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Titanium and Zirconium Complexes with Non-Salicylaldimine-Type Imine–Phenoxy Chelate Ligands: Syntheses, Structures, and Ethylene-Polymerization Behavior

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Abstract: New Ti and Zr complexes that bear imine–phenoxy chelate ligands, [{2,4-di-*t*Bu-6-(RCH=N)-C_6H_4O}$_2$MCl_2] (**1**: M=Ti, R=Ph; **2**: M=Ti, R=C_6F_5; **3**: M=Zr, R=Ph; **4**: M=Zr, R=C_6F_5), were synthesized and investigated as precatalysts for ethylene polymerization. ^{1}H NMR spectroscopy suggests that these complexes exist as mixtures of structural isomers. X-ray crystallographic analysis of the adduct **1**·HCl reveals that it exists as a zwitterionic complex in which H and Cl are situated in close proximity to one of the imine nitrogen atoms and the central metal, respectively. The X-ray molecular structure also indicates that one imine phenoxy group with the *syn* C=N configuration functions as a bidentate ligand, whereas the other, of the *anti* C=N form, acts as a monodentate phenoxy ligand. Although Zr complexes **3** and **4** with methylaluminoxane (MAO) or $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ displayed moderate activity, the Ti congeners **1** and **2**, in association with an appropriate activator, catalyzed ethylene polymerization with high efficiency. Upon activation with MAO at 25 °C, **2** displayed a very high activity of 19900 (kg PE) (mol Ti)$^{-1}$ h^{-1}, which is comparable to that for [Cp_2TiCl_2] and [Cp_2ZrCl_2], although increasing the polymerization temperature did result in a marked decrease in activity. Complex **2** contains a C_6F_5 group on the imine nitrogen atom and mediated nonliving-type polymerization, unlike the corresponding salicylaldimine-type complex. Conversely, with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ activation, **1** exhibited enhanced activity as the temperature was increased (25–75 °C) and maintained very high activity for 60 min at 75 °C (18740 (kg PE) (mol Ti)$^{-1}$ h^{-1}). ^{1}H NMR spectroscopic studies of the reaction suggest that this thermally robust catalyst system generates an amine–phenoxy complex as the catalytically active species. The combinations **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ and **2**/MAO also worked as high-activity catalysts for the copolymerization of ethylene and propylene.

Keywords: catalysts · complexes · polymerization · titanium · zirconium

Introduction

Since the advent of highly active Group 4 metallocene catalysts for olefin polymerization,[1] well-defined transition-metal complexes with various ligand sets have been studied extensively as potentially viable catalysts. This is because homogeneous catalysts based on well-defined transition-metal complexes can control the molecular weights and microstructures of the resultant polymers, unlike ill-defined heterogeneous catalysts.

As Group 4 metallocene and related catalysts have recently enjoyed success in the commercial production of a wide array of high-performance polymers,[2] there is a growing academic and industrial interest in the development of non-Cp-based catalysts (Cp=cyclopentadienyl). Intense research efforts centered on the design and synthesis of transition-metal complexes for olefin polymerization have introduced numerous new high-activity catalysts based on transition-metal complexes that incorporate non-Cp ligands.[3] Notable examples include Ni and Pd complexes with diimine li-

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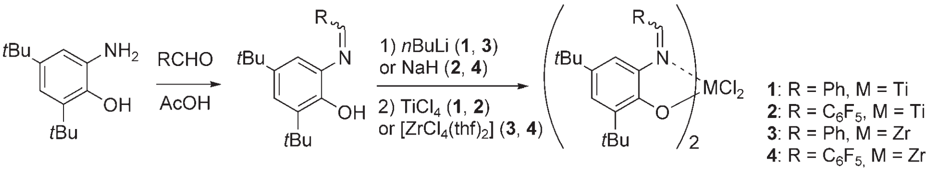
gands,[4] Ni complexes with phenoxy–imine ligands,[5] Fe and Co complexes with diimine–pyridine ligands,[6] Ti complexes with diamide,[7] phosphinimide,[8] or phenoxy–thioether ligands,[9,10] Zr complexes with phenoxy–quinoline ligands,[11] Zr and Hf complexes with phenoxy–oxazoline ligands,[12] Ti, Zr, and Hf complexes with diamide–ether,[13] diamide–amine,[14] bisphenoxy–amine,[15] tris(pyrazolyl)borate,[16] or phenoxy–phosphine ligands,[17] V complexes with imide–phenoxy ligands,[18] and Ta complexes with amide–pyridine ligands.[19,20] These complexes (with methylaluminoxane (MAO) or borate activation) show high catalytic activity, and some of them exhibit unique catalysis in polymerization to furnish distinctive polymers (e.g., hyperbranched polyethylenes (PEs), monodispersed poly(higher α olefin)s, ethylene/polar monomer copolymers, α olefin based block copolymers).

For our part, we investigated well-defined transition-metal complexes that bear nonsymmetric ligands with electronically flexible properties (ligand-oriented catalyst design) in an effort to obtain new and highly active catalysts.[21] As a consequence, we developed new families of transition-metal complexes,[22–37] which include complexes that feature phenoxy–imine (with early transition metals; FI catalysts),[22–30] pyrrolide–imine (with Ti, Zr, and Hf; PI catalysts),[32] indolide–imine (with Ti; II catalysts),[33] and phenoxy–ether ligands (with Ti; FE catalysts)[35] for olefin polymerization. These complexes, with appropriate activators (e.g., MAO, $[Ph_3C]^+[B(C_6F_5)_4]^-/Al\textit{i}Bu_3$, $MgCl_2/R_nAl(OR')_m$, heteropolycompounds/R_3Al),[24] have many unique and practical features, such as the highly controlled living polymerization of ethylene, propylene, ethylene/α olefins, and ethylene/norbornene to form a variety of block copolymers with interesting molecular architectures.[23,25,26,32c,e,33b] Furthermore, these complexes have the potential to produce ultrahigh-molecular-weight PEs and ethylene/α olefin copolymers, ultrafine noncoherent particle PEs with ultrahigh molecular weights, well-defined and controlled multimodal PEs, highly isotactic and syndiotactic polypropylenes with exceptionally high T_m values, and stereo- and regioirregular high-molecular-weight poly(1-hexene)s.[27–30] Recent reviews cover much of this work.[21]



Scheme 1. Synthesis of complexes **1**–**4**.

