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C−H Activation of the Trimethylsilyl-Substituted Cyclopentadienyl Ligand in the "Cation-like" Complex $[Cp'''_2ZrMe][Me(B(C_6F_5)_3]$ ($Cp''' = \eta^5$-C_5H_2-1,2,4-$(SiMe_3)_3$)

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The substituted cyclopentadienyl zirconium complex $[Cp'''_2ZrMe_2]$ (**1**; $Cp''' = \eta^5$-C_5H_2-1,2,4-$(SiMe_3)_3$) reacts with tris(perfluorophenyl)borane, $B(C_6F_5)_3$, in pentane to give the two species $[Cp'''_2ZrMe][MeB(C_6F_5)_3]$ (**2**) and $[Cp'''(\eta^5$-C_5H_2-2,4-$(SiMe_3)_2$-1-η^1-$SiMe_2CH_2)Zr][MeB(C_6F_5)_3]$ (**3**). Complex **3** was characterized by an X-ray structure determination, showing the C−H activation of a $SiMe_3$ group attached to the cyclopentadienyl ligand. Complexes **2** and **3** could be described, respectively, as the active and inactive species which both arise from **1** and $B(C_6F_5)_3$ in the cationic polymerization.

Introduction

The main advance in mechanistic investigations for polymerization catalysis by cationic group 4 species is mainly related to the conjunction of dimethyl organometallic complexes with tris(perfluorophenyl)borane. In this field, the conventional dimethylzirconocene has received a large attention from many researchers.[1] From the related system $[Cp'_2ZrMe_2]/B(C_6F_5)_3$ ($Cp' = C_5H_5$, C_5H_4R, $C_5H_3R_2$, with R = Me, *t*-Bu, $SiMe_3$), different interesting models were found to explain the behavior of the cationic complex as an olefin polymerization catalyst.[2,3] Of great relevance, deactivation processes of the cationic complexes have provided valuable information concerning the decay of the polymerization rate. Particularly, decomposition pathways via C−H bond activation and different examples have been observed. Some of them concern the reaction of $B(C_6F_5)_3$ with $[(1,3\text{-}t\text{-}Bu_2C_5H_3)_2ZrMe_2]$ or $[(C_5H_4C(Me)_2NMe_2)_2ZrMe_2]$, in which $[(t\text{-}Bu_2C_5H_3)(t\text{-}BuC_5H_3CMe_2CH_2)ZrMeB(C_6F_5)_3]$ and $[(C_5H_4C(Me_2)NMe_2)(C_5H_4C(Me_2)N(Me)CH_2)ZrMeB(C_6F_5)_3]$ were identified.[2,4] This paper deals with the reactivity of the highly substituted cyclopentadienyl zirconocene complex $[Cp'''_2ZrMe_2]$ (**1**; $Cp''' = \eta^5$-C_5H_2-1,2,4-$(SiMe_3)_3$).[5] Previous work has shown that the unpredictable chemistry of **1** is related to the influence of three $SiMe_3$ groups attached to the cyclopentadienyl rings.[6] The complex **1** was recently studied with CO and gave the unexpected enolate hydride $[Cp'''_2ZrH(OC(Me){=}CH_2)]$.[5] We now describe its reactivity with the relatively strong Lewis acid borane $B(C_6F_5)_3$ and some C−H activation of the $SiMe_3$ group attached to the cyclopentadienyl ring.

