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μ-Benzyl and μ-Chloro Dinuclear Cationic Titanium Compounds

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Summary: The reaction of $[Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)_2]_2$ *with the Lewis acid* $B(C_6F_5)_3$ *in toluene at room temperature affords the new dinuclear monocationic species* $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}_2(CH_2Ph)_3]^+[PhCH_2B(C_6F_5)_3]^-$ *(**1**). This compound is thermally unstable and decomposes in aromatic solvents to give the paramagnetic mixed-valence species* $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}(CH_2Ph)]_2{}^+Q^-$ $(Q^- = [PhCH_2B(C_6F_5)_3]^-$ *(**2**),* $[B(C_6F_5)_4]^-$ *(**3**)). In chlorinated solvents **1** affords the μ-chloro complexes* $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)\}_2(\mu\text{-}Cl)]^+Q^-$ $(Q^- = [PhCH_2B(C_6F_5)_3]^-$ *(**4**),* $[B(C_6F_5)_4]^-$ *(**5**)). Different isomers of **1** are observed, depending on the temperature, as deduced by variable-temperature NMR spectroscopic studies.*

Group 4 metal−alkyl cationic compounds are of great interest, in view of their role as active species in homogeneous Ziegler−Natta catalysis[1] and as stoichiometric reagents in organometallic synthesis.[2,3] These species are extremely electrophilic and have a pronounced tendency to achieve electron stabilization by coordinating with any available nucleophile, such as solvent molecules or external Lewis bases,[4,7b] or by interaction with the counteranion.[5] The formation of dinuclear methyl complexes of the type $[(MCp_2Me)_2(\mu\text{-}CH_3)]^+$ (M = Zr, Hf) has been reported.[6]

Previously, we described the preparation of new dinuclear cationic zirconium complexes bridged by fulvalene and methyl or methylene ligands[7] and evaluated their behavior compared with related mononuclear cationic complexes. With the same aim, we have investigated the reaction of $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}(CH_2Ph)_2]_2$[8] with $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$ in a range of solvents and under contrasting thermal conditions.

Results and Discussion

The reaction of the tetrabenzyl complex $[Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)_2]_2$ with the strong Lewis acid $B(C_6F_5)_3$ in toluene at room temperature immediately afforded a dark red solid characterized by elemental analysis as the dinuclear compound $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}_2(CH_2Ph)_3]^+[PhCH_2B(C_6F_5)_3]^-$ (**1**). Compound **1** is thermally unstable in solution and the solid state, although it was sufficiently stable under inert atmosphere in the solid state to undergo elemental analysis. When the reaction mixture was stirred for 2 h at room temperature, **1** was transformed into a dark green oil which, after workup, afforded a dark green paramagnetic compound, characterized as the mixed-valence cationic complex $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}(CH_2Ph)]_2{}^+Q^-$ $(Q^- = [PhCH_2B(C_6F_5)_3]^-$ (**2**); Scheme 1) by elemental analysis and EPR spectroscopy. A similar reaction carried out with $[Ph_3C][B(C_6F_5)_4]$ gave the related salt with $Q^- = [B(C_6F_5)_4]^-$ (**3**). Elimination of toluene and 1,2-diphenylethane, observed by NMR spectroscopy, indicated that the

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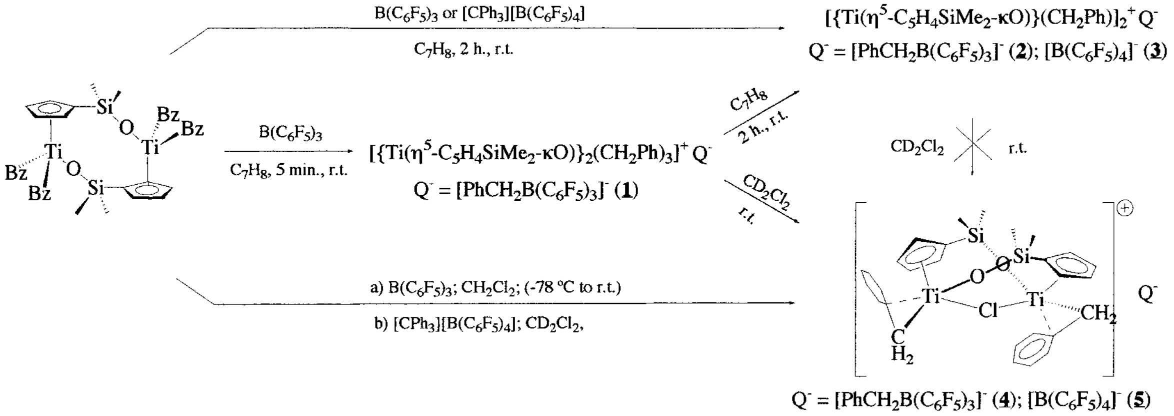
Scheme 1