As part of a program to develop new catalysts for olefin polymerization, we synthesized Group 4 transition-metal complexes that bear non-salicylaldimine-type imine–phenoxy chelate ligands with the general formula $[\{2,4\text{-di-}t\text{Bu-6-(RCH=N)C}_6\text{H}_4\text{O}\}_2\text{MCl}_2]$ (M = Ti or Zr, R = Ph or C_6F_5) and examined their potential as catalysts in olefin polymerization. This ligand design was chosen to investigate the effects of using ligands that are structurally different but contain the same coordination sites on the catalytic properties of the resulting complexes.

Herein, we report on the syntheses and ethylene-polymerization behavior of new Ti and Zr complexes with imine–phenoxy chelate ligands and compare them with the structurally related salicylaldimine-type bis(phenoxy–imine) complexes (FI catalysts). We also describe the molecular structure of an HCl adduct with one of the complexes, which constitutes a zwitterionic complex. Part of this work has been communicated previously.[35]

Results and Discussion

Syntheses and Characterization

The synthetic route used to prepare the complexes employed herein, bis(imine–phenoxy)–Ti or –Zr complexes **1**–**4**, is outlined in Scheme 1. The reaction of an aminophenol with a benzaldehyde yielded an imine–phenoxy ligand (R = Ph: 80 %; R = C_6F_5: 68 %). Complex formation was performed by treating the lithium or sodium salts of the imine–phenoxy ligand with $TiCl_4$ or $[ZrCl_4(thf)_2]$ (**1**: 82 %; **2**: 59 %; **3**: 59 %; **4**: 47 %; **1**, **2**: reddish-brown powder; **3**, **4**: orange powder).

Complexes **1**–**4** were characterized by field desorption mass spectrometry (FD MS; **1**–**4**), elemental analysis (**1**–**4**), and X-ray analysis (**1**·HCl; see following section). As **1**–**4** contain a pair of nonsymmetric bidentate ligands with imine (RCH=NR′) moieties, they consist of multiple isomers resulting from the different modes of ligand coordination, the attached/detached state of the imine nitrogen atoms, and *syn*/*anti* configurations with respect to the C=N double bonds.

Complex **1** in C_6D_6 at 25 °C exhibited involved ^{1}H NMR signals derived from the *tert*-butyl groups (Figure 1 a), which suggest that this complex exists as a mixture of structural isomers. Interestingly, however, these complicated signals were irreversibly simplified into three pairs of peaks at 75 °C (Figure 1 b). This spectral simplification was not caused by the decomposition of the complex, because the solution displayed FD MS peaks that were identical to those of the original solution. Therefore, the structural isomers seem to be reorganized into three energetically favorable and symmetrical isomers in solution at 75 °C, although their structures are presently unclear owing to a large number of possible isomers.[38]

In contrast, complex **2** with a C_6F_5 group on the imine carbon atom at 25 °C exhibited a relatively simple ^{1}H NMR spectrum, which included a set of major peaks that can be

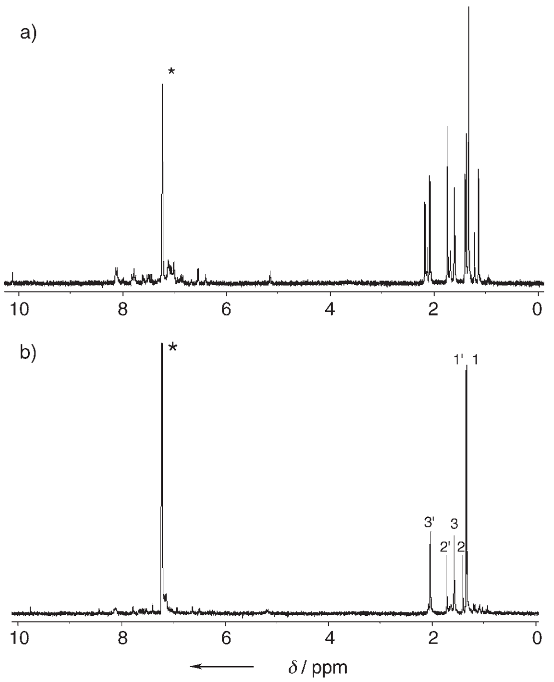


Figure 1. ^{1}H NMR spectra of complex **1** observed at a) 25 °C and b) 75 °C in C_6D_6. * = Residual solvent peak.

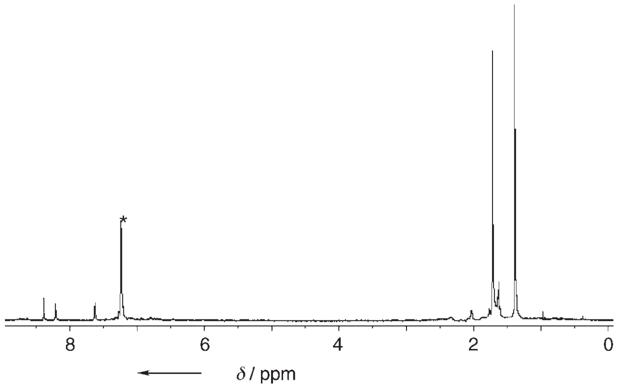


Figure 2. ^{1}H NMR spectra of complex **2** observed at 25 °C in C_6D_6. * = Residual solvent peak.

assigned to a symmetrical structure (Figure 2). Notably, a salicylaldimine-type Ti complex with a C_6F_5 group on the imine nitrogen atom displays a simpler ^{1}H NMR spectrum than the corresponding nonfluorinated compound.[23a,b,25b,c,28d,e] Zr complexes **3** and **4** exhibited similar NMR behavior to the corresponding Ti congeners. The results described herein, along with our previous, indicate that a bis(phenoxy–imine)-type Group 4 transition-metal complex can exist as a mixture of isomers in solution,[21] presumably an intrinsic feature of complexes of this type.

X-ray Analysis

Although all attempts to prepare single crystals of the complexes suitable for X-ray analysis failed and resulted in the formation of fine powders, a solution of complex **1** in CH_2Cl_2 afforded a small number of crystals, and these turned out to consist of **1**·HCl adduct.[39] X-ray analysis showed that the adduct exists as a zwitterionic complex, in which H and Cl are located in close proximity to one of the imine nitrogen atoms and Ti, respectively (Figure 3 and Table 1). This is a rare example of a zwitterionic complex with an iminium structure.[40a] The X-ray molecular structure of the zwitterionic complex provides some important structural information about complexes of this type.