Results and Discussion

The reaction of **1** with $B(C_6F_5)_3$ was studied in different solvents (toluene, THF, CH_2Cl_2) and analyzed by ^1H NMR, giving rise to spectra in which a multitude of $SiMe_3$ signals were observed, showing the formation of various complexes. Nevertheless, the reaction of **1** with $B(C_6F_5)_3$ in pentane (see Experimental Section) immediately gives a pale yellow precipitate. This solid was analyzed by ^1H and ^{13}C NMR in deuterated THF at low temperature (−80 °C), and a clear NMR spectrum was observed, justifying the formation of the expected complex $[Cp'''_2ZrMe(THF\text{-}d_8)][CH_3B(C_6F_5)_3]$ (**2**(THF-d_8)). In particular, a broad signal at 0.50 ppm as well as a well-resolved single one at 1.04 ppm are assigned to the methyl bridged to the borane and to the methyl on the zirconium atom, respectively. Interaction of the $[MeB(C_6F_5)_3]$ anion with the cationic metal center can be ruled out if we consider the significant downfield shift of the methyl group compared to the methyl group of **1** (δ 0.06) and the ^{19}F NMR data, where a $\delta(p\text{-}F-m\text{-}F)$ value larger than 3 ppm is indicative of significant interaction (**2**: $\delta(p\text{-}F-m\text{-}F) = 2.6$ ppm).[7] When the filtrate of the reaction mixture is allowed to stand for 2 days, or when a diluted mixture of the reactants is used as the starting material, the formation of crystalline $[Cp'''(\eta^5$-C_5H_2-2,4-$(SiMe_3)_2$-1-η^1-$SiMe_2CH_2)Zr][MeB(C_6F_5)_3]$ (**3**) is obtained, fully characterized by NMR (^1H, ^{13}C) and by an X-ray analysis (Figure 1). The main feature of the structure is the formation of a methylene bridge between the zirconium atom and one Si atom attached to the cyclopentadienyl ring. The $Zr-CH_2$

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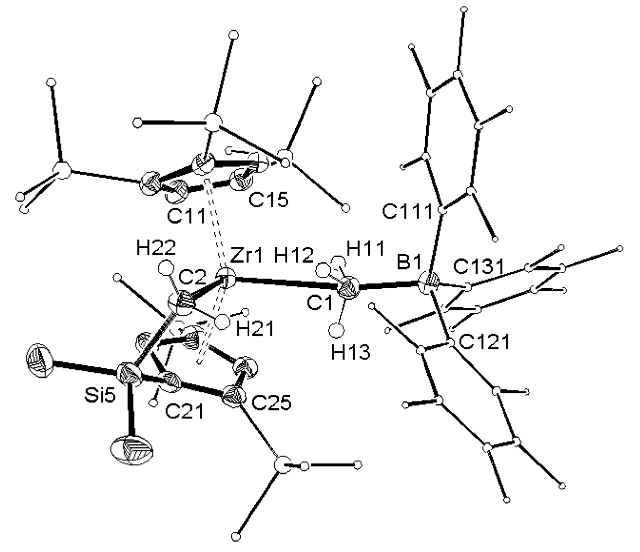
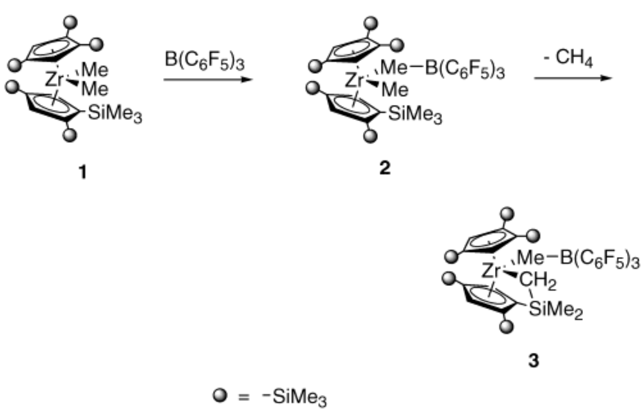


Figure 1. Molecular structure of **3** showing the labeling scheme. Hydrogen atoms of $SiMe_3$ groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Zr−C(1) = 2.641(2), Zr−C(2) = 2.294(2), B−C(1) = 1.692(3), Si(5)−C(2) = 1.847(2), Cp1−Zr = 2.221, Cp2−Zr = 2.219; Zr−C(1)−B(1) = 172.13(14), C(2)−Si(5)−C(21) = 91.47(10), Si(5)−C(2)−Zr = 103.41(10), C(2)−Zr−C(1) = 98.83(7), Cp1−Zr−Cp2 = 135.19. Cp1 and Cp2 are the centroids of the C(11)−C(15) and C(21)−C(25) rings, respectively.

