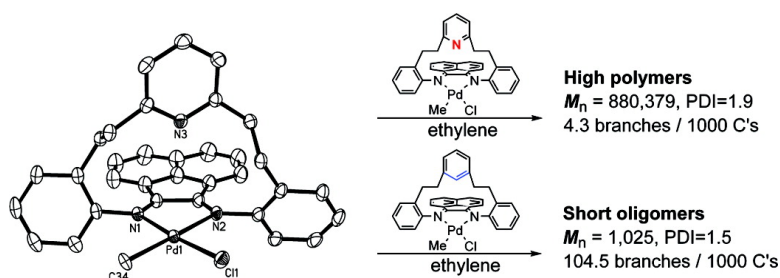


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## Axial Donating Ligands: A New Strategy for Late Transition Metal Olefin Polymerization Catalysis

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Late transition metal polymerization catalysts are under intense investigation because they offer unique features that early metal systems do not have.<sup>1</sup> A key insight from Brookhart and co-workers is that the incorporation of sterically bulky axial substituents in the  $\alpha$ -diimine ligand is essential in the generation of high molecular weight polymer.<sup>2</sup> On the basis of Brookhart's mechanistic model, prior to monomer insertion, the catalytically active  $14 e^-$  cationic complex containing the growing polymer chain can undergo reversible  $\beta$ -hydride elimination to form a square planar  $16 e^-$  olefin hydride intermediate. This olefin complex is susceptible to associative ligand exchange by coordination of a new olefin at the axial site, leading to premature chain termination.<sup>1a,2</sup> Catalysts with axial steric bulk can effectively prevent this from occurring. Many ligand modifications have been explored, including steric and electronic tuning, changing the backbone structure, and varying the chelating groups.<sup>1</sup> Despite these studies, bulky substituents are still required for the preparation of high molecular weight polymers. Herein, we report a fundamentally different approach: olefin polymerization catalysts that bear axial donating ligands.

We initially envisioned that a donating group at the axial site could interact with the metal through the empty p orbital.<sup>3</sup> This would prevent interception of the olefin hydride intermediate by axial coordination of a new monomer but still allow equatorial insertion of new monomers in the active cationic species. Significantly, unlike other  $\alpha$ -diimine-based late metal catalysts that require steric bulk at the top and bottom axial sites,<sup>1,2b</sup> our complexes would leave the bottom face open, yet produce polyethylene (PE) with high molecular weight. To the best of our knowledge, this represents the first example of  $\alpha$ -diimine ligand-based late transition metal catalysts that yield high molecular weight polymers without the need for bulky substituents.

We prepared ligand **1** that incorporates a pyridine donor (Figure 1). Ligand **1** was characterized by X-ray diffraction (see Supporting Information). In order to dissect axial interaction from steric effects, we also prepared ligand **2**, containing a nondonating phenyl group in place of the pyridine. Complexation to nickel and palladium precursors afforded the corresponding metal complexes (Figure 1). The crystal structure of **5** revealed that the Pd<sup>II</sup> center is chelated by the  $\alpha$ -diimine nitrogens in a square planar fashion with the pyridine donor situated above the metal center (Figure 2). While in the crystal form of the neutral complex the pyridine nitrogen is beyond bonding distance to the metal, the flexible alkyl tethers may allow for metal coordination in the activated cationic species in solution.

We first investigated the ethylene polymerization behavior of nickel complex **3** with a number of aluminum activators (Table 1). While only negligible yields were obtained with MAO or AlMe<sub>3</sub>, the addition of AlMe<sub>2</sub>Cl resulted in a highly active polymerization catalyst. Despite lacking steric bulk at the bottom face, catalyst **3** produces PE with high molecular weight and relatively narrow polydispersities (PDI). Similar to other  $\alpha$ -diimine-based catalysts, both the activity and molecular weight of PE formed fall as

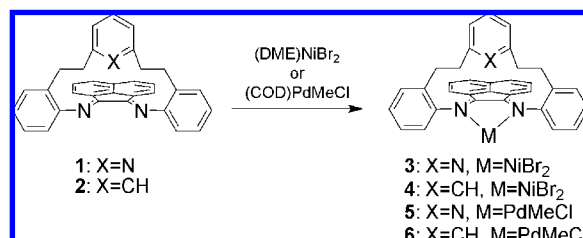


Figure 1. Axial donating ligand and metal complexes.

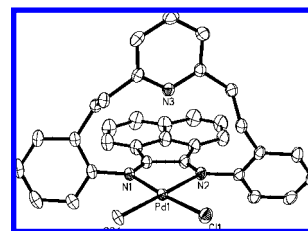


Figure 2. ORTEP drawing of Pd complex **5** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths: N(3)–Pd(1) 3.814 Å, N(1)–Pd(1) 2.054 Å, N(2)–Pd(1) 2.195 Å.

