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Observation and Identification of the Catalytically Active Species of Bis(phenoxy-imine) Group 4 Transition Metal Complexes for Olefin Polymerization Using ^{1}H NMR Spectroscopy

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Summary: Solution structures of bis(phenoxy-imine) group 4 transition metal complexes (FI Catalysts) were investigated using ^{1}H NMR spectroscopy. At least two isomers exist in equilibrium for FI Catalysts precursors, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (**1**), and bis[*N*-(3,5-dicumylsalicylidene)anilinato]zirconium(IV) dichloride (**2**), while bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**3**) exhibits only one isomer under the conditions examined. Upon activation with MAO, all FI Catalysts (**1-3**) generate two species at ambient temperature judging from some key signals in the ^{1}H NMR. When temperature is raised (up to 75 °C), one species (**1a-3a**) converts irreversibly to the other species (**1b-3b**). The resulting species, **1b-3b,** are stereochemically rigid, in contrast to precursors **1** and **2**. Species **3b,** derived from a living FI Catalyst, exhibited virtually no reactivity toward olefin insertion. The imine protons of species **1b-3b** are temperature and solvent polarity sensitive. Two possibilities are proposed for the assignment of species **1b-3b**, i) heterobinuclear complexes of group 4 metal and alkylaluminum with methyl and/or chlorine as bridging groups and ii) phenoxy-imine ligated aluminum complexes whose ligands are transferred from the group 4 metal. The latter is more probable from the separate synthesis of $LAlMe_2$ (L: phenoxy-imine ligand). When **3** was activated with MAO in the presence of olefins, a new imine signal was observed. This species (**3c** for ethylene and **3d** for propylene) is thermally more robust than **3a** toward transformation to **3b** and assignable to the living propagating species.

Keywords: dynamic behavior; FI Catalysts; living polymerization; NMR; solution structure

Introduction

One important development in the field of single-site olefin polymerization catalysis has been the elucidation of a relationship between the dynamic structure of the active catalyst species and the

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structure of resulting polyolefins. Taking advantage of this dynamic nature, unique polymerization processes based on the reversible transformation of catalytically active species have been developed.[1] Transformation of the catalyst species proceeds at a rate either much slower than chain-propagation, where the catalytic system will take on a multi-site character, or significantly faster than chain-propagation, where the system will apparently follow single-site polymerization mechanisms. When the transformation takes place on a time scale between catalyst initiation and polymer chain termination, the structural changes of the active species are reflected in the microstructures of individual polymer chains, which allows us unusual control over each monomer enchainment and syntheses of unique polymers with unprecedented structures. Fluxional processes of transition metal complexes that are observable on the NMR time scale (10^{-2} to 10^{-5} s) are similar in frequency to a typical propagation reaction in olefin polymerization. Therefore, such fluxionality can have an affect on polymerization reactivity or selectivity.

Significant time and effort have gone into exploring the potential of bis(phenoxy-imine) group 4 transition metal complexes as olefin polymerization catalysts (FI Catalysts).[2] By choosing the appropriate metal center, cocatalysts, and diversified ligand structures, these catalysts mediate ethylene polymerization with exceptionally high activity and desired molecular weight (molecular weight distribution),[3] living ethylene polymerization at ambient temperature or higher,[4] and living propylene polymerization with high syndiotacticity.[5,6] Schematically, FI Catalysts can have at least five isomers depending on the ligand coordination modes in an octahedral configuration.[2] In most cases, a stable *cis-N*, *trans-O*, *cis-Cl* isomer could be isolated in the solid state. However, we sometimes encountered multi-site characteristics with the FI Catalysts, which can probably be attributed to the presence of isomers in solution through intramolecular ligand rearrangement. One example includes the synthesis of polyethylene with controllable unimodal, bimodal, and trimodal molecular weight distributions by a Zr-FI catalyst, bis[*N*-(3,5-dicumylsalicylidene)anilinato]zirconium(IV) dichloride (**2**) / MAO.[3] Recently, a theoretical study involving the sydiospecific polymerization of propylene by bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**3**) and MAO suggested that the specificity was a result of rapid isomerization between active catalyst diastereomers.[7] Qualitatively, the theoretical results are in good agreement with experimental observations obtained from *'ligand-directed chain-end controlled'* syndiospecific propylene polymerizations.[2,5c]

