

Highly Active Titanium-Based Olefin Polymerization Catalysts Supported by Bidentate Phenoxyamide Ligands

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Phenoxyamide complexes of Ti-containing 2,6- $X_2C_6H_3$ ($X = Cl, Br$) substituents, when activated by methyl aluminoxane, afford catalysts with very high activities for the polymerization of ethylene and with good incorporation of 1-hexene.

Bidentate phenoxyimine ligands have made a dramatic impact on group 4 metal olefin polymerization catalysis.^{1–6} Such ligands are attractive because of their ease of synthesis and elaboration by straightforward Schiff base condensation procedures. An additionally attractive yet, to date, little exploited feature of the reaction chemistry of phenoxyimines is their ready reduction to phenoxyamines, which may serve as convenient precursors to phenoxyamide ligands. The wide range of ligand substitution patterns already elaborated for their phenoxyimine precursors highlights the potential for forming a similarly extensive library of dianionic ligands based on the phenoxide and amide donor combination.

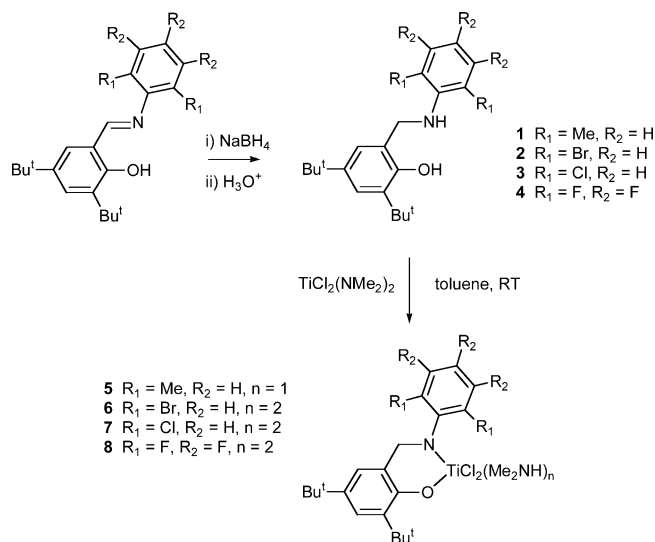
Recently, we described highly active ethylene polymerization catalysts supported by tridentate phenoxyamide ligands⁷ but, at the same time, found surprisingly low activities for a simple bidentate derivative containing the bulky 2,6- $Pr_2C_6H_3$ imino substituent. Here we show that incorporation of halo substituents within the amido aryl units leads to catalysts with dramatically improved ethylene polymerization activities and excellent 1-hexene incorporation.

The aminophenol proligands **1–4** were readily synthesized in good yields via the reduction of the corresponding iminophenols and isolated as colorless crystalline solids

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Scheme 1



according to Scheme 1. Treatment of **1–4** with $TiCl_2(NMe_2)_2$ gave the phenoxyamide complexes **5–8** with concomitant formation of dimethylamine. The hydrocarbon derivative **5** retains one molecule of dimethylamine within the metal's coordination sphere, whereas complexes **6–8** retain two molecules, reflecting the enhanced electrophilicity of the metal center in the halo-substituted products. Crystals of **8** suitable for an X-ray structure determination (see the Supporting Information for details) were grown from a saturated pentane solution. The geometry at Ti is slightly distorted octahedral (Figure 1) with cis angles in the range of 83.18(14)–94.7(2)°; the trans angles are between 171.3(2) and 176.42(16)°. The six-membered chelate ring adopts a shallow boat conformation with O(1) and C(7) lying +0.12 and +0.28 Å, respectively, out of the plane of the other four atoms, which are coplanar to better than 0.01 Å. The C_6F_5 ring is oriented orthogonally (ca. 89°) to this latter plane, a conformation perhaps stabilized by a pair of weak $N-H\cdots F$ interactions. The amide character of the C(7)–N(7) linkage is clearly evident from its bond length of 1.491(6) Å, and the Ti–N distance to this formally anionic N [1.965(4) Å] is very much shorter than those to the neutral dimethylamine ligands [2.232(5) and 2.243(6) Å]. The geometry at N(7) is distorted trigonal planar with the N lying ca. 0.07 Å out of

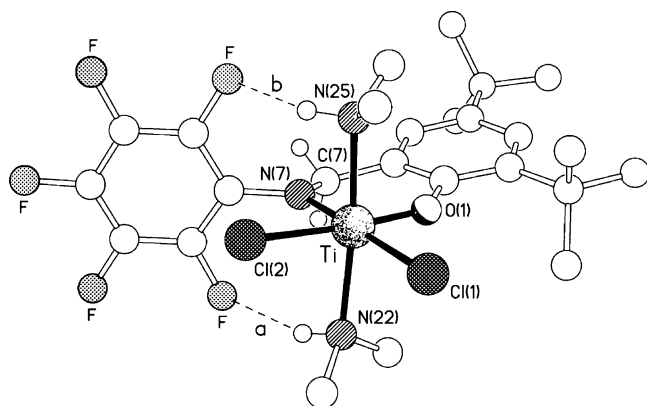


Figure 1. Molecular structure of **8**. The geometries of the N–H...F interactions are [N...F], [H...F] (Å), and [N–H...F] (deg): (a) 3.148(9), 2.29, and 161; (b) 3.081(6), 2.35, and 139.