Table 1. Ni Ethylene Polymerization Reactions and Results<sup>a</sup>

entry	catalyst	activator	temp <sup>b</sup>	TOF <sup>c</sup>	$M_n^d$	PDI	branches <sup>e</sup>	$T_m^f$
1	<b>3</b>	MAO	35	<5 <sup>g</sup>	n.d.	n.d.	n.d.	n.d.
2	<b>3</b>	AlMe <sub>3</sub>	35	<5 <sup>g</sup>	n.d.	n.d.	n.d.	n.d.
3	<b>3</b>	AlMe <sub>2</sub> Cl	5	187	109224	2.1	1.4	137
4	<b>3</b>	AlMe <sub>2</sub> Cl	15	535	39337	3.2	3.4	134
5	<b>3</b>	AlMe <sub>2</sub> Cl	35	588	56464	2.2	3.6	131
6	<b>3</b>	AlMe <sub>2</sub> Cl	55	428	17587	3.9	11.3	125
7	<b>3</b>	AlEt <sub>2</sub> Cl	5	104	91782	2.6	1.9	137
8	<b>3</b>	Al( <i>i</i> Bu) <sub>2</sub> Cl	5	35	61628	2.9	5.0	133
9	<b>4</b>	MAO	35	561	5648	7.2	11.3	126
10	<b>4</b>	AlMe <sub>3</sub>	35	294	6994	6.6	11.6	123
11	<b>4</b>	AlMe <sub>2</sub> Cl	35	348	6931	5.6	12.9	122

<sup>a</sup> Polymerization conditions: 2  $\mu$ mol catalyst, 6 mmol activator, 100 mL of toluene, 200 psig ethylene, 10 min. <sup>b</sup> Reaction temperature in  $^{\circ}$ C. <sup>c</sup>  $\times 10^{-3}$ /h. <sup>d</sup> Determined by GPC with polystyrene standards. <sup>e</sup> Determined by <sup>1</sup>H NMR and is the number of Me's per 1000 carbons. <sup>f</sup> Determined by DSC in  $^{\circ}$ C. <sup>g</sup> Only trace amounts of polyethylene formed.

temperature is raised. This may be due to low thermal stability of the active catalytic species or disruption of the pyridine interaction by higher thermal energy.

In sharp contrast, nickel catalyst **4**, containing a nondonating phenyl group, only afforded low molecular weight oligomers with broad PDI when using MAO, AlMe<sub>3</sub>, or AlMe<sub>2</sub>Cl as activators. This result is consistent with our initial proposal that the axial donating pyridine group in catalyst **3** can prevent chain transfer. The lack of such axial interactions in catalyst **4** results in high susceptibility to chain transfer from the open bottom face, leading to low molecular weight oligomers.

**Table 2.** Pd Ethylene Polymerization Reactions and Results<sup>a</sup>

entry	catalyst	P (atm)	TON	$M_n^b$	PDI	branches <sup>c</sup>	$T_m^d$
1	<b>5<sup>e</sup></b>	1	535	880379	1.9	5.1	133
2	<b>5<sup>e</sup></b>	6	1872	730999	2.2	2.5	134
3	<b>6</b>	1	1248	1025	1.5	104.5	n/a
4	<b>6</b>	6	2941	1121	1.6	105.8	n/a

<sup>a</sup> Polymerization conditions: 10  $\mu$ mol catalyst, 20 mL of toluene, 25  $^{\circ}$ C, 24 h. <sup>b</sup> Determined by GPC using polystyrene standards. <sup>c</sup> Determined by <sup>1</sup>H NMR and is the number of Me's per 1000 carbons. <sup>d</sup> Determined by DSC in  $^{\circ}$ C. <sup>e</sup> With 1 mmol AlMe<sub>2</sub>Cl added.

In addition to the dramatic increase in molecular weight when using the pyridine-based catalysts, DSC and <sup>1</sup>H NMR spectroscopic analyses revealed that the PE formed from catalysts **3** and **4** have different microstructures. Under identical polymerization conditions (Table 1, entries 5 and 11), catalyst **3** produces more linear PE with significantly higher melting temperatures ( $T_m$ ) than catalyst **4**. This suggests that the axial pyridine donor not only inhibits associative chain transfer but also suppresses  $\beta$ -hydride elimination and catalyst chain walking,<sup>4</sup> resulting in highly linear polymer.

We next investigated the ethylene polymerization activity of the corresponding palladium catalysts (Table 2). While direct activation of phenyl catalyst **6** with NaBARf in the presence of ethylene resulted in the formation of low molecular weight PE oils, surprisingly no activity was observed with pyridine catalyst **5** under the same conditions. However, addition of AlMe<sub>2</sub>Cl to the mixture of **5** and NaBARf resulted in formation of highly linear PE. Remarkably, the PE formed by catalyst **5** is of extremely high molecular weight. In addition, the PEs obtained from catalyst **5** have remarkably low branching densities and high  $T_m$ 's. While linear PE has recently been obtained by phosphine-sulfonate palladium catalysts,<sup>5c-g</sup> most palladium catalysts, especially other Pd<sup>II</sup>- $\alpha$ -diimine systems, generate highly branched PE due to catalyst chain walking.<sup>4a,5</sup> To our knowledge, this is the first example of a Pd<sup>II</sup>- $\alpha$ -diimine catalyst which produces highly linear PE with high molecular weight.

