Synthesis of Bis(phenoxyimine) Ti Alkyl Complexes and Observation of Living Species by ^{1}H NMR Spectroscopy

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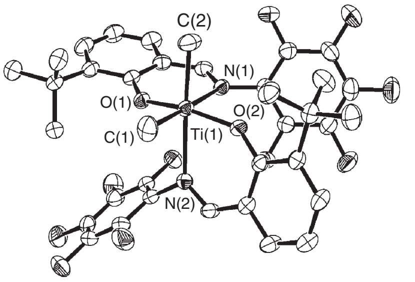
Synthesis of $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_3\text{-}3\text{-}R)]_2TiMeX$ (R: ^{t}Bu; X: Br (**2**), R: ^{t}Bu; X: Me (**3**), R: H; X: Me (**4**)) was achieved by the reaction of methylated titanium halides with sodium salts of the phenoxyimine ligands. These complexes can be activated with equimolar amounts of $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$ to form methyl cationic species, which, upon addition of a small amount of ethylene monomer allows room temperature observation of cationic polymeryl species.

Synthesis of alkyl complexes is of great value since such complexes can be activated in a well-defined manner using an equimolar amount of perfluoroaryl borane or borate salts without the need for alkylaluminums. Direct observations of these alkyl cationic species have contributed to fundamental understanding of olefin polymerization mechanisms with metallocenes and related complexes.[1]

We have reported the unique and versatile olefin polymerizations with Group 4 bis(phenoxyimine) complexes (FI Catalysts) activated with MAO or ^{i}Bu$_3$Al/$Ph_3CB(C_6F_5)_4$,[2] which include living (syndioselective) polymerizations of ethylene and propylene by fluorinated Ti-FI complexes,[3] e.g., $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_3\text{-}3\text{-}{}^tBu)]_2TiCl_2$ (**1**). However, attempts to synthesize alkylated FI complexes have been hampered by various side reactions, including nucleophilic attacks of alkylating agents on imine functions, reduction of Ti(IV) to Ti species with lower oxidation states, intramolecular migration of the alkyl group,[4] and ligand transfer to alkylaluminum.[5] Alkylation of **1** is even more difficult because electron-withdrawing perfluorophenyl groups make the imines more electrophilic. We now report on the successful synthesis of $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_3\text{-}3\text{-}R)]_2\text{-}TiMeX$ (R: ^{t}Bu; X: Br (**2**), R: ^{t}Bu; X: Me (**3**), R: H; X: Me (**4**)) by taking a new synthetic approach, i.e., synthesis of $Me_{2-n}TiX_{2+n}$ ($n = 1$, X = Br (**6**) or $n = 0$, X = Cl (**7**)) followed by complexation with sodium salt of phenoxyimine ligands.

A titanium precursor **6** was prepared in 70% yield according to modified procedure of the literature.[6] The reaction of **6** and 2 equiv. of $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_3\text{-}3\text{-}{}^tBu)]Na$ in toluene at $-78\,^\circ$C afforded complex **2** as reddish brown powder (71%). ^{1}H NMR spectrum of **2** exhibits two sets of ligand signals, indicating collapse of C_2 symmetry seen for **1**, as well as a H_3C-Ti signal at 1.97 ppm.[7] Dimethyltitanium dichloride (**7**) was generated in situ by the reaction of 1,2-dimethoxyethane adduct of $TiCl_4$ ($TiCl_4{\cdot}DME$) and 2 equiv. of MeLi in diethyl ether at $-30\,^\circ$C[8] and used without isolation in subsequent reactions with the sodium salts. After removal of inorganic salts by filtration, complex **3** was precipitated from pentane solution as dark red crystallite.[9] The molecular structure of **3** shown in Figure 1 adopts a distorted octahedral structure having a *trans*-O, *cis*-N, and *cis*-Me disposition as is commonly observed for FI dichloride complexes and is consistent with the observed NMR spectra. To the best of our knowledge, this represents the first structurally characterized alkyl complex bearing bis(phenoxyimine) ligands. Complex **4** was prepared by a similar manner to complex **3** and obtained as orange tan powder.[10]