reaction proceeded via homolytic cleavage of a Ti−CH$_2$-Ph bond. We propose that compounds **2** and **3** contain one cationic titanium(IV) center and one neutral titanium(III) center formed in a reductive benzyl-elimination process.

The EPR spectrum of **2** in THF shows a single peak (5.3 G) with a *g* value of 1.973, in good agreement with the values measured for other Ti(III) compounds.[9] Peaks due to the radical species generated during polymerization of the solvent (THF) are also present in the spectrum. Compounds **2** and **3** are stable in the solid state and can be stored under an argon atmosphere. They react with chlorinated solvents to give unidentified paramagnetic products, rather than the expected oxidative chloro-addition product.

Compound **1** decomposed in chlorinated solvents at room temperature to give the *μ*-chloro cationic complex $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)\}_2(\mu\text{-}Cl)]^+[PhCH_2B(C_6F_5)_3]^-$ (**4**), isolated as an orange-red solid identified by elemental analysis. Compound **4** was also obtained by reaction of $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}(CH_2Ph)_2]_2$ with $B(C_6F_5)_3$ in CH_2Cl_2 or $CHCl_3$ at room temperature. Formation of the related salt $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)\}_2(\mu\text{-}Cl)]^+[B(C_6F_5)_4]^-$ (**5**) was observed when the reaction with $[CPh_3][B(C_6F_5)_4]$ in CD_2Cl_2 at room temperature was monitored by NMR spectroscopy. Elimination of toluene and 1,2-diphenylethane in the reaction suggests that the chloride exchange proceeded via homolytic cleavage of the Ti−CH$_2$Ph bond[10] and subsequent halide abstraction, although direct chloride abstraction cannot be ruled out.[4a,c]

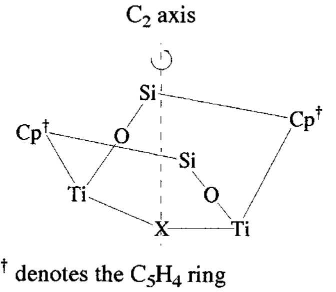


Figure 1. Central core of the dinuclear cationic complexes **1b**, **4**, and **5**.

The lack of solubility of all these complexes in nonpolar solvents is consistent with their marked ionic character. In contrast with complexes **1**−**3**, the *μ*-chloro derivatives **4** and **5** are stable in chlorinated solvents, allowing their characterization by NMR spectroscopy in CD_2Cl_2 at room temperature. The ^1H and ^{13}C NMR spectra of **4** display resonances consistent with a static C_2-symmetric compound on the NMR time scale, in the temperature range 298−203 K. The large value of $^1J_{C-H}$ (∼154 Hz) and the high-field-shifted *ipso*-C_6H_5 (δ 125.4) indicate the presence of a benzallylic interaction in **4**.[11] Spectroscopic features that confirm such a disposition are a higher difference in chemical shifts between the two diastereotopic benzylic CH_2 protons ($\Delta\delta = 1.12$) and a reduction in the value of $^2J_{H-H}$ (6.5 Hz) with respect to the neutral $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}(CH_2Ph)_2]_2$ compound ($\Delta\delta = 0.26$, $^2J_{H-H} = 9.5$ Hz).[8] We assume the central core, initially open in the starting tetrabenzyl compound, bends with respect to the Ti−Ti axis in the dinuclear cation of **4**, adopting a butterfly configuration (Figure 1). This disposition allows the chloride ligand to link both titanium atoms, maintaining the almost linear Ti−O−Si unit.[8]