distance (Zr−C(2) = 2.294(2) Å) is in the expected range for a Zr−C distance. The methyl counteranion is bonded to the zirconium and boron atoms (Zr−C(1) = 2.641(2) Å, B(1)−C(1) = 2.692(3) Å) with a nearly linear Zr(1)−C(1)−B(1) angle (172.14(15)°), indicating that the cation and anion are relatively separate by comparison to previous similar cationic zirconium structures.[2] Although some methyl Zr−C−H angles are quite acute (67.2, 66.0, 77.1°), the Zr−H distances are longer than expected for a Zr−H agostic interaction (2.434, 2.413, 2.599 Å).[8] The two protons of the methylene, which were located and refined, are inequivalent, as shown in the Zr−C(2)−H angles observed in the solid state (97.6, 117.6°) with Zr⋯H distances that also exclude any agostic interaction (2.605, 2.859 Å). Planes defined by [Cp centroids] with Zr (as P1) and C(2), Zr, C(1) (as P2) are nearly perpendicular (86.3°), which establishes that C(2) is nearly located in the plane containing the Zr-based LUMO.[9]

The cationic complex **3** is soluble in benzene or toluene (or their corresponding deuterated solvents), due to the presence of the TMS ligand on the cyclopentadienyl ring, which increases its solubility but decomposes rapidly to give, as shown by ^1H NMR, a large number of $SiMe_3$ signals. Nevertheless, the ^1H and ^{13}C NMR of a deuterated THF solution of **3** prepared at low temperature (−80 °C) give clean spectra, in agreement with the structural geometry. Two proton signals for each cyclopentadienyl ligand and five nonequivalent $SiMe_3$ signals were observed. The CH_2 methylene moiety shows two diastereotopic AB system protons (2.37 and −2.91 ppm). For the high-field shift, a reduced J_{C-H} coupling value (106 Hz) is observed, and this reflects the presence of a weak agostic C−H interaction in solution.[8] The expected broad signal of the methyl ligand attached to the boron atom is overlapped in part by the $SiMe_3$ signal in ^1H NMR (0.50 ppm) but could be observed by ^{13}C NMR at the expected value[9] (9.9 ppm with $^1J_{C-H}$ = 122 Hz, excluding any C−H agostic interaction with the Zr atom).[10] In solution a THF adduct with the cationic zirconium center is suggested, by comparison with the ^1H and ^{13}C NMR shifts observed of the counteranion with those of **2.** This is confirmed by the observation in the ^{13}C NMR of two sets of THF resonances attributable to free and coordinated THF.

Scheme 1



This complex arises from an intramolecular C−H activation of a methyl group of $SiMe_3$ attached to a cyclopentadienyl ring with the alkyl methyl ligand bound to the zirconium atom, and the isolated complex **2** is suggested to be an intermediate in its formation (Scheme 1). The ease of C−H activation of a methyl group of a $SiMe_3$ was well studied and established.[11,12] In relation to these findings, complexes **2** and **3** were tested toward ethylene polymerization (solvent toluene, 1 bar of ethylene, room temperature, 15 min). At first, we verified that a freshly stoichiometric mixture of **1** and $B(C_6F_5)_3$ in toluene yields polyethylene (1.4×10^4 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1}) but a rapid loss of

