A Novel Heteroligated Phenoxy-based Titanium Complex: Structure, Stability, and Ethylene Polymerization Behavior

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A new phenoxy–imine and phenoxy–ketone heteroligated titanium complex was obtained by hydrolysis of one of the two imine moieties of a bis(phenoxy–imine)Ti complex. X-ray diffraction analysis revealed that the complex assumes an octahedral coordination geometry with a *cis*-phenoxy-O's and *cis*-Cl's disposition. NMR studies demonstrated that the complex does not undergo disproportionation. In association with methylaluminoxane, the complex behaved as a non-living-type single-site catalyst for ethylene polymerization.

Among the several types of non-metallocene olefin polymerization catalysts,[1] of note are group 4 transition-metal complexes of bis(phenoxy–imine) including bis(phenoxy–ketimine) (known as FI Catalysts) that were developed at Mitsui Chemicals.[2] With appropriate cocatalysts, these complexes display many distinctive and practical features, including high activity, precise control of molecular weight and molecular weight distribution, highly syndioselective and isoselective propylene polymerization, and living ethylene and/or propylene polymerization.[2–4]

One way to expand the framework of the phenoxy-based catalyst family is to devise mixed ligand complexes. In fact, phenoxy–imine/Cp complexes, phenoxy–imine/pyrrolide–imine complexes, and structurally-diverse phenoxy–imine ligated complexes have already been reported by us and others.[5,6] However, there have been no reports covering the synthesis and olefin polymerization behavior of transition metal complexes bearing different phenoxy-based ligands, even though such complexes may give information on the structure and catalytic performance relationships. Herein, we report the first example of a titanium complex that possesses both phenoxy–imine and phenoxy–ketone chelate ligands (a heteroligated phenoxy-based titanium complex). Additionally, we discuss its molecular structure, stability against disproportionation, and its catalytic behavior for the polymerization of ethylene by comparing it with the parent FI Catalyst.

A heteroligated complex **2** was unexpectedly obtained during the synthesis of a conventional homoligated complex **1** (Figure 1). After the collection of purified complex **1**, the filtrate (a CH_2Cl_2/n-pentane solution of complex **1** and impurities) was left in contact with air, and yielded a small amount of crystalline product. NMR spectroscopy and mass spectrometry revealed that these crystals have the structure that we now assign to complex **2**.[7] Subsequent trials to prepare complex **2** deliberately were successful and reproducible. Namely, the slow introduction of water by way of vapor diffusion with the aid of *n*-pentane into a benzene solution of complex **1** afforded distinctive reddish-brown crystals of complex **2** (isolated yield: 17–29%).

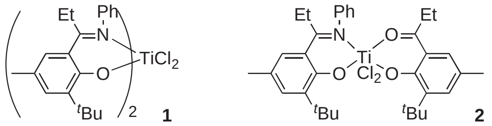

Figure 1. Homoligated complex **1** and heteroligated complex **2**.

We were interested in the coordination geometry of the heteroligated titanium complex **2**, since it has been reported that an existing bis(phenoxy–imine)Ti complex favors a *trans*-phenoxy-O and *cis*-Cl disposition in a distorted octahedral structure,[2] whereas a related bis(phenoxy–aldehyde)Ti complex is known to assume a *cis*-phenoxy-O and *cis*-Cl arrangement.[8] DFT calculation studies show that, among the six possible isomers that are labeled **a**–**f** in Figure 2, complex **2** favors the conformation adopted by isomer **c**, with the two phenoxy-O's in *cis*-positions.

The molecular structure of the heteroligated complex was established by X-ray crystallographic analysis.[9] As shown in Figure 3, the complex assumes a distorted octahedral geometry with a *cis*-phenoxy-O, *cis*-Cl, and *trans*-N/Cl arrangement, which agrees with the prediction of DFT calculations. The *cis*-relationship between the phenoxy-O's is rare for a phenoxy–imine-based transition-metal complex.[10] An important feature of this complex is that the chlorines occupy mutually *cis*-coordinated sites, which is potentially significant for generating an efficient polymerization active center. It is interesting to note that the two chelate ligands coordinate differently, i.e., the dihedral angle between the [N, C12, C6, C1, O1] least-squares plane and the [N, Ti, O1] plane is as large as 28.12°, while the [O2, C21, C26, C32, O3] least-squares plane and the [O2, Ti, O3] plane with a dihedral angle of 8.66°.[11]