In general, octahedral complexes are considered to be fairly stereochemically rigid unless metal-ligand bond cleavage is involved.[8] However, there is growing evidence of stereochemical nonrigidity with FI Catalysts[3] and other related octahedral complexes[9] with $[N_2O_2]^{2-}$ donor ligands. These complexes isomerize under the safe assumption that dissociation of a neutral coordinating atom is relatively easy. Even a non-dissociation mechanism may be allowed in the case of Ziegler-type polymerization catalysis where one ligand of the catalytically active cationic species is a loosely bound counter anion.

Investigation into the solution structures of FI Catalysts is of fundamental importance to understanding polymerization kinetics, selectivity, and polymer microstructures. Herein, we describe our attempts to observe the solution structures of some FI Catalysts, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (**1**), bis[*N*-(3,5-dicumylsalicylidene)anilinato]zirconium(IV) dichloride (**2**), and bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**3**), where fluxional processes between configurational isomers might lead to multimodal molecular weight distributions or syndiotactic polymers.

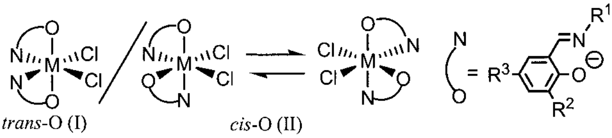
Experimental

Materials and Methods. All manipulations of air-sensitive materials were performed in Schlenk-type glassware on a dual-manifold Schlenk line or in a nitrogen-filled glove box with a high capacity recirculator (< 1 ppm O_2). Deuterated solvents were obtained from Cambridge Isotope Laboratories (all ≥ 99 atom %D), freeze-pump-thaw-degassed, dried over activated molecular sieves, and stored in resealable flasks. Precatalysts **1**-**3** were prepared as described in our previous papers.[3,4,10] Commercially available MAO (Albemarle, 1.2 M in toluene) was dried under vacuum to obtain white powder, dissolved in deuterated toluene, and dried again to remove a trace amount of residual non-deuterated toluene. This dried MAO (DMAO) was added as a powder whose molecular weight is 58 based on $-Al(CH_3)O-$ unit.

Physical and Analytical Measurements. NMR spectra were recorded on JEOL GSX 270 spectrometer (FT, 270 MHz, ^1H). Chemical shifts were referenced using internal solvent resonances and are reported relative to tetramethylsilane. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J. Young). In VT-NMR experiments, each temperature transition was conducted at intervals around 5–10 min including temperature equilibration and data collection.

Results and Discussion

In our previous paper,[3] fluxional processes for the FI Catalyst precursors, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (**1**), and bis[*N*-(3,5-dicumylsalicylidene)-anilinato]zirconium(IV) dichloride (**2**) were observed by ^{1}H and ^{15}N NMR spectroscopy. The isomers detected in solution were assigned to a *cis-N*, *trans-O*, *cis-Cl* isomer with C_2 symmetry (I) and a *cis-N*, *cis-O*, *cis-Cl* isomer with C_1 symmetry (II) that has a chemically nonequivalent phenoxy-imine ligand pair (Scheme 1). In general, with early transition metal complexes, shorter metal-O bonds are trans to one another to alleviate repulsion between valence shell electron pairs.[9] This is observed with the major solution-state isomer for **1.** However, the major isomer for **2** was found to have a *cis-N*, *cis-O*, *cis-Cl* configuration.[3] On the other hand, at room temperature the titanium complex, bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoro-anilinato]titanium(IV) dichloride (**3**), exhibits a set of sharp signals for one isomer in solution (toluene-d_8 or $CDCl_3$), which is in sharp contrast to the broad, fluxional signals observed for the Zr complexes **1** and **2** under the same conditions. Considering the crystallographically characterized structure as well as the relative formation energy calculated by DFT for **3**,[4b] the dominant species of **3** in solution is most likely the *cis-N*, *trans-O*, *cis-Cl* isomer.