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[12] C−H activation of the trimethylsilyl group attached to a cyclopentadienyl ring was observed when the dichlorozirconocene $[Cp'''_2ZrCl_2]$ is reduced by Mg in THF. A clear EPR 1:2:1 triplet is obtained (g = 1.989; $a(^1H)$ = 6.2 G), in agreement with the coupling of an unpaired electron of a Zr^{III} nucleus with two equivalent protons.[11a−c] Addition of DCl to the solution gives nearly quantitative dichlorozirconocene complex, in which the incorporation of labeled deuterium into the $SiMe_3$ ligand is observed by ^2H NMR (^1H NMR (toluene-d_8; δ, ppm) 7.29 (s, $C_5H_2(SiMe_3)_3$), 0.69 (s, 2$SiMe_3$), 0.57 (s, $SiMe_3$); ^2H NMR (toluene/toluene-d_8 as standard; δ, ppm): 0.68 (s, $SiMe_3$). In the absence of an X-ray structure determination, we could suggest a magnesium hydride zirconium complex containing a C−H activated $SiMe_3$ group or $[Cp'''(\eta^5{:}\eta^1\text{-}C_5H_2(SiMe_3)_2SiMe_2CH_2)Zr^{III}]$ by comparison with the structures recently published by Mach and co-workers.[11a−c] It is worth noting that chemical reduction of other dichlorozirconocene species $[(C_5H_4R)_2ZrCl_2]$ (R = H, tBu, $SiMe_3$) by Mg in THF leads to an EPR doublet spectrum due to the formation of a zirconocene(III) hydride species (R = H, g = 1.997, $a(^1H)$ = 7.2 G; R = tBu, g =1.987, $a(^1H)$ = 5.2 G; R = $SiMe_3$, g = 1.988, $a(^1H)$ = 6.4 G). (a) Choukroun, R. Unpublished results. (b) Samuel, E. *Inorg. Chem.* **1983**, *22*, 2967.

polymerization activity is observed. Surprisingly, **2** was found to be inactive, which is certainly related to its fast decomposition in toluene at room temperature (vide supra). Nevertheless, a suspension of **2** in pentane shows a moderate activity toward ethylene polymerization (9×10^3 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1}). As expected, complex **3** is catalytically inactive. From these results, the main feature remains that **2** and **3** could be described, respectively, as the active and inactive species which both arise from **1** and $B(C_6F_5)_3$ in the cationic polymerization.

In summary, complex **1** has been activated with $B(C_6F_5)_3$ and the two cationic products **2** and **3** were isolated from the mother solution. Complex **2** was found to be efficient for ethylene polymerization, whereas **3** was inactive due to the C−H activation of one $SiMe_3$ group of the subtituted cylopentadienyl ligand with the alkyl methyl ligand bound to the zirconium atom. Deactivation of cationic catalysts by cyclopentadienyl ligand degradation is again confirmed.[2,4,13]

Experimental Section

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon, collected by distillation, and stored in a drybox over activated 4 Å molecular sieves. Deuterated solvents were degassed and dried over activated 4 Å molecular sieves. NMR data were recorded using Bruker AMX-400, DPX-300, and AC-200 spectrometers and referenced internally to residual protio solvent (^1H) resonances and are reported relative to tetramethylsilane (δ 0 ppm). Assignments in the ^1H and ^{13}C NMR spectra for **3** were confirmed through COSY spectra. ^{19}F NMR (188.298 MHz) spectra were recorded on a Bruker AC-200 spectrometer (reference CF_3CO_2H). EPR spectra were obtained by using a Bruker ESP300E spectrometer. Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) (C, H, N). $[Cp'''_2Zr(CH_3)_2]$ ($Cp''' = C_5H_2(SiMe_3)_3$)[5] was prepared as previously described, and $B(C_6F_5)_3$ was prepared according to the literature.[14]

$[Cp'''_2ZrMe][MeB(C_6F_5)_3]$ (2) and $[Cp'''(\eta^5\text{-}C_5H_2\text{-}2,4\text{-}(SiMe_3)_2\text{-}1\text{-}\eta^1\text{-}SiMe_2CH_2)Zr][MeB(C_6F_5)_3]$ (3) ($Cp''' = \eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}(SiMe_3)_3$). A solution of $B(C_6F_5)_3$ (75 mg, 0.15 mmol) in pentane (5 mL) was added dropwise to a solution of **1** (100 mg, 0.15 mmol) in pentane (5 mL) at room temperature. A pale yellow microcrystalline solid was filtered off after 20 min and characterized as **2** (60 mg, 34%). The filtrate was allowed to crystallize. After 24 h, yellow crystals are filtered off and characterized as **3** (15 mg, 9%). In another synthesis, a solution of $B(C_6F_5)_3$ (15 mg, 0.03 mmol) in pentane (1 mL) was added dropwise to a solution of **1** (20 mg, 0.03 mmol) in pentane (0.5 mL) at room temperature. A pale yellow solid was filtered off after 5 min and characterized as **2** (23 mg, 65%). The yield of **2** was dependent on the reaction time before its filtration out of the solution.