NMR studies demonstrate that complex **2** exists predominantly as a single isomer in both $CDCl_3$ and C_6D_6 solutions.[7] The aromatic regions of the ^1H and ^{13}C NMR spectra show nine or eighteen discrete peaks, respectively, meaning that the phenyl group attached to the imine-N has non-equivalent *ortho*- and

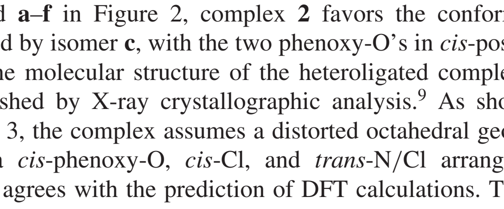

Figure 2. Calculated relative formation energies (kJ/mol) of the possible isomers of complex **2**. Neutral oxygens are labeled with asterisk.

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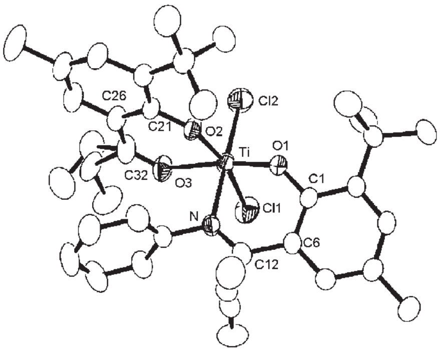

Figure 3. ORTEP diagram of the molecular structure of complex **2**. Ethyl groups are drawn as observed in disorder. Selected bond lengths (Å), bond angles (°): Ti–O1, 1.821(2); Ti–O2, 1.863(2); Ti–O3, 2.084(2); Ti–N, 2.198(2); Ti–Cl1, 2.3194(8); Ti–Cl2, 2.3186(8); O1–Ti–O2, 95.50(8); O1–Ti–N, 81.24(7); O1–Ti–Cl1, 97.01(6); O1–Ti–Cl2, 99.08(6); O2–Ti–O3, 81.33(7); O2–Ti–N, 89.17(8); O2–Ti–Cl2, 91.98(6); O3–Ti–N, 88.59(8); O3–Ti–Cl1, 85.01(6); O3–Ti–Cl2, 91.15(6); N–Ti–Cl1, 85.27(6); Cl1–Ti–Cl2, 93.50(3).

meta-positions. This observation can probably be ascribed to the restricted rotation of the phenyl group on the NMR time scale,[10a] due to steric congestion derived from the ethyl group on the imine-C.

Since complex **2** is well-suited for use in studying ligand exchange between complexes, the stability of complex **2** against disproportionation was investigated. No peaks arising from complex **1** appear in the ^{1}H NMR spectrum of complex **2** up to 75 °C in C_6D_6. Moreover, we observed that complex **2** does not show any distinct change in its NMR spectrum in $CDCl_3$ over a temperature range between 23 and −50 °C, and that a mixture of complexes **1** and **2** in C_6D_6 only exhibits peaks stemming from each of complexes **1** and **2** at 75 °C.[7] These results indicate that complex **2** is highly robust against disproportionation under the conditions examined.

In addition to the molecular structure, the ethylene polymerization behavior of heteroligated titanium complex **2** has attracted interest because a bis(phenoxy–imine)Ti complex has (some) characteristics of living ethylene polymerization, as reported by us and others,[2] and a related bis(phenoxy–aldehyde)Ti complex does not (which behaves as a multi-site catalyst and provides broad molecular weight distribution polyethylene).[8] Ethylene polymerization results for complexes **1** and **2** with MAO activation are compared (25 °C, 5 min, atmospheric pressure, toluene solution, [Ti] = 0.02 mM, and [Al] = 5 mM). As expected, complex **1** produced nearly monodisperse polyethylene (M_w/M_n 1.06, M_n 26200, and activity 266 kg-PE/mol-Ti•h).[2] Interestingly, heteroligated complex **2** displayed normal single-site catalysis and formed polyethylene with a molecular weight distribution (M_w/M_n) of 2.04 (M_n 10400 and activity 104 kg-PE/mol-Ti•h). Complex **1** probably generates homotopic polymerization sites, while complex **2** apparently forms non-equivalent catalytic sites. At this point, it is not clear how these features reflect the polymerization catalysis of complexes **1** and **2**. Further studies on heteroligated complexes would provide insight into the role played by the phenoxy, imine, and carbonyl donors in the catalytic properties and mechanistic behavior.