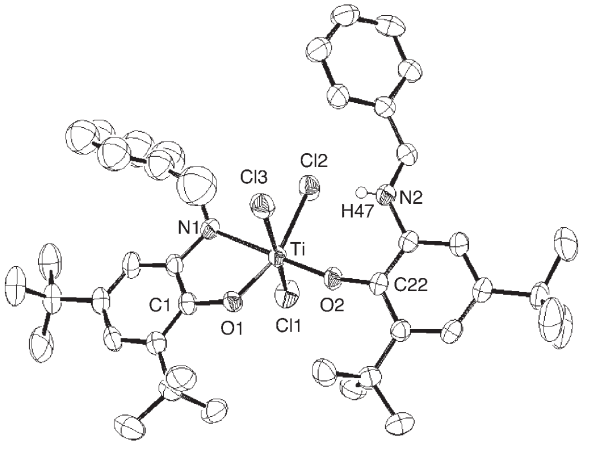


Figure 3. ORTEP view of the molecular structure of the zwitterionic complex **1**·HCl. Selected bond lengths (Å) and angles (°): Ti–Cl1 2.325(1), Ti–Cl2 2.414(1), Ti–Cl3 2.406(1), Ti–O1 1.831(3), Ti–O2 1.827(3), Ti–N1 2.260(3), N2–H47 0.67; Cl1-Ti-O1 90.1(1), Cl1-Ti-O2 97.2(1), Cl1-Ti-N1 84.9(1), Cl1-Ti-Cl2 86.95(5), Cl3-Ti-O1 92.81(10), Cl3-Ti-O2 88.8(1), Cl3-Ti-N1 89.1(1), Cl3-Ti-Cl2 87.89(5), O1-Ti-N1 76.7(1), N1-Ti-Cl2 81.95(10), Cl2-Ti-O2 98.36(9), O2-Ti-O1 103.0(1), Ti-O1-C1 124.3(3), Ti-O2-C22 165.7(3).

Table 1. Crystallographic data for **1**·HCl.

Empirical formula	$C_{42}H_{53}Cl_3N_2O_2Ti$	β [°]	95.186(5)
FW	772.15	V [Å^3]	4215.0(6)
Crystal size [mm]	0.20×0.10×0.10	Z	4
Crystal color	red	d_{calcd} [g cm^{-3}]	1.22
T [K]	150	μ [cm^{-1}]	4.3
Crystal system	monoclinic	R_1[a]	0.092
Space group	$P2_1/c$ (No. 14)	wR_2[b]	0.217
a [Å]	12.4805(6)	Goodness of fit	1.84
b [Å]	17.998(2)		
c [Å]	18.841(2)		

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ for $I>2\sigma(I)$.

X-ray studies revealed that one of the imine–phenoxy groups functions as a bidentate ligand with *syn*-imine configuration (i.e., the phenyl group was directed outwards), [40b] whereas the other functions as a monodentate phenoxy ligand with the intrinsically stable *anti*-imine configuration (i.e., the phenyl group was directed inwards). The coordination around the central metal was pseudooctahedral with two elongated Ti–Cl bonds (Ti–Cl2 and Ti–Cl3). Notably, the two phenoxy oxygen atoms, which normally favor a *trans*-located arrangement because of their highly anionic and short-bond-length nature, are *cis*-located. In this case, a phenoxy oxygen and an anionic chlorine atom are in a *trans* configuration.[37]

^{1}H NMR spectroscopic analysis at 25 °C showed that the adduct displays a ^{1}H NMR spectrum similar to that of complex **1**; the resonance of H47 was missing. At 75 °C, it yielded practically an identical ^{1}H NMR spectrum to that observed for **1** at the same temperature. Upon activation with $[Ph_3C]^+[B(C_6F_5)_4]^-/Al\textit{i}Bu_3$, the adduct provided ethylene-polymerization results similar to those for **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-/Al\textit{i}Bu_3$, which are described below.

Ethylene Polymerization with MAO Activation

Complexes **1**–**4** were screened as catalysts for ethylene polymerization in the presence of MAO under ethylene at atmospheric pressure. The results are presented in Table 2.

Table 2. Ethylene polymerization with MAO activation.[a]

Entry	Catalyst ([μmol])	T [°C]	Yield [mg]	Activity[b]	M_v [10^{-4}]
1	**1** (5)	25	54	130	268
2	**1** (5)	50	53	130	236
3	**1** (5)	75	45	110	224
4	**2** (0.2)	25	331	19900	2.6
5	**2** (5)	50	174	420	3.7
6	**2** (5)	75	38	90	48
7	**3** (5)	25	54	130	142
8	**3** (5)	50	53	130	99
9	**3** (5)	75	22	50	–[c]
10	**4** (5)	25	16	40	–[c]
11	**4** (5)	50	13	30	–[c]
12	**4** (5)	75	7	30	–[c]

[a] Conditions: reaction time 5 min, toluene 250 mL, ethylene gas flow 100 L h^{-1}, pressure 0.1 MPa, MAO 1.25 mmol. [b] (kg PE) (mol metal)$^{-1}$ h^{-1}. [c] Unavailable owing to low polymer yield.

Complexes **1** and **3** with MAO at 25 °C polymerized ethylene to produce high-molecular-weight PEs with a moderate activity of 130 (kg PE) (mol metal)$^{-1}$h^{-1}, which is substantially lower than those attained for the relevant salicylaldimine-type complexes (i.e., FI catalysts) under analogous conditions.[22a–d] The activity of **4**/MAO was too low to allow meaningful product analysis. Changes in the polymerization temperature for **1**, **3**, and **4** had no significant influence on catalytic activity.