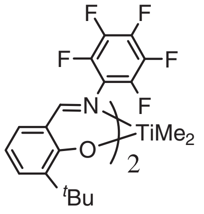


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Figure 1. Molecular structure of a Ti-FI dimethyl complex, $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_3\text{-}3\text{-}{}^tBu)]_2TiMe_2$ (**3**). Selected bond lengths (Å) and bond angles (deg): Ti–O(1) 1.869(2); Ti–O(2) 1.872(2); Ti–N(1) 2.345(3); Ti–N(2) 2.371(3); Ti–C(1) 2.111(4); Ti–C(1) 2.102(4); O(1)–Ti–O(2) 160.3(1); N(1)–Ti–N(2) 93.9(1); C(1)–Ti–C(2) 93.9(2).

Complex **2**, upon activation with an equimolar amount of $NaB(C_6F_5)_4$, exhibited lower ethylene polymerization activity than MAO activation under the same conditions (5700 g mmol^{-1} h^{-1} for borate; 35,800 g mmol^{-1} h^{-1} for MAO[3a]) and was practically inactive for propylene polymerization. Complex **3** upon activation with $Ph_3CB(C_6F_5)_4$ displayed comparable activities with MAO for ethylene (23,400 g mmol^{-1} h^{-1}) and propylene polymerizations (2.9 kg mol^{-1} h^{-1} for MAO;[3b] 1.3 kg mol^{-1} h^{-1} for borate). The ^{1}H NMR spectra of complex **2** activated with $NaB(C_6F_5)_4$ indicated a set of ligand signals as a main component (**2***), showing a symmetric structure on an NMR time scale. However, the signals of **2*** are significantly up-field shifted (0.56 ppm for *H*C=N) relative to MAO activated species.[5] This can be attributed to less cationic nature of **2*** presumably derived from formation of Br-bridged dinuclear monocationic complex, $[\{C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_3\text{-}3\text{-}{}^tBu)\}_2TiMe]_2\text{-}Br^+$.[11] On the other hand, activation of **3** with the trityl salt caused immediate precipitation of a dark red oily product (**3***) indicative of a species with strong ionic character. The reaction in bromobenzene-d_5 resulted in homogeneous solution of **3***, whose ^{1}H NMR exhibited a set of ligand signals and methyl groups of Ph_3CMe and Me–Ti at 1.88 and 1.78 ppm, respectively, corroborating the formation of $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_3\text{-}3\text{-}{}^tBu)]TiMe^+B(C_6F_5)_4{}^-$. Activation of **3** with $B(C_6F_5)_3$, which usually affords more soluble and more stable inner sphere ion

