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Living Polymerization of α-Olefins: Catalyst Precursor Deactivation via the Unexpected Cleavage of a B−C_6F_5 Bond

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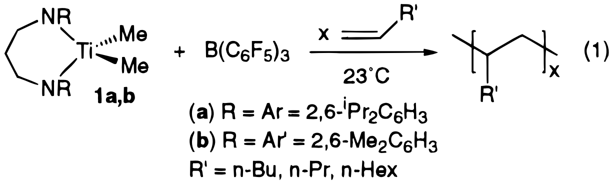
*Summary: The titanium diamide complex [ArN(CH_2)$_3$NAr]TiMe_2 (**1a**; Ar = 2,6-^{i}$Pr_2C_6H_3$) reacts with B(C_6F_5)$_3$ in pentane to give an insoluble yellow-orange solid (**2a**). Complex **2a** is a catalyst for the living polymerization of 1-hexene. Pentane suspensions of **2a** slowly evolve methane over the course of several hours to give the new pentane-soluble derivative [ArN(CH_2)$_3$NAr]Ti[CH_2B(C_6F_5)$_2$](C_6F_5) (**3a**), which was structurally characterized. Addition of a B−C_6F_5 group across an intermediate Ti=CH_2 unit is proposed. Compound **3a** is inactive for the polymerization of α-olefins.*

Introduction

The design and synthesis of single-site olefin polymerization catalysts has developed rapidly in the last few decades, with the group 4 metallocene class of compounds receiving the most attention.[1,2] Studies in this area have been concerned with the way in which the catalytic activity, comonomer incorporation, and stereoregularity can be altered with changes to the Cp ligand(s). There is, however, a growing interest in new non-Cp ligand environments as possible alternatives for olefin polymerization catalysts; in particular, amide ligands[3−9] have recently received considerable attention.

As part of our program to investigate the chemistry of early-transition-metal amide derivatives,[10−12] we recently reported that chelating diamide complexes of titanium serve as precursors for the living[13] polymerization of α-olefins. These living systems are derived from equimolar amounts of the titanium dimethyl complex [ArN(CH_2)$_3$NAr]TiMe_2 (**1a**; Ar = 2,6-^{i}$Pr_2C_6H_3$) or [Ar′N(CH_2)$_3$NAr′]TiMe_2 (**1b**; Ar′ = 2,6-$Me_2C_6H_3$)[14] and B(C_6F_5)$_3$[15] (eq 1).



Herein we report that an *inactive* compound is formed quantitatively in the absence of monomer, representing a formal deactivation of these living systems.

Results and Discussion

The addition of a pentane solution of compound **1a** or **1b** to a pentane solution of B(C_6F_5)$_3$ at 23 °C yields an insoluble yellow-orange solid (**2a,b**) in nearly quantitative yield. Although it has so far proven very difficult to spectroscopically identify compounds **2a,b**, their reactivity is consistent with a cationic[4,16] complex of the type {[RN(CH_2)$_3$NR]TiMe}$^+$[MeB(C_6F_5)$_3$]$^-$ (R = Ar, Ar′). For example, compounds **2a,b** react rapidly with CD_2Cl_2 to give the known dichloride derivatives [RN(CH_2)$_3$NR]TiCl_2 (R = Ar, Ar′).[14] It should be noted that the dimethyl complexes **1a,b** are stable in CD_2Cl_2. Deep red insoluble oils are formed when compounds **2a,b** are "dissolved" in aromatic solvents or when **1a,b** and B(C_6F_5)$_3$ are mixed in these solvents. The oils generated from toluene as well as compounds **2a,b** (isolated solids) are catalysts for the living polymerization of 1-hexene.[17]

Although pentane suspensions of compound **2b** are stable for days, complex **2a** slowly evolves methane (confirmed by NMR spectroscopy) over the course of several hours to give a new pentane-soluble derivative (**3a**) in quantitative yield by NMR spectroscopy (Scheme 1). Piers *et al.* have reported a similar reaction between Cp_2ZrMe_2 and HB(C_6F_5)$_2$, which evolves methane to give the complex [Cp_2Zr](μ-CH_2)(μ-H)[B(C_6F_5)$_2$].[18] Compound **3a** can be isolated in high yield from pentane at −30 °C and is soluble in most organic solvents with no decomposition.