Remarkably, **2**/MAO at 25 °C exhibited a very high activity of 19900 (kg PE) (mol Ti)$^{-1}$ h^{-1}, which is comparable to that found for early Group 4 metallocene catalysts under the same polymerization conditions (e.g., $[Cp_2TiCl_2]$ 1670 (kg PE) (mol Ti)$^{-1}$ h^{-1}, $[Cp_2ZrCl_2]$ 2000 (kg PE) (mol Zr)$^{-1}$ h^{-1}). Indeed, this activity represents one of the highest values reported to date for Ti-based non-metallocene catalysts under conditions of atmospheric pressure. The high activity may be attributed to the effect of the electron-withdrawing C_6F_5 group on the imine carbon atom, which makes the central metal more electron-deficient and, thus, more reactive toward ethylene. A similar, but less remarkable, effect of an electron-withdrawing substituent on catalytic activity was observed for the salicylaldimine-type bis(phenoxy–imine) Group 4 metal complexes.[41]

By analogy with the polymerization behavior of a salicylaldimine-type bis(phenoxy–imine)–Ti complex that contains a C_6F_5 group on the imine nitrogen atom, one would expect that complex **2** would initiate living ethylene polymerization induced by an attractive interaction between the F atom and a β-H atom on a growing polymer chain.[21b,f,23,42] The PE formed from this catalyst system has a broad molecular-weight distribution (M_w/M_n) of 5.21 ($M_w = 15000$), suggesting that multiple active species are in operation in the polymerization. In fact, this is unsurprising, as we have often observed multimodal behavior with a structurally related bis(phenoxy–imine) complex/MAO system,[27b,c] which is probably due to the presence of structural isomers of the active species. Density functional theory (DFT) calculations on the most-probable isomer with the *syn*-imine configuration suggest that there is practically no interaction between the F and β-H atoms (3.66 Å), and that a strong β agostic interaction exists between the Ti and β-H atoms (0.69 Å) (Figure 4), which is consistent with the observation that **2**/MAO catalyzed nonliving-type polymerization and furnished low-molecular-weight PEs.

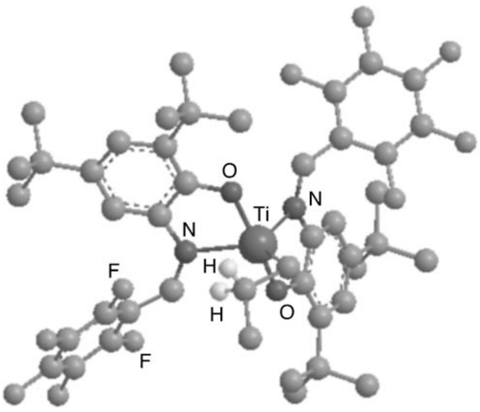


Figure 4. DFT-optimized structure of a plausible catalytically active species. The central metal is positively charged and bound to an *n*-propyl group (polymer-chain model). Only β-hydrogen atoms are shown for clarity.

For the **2**/MAO system, an increase in the polymerization temperature led to a marked decrease in catalytic activity (Table 2). This behavior is probably due to catalyst decay. Although the mode of catalyst decay is unknown, the fact that the reaction of **2** with MAO for 30 min at 75 °C followed by protonolysis resulted in the recovery of the original imine–phenoxy ligand in 87 % yield suggests that catalyst decay is not caused by the nucleophilic addition of a methide group to the imine moiety.[43]

Ethylene Polymerization with $[Ph_3C]^+[B(C_6F_5)_4]^-$/AliBu$_3$ Activation

The ethylene-polymerization behavior of complexes **1**–**4** was also investigated with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ activation under atmospheric pressure. A summary of the polymerization results is shown in Table 3. Complexes **3** and **4** displayed moderate activities and formed PEs with high to very high molecular weights over a temperature range of 25–75 °C.

Table 3. Ethylene polymerization with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ activation.[a]

Entry	Catalyst ([μmol])	T [°C]	Yield [mg]	Activity[b]	M_v [10^{-4}]
1	**1** (5)	25	34	70	–[c]
2	**1** (5)	50	1576	1380	117
3	**1** (0.2)	75	357	21420	64
4[d]	**1** (0.2)	75	3748	18740	59
5	**2** (5)	25	67	160	171
6	**2** (5)	50	81	200	161
7	**2** (5)	75	128	310	166
8	**3** (5)	25	73	180	–[c]
9	**3** (5)	50	213	510	72
10	**3** (5)	75	149	360	133
11	**4** (5)	25	34	80	–[c]
12	**4** (5)	50	63	150	151
13	**4** (5)	75	45	110	142

[a] Conditions: reaction time 5 min, toluene 250 mL, ethylene gas flow 100 L h^{-1}, pressure 0.1 MPa, MAO 1.25 mmol. [b] (kg PE) (mol metal)$^{-1}$ h^{-1}. [c] Unavailable owing to low solubility of the polymer produced in decalin under the conditions for intrinsic viscosity measurements. [d] Reaction time 60 min.

The polymerization characteristics of complexes **1** and **2** are considerably different from those observed for MAO activation. Complex **2** with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ at 25 °C afforded a high-molecular-weight PE with moderate activity ($M_v = 1710000$, 160 (kg PE) (mol Ti)$^{-1}$ h^{-1}), whereas, as described, **2** with MAO provided a low-molecular-weight PE with a very high activity ($M_w = 15000$, 19900 (kg PE) (mol Ti)$^{-1}$ h^{-1}). Furthermore, unlike with MAO activation, **1** with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ is a highly active catalyst and forms high-molecular-weight PEs.

One striking feature that was observed is that complex **1** with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ exhibited enhanced activity with an increase in polymerization temperature. The activity of 21420 (kg PE) (mol Ti)$^{-1}$ h^{-1} that was obtained at 75 °C is one of the highest for ethylene polymerization ever recorded among Ti-based homogeneous catalysts under atmospheric pressure. Analysis of the PE formed with **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ at 75 °C by gel permeation chromatography (GPC) revealed a narrow molecular-weight distribution (M_w/M_n) of 2.26 ($M_w = 374000$), which is consistent with the operation of a single-site catalyst, despite the catalyst precursor being a mixture of isomers. Notably, at 75 °C, this catalyst system was long-lived and virtually maintained its very high activity for 1 h (18740 (kg PE) (mol Ti)$^{-1}$ h^{-1}). These results indicate a very high potential for **1** with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ to act as a catalyst for olefin polymerization. No enhancing effect on catalytic activity due to the C_6F_5 group was observed for **2**, unlike with MAO activation. As for the catalytic performance of $TiCl_4$ combined with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ (75 °C, activity 320 (kg PE) (mol Ti)$^{-1}$ h^{-1}, $M_v = 1760000$), which is similar to that for **2** with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$, it is possible that the decomposition of the active species derived from **2**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ is responsible. The zwitterionic complex (**1**·HCl) combined with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ exhibited essentially the same ethylene-polymerization behavior (75 °C, 20910 (kg PE) (mol Ti)$^{-1}$ h^{-1}) as **1** with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ activation. During the course of our study into ethylene polymerization, we noted the presence of an induction period for polymerization with the **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ catalyst system.[35]

The great difference in catalytic performance observed between MAO and $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ activation for complexes **1** and **2**, together with the presence of the induction period for the $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ activation system, suggest that activation of these complexes with MAO and $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ results in a structurally different active species with different ethylene-polymerization behavior.