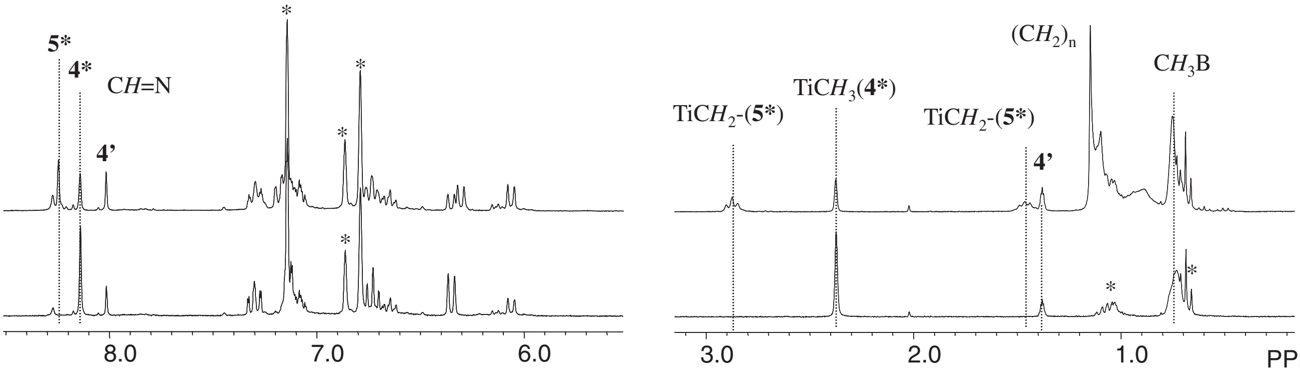

Figure 2. ^{1}H NMR spectra (270 MHz: BrC_6D_5) of $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_4)]TiMe^+[MeB(C_6F_5)_3]^-$ (**4***, bottom) and $[C_6F_5N{=}CH(2\text{-}O\text{-}C_6H_4)]Ti(CH_2CH_2)_nMe^+[MeB(C_6F_5)_3]^-$ (**5***, top). The asterisks indicate protio impurities of NMR solvent and pentane.

pairs with metallocene dialkyls,[1] also resulted in oily precipitation in toluene at 8.1 mM [Ti], implying significant cation–anion separation of this species.[12] Sterically much less encumbered complex **4** with $B(C_6F_5)_3$ also gave an oily species (**4***) in toluene-d_8 (13.3 mM [Ti]), thus the origin of the ion separation is not primarily steric. ^{1}H NMR spectra of **4*** verify the formation of a cationic methyl species with some minor species (**4′**) that is not observed for **3***. The identity of the minor species is unknown at this moment but could be a Me-bridged dinuclear species due to reduced steric bulk of **4***. The ^{1}H NMR shifts of $MeB(C_6F_5)_3^-$ for **4*** as a measure of ionic character[13] are ca. 0.8 ppm in both toluene and bromobenzene that is almost identical to $LiMeB(C_6F_5)_3$. We attribute this enhanced ion separation to the formation of sterically more relaxed five-coordinated trigonal bipyramidal cationic species that can compensate for the energy gain due to the charge separation.

Upon addition of ethylene (ca. 5 equiv. to [Ti]) to **4*** in bromobenzene-d_5, peak intensity of species **4*** decreases along with the appearance of new signals as shown in Figure 2. Particularly notable are the signals at 2.88 and 1.45 ppm that are assignable to the diastereotopic α-methylene protons of the propagating "*living*" species (**5***). The minor species (**4′**) is virtually inactive to ethylene polymerization and there is no double bond formation indicative of chain transfers. It should be noted that NMR experiments were conducted at room temperature and that after 9 h, species **5*** remained almost unchanged though **4*** slightly decreased in intensity. The same experiment for **3*** also exhibits a living propagating species (4.59 and 3.15 ppm for $-CH_2Ti$), although it was rather difficult to control the reaction due to the high activity of this species[14] under the conditions currently applied.

In conclusion, we have shown that monomethyl and dimethyl Ti-FI catalysts with perfluorinated *N*-aryl groups are accessible. These complexes can be activated by common boron cocatalysts without the use of alkylaluminums and thus without reduction of the imine and Ti. The species obtained are similar to MAO derived species in character and prove the extraordinary robust livingness. The living propagating species can be observed even at room temperature. In order to investigate dynamic solution structure and polymerization mechanism of FI Catalysts, including the proposed ortho-F–β-H interaction,[3] and configurational fluxionality,[3b,15] more extensive NMR and other spectroscopic studies are currently underway and will be reported in due course.