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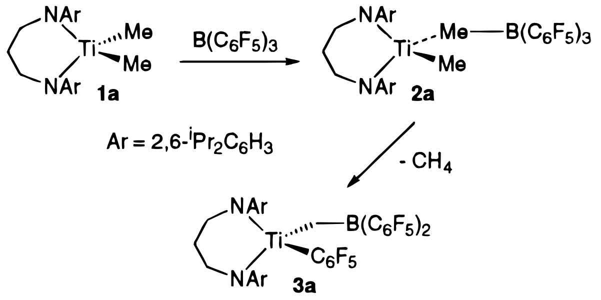
S0276-7333(96)01034-5 CCC: $14.00

Scheme 1



The proton NMR spectrum of **3a** reveals that the complex has C_s symmetry coupled with restricted rotation[11] about the N−C$_{ipso}$ bonds of the ligand. A broad singlet at 3.92 ppm is assigned to the methylene protons, which are split into a doublet ($^1J_{CH}$ = 114 Hz) in the isotopically labeled complex $[ArN(CH_2)_3NAr]Ti[^{13}CH_2B(C_6F_5)_2](C_6F_5)$ (***^{13}C-3a***) prepared from $[ArN(CH_2)_3NAr]Ti(^{13}CH_3)_2$ (***$^{13}C_2$-1a***). For comparison, the methylene protons in the complex $Cp_2Zr(\mu\text{-}CH_2)(\mu\text{-}H)B(C_6F_5)_2$ appear at 5.30 ppm (no carbon NMR data are reported for this compound).[18] The carbon NMR spectrum of compound **3a** shows a broad resonance at 109.5 ppm for the methylene carbon bridging the titanium and boron. The ^{19}F NMR spectrum of **3a** shows six different fluorine resonances (two ortho, two meta, and two para) consistent with migration[19] of one of the perfluorophenyl groups to titanium. The ^{11}B NMR spectrum of **3a** shows a peak at 79.4 ppm, which compares well with $[\eta^5\text{-}C_5H_4(CH_2)_3B(C_6F_5)_2]_2ZrCl_2$ (73.9 ppm)[20] and is typical for three-coordinate boron.[21]

The solid-state structure of **3a** was determined by X-ray crystallography (Table 1). The molecular structure of complex **3a** can be found in Figure 1, and relevant bond distances and angles in Table 2. The structure is best described as a distorted tetrahedron with the boromethyl group occupying one site. The titanium−amide and titanium−carbon bond lengths are comparable to the distances in the dimethyl complex $[Ar'N(CH_2)_3NAr']TiMe_2$.[14] The Ti(1)−C(34)−B(1) angle is more obtuse than is expected for an sp^3-hybridized carbon, likely due to steric interactions between $B(C_6F_5)_2$ and the pentafluorophenyl group bound to titanium. A close contact exists between the ortho fluorine F(1) and the boron atom (B(1)−F(1) = 2.94 Å); however, the boron center is trigonal-planar, as evidenced by the sum of the angles about boron (360.0°).

Complex **3a** is significant because of its *inactivity* as an α-olefin polymerization catalyst. In the absence of α-olefin, we propose that the methylborate adduct **2a** loses methane to give an intermediate 12-electron titanium methylidene complex (e.g., $[ArN(CH_2)_3NAr]Ti{=}CH_2$) which may be stabilized by the released borane. Notably, Gambarotta *et al.* have reported that the cyclohexylamide complex $(Cy_2N)_2TiMe_2$ slowly evolves methane in the absence of a Lewis acid to give the methylene-bridged dimer $[(Cy_2N)_2Ti]_2(\mu\text{-}CH_2)_2$,[8] suggesting that this may be a common mode of decomposition for four-coordinate amide complexes bearing methyl groups at titanium. In our system this elimination seems to be accelerated by the presence of a Lewis acid; hence, we are exploring alternative routes to diamide-stabilized alkylidene species. Addition of the B−C$_6$F$_5$ group across the proposed Ti=CH$_2$ unit yields the final product **3a**. Deactivation of metallocene/MAO (MAO =

Table 1. Crystallographic Data for 3a·CH$_2$Cl$_2$[a]

formula	$C_{46}H_{42}BF_{15}N_2Ti{\cdot}CH_2Cl_2$
fw	1051.47
color, habit	yellow, needle
cryst size, mm	0.08 × 0.25 × 0.60
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	20.292(2)
b, Å	11.253(2)
c, Å	23.459(2)
β, deg	114.967(7)
V, Å^3	4856(1)
Z	4
T, °C	21
D_c, g/cm^3	1.438
F(000)	2144
μ(Cu Kα), cm^{-1}	33.36
transmissn factors	0.70−1.00
scan type	$\omega-2\theta$
scan range (in ω), deg	$0.89 + 0.20 \tan\theta$
scan speed, deg/min	16 (up to 8 rescans)
data collected	$+h,+k,\pm l$
$2\theta_{max}$, deg	155
cryst decay, %	1.8
total no. of rflns	10 798
no. of unique rflns	10 503
R_{merge}	0.037
no. of rflns with $I \geq 3\sigma(I)$	3442
no. of variables	637
R	0.041
R_w	0.034
GOF	1.64
max Δ/σ	0.002
residual density, e/Å^3	−0.19, 0.20

[a] Conditions and definitions: Rigaku AFC6S diffractometer, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), Cu Kα radiation (λ = 1.541 78 Å), graphite monochromator, $\sigma^2(F^2) = [S^2(C + 4B)]/(Lp)^2$ (S = scan speed, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I \geq 3\sigma(I)$.

