 1443, 1332, 1202, 1028, 932, 837, 742, 687 cm^{-1}. $C_{32}H_{34}N_2PdS$ (585.11): calcd. C 65.69, H 5.86, N 4.79; found C 65.80, H 5.95, N 4.69.

Complex 5: A similar procedure to that used for the preparation of complex **4** was employed. L2 (0.44 g, 1.07 mmol), *n*-butyllithium (2.86 M in hexane, 0.38 mL, 1.08 mmol), and (cod)PdMeCl (0.28 g). Yield: 0.32 g (56%). MS (ESI): *m*/*z* = 527, 528, 529, 530, 531, 532, 533, 534, 535 [isotope, M^+]: 511, 512, 513, 514, 515, 516, 517, 518,

Table 3. Crystallographic date and refinement for L2 and complexes **1** and **2**.

	L2	**1**	**2**
Formula	$C_{27}H_{24}N_2S$	$C_{62}H_{62}Br_2N_4Ni_2S_2$	$C_{54}H_{46}Br_2N_4Ni_2S_2$
Fw	408.54	1204.52	1092.31
T [K]	173(2)	173(2)	173(2)
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	10.125(2)	17.7626(16)	20.513(2)
b [Å]	8.0233(18)	19.7558(17)	13.5870(15)
c [Å]	26.920(6)	16.6084(15)	18.720(2)
α [°]	90	90	90
β [°]	98.449(4)	109.901(2)	114.605(2)
γ [°]	90	90	90
V [Å^3]	2163.1(8)	5480.1(8)	4743.7(9)
Z	4	4	4
$D_{calcd.}$ [g/cm^3]	1.254	1.460	1.529
Absorp. coeff. [mm^{-1}]	0.166	2.265	2.608
F(000)	864	2480	2224
Crystal size [mm]	0.48 × 0.45 × 0.30	0.44 × 0.32 × 0.28	0.48 × 0.42 × 0.19
θ [°]	1.53–27.10	1.22–27.09	1.09–27.06
No. of date collected	10388	28030	23990
No. of unique date	4665 R_{int} = 0.0354	11937 R_{int} = 0.0519	10189 R_{int} = 0.0318
Goodness-of-fit on F^2	1.053	1.002	1.005
Final *R* indexes [$I > 2\sigma(I)$]	R_1 = 0.0510 wR_2 = 0.1537	R_1 = 0.045 wR_2 = 0.0943	R_1 = 0.0375 wR_2 = 0.0973
R indexes (*all data*)	R_1 = 0.0690, wR_2 = 0.1707	R_1 = 0.1012, wR_2 = 0.1148	R_1 = 0.0659, wR_2 = 0.1150

Table 4. Crystallographic date and refinement for complexes **4**, **5**, and **6**.

	4	**5**	**6**
Formula	$C_{32}H_{35}N_2PdS$	$C_{28}H_{26}N_2PdS$	$C_{26}H_{22}N_2PdS$
Fw	586.08	528.97	500.92
T [K]	173(2)	173(2)	173(2)
λ(Mo-K_a) [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	10.8867(17)	10.775(2)	10.156(3)
b [Å]	11.1754(17)	11.479(2)	10.666(3)
c [Å]	12.694(2)	18.635(4)	11.179(4)
α [°]	89.271(2)	90	102.810(5)
β [°]	76.702(2)	93.410(3)	99.588(5)
γ [°]	64.493(2)	90	109.301(5)
V [Å^3]	1349.9(4)	2300.9(8)	1076.0(6)
Z	2	4	2
$D_{calcd.}$ [g/cm^3]	1.442	1.527	1.546
Absorp. coeff. [mm^{-1}]	0.788	0.916	0.975
F(000)	606	1080	508
Crystal size [mm]	0.48 × 0.48 × 0.36	0.36 × 0.25 × 0.16	0.37 × 0.32 × 0.18
θ [°]	1.66–27.10	2.08–27.14	1.94–25.99
No. of date collected	11466	11280	8076
No. of unique date	5809 R_{int} = 0.0203	5027 R_{int} = 0.0356	4083 R_{int} = 0.0255
Goodness-of-fit on F^2	1.074	1.001	1.023
Final *R* indexes [$I > 2\sigma(I)$]	R_1 = 0.0302 wR_2 = 0.0867	R_1 = 0.0416 wR_2 = 0.1094	R_1 = 0.0403 wR_2 = 0.1328
R indexes (*all data*)	R_1 = 0.0380, wR_2 = 0.093	R_1 = 0.0615, wR_2 = 0.1267	R_1 = 0.0496, wR_2 = 0.1474