Table 1. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for Compound 3

formula	$C_{47}H_{58}BF_{15}Si_6Zr$
fw	1180.52
temp (K)	160(2)
wavelength (Å)	0.710 73
cryst syst, space group	triclinic, $P\bar{1}$
a (Å)	12.805(5)
b (Å)	13.873(5)
c (Å)	17.953(5)
α (deg)	79.763(5)
β (deg)	81.826(5)
γ (deg)	62.677(5)
V (Å^3)	2781.6(17)
Z	2
F(000)	1212
density (g cm^{-3})	1.409
abs coeff (mm^{-1})	0.409
cryst descripn	parallelepiped
cryst size (mm)	$0.50 \times 0.37 \times 0.25$
collecn method	φ rotation
2θ range for data collecn (deg)	3.3−52.1
index ranges	$-15 \le h \le 15$ $-17 \le k \le 17$ $-22 \le l \le 22$
no. of rflns collected/unique	27 546/10 184 (R_{int}=0.0231)
completeness to 2θ (%)	90.8
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	10 184/0/668
GOF on F^2	1.053
final R indices ($I > 2\sigma(I)$)	R1 = 0.0312, wR2 = 0.0793
R indices (total)	R1 = 0.0384, wR2 = 0.0864
largest diff peak and hole (e Å^{-3})	0.452 and −0.348

2: ^1H NMR (THF-d_8; 203 K; δ, ppm) 0.37 (s, 18H, $Si(CH_3)_3$), 0.42 (s, 36H, $Si(CH_3)_3$), 0.50 (broad s, 3H, $H_3C{-}B(C_6F_5)_3$), 1.04 (s, 3H, CH_3), 1.81, 3.64 (coordinated THF; free THF at 1.77, 3.60), 6.99 (s, 2H, C_5H_2), 7.18 (s, 2H, C_5H_2); $^{13}C\{^1H\}$ NMR (THF-d_8; 203 K; δ, ppm) 0.7, 0.8, 1.6 ($Si(CH_3)_3$), 9.8 ($H_3CB(C_6F_5)_3$), 25.2, 67.6 (coordinated THF; free THF at 24.9, 67.2), 128.6 ($CSiMe_3$), 129.2 (ipso-C, $B(C_6F_5)_3$), 129.3 ($CSiMe_3$), 130.3 (C_5H_2), 136.4 (d, $^1J_{C-F} = 240.0$ Hz, m-C, $B(C_6F_5)_3$), 137.1 (C_5H_2), 137.6 (d, $^1J_{C-F} = 240.0$ Hz, p-C, $B(C_6F_5)_3$), 146.5 ($CSiMe_3$), 148.5 (d, $^1J_{C-F} = 240.0$ Hz, o-C, $B(C_6F_5)_3$) (^{13}C resonance of the terminal methyl group not detected, due to the overlapping of the $SiMe_3$ resonance in the same chemical shift range); ^{19}F NMR (THF-d_8; 203 K; δ, ppm) −57.32, −89.31, −91.90 (o-F, p-F, m-F (C_6F_5)).