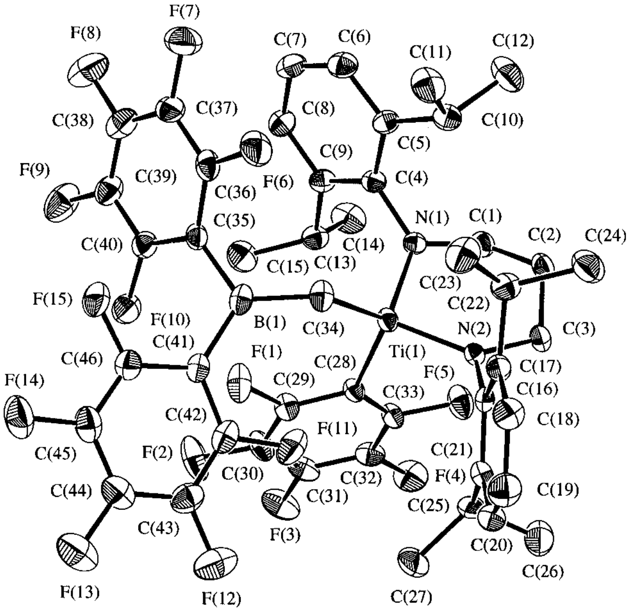


Figure 1. Molecular structure of **3a** (33% probability thermal ellipsoids are shown for the non-hydrogen atoms).

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $3a{\cdot}CH_2Cl_2$

Bond Distances			
Ti(1)−N(1)	1.846(4)	Ti(1)−N(2)	1.849(3)
Ti(1)−C(28)	2.191(4)	Ti(1)−C(34)	2.111(4)
C(34)−B(1)	1.503(6)	C(35)−B(1)	1.567(7)
C(41)−B(1)	1.584(7)	B(1)−F(1)[a]	2.94
Bond Angles			
N(1)−Ti(1)−N(2)	100.8(2)	N(1)−Ti(1)−C(28)	102.8(2)
N(1)−Ti(1)−C(34)	113.5(2)	N(2)−Ti(1)−C(28)	104.8(2)
N(2)−Ti(1)−C(34)	111.2(2)	C(28)−Ti(1)−C(34)	121.5(2)
Ti(1)−N(1)−C(1)	119.1(3)	Ti(1)−N(1)−C(4)	124.5(3)
C(1)−N(1)−C(4)	116.3(4)	Ti(1)−N(2)−C(3)	122.8(3)
Ti(1)−N(2)−C(16)	122.7(3)	C(3)−N(2)−C(16)	114.6(3)
Ti(1)−C(28)−C(29)	120.9(3)	Ti(1)−C(28)−C(33)	127.7(4)
Ti(1)−C(34)−B(1)	125.1(3)	C(34)−B(1)−C(35)	120.9(5)
C(34)−B(1)−C(41)	122.0(5)	C(35)−B(1)−C(41)	117.1(4)

[a] Close contact.

methylaluminoxane) systems concomitant with methane evolution has been observed.[22] Perhaps the formation of complex **3a** can be viewed as a model for this process.

Conclusion

A living α-olefin polymerization system is generated from the titanium dimethyl complexes **1a,b** and $B(C_6F_5)_3$ (**2a,b**). In the absence of monomer, compound **2b** is stable; however, the bulkier complex **2a** deactivates to give the methylene derivative **3a**. In principle, migration of the pentafluorophenyl group back to boron could generate a single-component catalyst. The titanium is clearly more electrophilic than boron in this instance, precluding formation of this species. We are currently exploring the interaction of other group 13 Lewis acids, for example $AlClMe_2$, in the hope of generating chelating diamide analogues of Tebbe's reagent $[Cp_2Ti](\mu\text{-}CH_2)(\mu\text{-}Cl)[AlMe_2]$.[23]

