# Cationic *ansa*-($\eta^5$-Cyclopentadienyl)($\eta^6$-arene) Complexes of Titanium[≠]

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The half-sandwich titanium trimethyl complex ($\eta^5$-$C_5H_4CMe_2Ar$)$TiMe_3$ (Ar = 3,5-$Me_2C_6H_3$) reacts with the Lewis acid $B(C_6F_5)_3$ to give the ionic $Ti^{IV}$ *ansa*-cyclopentadienyl-arene complex [($\eta^5$,$\eta^6$-$C_5H_4CMe_2Ar$)$TiMe_2$][$MeB(C_6F_5)_3$]. In bromobenzene solvent, addition of more $B(C_6F_5)_3$ leads to $C_6F_5$/Me exchange and, subsequently, to formation of an unusual dimeric $Ti^{III}$ dicationic species, {[($\eta^5$,$\eta^6$-$C_5H_4CMe_2Ar$)Ti($\mu$-Br)]$_2$}[$B(C_6F_5)_4$]$_2$, which was structurally characterized. Its formation involves reduction of the transition-metal center, solvent C–Br cleavage and perfluoroaryl-group scrambling.

## Introduction

Cationic titanium half-sandwich (mono-cyclopentadienyl) species show interesting catalytic activity, especially in the syndiotactic polymerization of styrene[1] and the polymerization of propene to high molecular weight atactic polypropene.[2] There has been some debate in the literature about the nature of the actual active species in these systems, e.g. whether $Ti^{IV}$ or $Ti^{III}$ species are involved, or both.[3] As the cationic species [($\eta^5$-$C_5R_5$)$TiMe_2$]$^+$ are highly electron-deficient we sought ways of stabilizing these, without resorting to strong heteroatom-based Lewis basic moieties, in order to study their reactive properties. Baird et al. found that [($\eta^5$-$C_5Me_5$)$MMe_2$]$^+$ cations (M = Ti, Zr, Hf) can bind arenes reversibly,[4] and that this interaction is significantly stronger for Zr and Hf (for which a related crystal structure has been reported[5]) than for Ti. We thus set out to prepare half-sandwich titanium complexes with benzyl-substituted Cp-ligands to use these interactions in an intramolecular fashion. The feasibility of this was suggested by observations of Chien, Rausch et al. on the [$\eta^5$-$C_5Me_4(CH_2CH_2Ph)$]$TiMe_3$ + [$Ph_3C$][$B(C_6F_5)_4$] system, where NMR evidence was obtained for $\eta^6$-coordination of the arene moiety in the thermally labile cationic dimethyl species.[6] In this contribution we describe the synthesis of neutral and cationic titanium complexes with the benzyl-substituted cyclopentadienyl ligand [$C_5H_4CMe_2Ar$]$^-$ (Ar = 3,5-dimethylphenyl).

The cationic *ansa*-cyclopentadienyl-arene complex [($\eta^5$,$\eta^6$-$C_5H_4CMe_2Ar$)$TiMe_2$][$MeB(C_6F_5)_3$] was found to be quite stable in bromobenzene solution at ambient temperature, but it reacts with the Lewis acid $B(C_6F_5)_3$ via Me/$C_6F_5$ scrambling. This species subsequently undergoes a highly unusual transformation, resulting in a dicationic dimeric $Ti^{III}$ complex. The crystal structure of this product represents the first structural characterization of an *ansa*-cyclopentadienyl-arene early transition-metal compound.

## Results and Discussion

The synthesis of the benzyl-cyclopentadienyl salt Li[$C_5H_4CMe_2Ar$] (Ar = 3,5-dimethylphenyl) is straightforward, proceeding through addition of ArLi (obtained from ArBr and *n*BuLi) to 6,6-dimethylfulvene, analogous to the preparation of Li[$C_5H_4CMe_2Ph$].[7] The 3,5-(dimethyl)-phenyl group was chosen initially to provide a stronger donor interaction (in [Cp*$MMe_2$(arene)]$^+$ toluene is more strongly bound than benzene[4]) and to make arene cyclometallation[8] less favorable. Reaction of this Li salt with $TiCl_4$ in dichloromethane afforded ($C_5H_4CMe_2Ar$)$TiCl_3$, which was methylated in benzene solvent using $Me_2Mg$(dioxane) to give the trimethyl derivative ($C_5H_4CMe_2Ar$)$TiMe_3$ (**1**).

In [$D_2$]-1,1,2,2-tetrachloroethane or [$D_5$]bromobenzene solvent, **1** reacts with 1 equiv. of the Lewis acid $B(C_6F_5)_3$ to give deep red solutions of a species that was identified by 1D and 2D NMR techniques as the ionic *ansa*-cyclopentadienyl-arene complex [($\eta^5$,$\eta^6$-$C_5H_4CMe_2Ar$)$TiMe_2$][$MeB(C_6F_5)_3$] (**2**, Scheme 1).