The polymerization results suggest that a modification of our initial mechanistic hypothesis is necessary to account for the peculiar role of AlMe<sub>2</sub>Cl. Instead of a direct axial coordination between the pyridine donor group and the metal center, AlMe<sub>2</sub>Cl appears to play a specific and active role in generating the active species for the pyridine-based complexes. While phenyl-based Ni complex **4** shows no selectivity between MAO, AlMe<sub>3</sub>, and AlMe<sub>2</sub>Cl activators, only AlMe<sub>2</sub>Cl is effective in activating pyridine complex **3**. Similarly for pyridine-based Pd complex **5**, addition of AlMe<sub>2</sub>Cl is critical to generate the active catalyst for polymerization. In contrast, addition of AlMe<sub>2</sub>Cl to phenyl-based Pd complex **6** resulted in decreased activity and formation of short oligomers. Previous studies have shown that AlR<sub>2</sub>Cl reagents are effective activators for nickel catalysts,<sup>6</sup> and there is some evidence for the formation of bimetallic Ni–Al complexes bridged by the halide.<sup>6d</sup> Specific reactivity with AlR<sub>2</sub>Cl reagents has been seen for lanthanide polymerization catalysts which may also involve a bimetallic species.<sup>7</sup> Whereas the exact mechanism is still elusive at this moment,<sup>8</sup> we propose that the pyridine nitrogen in our system may be interacting directly with AlMe<sub>2</sub>Cl, bringing it close to the metal center to form an active bimetallic species bridged by the chlorine atom. Presumably, this axial coordination suppresses  $\beta$ -hydride elimination process and chain transfer, hence resulting high molecular weight, linear polymer structures.

In support of this hypothesis, indirect evidence for a specific interaction of AlMe<sub>2</sub>Cl with the pyridine-based catalysts has been obtained. Significantly lower polymerization activity was observed for pyridine catalyst **3** with more sterically bulky AlR<sub>2</sub>Cl reagents such as AlEt<sub>2</sub>Cl and Al(*i*Bu)<sub>2</sub>Cl, which is consistent with a site-

specific interaction with the pyridine group (Table 1, entries 7 and 8). Although having similar Lewis acidity, larger aluminum reagents may encounter unfavorable steric interactions with the catalyst, leading to decreased activity. Furthermore, no polymerization activity was observed when BF<sub>3</sub>·Et<sub>2</sub>O was added as a competitive Lewis acid additive for the pyridine donor site, suggesting that pyridine interaction with AlMe<sub>2</sub>Cl plays an active role in the polymerization process.

In conclusion, we have demonstrated a new strategy for the design of late transition metal olefin polymerization catalysts that utilize axial donor ligands. In this study, a pyridine group was introduced to an  $\alpha$ -diimine ligand to interact with the metal through the axial site. The pyridine, facilitated by AlMe<sub>2</sub>Cl, has been shown to play an active role in inhibiting chain transfer and producing high molecular weight PE. This interaction also results in significant changes in the polymer microstructures for both the nickel and palladium systems, yielding highly linear polymer. We have demonstrated that the use of axial donating ligands is a powerful approach for controlling catalyst activity and polymer properties. Studies at expanding the scope of this concept and exploring the nature of the interaction between the axial donor group and AlMe<sub>2</sub>Cl are currently underway.

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**Supporting Information Available:** Experimental details for the synthesis and characterization of compounds, polymerization data, NMR experiments, and X-ray crystal structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325–351. (d) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315. (e) Camacho, D.; Salo, E. V.; Ziller, J. W.; Guan, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821–1825.
- (2) (a) Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 10634–10635. (b) Gates, D. P.; Svejda, S. A.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320–2334.
- (3) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin, Inc.: New York, 1966.
- (4) (a) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059–2062. (b) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068–3081. (c) Rose, J. M.; Cherian, A. E.; Coates, G. W. *J. Am. Chem. Soc.* **2006**, *128*, 4186–4187.
- (5) (a) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888–899. (b) Popeney, C.; Guan, Z. *Organometallics* **2005**, *24*, 1145–1155. (c) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744–745. (d) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. *Organometallics* **2007**, *26*, 6624–6635. (e) Burns, C. T.; Jordan, R. F. *Organometallics* **2007**, *26*, 6737–6749. (f) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948–8949. (g) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033–2038.
- (6) (a) Kumar, K. R.; Sivaram, S. *Macromol. Chem. Phys.* **2000**, *201*, 1513–1520. (b) Maldanis, R. J.; Wood, J. S.; Chandrasekaran, A.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **2002**, *645*, 158–167. (c) de Souza, C. G.; de Souza, R. F.; Bernardo-Gusmao, K. *Appl. Catal., A* **2007**, *325*, 87–90. (d) de Souza, R. F.; Simon, L. C.; Alves, M. C. M. *J. Catal.* **2003**, *214*, 165–168.
- (7) Evans, W. J.; Champagne, T. M.; Giarikos, D. G.; Ziller, J. W. *Organometallics* **2005**, *24*, 570–579.
- (8) We have attempted low temperature NMR and a number of other mechanistic studies; unfortunately, thus far direct detection of the active catalytic species has been unsuccessful.

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