1: $R^1 = C_6H_5$; $R^2 = C(CH_3)_3$; $R^3 = H$; M = Zr; I / II = 84/16[3]
2: $R^1 = C_6H_5$; R^2, $R^3 = C(CH_3)_2Ph$; M = Zr; I / II = 12/88[3]
3: $R^1 = C_6F_5$; $R^2 = C(CH_3)_3$; $R^3 = H$; M = Ti; I / II = 100/0

Scheme 1

Upon activation of **1** with DMAO (Al/Zr = 110, [Zr] = 7.0 μmol) at ambient temperature in toluene-d_8, two new imine signals appear at 7.81 and 7.51 ppm distinct from the peak at 7.54 ppm for **1** (Figure 1A). With increased temperature, the imine peak at 7.81 ppm decreases in intensity and shifts downfield slightly (7.85 ppm at 50 °C). The imine peak around 7.81 ppm disappears at about 50 °C, while the peak at 7.51 ppm increases in intensity and shifts downfield significantly (7.60 ppm at 50 °C and 7.65 ppm at 75 °C). This indicates that two species are generated and that one species (**1a**, Figure 1) is transformed into the other (**1b**, Figure 1). After cooling to room temperature, the signals for **1b** remain but those for **1a** do not reappear, whichsuggests that the transformation of **1a** to **1b** is irreversible. At all temperatures examined, judging by the single imine in the ^{1}H NMR spectra, species **1a** and **1b** seem to have one set of ligand signals and are stereochemically rigid except for the temperature-sensitive imine proton of **1b**, which may be involved in dynamic processes. Another feature is the appearance and growth of a sharp singlet at 0.18 ppm during the transformation of **1a** to **1b** (Figure 1B), which turns out to be assignable to methane by comparison with an authentic sample. This methane formation is observed in all experiments below.

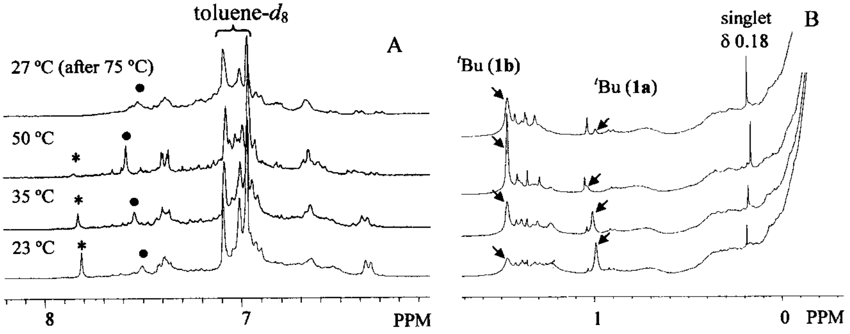


Figure 1. Variable-temperature ^{1}H NMR spectra of aromatic (A) and aliphatic region (B) of **1**/DMAO. The imine signals for species **1a** and **1b** are marked * and •, respectively.