To establish the structure of **1**, the reaction of $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}(CH_2Ph)_2]_2$ with $B(C_6F_5)_3$ was monitored by ^1H NMR spectroscopy at variable temperature. The tetrabenzyl complex was mixed with the Lewis acid in CD_2Cl_2 at −78 °C in a sealed NMR tube. The spectroscopic data at −90 °C reveal the transfer of one benzyl group from titanium to boron, confirmed by the characteristic signals of the triarylborate anion $[PhCH_2B(C_6F_5)_3]^-$, and the formation of a unique cationic species.

The ^1H NMR spectrum at −90 °C exhibits two ABCD spin systems for the protons of two nonequivalent cyclopentadienyl rings and two pairs of broad signals which are in a slow spin exchange at −80 °C (saturation transfer experiments). The two pairs are assigned to the methylene (δ 2.97 (1H), 4.52 (1H); δ_{av}= 3.74 ppm; $\Delta\delta$ =

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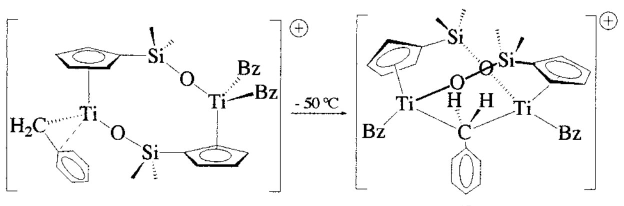
Scheme 2



1a **1b**

1.55 ppm) and ortho phenyl protons (δ 6.0 (1H), 7.8 (1H); $\delta_{av} = 6.9$ ppm; $\Delta\delta = 1.8$ ppm) of a benzallylic twisted benzyl ligand.[11b] Two broad signals are also observed for the two SiMe_2 groups (δ 0.23 (6H), 0.48 (6H); $\Delta\nu \approx$ 14 Hz) and two broad signals for the diastereotopic CH_2-Ph ligands (δ 2.63 (2H), 2.93 (2H); $\Delta\delta = 0.3$ ppm), rather than the four signals expected in each case. This is may be explained by a rapid spin exchange between these resonances at this temperature ($\Delta G^{\ddagger}$(183 K) < 8.3 kcal/mol). The spectroscopic data are consistent with the proposed open structure **1a** (Scheme 2) containing two titanium atoms in different ligand environments (cationic and neutral titanium centers).

The ^{1}H NMR spectrum at −60 °C shows the collapse of the methylene proton resonances (δ 3.72) of the benzallylic group ($\Delta G^{\ddagger}$(213 K) = 10.3 kcal/mol) and two AA′BB′ spin systems for the ring protons, consistent with the loss of the benzallylic interaction in **1a**. The collapse of ortho phenyl protons is not observed by overlapping with other resonances in the region near to 7 ppm.

When the sample is warmed to −50 °C, a new set of signals appears in the ^{1}H NMR spectrum, and after 2 h only these new resonances are observed. The spectrum exhibits two broad resonances (δ 0.37 and 0.58; $\Delta\nu$ = 18 Hz) for SiMe groups and four broad signals (δ 5.9, 6.1, 6.2, and 7.8) for ring protons. Furthermore, one singlet at δ 3.22 ($\Delta\nu$ = 6 Hz) assignable to the bridging benzyl methylene protons and one AB spin system (δ 2.67 and 2.75; $^2J_{H-H}$ = 9.7 Hz) for the diastereotopic CH_2 resonances of two equivalent η^1 benzyls are observed. These data are in agreement with C_2 symmetry. We propose **1a** is transformed, via an intramolecular rearrangement, into the chiral μ-benzyl-bridged isomer $[\{[Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)](CH_2Ph)\}_2(\mu\text{-}CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$ (**1b**; Scheme 2). **1b** adopts a bent configuration analogous to that of complex **4**, where one of the benzyl ligands bridges both titanium atoms. As far as we know, species **1b** is the first example of a dinuclear titanium cation bearing a μ-benzyl ligand, analogous to the more common μ-methyl derivatives.[6]