We elucidated from reaction ^{1}H NMR spectroscopic studies that the imine groups of the complexes are susceptible to reduction by Al*i*Bu$_3$ (and its contaminant Al*i*Bu$_2$H) to form an amine group, with the concurrent formation of isobutene (Figure 5). The treatment of complex **1** with Al*i*Bu$_3$ in an NMR tube resulted in the appearance of resonances characteristic of an AB system centered at 4.40 and 4.51 ppm ($^2J = 14.7$ Hz), which were attributed to diastereotopic benzyl protons, as well as a sharp multiplet resonance centered at 4.78 ppm, assigned to isobutene protons. These results show that the imine–phenoxy ligand was converted into an

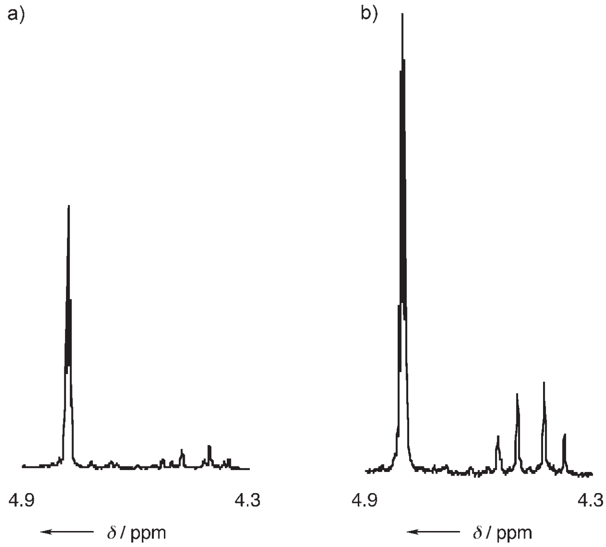


Figure 5. ^{1}H NMR spectra of **1**/Al*i*Bu$_3$ (0.02 M/0.25 M) in C_6D_6 after 10 min at a) 50 °C and b) 75 °C. The vertical scales were adjusted by using the residual solvent peaks as a reference.

amine–phenoxy ligand by reduction with Al*i*Bu$_3$ (and its contaminant Al*i*Bu$_2$H),[44] which also produced isobutene during the reaction. The reduction was complete after 10 min at 75 °C, whereas the same process took about 30 min at 50 °C and was incomplete even after 24 h at 25 °C.[45] The addition of $[Ph_3C]^+[B(C_6F_5)_4]^-$ followed by ethylene to the resulting mixture in the NMR tube afforded the PE.

The reduction of the imine moiety was further confirmed by the fact that protonolysis of a mixture of complex **1** and Al*i*Bu$_3$ (which was pretreated at 75 °C for 30 min) yielded an amine–phenoxy ligand in 91 % yield. The above results allow us to postulate the formation of a bis(amine–phenoxy)–Ti complex with Al*i*Bu$_2$ attached to the amine donor as a catalytically active species for the **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ system. Although we observed a similar reduction of bis(phenoxy–imine)–Ti, –Zr, or –Hf complexes with Al*i*Bu$_3$,[22c,27a,28a,46] it is noteworthy that the reduced species is more catalytically active in this case.

As described above, a high temperature is required for efficient conversion of the imine into the amine, resulting in the formation of a highly active species for ethylene polymerization. The reduced species derived from complex **1** displayed a very high activity at 75 °C, whereas low activity was encountered at 25 °C (Table 4, entries 1 and 2). Thus, a higher temperature is necessary for both the formation of an active species with amine–phenoxy ligands and for efficient catalysis. As expected, **1**/Al*i*Bu$_3$ in the absence of $[Ph_3C]^+[B(C_6F_5)_4]^-$ hardly promoted ethylene polymerization (Table 4, entry 3), which is consistent with the general proposal that the active species is a cationic metal complex.

Table 4. Ethylene polymerization with **1**.[a]

Entry	Catalyst	Activator	T [°C]	Yield [mg]	Activity[b]
1	**1**/Al*i*Bu$_3$[c]	$[Ph_3C]^+[B(C_6F_5)_4]^-$	75	3125	7800
2	**1**/Al*i*Bu$_3$[c]	$[Ph_3C]^+[B(C_6F_5)_4]^-$	25	43	100
3	**1**	Al*i*Bu$_3$	75	2	10
4	**1**	$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$	75	2410	5780

[a] Conditions: reaction time 5 min, toluene 250 mL, ethylene gas flow 100 L h^{-1}, pressure 0.1 MPa, catalyst 5 μmol, $[Ph_3C]^+[B(C_6F_5)_4]^-$ 6 μmol, Al*i*Bu$_3$ 0.25 mmol. [b] (kg PE) (mol Ti)$^{-1}$ h^{-1}. [c] Pretreated at 75 °C for 5 min before the addition of $[Ph_3C]^+[B(C_6F_5)_4]^-$.

Ethylene/Propylene Copolymerization

Ethylene/propylene copolymerization with complex **1** or **2** was performed under conditions that provided the highest ethylene-polymerization activity for each of the complexes (Table 5). Both **1** with $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ at 75 °C and **2** with MAO at 25 °C were found to produce copolymers with high efficiency. The **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ system displayed a greater ability to incorporate propylene and formed a copolymer with higher propylene content and molecular weight than **2**/MAO. The advantage of **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ in terms of propylene incorporation may be attributed to the more-electrophilic and sterically open nature of the active species, which stems from the lower coordination ability of an amine relative to an imine donor.