Precatalyst **2** (Al/Zr = 130, [Zr] = 6.0 µmol) was similarly activated with DMAO at ambient temperature in toluene-d_8. The ^{1}H NMR spectra involving DMAO activated precatalyst **2** are more complicated than those of activated precatalyst **1** and rather uninformative. However, as the temperature is increased, broad signals at 7.95 ppm decrease in intensity and disappear around 75 °C. A new imine signal similar in chemical shift to that of **1b** as well as another signal at 7.7 ppm appears. Irreversible increase or decrease in intensity of the other signals, which are poorly resolved and unassignable, suggests that a transformation from **2a** to **2b** proceeds in a similar manner to the **1**/DMAO system. After complete formation of species **2b** the spectra are less complicated. The temperature-sensitive imine signal of **2b** (• in Figure 2) is clearly seen as a singlet. In addition, a doublet around 7.7 ppm (J = 2.31 Hz, denoted as × in Figure 2), whose chemical shift is rather temperature independent, can be observed (Figure 2A). In order to investigate solvent effects, all volatiles were then removed from the NMR tube *in vacuo* and deuterated tetrachloroethane ($C_2D_2Cl_4$) was added (Figure 2B). Using $C_2D_2Cl_4$ as a solvent, resolution was significantly improved. Notable is the dramatically downfield shifted singlet imine proton (~0.7 ppm at 25 °C, • in Figure 2B), which demonstrates that the structure of species **2b** is sensitive to solvent polarity as well as the temperature. In contrast, the chemical shift of the doublet around 7.6 ppm (× in Figure 2B) does not shift significantly in $C_2D_2Cl_4$. These two signals are almost equal in intensity at all temperatures examined and the integration approximates one proton for each signal. The imine protons of FI Catalysts or phenoxy-imine ligands usually appear as singlets but sometimes as poorly resolved doublets or multiplets. In the latter cases, the coupling constants observed with the imine proton usually do not match those on the phenol ring, indicating that the multiplicity on imine protons is not caused by a long-range coupling between the imine proton and 6-H of 3-alkylsalicylidene moiety.[11] Since two other doublets having equal coupling constants of 2.31 Hz are observed at 6.86 ppm and 7.36 ppm (75 °C), the doublet at 7.62 ppm is assignable to an aromatic proton on a phenol-ring. Since neither peak broadening nor coalescence are observed (Figure 2), a configurational isomerization does not take place with **2b,** but some dynamic processes must be considered for the temperature and solvent sensitive imine chemical shifts. A sharp singlet at 0.18 ppm (methane) appeared in a similar manner to the reaction of **1**/DMAO.

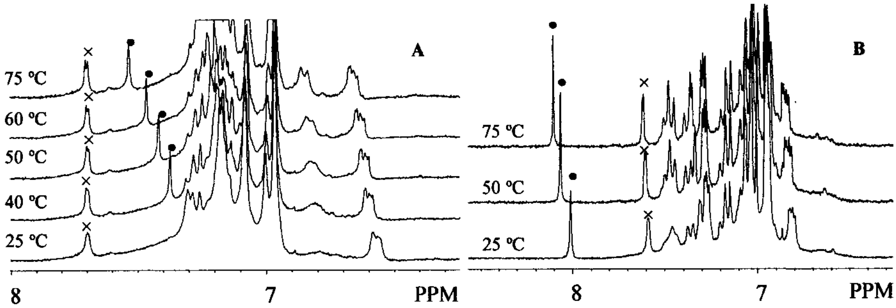


Figure 2. VT-^{1}H NMR spectra of **2**/DMAO in toluene-d_8 (A) and in $C_2D_2Cl_4$ (B), respectively (Al/Zr = 224, [Zr] = 6.3 mmol).

To further examine the generality of the observations made with precursors **1** and **2**, bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**3**) was chosen as a precursor in the next experiment. There are several advantages of investigating this complex: i) the perfluorinated phenyl ring simplifies the aromatic region of spectra; ii) greater solubility improves resolution even at room temperature; and iii) the living nature of this catalyst allows in-situ observation of subsequent reactions with olefins. In $CDCl_3$ or toluene-d_8 at room temperature, **3** shows only a single set of ligand signals in contrast to **1** and **2** under the same conditions. This indicates that **3** exists as a single isomer possessing C_2 symmetry (Scheme 1). Activation of **3** with DMAO at room temperature leads to the formation of two species (Figure 3). With the perfluorinated ligand, each species is fairly well separated from each other and the solvent signals, which allowed us to determine that both species have only one set of ligand signals. Thus, as shown in Figure 3, each species gives rise to five signals (*i.e.*, imine (s, 1H), phenol (dd, dd, t, 3H) and *tert*-butyl (s, 9H) signals) though one triplet overlaps with the solvent signals. In addition to these signals assignable to the ligands, another broad singlet appears at 1.97 ppm. Upon increasing the temperature, the signals of the dominant species at room temperature (**3a**) decreases in intensity and the signals for the other minor species (**3b**) increases. The singlet at 1.97 ppm decreases in intensity in accordance with the decrease in intensity of the signals derived from **3a**. The singlet integrates to 3H when the imine proton of **3a** at 8.20 ppm is integrated to 2H.