At −35 °C the ^{1}H NMR spectrum shows the collapse point for SiMe signals ($\Delta G^{\ddagger}$(238 K) = 11.3 kcal/mol). At −10 °C an AA′BB′ spin system (δ 6.16 (4H) and 7.36 (4H)) for cyclopentadienyl and one singlet (δ 0.55 (12H)) for methylsilyl protons are observed. The spectrum also exhibits a broad signal located at δ 3.03 (6H) for three methylene Ti−CH_2Ph groups along with a unique set of resonances (integrated for 3, 6, and 6 protons) for the phenyl protons Ti−CH$_2$Ph. These spectroscopic features indicate a typical spin exchange process between the benzyl groups and all of the SiMe resonances. This dynamic behavior can be described as “configuration fluttering”, as illustrated in Scheme 3.

The dissociation of the μ-benzyl group through either of two pathways, i or ii, proceeds with simultaneous opening of the butterfly configuration, affording the open structure isomer **1a**. This may then return to the bent configuration isomer in either of two ways. One route simply recovers the original enantiomeric conformation A, while the other places the erstwhile μ-benzyl in the terminal position and the erstwhile terminal benzyl group in the bridging position, yielding the enantiomeric conformation B. As the coordination of the latter benzyl group to the second metal center takes place on the opposite face, the global process involves the equilibration of benzyl ligands, the methyl groups of the SiMe$_2$ units, and α- and β-protons of the cyclopentadienyl rings.

In conclusion, this report shows that dinuclear complexes with two Ti atoms held in close proximity offer a valuable strategy for designing new cationic derivatives, unprecedented for related mononuclear complexes. Addition of Lewis acids to the tetrabenzyl derivative $[Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)_2]_2$ in chlorinated solvents results in the clean formation of the $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}_2(CH_2Ph)_3]^+$, $[\{[Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)](CH_2Ph)\}_2(\mu\text{-}CH_2Ph)]^+$, and $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)\}_2(\mu\text{-}Cl)]^+$ cationic species, depending on the temperature. When the same reaction was carried out in aromatic solvents, the mixed-valence species $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}(CH_2Ph)]_2{}^+$ were isolated. This reaction provides an interesting example in which Ti(III) species are generated by reaction of a Ti(IV) alkyl complex with a Lewis acid activator.

Experimental Section

All manipulations were performed under argon using Schlenk and high-vacuum-line techniques or a glovebox (Model HE-63). The solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. $[Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)_2]_2$,[8] $B(C_6F_5)_3$,[12] and $[Ph_3C][B(C_6F_5)_4]$[13] were prepared by literature methods. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. The carbon analytical value found for **4** was incorrect, due to its air sensitivity and difficulties in the manipulation of the sample. NMR spectra were recorded on a UnityPlus 500 (Varian NMR system) spectrometer, and chemical shifts were referenced to residual solvent protons relative to TMS. ^{19}F (470.3 MHz) spectra are referenced to external CFCl$_3$.

Synthesis of $[\{Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)\}_2(CH_2Ph)_3]^+[PhCH_2B(C_6F_5)_3]^-$ (1). A toluene (25 mL) solution of $B(C_6F_5)_3$ (3.46 g, 6.76 mmol) was added to a solution of $[Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\kappa O)(CH_2Ph)_2]_2$ (5 g, 6.76 mmol) in toluene (50 mL) at ambient temperature. The solution rapidly turned dark, and a brownish red oil was deposited. The solution was immediately separated and the oil obtained dried to afford **1** as an analytically pure dark red solid (7.68 g, 91%). Anal. Calcd for $C_{60}H_{48}BF_{15}O_2Si_2Ti_2$: C, 57.31; H, 3.87. Found: C, 57.47; H, 3.95. ^{1}H NMR of the isomer **1a** (500 MHz, CD$_2$Cl$_2$, −50 °C): δ 0.25, 0.50 (br s, 2 × 6H, SiMe_2), 2.80 (br, 2H, BCH_2Ph), 2.65, 2.95 (br s, 2 ×