Table 5. Ethylene/propylene polymerization with titanium complexes **1** and **2**.[a]

Catalyst	Activator	T [°C]	Yield [mg]	Activity[b]	M_v [10^{-4}]	Propylene [mol %]
1	$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$	75	683	820	5.8	14.6
2	MAO	25	925	1110	1.2	4.2

[a] Conditions: reaction time 10 min, toluene 250 mL, ethylene gas flow 50 L h^{-1}, propylene gas flow 150 L h^{-1}, pressure 0.1 MPa, catalyst 5 μmol, $[Ph_3C]^+[B(C_6F_5)_4]^-$ 6 μmol, Al*i*Bu$_3$ 0.25 mmol, MAO 1.25 mmol. [b] (kg polymer) /(mol Ti)$^{-1}$ h^{-1}.

Conclusions

In summary, we have demonstrated that Ti and Zr complexes **1**–**4** supported by non-salicylaldimine-type imine–phenoxy ligands are readily synthesized and provide active catalysts for the polymerization of ethylene after activation with MAO or $[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$. In particular, Ti complexes **1** and **2** polymerized ethylene with very high efficiency when combined with an appropriate activator. The combinations **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ and **2**/MAO displayed very high activities that are comparable to those observed for $[Cp_2TiCl_2]$ and $[Cp_2ZrCl_2]$. These catalyst systems also efficiently promoted the copolymerization of ethylene and propylene. We have revealed that **1**/$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ generates an amine–phenoxy complex as a catalytically active species; this is a long-lived catalyst that maintains a very high activity for 1 h at 75 °C. The results reported herein further indicate the high potential of transition-metal complexes that incorporate phenoxy-based ligands for olefin polymerization.[3d]

Experimental Section

General

All manipulations were carried out under an inert atmosphere of argon or nitrogen by using standard Schlenk or glovebox techniques. Anhydrous ethanol, *n*-hexane, *n*-pentane, and toluene were purchased from Kanto Chemical Co., Inc. and used without further purification. THF, CH_2Cl_2, and Et_2O were dried with columns of molecular sieves and activated Al_2O_3 under N_2. The toluene that was used as a polymerization solvent was obtained from Wako Pure Chemical Industries, Ltd. and dried over Al_2O_3 under N_2. MAO was purchased from Albemarle as a solution in toluene (1.2 M), and the remaining trimethylaluminum was evaporated under vacuum, providing a solid white powder. Al*i*Bu$_3$ (Tosoh-Akzo Co., Ltd.) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (Asahi Glass Co.) were used as received. Synthesis details with regard to 2-amino-4,6-di-*tert*-butylphenol are described in the Supporting Information. Polymerization-grade ethylene and propylene were obtained from Sumitomo Seika Co., Ltd. and Mitsui Chemicals, Inc., respectively. All other chemicals were obtained commercially and used as received.

^1H NMR spectra were recorded on a JEOL 270 spectrometer (270 MHz). $CDCl_3$ and C_6D_6 were dried over activated alumina. Chemical shifts are referenced to the residual solvent peaks and reported relative to tetramethylsilane. FD MS was performed on an SX-102 A spectrometer from Japan Electron Optics Laboratory Co., Ltd. Elemental analysis for C, H, and N was performed by a CHNO-type instrument from Helaus Co. Gas liquid chromatography (GLC) was carried out on a Shimadzu GC-14 A (FID) chromatograph with a DB-1701 column (J&W Scientific).

Syntheses

2-Benzilideneamino-4,6-di-*tert*-butylphenol: Acetic acid (1 mL) was added to a stirred solution of 2-amino-4,6-di-*tert*-butylphenol (2.83 g, 12.8 mmol) and benzaldehyde (1.63 g, 15.3 mmol) in dried ethanol (50 mL) at room temperature. The mixture was stirred at room temperature for 12 h. The resulting mixture was concentrated under vacuum to yield the crude product, which was purified by column chromatography on silica gel with EtOAc/hexanes as eluent to yield yellow crystals (3.16 g, 80.0 %). ^{1}H NMR ($CDCl_3$, 27 °C): $\delta = 8.70$ (s, 1 H, O*H*), 7.96–7.92 (m, 2 H, Ar*H*), 7.73 (s, 1 H, NC*H*), 7.48–7.43 (m, 3 H, Ar*H*), 7.25 (d, $^4J =$ 2.2 Hz, 1 H, Ar*H*), 7.17 (d, $^4J = 2.2$ Hz, 1 H, Ar*H*), 1.46 (s, 9 H, CC*H*$_3$), 1.35 ppm (s, 9 H, CC*H*$_3$).

2,4-Di-*tert*-butyl-6-pentafluorobenzilideneaminophenol: Acetic acid (0.3 mL) was added to a stirred solution of 2-amino-4,6-di-*tert*-butylphenol (2.82 g, 12.8 mmol) and pentafluorobenzaldehyde (2.50 g, 12.8 mmol) in dried ethanol (30 mL) at room temperature. The mixture was stirred at room temperature for 12 h to yield yellow crystals, which were collected by filtration, washed with cool methanol (1 mL), and dried (1.09 g, 27.3 %). The filtrate was concentrated under vacuum to afford the crude product, which was purified by column chromatography on silica gel with EtOAc/hexanes as eluent to yield yellow crystals (2.06 g, 40.3 %; altogether 3.15 g, 67.6 %). ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 8.79$ (s, 1 H, O*H*), 7.75 (s, 1 H, NC*H*), 7.36 (d, $^4J = 2.1$ Hz, 1 H, Ar*H*), 7.20 (d, $^4J = 2.1$ Hz, 1 H, Ar*H*), 1.43 (s, 9 H, CC*H*$_3$), 1.31 ppm (s, 9 H, CC*H*$_3$).