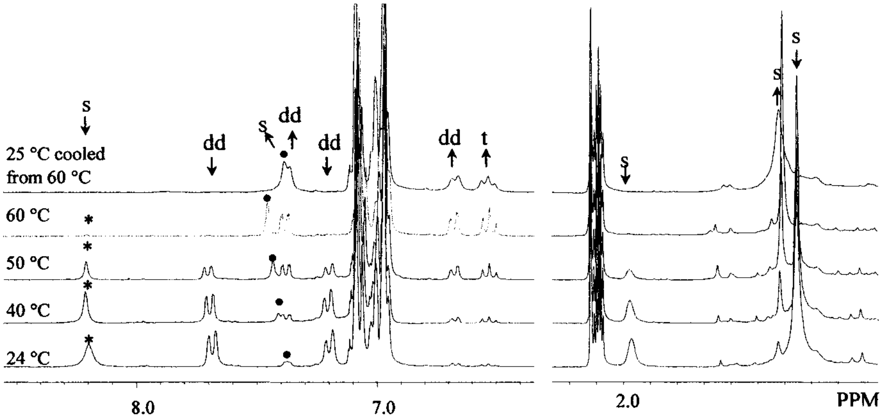


Figure 3. VT-^{1}H NMR spectra of **3**/DMAO in toluene-d_8 (Al/Ti = 108, [Ti] = 14.0 mmol). Symbols denote the imine protons of **3a** (*) and **3b** (•).

Thus, the singlet can be assigned to the methyl group attached to titanium; therefore, **3a** may be identified as the cationic methyl species, $L_2TiCH_3^+$(L: phenoxy-imine ligand). The conversion of **3a** to **3b** is irreversible and the imine signal for **3b** shifts downfield with increased temperature in contrast to the other temperature independent signals. In addition, the formation of methane is again observed. These observations are similar to those seen in the previously described reactions involving precursors **1** and **2**, demonstrating that these characteristics have generality in the activation processes of FI Catalysts with MAO. Since MAO does not produce methane upon heating, the cationic species would be involved in the methane formation probably via C–H bond activation.

To identify species **3b**, various olefins were added to investigate whether or not olefin insertion will occur. Introduction of ethylene to the in-situ generated **3b** (Al/Ti = 53; ethylene/Ti ≈ 2) leads to formation of solid polyethylene. The ^{1}H NMR spectra of the reaction mixture shows large signals of **3b** remaining in the mixture and additional small broad signals in conjunction with broad polyethylene signals (spectrum iii in Figure 4). Unfortunately, it is almost impossible to ensure uniform reaction conditions in the NMR tube because the high MAO concentration tends to solidify the reaction mixture especially at the low temperatures preferable for reaction NMR experiments. To prevent this from occurring slower reactions with bulkier olefins were examined. Styrene did not react with **3b** even at 75 °C. With the reaction of **3b** with 1-hexene, only isomerization to internal olefins was observed. The low reactivity toward α-olefin insertion leads to the postulation that species **3b** (and presumably **1b** and **2b**) is not the active species during olefin polymerization.