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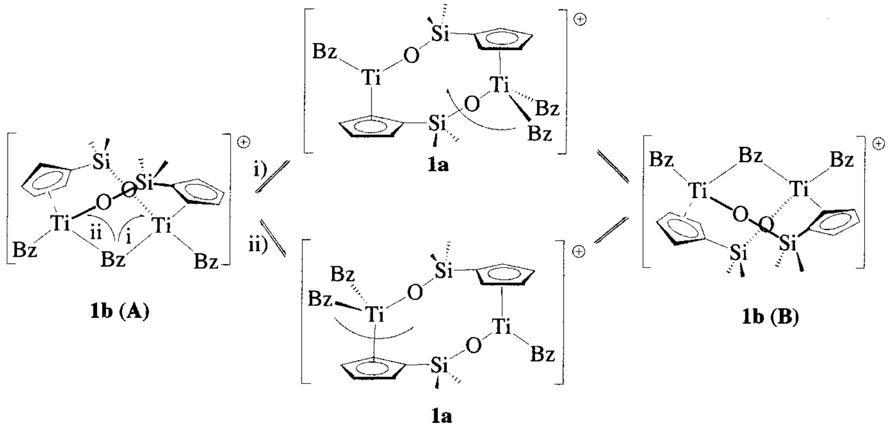
Scheme 3



2H, TiCH_2Ph), 3.72 (br s, 2H, TiCH_2Ph), 6.0, 6.5, 6.7, 7.5 (4 × 2H, two AA′BB′ spin systems, C_5*H_4*), 6.7, 6.9, 7.2, 7.5 (m, 2H, 6H, 6H, 1H, TiCH$_2$*Ph*), 6.7, 6.8, 6.9 (m, 2H, 1H, 2H, BCH$_2$*Ph*). ^{1}H NMR of the isomer **1b** (500 MHz, CD_2Cl_2, −50 °C): δ 0.37, 0.58 (br s, 2 × 6H, Si*Me*$_2$), 2.80 (br, 2H, BCH_2Ph), 2.67, 2.75 (AB spin system, $^2J_{H-H} = 9.7$ Hz, 2 × 2H, TiCH_2Ph), 3.22 (br, 2H, Ti−μ-CH_2Ph−Ti), 5.9, 6.1, 6.2, 7.8 (4 × 2H, two AA′BB′ spin systems, C_5*H_4*), 6.7, 6.9, 7.2, 7.5 (m, 2H, 6H, 6H, 1H, TiCH$_2$*Ph*), 6.7, 6.8, 6.9 (m, 2H, 1H, 2H, BCH$_2$*Ph*). ^{19}F NMR (470.3 MHz, CD_2Cl_2, −50 °C): δ −131.9 (m), −164.2 (m), −167.2 (m).

Synthesis of [{Ti(η^5-$C_5H_4SiMe_2$-κO)}(CH_2Ph)]$_2^+$[$PhCH_2B(C_6F_5)_3$]$^-$ (2). A toluene (20 mL) solution of $B(C_6F_5)_3$ (0.7 g, 1.37 mmol) was added to a solution of [Ti(η^5-$C_5H_4SiMe_2$-κO)($CH_2Ph)_2$]$_2$ (1 g, 1.36 mmol) in toluene (30 mL) at ambient temperature. The solution turned dark, and a brownish red oil was deposited. The reaction mixture was stirred for 2 h, and the color of the oil and the solution became dark green. The solution was separated and the oil dried and washed with *n*-hexane (2 × 30 mL) to afford **2** as an analytically pure dark green solid (1.25 g, 80%). Anal. Calcd for $C_{53}H_{41}BF_{15}O_2Si_2Ti_2$: C, 55.0; H, 3.57. Found: C, 54.85; H, 3.87.