Experimental Section

General Details. All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques or in an Innovative Technology Inc. glovebox. Pentane was treated with 5% HNO_3 in H_2SO_4 to remove any olefins prior to being distilled under argon from sodium/benzophenone ketyl. The compounds $[ArN(CH_2)_3NAr]TiMe_2$ (**1a**; Ar = 2,6-$^iPr_2C_6H_3$) and $[Ar'N(CH_2)_3NAr']TiMe_2$ (**1b**; Ar′ = 2,6-$Me_2C_6H_3$)[14] and $B(C_6F_5)_3$[15] were prepared according to literature procedures. $[ArN(CH_2)_3NAr]Ti(^{13}CH_3)_2$ (***$^{13}C_2$*-1a**) was prepared from 2 equiv of $^{13}CH_3MgI$ and $[ArN(CH_2)_3NAr]TiCl_2$ in ether.[14] Proton (300 MHz), carbon (75.5 MHz), boron (96.2 MHz), and fluorine (282.2 MHz) NMR spectra were recorded in d_8-toluene at approximately 23 °C on a Varian XL-300 spectrometer. The proton chemical shifts were referenced to internal $C_6D_5CD_2H$ (δ 2.09 ppm) and the carbon resonances to C_{ipso}-C_6D_5-CD_3 (δ 137.5 ppm). Fluorine and boron chemical shifts were referenced externally to $CFCl_3$ (δ 0.0 ppm) and $BF_3{\cdot}Et_2O$ (δ 0.0 ppm), respectively. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

$[ArN(CH_2)_3NAr]Ti[CH_2B(C_6F_5)_2](C_6F_5)$ (3a). $B(C_6F_5)_3$ (76 mg, 0.15 mmol) in pentane (5 mL) was added dropwise at 23 °C to $[ArN(CH_2)_3NAr]TiMe_2$ (**1a**; 70 mg, 0.15 mmol) dissolved in pentane (5 mL) to give a yellow-orange precipitate. After ∼2 h the solution turned homogeneous. Stirring was continued for 16 h. The clear solution was passed through a plug of Celite, concentrated to ∼2 mL, and cooled to −30 °C. **3a** (120 mg, 0.12 mmol, 83%) was obtained as an orange crystalline solid. ^1H NMR: δ 7.12 (m, 3H, Ar), 7.01 (m, 3H, Ar), 4.58 (m, 2H, NCH_2), 3.92 (br s, 2H, $TiCH_2$), 3.31 (sept, 2H, $CHMe_2$), 3.28 (sept, 2H, $CHMe_2$), 3.20 (m, 2H, NCH_2), 1.42 (m, 1H, NCH_2CH_2), 2.29 (m, 1H, NCH_2CH_2), 1.30 (d, 6H, $CHMe_2$), 1.04 (d, 6H, $CHMe_2$), 0.95 (d, 6H, $CHMe_2$), 0.78 (d, 6H, $CHMe_2$). $^{13}C\{^1H\}$ NMR: δ 145.4, 144.0, 141.4, 129.4, 125.0, 109.5 ($TiCH_2$), 65.0, 33.4, 29.5, 28.2, 27.0, 26.2, 22.6, 22.4 (the carbon resonances for the perfluorophenyl groups appear as multiplets from 150−135 ppm). $^{19}F\{^1H\}$ NMR: δ −119.4 (d, 2F, F_o), −132.3 (d, 4F, F_o), −154.0 (t, 2F, F_p), −155.1 (t, 1F, F_p), −163.2 (m, 2F, F_m), −164.2 (m, 4F, F_m). $^{11}B\{^1H\}$ NMR: δ 79.4. Anal. Calcd for $C_{33}H_{53}ClN_2Ti$: C, 57.16; H, 4.38; N, 2.90. Found: C, 57.49; H, 4.81; N, 2.69.

X-ray Crystallographic Analysis of $3a{\cdot}CH_2Cl_2$. Crystallographic data appear in Table 1. The final unit cell parameters were obtained by least squares on the setting angles for 25 reflections with $2\theta = 31.5-45.6°$. The intensities of three standard reflections, measured every 200 reflections, decayed linearly by 1.8%. The data were processed[24] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans). The structure was solved by direct methods. The dichloromethane molecule was severely disordered. The 6 largest peaks in the solvent region were refined as chlorine and the next 4 peaks as carbon. The occupancy factors and isotropic thermal parameters were refined for all 10 solvent peaks. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms (excluding those associated with the solvent) were fixed in idealized positions (C−H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). A secondary extinction correction (Zachariasen type, isotropic) was applied, the final value of the extinction coefficient being $[2.6(3)] \times 10^{-7}$. Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from ref 25. Selected bond lengths and angles for **3a** appear in Table 2.

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Supporting Information Available: Text giving experimental details and tables giving final atomic coordinates and equivalent isotropic thermal parameters, all bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for **3a** (20 pages). Ordering information is given on any current masthead page.

OM961034B

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