In the real polymerization experiments, activation of FI Catalysts with MAO is usually conducted in the presence of a monomer. Polymerization starts without an induction period even below room temperature indicating extremely rapid formation of active species. Therefore, it is reasonable to assume that an immediately formed active species, **3a**, turns gradually into an inactive species, **3b**, in the absence of a reacting monomer. Activation in the presence of ethylene was conducted by injecting a toluene solution of **3** into DMAO (~70 equiv to Ti) and ethylene (1.4 or 7 equiv to Ti) dissolved in toluene at 0 °C. After removing all volatiles *in vacuo*, the residue was dissolved in toluene-d_8. A new set of signals (species **3c**) was observed in addition to those of **3b** and growing polyethylene signals (spectra iv and v in Figure 4). The peaks corresponding to **3c** are similar to those of **3a** except for the imine chemical shift, which appears slightly upfield (7.9 – 8.0 ppm) in comparison to the corresponding signal of **3a** (8.19 ppm) but much further downfield than the signal of **3b** (7.37 ppm). There are some signals in the olefinic region (4.8 – 6.6 ppm) which are unassignable at this time.

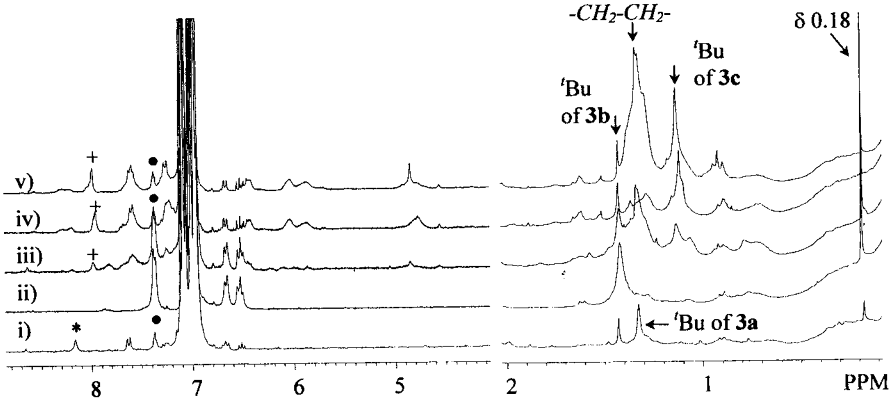
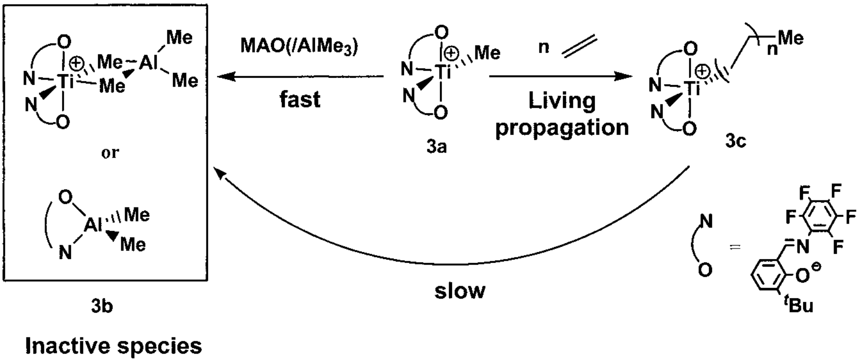


Figure 4. ^{1}H NMR spectra of **3**/DMAO prepared under various conditions. i) **3**/DMAO (1/108) at 24 °C; ii) **3**/DMAO (1/108) after reaction at 60 °C; iii) **3**/DMAO (1/53) after reaction at 60 °C for 5 min, ethylene (2 equiv to Ti) was added; iv) activation in the presence of ethylene, DMAO/ethylene/**3** (67/1.4/1); v) activation in the presence of ethylene, DMAO/ethylene/**3** (71/7/1). Characteristic imine signals are marked with * for **3a**, • for **3b**, and + for **3c**.