In summary, the formation, molecular structure, stability against disproportionation, and ethylene polymerization behavior of a new Ti complex ligated with phenoxy–imine and phenoxy–ketone has been described. The results introduced herein suggest that only a partial change in the ligand structure can have a significant effect on complex structure and catalyst performance. Further investigations are now in progress to define the scope and limitations of this partial hydrolysis method for the preparation of transition-metal complexes ligated with phenoxy–imine and phenoxy–ketone (or aldehyde) from readily-available bis(phenoxy–imine) complexes.

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References and Notes

1 V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, **103**, 283 (2003).
2 For recent reviews: a) Y. Suzuki, H. Terao, and T. Fujita, *Bull. Chem. Soc. Jpn.*, **76**, 1493 (2003). b) M. Mitani, J. Saito, S. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka, and T. Fujita, *Chem. Rec.*, **4**, 137 (2004). c) H. Makio and T. Fujita, *Bull. Chem. Soc. Jpn.*, **78**, 52 (2005). d) R. Furuyama, J. Saito, S. Ishii, H. Makio, M. Mitani, H. Tanaka, and T. Fujita, *J. Organomet. Chem.*, in press.
3 The developmental history of FI Catalysts for syndioselective propylene polymerization seems confused. To the best of our knowledge, syndioselective propylene polymerizations with Ti–FI Catalysts were first reported by researchers at Mitsui Chemicals in January 2000 (WO-0155231), which represents the first examples of syndioselective propylene polymerization using FI Catalysts and related complexes.
4 For some recent research: a) R. Furuyama, M. Mitani, J. Mohri, R. Mori, H. Tanaka, and T. Fujita, *Macromolecules*, **38**, 1546 (2005). b) J. Saito, Y. Tohi, N. Matsukawa, M. Mitani, and T. Fujita, *Macromolecules*, **38**, 4955 (2005). c) H. Makio, T. Oshiki, K. Takai, and T. Fujita, *Chem. Lett.*, **34**, 1382 (2005).
5 a) T. Fujita, Y. Tohi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio, and T. Tsutsui, Eur. Patent EP-0874005 (1998). b) M. Nitabaru, K. Tsuru, S. Matsui, and T. Fujita, Jpn. Tokkyo Kokai Koho JP-072810 (2000).
6 a) J. Huang, B. Lian, Y. Qian, W. Zhou, W. Chen, and G. Zheng, *Macromolecules*, **35**, 4871 (2002). b) R. K. J. Bott, D. L. Hughes, M. Schormann, M. Bochmann, and S. J. Lancaster, *J. Organomet. Chem.*, **665**, 135 (2003). c) D. A. Pennington, S. J. Coles, M. B. Hursthouse, M. Bochmann, and S. J. Lancaster, *Chem. Commun.*, **2005**, 3150. d) A. F. Mason and G. W. Coates, *J. Am. Chem. Soc.*, **126**, 10798 (2004).
7 Details of the experimental results are supplied as Supporting Information files.
8 L. Matilainen, M. Klinga, and M. Leskelä, *J. Chem. Soc., Dalton Trans.*, **1996**, 219.
9 Crystal data: $C_{34}H_{43}Cl_2NO_3Ti$, MW = 632.52, triclinic, $P\bar{1}$ (No. 2). $a = 9.9193(2)$ Å, $b = 10.0822(4)$ Å, $c = 17.4856(3)$ Å, $\alpha = 85.748(5)°$, $\beta = 89.698(1)°$, $\gamma = 76.677(7)°$, $V = 1696.84(9)$ Å^3, $Z = 2$, $D_{calcd} = 1.238\ \mathrm{g\,cm^{-3}}$. $T = 296$ K, $\lambda = 0.71069$ Å. The final structure was refined to $R_1 = 0.054$, $wR_2 = 0.139$, and GOF = 1.934 for all 6997 reflections ($2\theta < 54.95$) and 407 parameters.
10 a) J. Strauch, T. H. Warren, G. Erker, R. Fröhlich, and P. Saarenketo, *Inorg. Chim. Acta*, **300–302**, 310 (2000). b) Y. Tohi, H. Makio, S. Matsui, M. Onda, and T. Fujita, *Macromolecules*, **36**, 523 (2003). c) Y. Tohi, T. Nakano, H. Makio, S. Matsui, T. Fujita, and T. Yamaguchi, *Macromol. Chem. Phys.*, **205**, 1179 (2004).
11 The corresponding dihedral angles for bis(phenoxy–aldehyde)Ti complexes are 1.89 and 12.89°, respectively. The dihedral angles for bis(phenoxy–imine)Ti complexes are usually within 15°.

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