References and Notes

1 E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, **100**, 1391 (2000).
2 H. Makio, N. Kashiwa, and T. Fujita, *Adv. Synth. Catal.*, **344**, 477 (2002).
3 a) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, **124**, 3327 (2002). b) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, H. Tanaka, and T. Fujita, *J. Am. Chem. Soc.*, **125**, 4293 (2003).
4 P. D. Knight, A. J. Clarke, B. S. Kimberley, R. A. Jackson, and P. Scott, *J. Chem. Soc., Chem. Commun.*, **2002**, 352.
5 H. Makio and T. Fujita, *Macromol. Symp.*, **213**, 221 (2004).
6 K.-H. Thiele, P. Zdunneck, and D. Baumgart, *Z. Anorg. Allg. Chem.*, **378**, 62 (1970).
7 ^{1}H NMR (270 MHz, benzene-d_6) δ 7.55 (s, 1H, *H*C=N), 7.47 (s, 1H, *H*C=N), 7.44 (dd, $J = 3.6$, 1.7 Hz, 1H, ArH), 7.41 (dd, $J = 3.6$, 1.7 Hz, 1H, ArH), 6.91 (dd, $J = 7.9$, 1.7 Hz, 1H, ArH), 6.81 (dd, $J = 7.9$, 1.7 Hz, 1H, ArH), 6.69 (dt, $J = 7.6$, 1.7 Hz, 2H, ArH), 1.97 (d, $J = 2.0$ Hz, 3H, CH_3-Ti), 1.57 (s, 9H, ^{t}Bu), 1.51 (s, 9H, ^{t}Bu); ^{13}C NMR (67.5 MHz, benzene-d_6) δ 174.7, 174.0, 163.7, 162.9, 140.2, 139.2, 136.2, 135.1, 134.6, 134.1, 124.6, 123.7, 121.0, 86.3, 35.5, 29.8–29.3; Anal. Found: C, 51.16; H, 2.86; N, 3.44%. Calcd for $C_{28}H_{16}F_{10}N_2O_2Ti$: C, 50.81; H, 3.53; N, 3.39%. The discrepancy in elemental analyses is due to instability of the complex.
8 D. Duncan and T. Livinghouse, *Organometallics*, **18**, 4421 (1999).
9 ^{1}H NMR (270 MHz, benzene-d_6) δ 7.52 (s, 2H, *H*C=N), 7.45 (dd, $J = 7.6$, 1.7 Hz, 2H, ArH), 6.88 (dd, $J = 7.6$, 1.7 Hz, 2H, ArH), 6.72 (t, $J = 7.7$ Hz, 2H, ArH), 1.65 (s, 6H, CH_3-Ti), 1.58 (s, 18H, ^{t}Bu); ^{19}F NMR (471 MHz, benzene-d_6) δ -149.3 (d, *o*-F), -160.3 (t, *p*-F), -164.2 (m, *m*-F); Anal. Found: C, 56.12; H, 3.07; N, 3.60%. Calcd for $C_{36}H_{32}F_{10}N_2O_2Ti$: C, 56.71; H, 4.23; N, 3.67%. The discrepancy in elemental analyses is due to instability of the complex.
10 ^{1}H NMR (270 MHz, toluene-d_8) δ 7.38 (s, 2H, *H*C=N), 7.11–7.05 (m, 2H, ArH), 6.81–6.77 (m, 4H, ArH), 6.59 (dt, $J = 7.6$, 1.0 Hz, 2H, ArH), 1.67 (s, 6H, CH_3-Ti); ^{19}F NMR (471 MHz, benzene-d_6) δ -147.0, -149.5 (br, *o*-F), -160.9 (t, *p*-F), -163.3, -164.6 (br, *m*-F); Anal. Found: C, 50.69; H, 1.33; N, 4.22%. Calcd for $C_{28}H_{16}F_{10}N_2O_2Ti$: C, 51.72; H, 2.48; N, 4.31%. The discrepancy in elemental analyses is due to instability of the complex.
11 In fact, a 1:1 mixture of **3*** and **2** gave a similar spectrum to **2***.
12 C. Zuccaccia, N. G. Stahl, A. Macchioni, M.-C. Chen, J. A. Roberts, and T. J. Marks, *J. Am. Chem. Soc.*, **126**, 1448 (2004).
13 S. Beck, S. Lieber, F. Schaper, A. Geyer, and H.-H. Brintzinger, *J. Am. Chem. Soc.*, **123**, 1483 (2001).
14 R. Furuyama, M. Mitani, J. Mohri, R. Mori, H. Tanaka, and T. Fujita, *Macromolecules*, **38**, 1546 (2005).
15 Y. Tohi, H. Makio, S. Matsui, M. Onda, and T. Fujita, *Macromolecules*, **36**, 523 (2003).