519 [isotope, $(M – CH_3)^+$]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (s, 1 H, CH=N), 7.71 (s, 1 H, Ar–H), 7.68 (s, 1 H, Ar–H) 7.59–7.53 (m, 2 H, Ar–H), 7.31–7.26 (m, 3 H, Ar–H), 7.21–6.98 (m, 7 H, Ar–H), 6.59 (t, 1 H, Ar–H), 6.50 (t, 1 H, Ar–H), 2.24 (s, 6 H, CH_3), –0.49 (s, 3 H, Pd–CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1601, 1580, 1526, 1445, 1432, 1329, 1211, 1153, 1127, 1089, 1030, 837, 742, 690 cm^{-1}. $C_{28}H_{26}N_2PdS$ (529.00): calcd. C 63.57, H 4.95, N 5.30; found C 63.29, H 4.87, N 5.11.

Complex 6: A similar procedure to that used for the preparation of complex **4** was employed. L3 (0.75 g, 1.97 mmol), *n*-butyllithium (2.86 M in hexane, 0.7 mL, 2.0 mmol), and (cod)PdMeCl (0.53 g). Yield: 0.65 g (66%). MS (ESI): *m*/*z* = 1002 $[2M]^+$; 524, 525, 526, 527, 528, 529, 530, 531 [isotope, $[M + Na]^+$]; 499, 500, 501, 502, 503, 504, 505, 506 [isotope, $[M]^+$]; 485, 486, 487, 488, 489, 490, 491 [isotope, $(M – CH_3)^+$]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (s, 1 H, CH=N), 7.69–7.62 (m, 2 H, Ar–H), 7.59–7.52 (m, 2 H, Ar–H), 7.36–7.24 (m, 6 H, Ar–H), 7.21–7.01 (m, 6 H, Ar–H), 6.61 (t, 1 H, Ar–H), 6.48 (t, 1 H, Ar–H), –0.24 (s, 3 H, Pd–CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1602, 1780, 1527, 1473, 1447, 1425, 1332, 1217, 1152, 1123, 1026, 933, 836, 740, 691 cm^{-1}. $C_{26}H_{22}N_2PdS$ (500.95): calcd. C 62.34, H 4.43, N 5.59; found C 62.51, H 4.65, N 5.49.

Ethylene Oligomerization: The oligomerization under 1 atm of ethylene was carried out in a typical procedure as follows. Appropriate MAO solid was added into a 50-mL flask. The flask was backfilled twice with ethylene, and then freshly distilled toluene (20 mL) was added by syringe under an ethylene atmosphere at the desired polymerization temperature. The resulting mixture was stirred for a further 10 min, and the catalyst precursor in toluene was injected by syringe. The reaction solution was vigorously stirred under 1 atm of ethylene for the desired time. The flask was cooled to –10 °C and then quenched with concentrated HCl in ethanol (10 mL, HCl/ethanol, 5:95, v/v). About 2 mL of organic solution was dried with anhydrous Na_2SO_4 for GC–MS analysis.

Norbornene Polymerization: In a typical procedure, the appropriate MAO solid was added into a 50-mL flask, and then freshly distilled toluene and norbornene dissolved in toluene (0.4 g/mL) was added by syringe at the desired polymerization temperature. The resulting mixture was stirred for a further 10 min, and the catalyst precursor in toluene was injected by syringe. The polymerization was carried out for the desired time and then quenched with concentrated HCl in ethanol (150 mL, HCl/ethanol, 5:95, v/v). The precipitated polymer was collected and washed with ethanol, and then dried overnight under vacuum at 50 °C.

X-ray Structure Determination: The crystals were mounted on a glass fiber by using the oil drop scan method. Dates obtained with the *ω-2θ* scan mode were collected with a Bruker SMART 1000 CCD diffractometer with graphite-monochromated *Mo-*K_α radiation. The structures were solved by direct methods, whereas further refinement with full-matrix least-squares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anistotropically. Hydrogen atoms were introduced in calculated positions with the displacement factor of the host carbon atoms. Crystal data and processing parameters for L2 and complexes **1**, **2**, **4**, **5**, and **6** are summarized in Tables 3 and 4.

CCDC-673899 (for L2), -673900 (for **1**), -673901 (for **2**), -673902 (for **4**), -673903 (for **5**), and -673904 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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