Olefin polymerization mediated by FI Catalysts is conceived to be catalyzed by a cationic metal–alkyl species like other well-defined group 4 transition metal catalysts. Thus, downfield shift of imine protons is most likely attributed to an increase in cationic nature. This assumption rationalizes the chemical shifts of imine protons observed in ^{1}H NMR, *e.g.*, two reactive species which appear downfield are assignable to the cationic methyl species, $L_2Ti^+-CH_3$ (**3a**) and the cationic propagating species, $L_2Ti^+-(CH_2CH_2)_n-CH_3$ (**3c**), respectively. The less reactive species **3b** with a diminished cationic character may be assigned to i) a heterobinuclear complex with alkylaluminum compounds, $[L_2Ti-\mu_2-(CH_3)(X)-Al(CH_3)(X)]^+$ (X: $-CH_3$ or -Cl) or ii) a L_nAlMe_{3-n} (n = 1 or 2) complex where L^- is transferred from the Ti center (Scheme 2). There are examples of the formation of similar complexes in metallocenes and other early transition metal complexes.[9a,12] The reaction between L–H and $AlMe_3$ (~0.5 equiv) in toluene-d_8 at room temperature monitored by ^{1}H NMR indicates the formation of a compound similar to **3b** as a major product, of which imine proton shows similar temperature dependence to that of **3b**. From the integration, the major product is assignable to $LAlMe_2$ (^1H NMR (δ, C_7D_8): 7.39-7.36 (m, 3H), 6.60 (dd, 1H), 6.51 (t, 1H), 1.43 (s, 9H), -0.35 (t, 6H)) which coexists with unreacted L–H, suggesting that **3b** is most likely to be $LAlMe_2$.



Scheme 2

Similar species were observed through the reaction of **3**, $AlMe_3$, and $Ph_3CB(C_6F_5)_4$. Two species very similar to **3a** and almost identical to **3b** are observed in the ^1H NMR spectrum (Figure 5). The signal of Ph_3CCH_3 is clearly seen at 2.0 ppm, indicating methide abstraction from titanium,[13] which in turn suggests the generation of a cationic titanium species. These observations are in agreement with the generation of $[L_2Ti\text{-}CH_3]^+[B(C_6F_5)_4]^-$ similar to **3a** with concomitant formation of **3b**.

The activation of **3** was attempted in the presence of propylene by the same method used to activate **3** in the presence of ethylene. As observed with the ethylene system, species **3b** (the

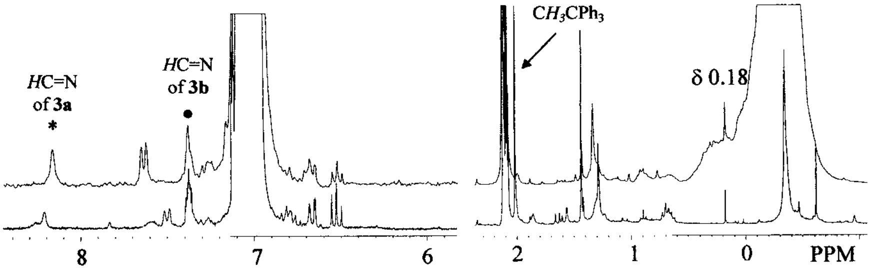


Figure 5. ^1H NMR spectra of **3** activated with DMAO (top; Al/Ti = 108) and $AlMe_3$ / $Ph_3CB(C_6F_5)_4$ (bottom; Al/Ti/B = 2.8/1/1.04).

imine protons are marked with • in Figure 6) and **3d** (supposedly with a propagating chain of propylene, the imine proton are marked with + in Figure 5) were observed. As temperature increases, **3d** is slowly transformed into **3b** but a significant amount of **3d** remains even at 75 °C for more than 15 min. Considering the fact that species **3a** turned to **3b** completely at 60 °C in the absence of propylene, the thermal resistance of **3d** toward formation of **3b** probably stems from a bulkier growing chain of propylene, which will discourage the formation of **3b**. This thermal stability is important in establishing the living nature of this species (Scheme 2).