Synthesis of [{Ti(η^5-$C_5H_4SiMe_2$-κO)(CH_2Ph)]$_2^+$[$B(C_6F_5)_4$]$^-$ (3). A toluene (20 mL) solution of [CPh_3][$B(C_6F_5)_4$] (0.32 g, 0.35 mmol) was added to a solution of [Ti(η^5-$C_5H_4SiMe_2$-κO)($CH_2Ph)_2$]$_2$ (0.25 g, 0.34 mmol) in toluene (30 mL) at room temperature. The solution turned dark, and a brownish red oil was deposited. The reaction mixture was stirred for 2 h, and the color of the oil and the solution became dark green. The solution was separated and the oil dried and washed with *n*-hexane (2 × 30 mL) to give **3** as an analytically pure dark green solid (0.31 g, 74%). Anal. Calcd for $C_{54}H_{34}BF_{20}O_2Si_2Ti_2$: C, 50.62; H, 2.78. Found: C, 50.28; H, 2.88.

Synthesis of [{Ti(η^5-$C_5H_4SiMe_2$-κO)($CH_2Ph)_2$}$_2$(μ-Cl)]$^+$[$PhCH_2B(C_6F_5)_3$]$^-$ (4). A solution of $B(C_6F_5)_3$ (1.39 g, 2.7 mmol) in 30 mL of CH_2Cl_2 at −78 °C was added to a solution of [Ti(η^5-$C_5H_4SiMe_2$-κO)($CH_2Ph)_2$]$_2$ (2 g, 2.7 mmol) in 30 mL of dichloromethane at −78 °C. The color of the reaction mixture immediately changed to orange. The reaction was stirred at −78 °C for 1/2 h and for a further 2 h at room temperature. The volatiles were removed under vacuum to afford an orange solid, which was washed with *n*-hexane and dried under vacuum to yield 2.75 g (85%) of **4**. Anal. Calcd for $C_{53}H_{41}BClF_{15}O_2Si_2Ti_2$: C, 53.35; H, 3.47. Found: C, 54.31; H, 3.56. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 0.45, 0.46 (s, 2 × 6H, Si*Me*$_2$), 2.83 (br, 2H, BCH_2Ph), 2.95, 4.07 (AB spin system, $J_{H-H} = 6.5$ Hz, 2 × 2H, TiCH_2Ph), 5.62, 6.26, 6.41, 7.67 (ABCD spin system, 4 × 2H, C_5*H_4*), 6.63, 7.25, 7.49 (*o*-, *m*-, *p*-, 4H, 4H, 2H, TiCH$_2$*Ph*), 6.76, 6.80, 6.88 (*o*-, *m*-, *p*-, 2H, 1H, 2H, BCH$_2$*Ph*). ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ −0.5, 2.1 (Si*Me*$_2$), ~30 (br, B*C*H$_2$Ph), 79.6 (dd, $^1J_{C-H} = 149.8$ Hz, $^1J_{C-H} = 153.9$ Hz, Ti*C*H$_2$Ph), 125.4 (C_{ipso}, *Ph*CH$_2$Ti), 119.4, 119.9, 121.8, 123.47, 126.53, 127.2, 128.6, 132.5, 133.15, 133.7, 134.3, 149.2, (*C*$_5$H$_4$), (TiCH$_2$*Ph*), (BCH$_2$*Ph*), 136.1, 137.4, 148.0 (*C*$_6$F$_5$). ^{19}F NMR (470.3 MHz, CD_2Cl_2, 25 °C): δ −132.3 (m), −164.5 (m), −167.3 (m).

[{Ti(η^5-$C_5H_4SiMe_2$-κO)}($CH_2Ph)_2$]$_2$(μ-Cl)]$^+$[$B(C_6F_5)_4$]$^-$ (5). A solution of [CPh_3][$B(C_6F_5)_4$] (37.6 mg, 40.7 × 10^{-6} mol) in CD_2Cl_2 (0.5 mL) was added at ambient temperature to a solution of [Ti(η^5-$C_5H_4SiMe_2$-κO)($CH_2Ph)_2$]$_2$ (30 mg, 40.7 × 10^{-6} mol) in CD_2Cl_2 (0.5 mL). The color changed instantaneously to dark red. The total conversion into **5** is confirmed by ^{1}H NMR spectroscopy. Compound **5** shows spectroscopic behavior identical with that described for **4**.

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