1: A solution of *n*BuLi (1.60 M, 19.1 mL) in hexane was added dropwise to a stirred solution of 2-benzilideneamino-4,6-di-*tert*-butylphenol (10.5 g, 34.03 mmol) in dried *n*-pentane (80 mL) at −78 °C. The mixture was warmed to room temperature. The yellow precipitate was collected by filtration, washed with dried *n*-pentane (20 mL), and dried under vacuum to afford lithium 2-benzilideneamino-4,6-di-*tert*-butylphenoxide (9.80 g, 31.05 mmol). The lithium salt (2.48 g, 7.86 mmol) was suspended in dried Et_2O (20 mL) and added dropwise to a stirred solution of $TiCl_4$ in dried toluene (0.2 M, 19.7 mL) at −30 °C. The mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was concentrated under vacuum, after which CH_2Cl_2 (25 mL) was added and stirred. The resulting mixture was filtered. The filtrate was concentrated under vacuum to about 5 mL, and dried *n*-pentane (30 mL) was added. The resulting precipitate was collected by filtration, washed with dried *n*-pentane (2 mL), and dried under vacuum to yield **1** as a reddish-brown powder (2.37 g, 81.9 %). ^{1}H NMR (C_6D_6, 75 °C, mixture of three isomers): $\delta = 8.12$ (br s, NC*H*), 6.21–7.01 (m, Ar*H*), 6.72 (br s, Ar*H*), 6.60 (br s, Ar*H*), 5.20 (br s, Ar*H*), 2.02 (s, CC*H*$_3$ of isomer 3), 1.78 (s, CC*H*$_3$ of isomer 2), 1.60 (s, CC*H*$_3$ of isomer 3), 1.42 (s, CC*H*$_3$ of isomer 2), 1.34 (s, CC*H*$_3$ of isomer 1), 1.33 ppm (s, CC*H*$_3$ of isomer 1) (the integral ratio for isomers 1, 2, and 3 is 1:0.26:0.22); MS (FD): $m/z = 734$; elemental analysis: calcd (%) for $C_{42}H_{52}Cl_2N_2O_2Ti$: C 68.57, H 7.12, N 3.81; found: C 68.72, H 6.91, N 3.83.

2: NaH (oil-free, 165 mg, 6.89 mmol) was suspended in dried THF (5 mL) and added dropwise to a stirred solution of 2,4-di-*tert*-butyl-6-pentafluorobenzilideneaminophenol (2.75 g, 6.89 mmol) in dried THF (20 mL) at −30 °C. The mixture was warmed to room temperature and stirred for 3 h. The resulting slurry was added dropwise to a stirred solution of $TiCl_4$ in dried toluene (0.2 M, 17.2 mL) at −30 °C. The mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was concentrated under vacuum, and dried CH_2Cl_2 (25 mL) was added and stirred. The resulting mixture was filtered. The filtrate was concentrated under vacuum to about 5 mL, and dried *n*-pentane (30 mL) was added. The resulting precipitate was collected by filtration, washed with dried *n*-pentane (2 mL), and dried under vacuum to give **2** as a reddish-brown powder (1.86 g, 59.2 %). ^{1}H NMR (C_6D_6, 25 °C, major isomer): $\delta = 8.42$(s, 2 H, NC*H*), 8.24 (br s, 2 H, ArH), 7.62 (d, $^4J = 2.0$ Hz, 2 H, Ar*H*), 1.73 (s, 18 H, CC*H*$_3$), 1.38 ppm (s, 18 H, CC*H*$_3$); MS (FD): $m/z =$ 914; elemental analysis: calcd (%) for $C_{42}H_{42}Cl_2F_{10}N_2O_2Ti$: C 55.10, H 4.62, N 3.06; found: C 55.21, H 4.89, N 3.31.

3: Lithium 2-benzilideneamino-4,6-di-*tert*-butylphenoxide (883 mg, 2.80 mmol) was suspended in dried THF (20 mL) and added dropwise to a stirred solution of $[ZrCl_4(thf)_2]$ (528 mg, 1.40 mmol) in dried THF (40 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was concentrated under vacuum, and dried toluene (40 mL) was added. The resulting mixture was filtered. The filtrate was concentrated under vacuum to about 2 mL, and dried *n*-pentane (40 mL) was added. The resulting precipitate was collected by filtration, washed with *n*-pentane (5 mL), and dried under vacuum to yield **3** as an orange powder (612 mg, 56.1 %). ^{1}H NMR ($CDCl_3$, 25 °C, mixture of isomers): $\delta = [9.31, 8.70, 8.59, 8.49, 8.45]$ (s, 2 H, NC*H*), 7.95–6.78 (m, 14 H, Ar*H*), [2.32, 1.66, 1.58, 1.41, 1.40, 0.96, 0.92, 0.85] ppm (s, 36 H, CC*H*$_3$); MS (FD): $m/z = 778$; elemental analysis: calcd (%) for $C_{42}H_{52}Cl_2N_2O_2Zr$: C 63.36, H 6.73, N 3.10; found: C 63.81, H 7.16, N 3.51.

4: NaH (oil-free, 166 mg, 6.91 mmol) was suspended in dried THF (5 mL) and added dropwise to a stirred solution of 2,4-di-*tert*-butyl-6-pentafluorobenzilideneaminophenol (2.76 g, 6.91 mmol) in dried THF (20 mL) at −30 °C. The mixture was warmed to room temperature and stirred for 3 h. The resulting slurry was added dropwise to a stirred solution of $[ZrCl_4(thf)_2]$ (1.30 g, 3.46 mmol) in dried THF (20 mL) at −5 °C. The mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was concentrated under vacuum, and dried CH_2Cl_2 (25 mL) was added. The resulting mixture was filtered. The filtrate was concentrated under vacuum to about 5 mL, and dried *n*-pentane (30 mL) was added. The resulting precipitate was collected by filtration, washed with dried *n*-pentane (2 mL), and dried under vacuum to yield **4** as an orange powder (1.85 g, 55.8 %). ^{1}H NMR ($CDCl_3$, 25 °C, major isomer): $\delta = 8.01$(s, 2 H, NC*H*), 7.40 (br s, 2 H, ArH), 7.22 (br s, 2 H, Ar*H*), 1.42 (s, 18 H, CC*H*$_3$), 1.30 ppm (s, 18 H, CC*H*$_3$); MS (FD): $m/z = 958$; elemental analysis: calcd (%) for $C_{42}H_{42}Cl_2F_{10}N_2O_2Zr$: C 52.61, H 4.41, N 2.92; found: C 52.90, H 4.49, N 2.71.

Reaction of Complexes with Alkylaluminum

Reaction NMR experiment: A J-Young NMR tube was charged with **1** (10.3 mg, 0.014 mmol), and a solution of Al*i*Bu$_3$ in C_6D_6 (0.25 M, 0.7 mL) was added at room temperature. An instrument probe was held at the designated temperature beforehand, after which the tube was introduced for analysis.