Table 1. Ethylene Polymerization and Copolymerization Results for Complexes **5–8**^a

entry	precatalyst (μmol)	pressure (bar)	yield (g)	activity (g mmol ⁻¹ bar ⁻¹ h ⁻¹)
1	5 (5.0)	1	0.17	70 ^c
2	5 (5.0)	4	0.72	72 ^c
3 ^b	5 (5.0)	4	0.68	68 ^c
4	6 (0.2)	1	0.16	1600 ^c
5	6 (0.5)	4	1.37	1370 ^c
6 ^b	6 (0.5)	4	0.95	950 ^d
7	7 (1.0)	1	3.10	6200 ^c
8	7 (1.0)	4	7.65	3825 ^c
9	7 (0.5)	4	7.60	7600 ^c
10	7 (0.2)	4	4.85	12130 ^c
11	7 (0.2)	3	3.85	12830
12	7 (0.2)	2	1.79	8950 ^c
13	7 (0.2)	1	1.02	10200 ^c
14 ^b	7 (1.0)	4	14.21	7110 ^e
15	8 (10.0)	1	0.25	50 ^c
16	8 (10.0)	4	0.80	40 ^c
17 ^b	8 (10.0)	4	0.40	20 ^c

^a General conditions: Fisher Porter reactor, heptane solvent (200 mL), MAO cocatalyst (4.0 mmol), 25 °C, 30 min of reaction. ^b 1-Hexene (20 mL). ^c $M_w > 2 \times 10^6$. ^d $M_w = 708\,000$, $M_n = 253\,300$, PDI = 2.8. ^e $M_w = 475\,200$, $M_n = 159\,100$, PDI = 2.9.

the plane of its substituents; the angles subtended at this center are 108.4(4), 124.5(3), and 126.6(4)°, with the smallest being for the C–N–C angle. There are no intermolecular interactions of note.

A comparison of the ethylene polymerization and 1-hexene copolymerization capabilities of **5–8** (Table 1) reveals that the chloro- and bromo-substituted ligands afford catalysts with much higher activities than their hydrocarbon or pentafluorophenyl relatives. Thus, whereas **5**/methyl aluminum-oxane (MAO) gave activities of ca. 70 g_{PE} mmol⁻¹ h⁻¹ bar⁻¹ (entries 1 and 2; PE = polyethylene), the 2,6-dibromophenyl derivative **6** afforded activities as high as 1600 g_{PE} mmol⁻¹ h⁻¹ bar⁻¹ (entries 4 and 5).

For the chloro derivative **7**, the activity is further raised to 6200 g mmol⁻¹ bar⁻¹ h⁻¹ (entry 7) under the same

conditions. Upon lowering of the catalyst loading for **7** (entries 8–10), the activity level was optimized in the region 12–13 000 g mmol⁻¹ bar⁻¹ h⁻¹ (entries 10 and 11). High-molecular-weight (> 2 × 10⁶), linear polyethylene was obtained in each case. Examination of the effect of the ethylene pressure on the polymer yield for **7** (entries 10–13) revealed a first-order dependence. Contrasting the impressive activities found for the 2,6-dichloro and dibromo derivatives, the pentafluorophenyl catalyst **8**/MAO gave poor activities in tests under the same conditions (entries 15 and 16).

Complexes **5–8** were tested for 1-hexene comonomer incorporation. For the low-activity catalysts **5**/MAO (entry 3) and **8**/MAO (entry 17), 1-hexene incorporation was insignificant (by NMR). By contrast, catalyst **6**/MAO (entry 6) afforded 4.5 mol % 1-hexene incorporation, which increased to 6.8 mol % for **7**/MAO (entry 14). Both copolymers afforded relatively narrow molecular weight distribution products. Interestingly, the activity for the copolymerization using **7** was raised substantially relative to that for ethylene homopolymerization (compare entries 8 and 14).

The enhanced activities of the 2,6-dichloro- and 2,6-dibromophenyl catalysts relative to their hydrocarbon analogue may be attributed to the increased electrophilicity of the metal center in the halo-substituted systems.^{8,9} However, the poor activity found for the pentafluorophenyl catalyst suggests a deactivating effect for this highly electron-withdrawing substituent, which contrasts its beneficial effect in phenoxyimine catalyst systems, where it not only has been found to support to good activities but also has been shown to suppress chain termination processes.^{4,10–12} It is possible that, for monochelate phenoxyamide catalysts, the smaller pentafluorophenyl-containing ligand offers inadequate steric protection of the active site, leading to catalyst deactivation.

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Supporting Information Available: Experimental and spectroscopic details for the ligands and precatalysts, crystal data for **8**, and polymerization procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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