3: ^1H NMR (THF-d_8; 203 K; δ, ppm): −2.91 (d, $^1J_{C-H} = 12.8$ Hz, 1H, $SiCH_aH_bZr$), 0.36 (s, 18H, $Si(CH_3)_3$), 0.44 (s, 9H, $Si(CH_3)_3$), 0.48 (s, 9H, $Si(CH_3)_3$), 0.49 (s, 9H, $Si(CH_3)_3$), 0.51 (broad s, $H_3C{-}B(C_6F_5)_3$), 2.37 (d, $^1J_{C-H} = 12.8$ Hz, 1H, $Si{-}CH_aH_b{-}Zr$), 6.07 (s, 1H, C_5H_2), 6.85 (s, 1H, C_5H_2), 6.90 (s, 1H, C_5H_2), 6.98 (s, 1H, C_5H_2); $^{13}C\{^1H\}$ NMR (THF-d_8; 203 K; δ, ppm) 0.9, 1.0, 1.1, 1.3 (q, $^1J_{C-H} = 118.9$ Hz, $Si(CH_3)_3$), 9.9 (broad q, $^1J_{C-H} = 118.9$ Hz, $H_3CB(C_6F_5)_3$), 25.0, 67.3 (coordinated THF; free THF at 24.9, 67.2), 40.5 (dd, $^1J_{C-H_a} = 106.0$ Hz, $^1J_{C-H_b} = 137.6$ Hz, $SiCH_aH_bZr$), 127.6 (s, $CSiMe_3$), 128.7 (d, $^1J_{C-H} = 164.1$ Hz, C_5H_2), 129.0 (d, $^1J_{C-H} = 164.3$ Hz, C_5H_2), 129.2 (broad s, ipso-C, $B(C_6F_5)_3$), 133.7 (s, $CSiMe_3$), 134.3 (s, $CSiMe_3$), 134.8 (d, $^1J_{C-H} = 167.7$ Hz, C_5H_2), 136.4 (d, $^1J_{C-F} = 240.0$ Hz, m-C, $B(C_6F_5)_3$), 137.6 (d, $^1J_{C-F} = 240.0$ Hz, p-C, $B(C_6F_5)_3$), 139.5 (s, $CSiMe_3$), 141.1 (s, $CSiMe_3$), 143.1 (d, $^1J_{C-H} = 158.0$ Hz, C_5H_2), 143.8 (s, $CSiMe_3$), 148.5 (d, $^1J_{C-F} = 240.0$ Hz, o-C, $B(C_6F_5)_3$).

Anal. Calcd for $C_{48}H_{64}BF_{15}Si_6Zr$ (**2**): C, 48.18; H, 5.39. Found: C, 47,12; H, 4.91. Calcd for $C_{47}H_{60}BF_{15}Si_6Zr$ (**3**): C, 47.82; H, 5.12. Found: C, 47.70; H, 4.96.

Typical Ethylene Polymerization Tests. The catalyst precursor **2** (30 mg) was suspended in 10 mL of pentane. Ethylene (1 atm) was introduced under stirring at room temperature. After 15 min, the polymerization was quenched with acidified methanol. The polyethylenes were filtered, washed with methanol and then acetone, and dried under vacuum at 80 °C for 24 h.

Crystallographic Data for 3. For structure **3** (Table 1), data were collected using a Stoe Imaging Plate Diffraction

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System (IPDS). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. No fluctuations of the intensity were observed over the course of the data collection. A semiempirical correction absorption[15] was applied to the data. The structure was solved by direct methods using SIR92[16] and refined by least-squares procedures on F^2 with the aid of SHELXL97[17] included in WinGX (version 1.63).[18] The atomic scattering factors were taken from ref 19. All hydrogen atoms were located on a difference Fourier map and refined with a riding model, except for a few specific hydrogen atoms which were isotropically refined (those on CH_3 and CH_2 groups). All the remaining non-hydrogen atoms were anisotropically refined, and in the last refinement cycles a weighting scheme was used where weights were calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Drawing of the molecules was performed using the program ORTEP32.[20] Criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviation being less than 0.1 and no significant features in final difference maps.

Supporting Information Available: Crystallographic data for compound **3** including ORTEP diagram, tables of crystal data and data, collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030167B

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