Reaction of **2** with MAO: A solution of MAO in toluene (1.25 M, 2 mL) was added by syringe to a stirred solution of **2** (147 mg, 0.16 mmol) in dried toluene (10 mL) at 75 °C. After being stirred for 30 min, the reaction mixture was cooled with an iced-water bath, and the reaction was quenched with methanol (5 mL). The mixture was stirred for 2 h and concentrated under vacuum. Water was added to the residue, and the resulting mixture was extracted with toluene (3 × 3 mL). The combined organic extracts were dried (Na_2SO_4). The solution was concentrated under vacuum to yield a solid, which was dried under vacuum. ^{1}H NMR spectroscopic analysis of the resulting solid indicated the presence of 2,4-di-*tert*-butyl-6-pentafluorobenzilideneaminophenol as the major material. GLC analysis with biphenyl as an internal standard indicated 87 % recovery of 2,4-di-*tert*-butyl-6-pentafluorobenzilideneaminophenol.

Reaction of **1** with Al*i*Bu$_3$: A solution of Al*i*Bu$_3$ in toluene (1.0 M, 3 mL) was added by syringe to a stirred solution of **1** (258 mg, 0.35 mmol) in dried toluene (10 mL) at 75 °C. After being stirred for 30 min, the reaction mixture was cooled in an iced-water bath, and the reaction was quenched with methanol (1 mL) and water (10 mL). The mixture was stirred for 5 h, and the toluene phase was separated. The remaining aqueous phase was extracted with toluene (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated under vacuum to yield a solid, which was identified as 2-benzylamino-4,6-di-*tert*-butylphenol (199 mg, 91 %) by ^{1}H NMR spectroscopy and FD MS. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.33$–7.27 (m, 5 H), 6.85 (d, $J = 2.1$ Hz, 1 H, Ar*H*), 6.73 (d, $J =$ 2.1 Hz, 1 H, Ar*H*), 5.95 (br s, 1 H, O*H*), 4.12 (s, 2 H, C*H*$_2$Ph), 3.20 (br s, 1 H, N*H*), 1.39 (s, 9 H, CC*H*$_3$), 1.20 (s, 9 H, CC*H*$_3$); MS (FD): $m/z = 311$.

X-ray Analysis

Crystals of **1**·HCl suitable for X-ray structure determination were grown from a solution of **1** in dried CH_2Cl_2, whose surface was covered with a layer of dried *n*-pentane. Elemental analysis: calcd (%) for $C_{42}H_{53}Cl_3N_2O_2Ti$: C 65.33, H 6.92, N 3.63; found: C 65.54, H 7.20, N 3.85.

Data collection: A suitable crystal was mounted in a glass capillary under argon atmosphere. Data were collected by a Rigaku RAIS-IV Imaging Plate diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The incident-beam collimator was 0.5 mm in diameter, and the crystal-to-detector distance was 100.00 mm with the detector at the zero swing position. Indexing was performed from 2 oscillations exposed for 4.0 min. The readout was obtained in the 0.100-mm pixel mode. A total of 32 plates of 3.00° oscillation images were collected, each having been exposed for 6.8 min. The cell parameters are listed in Table 1.

Data reduction: Of the 16894 reflections collected, 8765 were unique ($R_{int} = 0.062$); equivalent reflections were merged; absorption correction was not applied. The data were corrected for Lorentzian and polarization effects.

Structure determination and refinement: All calculations were performed with the teXsan crystallographic software package,[47] and illustrations were drawn with Ortep-3 for Windows.[48] Crystallographic calculations were performed on an SGI O_2 workstation at the Venture Business Laboratory, Graduate School of Okayama University. The structure was solved by heavy-atom Patterson methods and expanded with Fourier techniques. Some non-hydrogen atoms were refined anisotropically; the rest were refined isotropically. Some hydrogen atoms were refined isotropically; the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 8756 observed reflections ($I > -10.00\sigma(I)$) and 424 variable parameters. The minimized function was $\Sigma w\,(F_o^2 - F_c^2)^2$, where F_o and F_c are the amplitudes of the observed and calculated structure factors, respectively.

CCDC-622716 (**1**·HCl) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Ethylene or Ethylene/Propylene Polymerization

MAO activation: Toluene (250 mL) was placed in a 500-mL glass reactor equipped with a mechanical stirrer, a temperature probe, and a condenser under N_2 atmosphere and stirred vigorously (600 rpm). The toluene was maintained at the designated temperature, and the N_2 atmosphere was replaced with ethylene ($100\,L\,h^{-1}$) or ethylene/propylene (ethylene $50\,L\,h^{-1}$, propylene $150\,L\,h^{-1}$) by a gas feed to toluene. After 15 min, polymerization was initiated by adding a solution of MAO in toluene followed by a solution of **1** or **2** in toluene into the reactor. After the designated time, isobutyl alcohol (10 mL) was added to quench the polymerization, and the gas feed was stopped. The resulting mixture was added to acidic methanol (1.0 L, including 2 mL of conc. HCl). The polymer was collected by filtration, washed with methanol (2×200 mL), and dried in a vacuum oven for 10 h (80 °C for polyethylene, 130 °C for ethylene/propylene copolymer).

$[Ph_3C]^+[B(C_6F_5)_4]^-$/Al*i*Bu$_3$ activation: The procedure is similar to that described above. Polymerization was initiated by adding solutions in toluene of Al*i*Bu$_3$, **1** or **2**, and $[Ph_3C]^+[B(C_6F_5)_4]^-$, in that order, into the reactor.

Polymer Analysis

The molecular weights (M_w and M_n) and molecular-weight distributions (M_w/M_n) of the PEs were determined by using a Waters 50-C gel permeation chromatograph equipped with three TSK gel columns (two sets of TSKgelGMH$_{HR}$-H(S)HT and TSKgelGMH$_6$-HTL) at 145 °C with polyethylene calibration. 1,2-Dichlorobenzene was used as the solvent at a flow rate of $1.0\,mL\,min^{-1}$.

DFT Calculations

All calculations were performed at the gradient-corrected density functional BLYP level by means of the Amsterdam density functional program (ADF2003.01).[49] We used the triple-ζ plus polarization STO basis set for Ti, the double-ζ plus polarization STO basis set for Cl/O/N, and the double-ζ STO basis set for the other atoms to calculate the optimized geometries. For the energy calculations, the triple-ζ plus polarization STO basis set for Ti and the double-ζ plus polarization STO basis set for the other atoms were used, and quasirelativistic correction was also added.

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[45] It was observed that the amount of isobutene produced after the completion of the reduction is larger than that expected theoretically (roughly double). The reason for this is unclear at the present time.

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