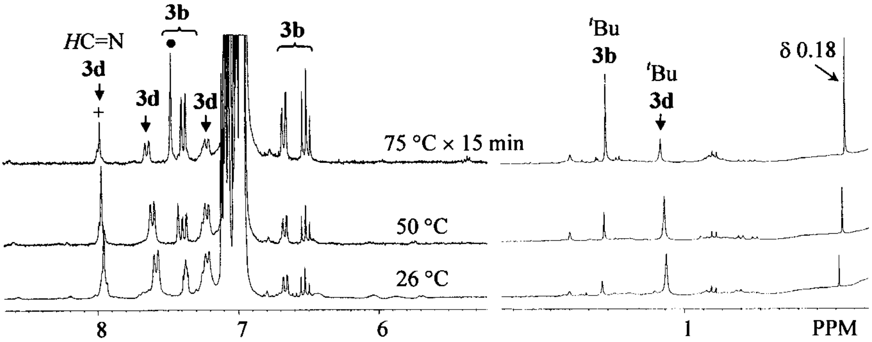


Figure 6. VT-^{1}H NMR spectra of **3** activated with DMAO in the presence of propylene (Al/Ti/propylene = 72/1/1.4). The imine proton of **3b** and **3d** is marked with • and +, respectively.

These interpretations qualitatively explain many general characteristics of olefin polymerizations mediated by FI Catalysts, *e.g.*, i) a bulky substituent next to the phenoxy-oxygen increase catalytic activity;[2,10] ii) DMAO exhibits higher activity than commercially available MAO (regular MAO) that contains a larger amount of $AlMe_3$ than DMAO;[14] and iii) reaction of FI Catalysts with a cocatalyst in the absence of a monomer lowers catalytic activity compared to activation in the presence of a monomer. These observations can be rationalized in terms of discouraging the formation of inactive species with $AlMe_3$ by i) steric hindrance of substituents close to reaction center, ii) lower $AlMe_3$ content in DMAO, and iii) steric protection by a bulkier growing polymer chain. To spectroscopically examine the phenomenon ii) mentioned above, trimethylaluminum was added to DMAO (DMAO: 1.4 mmol; $AlMe_3$: 0.35 mmol) to create similar conditions to those of regular MAO. Treatment of precursor **2** with the prepared MAO (**2**: 5.6 μmol, Al/Zr = 315) results in immediate formation of **2b** without heat, which verifies the hypothesis. The differences between DMAO and regular MAO have a significant effect on syndiotacticity in propylene polymerization with non-fluorinated Ti-FI Catalysts, that is, regular MAO affords higher syndiotacticity than DMAO.[14] This might not be explained in terms of the formation of inactive $LAlMe_2$ and therefore, direct interaction of $AlMe_3$ with active species, *e.g.*, $[L_2Ti\text{-}\mu_2\text{-}(CH_3)_2Al(CH_3)_2]^+$, cannot be excluded.

Conclusion

Reaction NMR experiments were conducted for the activation of three FI Catalyst precursors with DMAO. The chemical shifts of imine protons are well-separated at lower field and are sensitive to the structure and cationic character of the generated species to serve as a good probe for the identification of the catalytically active species. The results suggest that with all three precursors the active cationic methyl species are generated immediately and slowly transformed into inactive species, which are most likely to be aluminum complexes bearing phenoxy-imine ligands. Activation of the living precatalyst **3** in the presence of ethylene or propylene leads to the formation of a cationic propagating species, which is thermally more robust than the corresponding methyl species toward transformation to the aluminum species. These interpretations qualitatively explain general polymerization characteristics observed with FI Catalysts. Expected fluxionality between configurational isomers could not be examined in detail because the systems suffer from heterogeneity due to solidified MAO at lower temperatures and the formation of the aluminum complex at higher temperatures.

Acknowledgement

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[11] For example, at a lower temperature of −25 °C in $C_2D_2Cl_4$, the imine protons for **1** appears in doublet for both isomers shown in Scheme 1 (major: δ 8.12; 2.3 Hz, minor: δ 8.07 and 7.86; 2.3 Hz). The coupling on the imine is clearly larger than those on the double doublets of the phenol ring of **1** (7.8 Hz, 1.4 Hz).

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