The resonances for the [$MeB(C_6F_5)_3$]$^-$ anion are consistent with those for a noncoordinated anion,[9] and the resonances for the arene moiety show substantial coordination chemical shifts (downfield for *o*-C and *p*-C, upfield for *m*-C; the *o*-H proton resonances are found upfield shifted at $\delta = 5.91$). The chemical shift difference between the two sets of Cp protons also increases strongly ($\Delta\delta = 1.59$ in **2** and 0.14 in **1**). Compound **2** is a 16-electron complex and does not readily react with propene or styrene at ambient temperature (as seen from NMR-tube-scale experiments). This suggests that the arene moiety is fairly strongly bound. Addition of a drop of [$D_8$]THF to a $C_6D_5Br$ solution of **2** shows a shift of the Cp and aryl proton resonances back to

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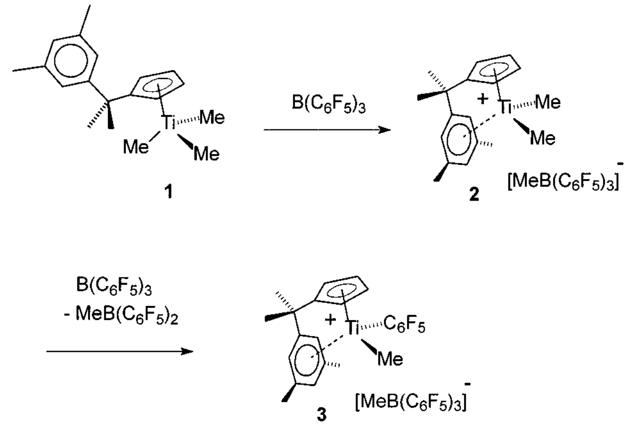

Scheme 1. Generation of the cationic species **2** and **3**

"normal" chemical shift ranges, indicating release of the arene moiety in the presence of a hard Lewis base to give a $[(\eta^5\text{-}C_5H_4CMe_2Ar)TiMe_2(THF)_x][MeB(C_6F_5)_3]$ species. Compound **2** is reasonably stable in $C_2D_2Cl_4$ or [D$_5$]bromobenzene and only very gradually decomposes at ambient temperature. Solutions of **2**, prepared in situ in [D$_5$]bromobenzene, produced a few deep brown-green crystals upon standing at ambient temperatures for several days (vide infra).

The presence of one equivalent of excess $B(C_6F_5)_3$ in bromobenzene solutions of **2** resulted in a reaction (complete in about 20–24 h at ambient temperature) forming $MeB(C_6F_5)_2$[10] and an organometallic species that, based on NMR spectroscopy, was identified as the mixed methyl/perfluoroaryl species $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ar)Ti(C_6F_5)Me][MeB(C_6F_5)_3]$ (**3**, Scheme 1). The $^{19}$F NMR spectrum shows a $C_6F_5$ group with a downfield shifted *o*-F resonance, and the $^{13}$C NMR spectrum a triplet with $^3J_{CF} = 7.3$ Hz at $\delta = 102.7$ for the Ti–Me group. These features are consistent with a $Ti(Me)(C_6F_5)$ species.[11] The $^1$H NMR resonances of **3** are broad at ambient temperature, but at –30 °C they reveal an asymmetric structure, and the retention of the $\eta^5,\eta^6$-coordination mode of the ancillary ligand. Thus the addition of an extra equivalent of the Lewis acid induces a scrambling of Ti-bound and B-bound hydrocarbyl groups. Upon standing at ambient temperature the solution produces brown-green crystals that (based on lattice parameters) are identical to those that are (more slowly) formed in solutions of **2**.

An X-ray structure determination showed that these crystals are of the salt $\{[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ar)Ti(\mu\text{-}Br)]_2\}[B(C_6F_5)_4]_2$ (**4**, Figure 1).

In this compound a dicationic dimeric Ti$^{III}$ *ansa*-cyclopentadienyl-arene bromide complex is complemented by two tetrakis(pentafluorophenyl)borate anions. The dication is centrosymmetric, with nearly equivalent Ti–Br bond lengths in the Ti($\mu$-Br)$_2$Ti bridge. The Ti–Br distances are, on average, 0.085 Å shorter than in the isoelectronic neutral $[(C_5H_4Me)_2Ti(\mu\text{-}Br)]_2$ complex[12] and this, combined with the wider Br–Ti–Br' angle, results in a Ti···Ti distance of 3.7858(9) Å in **4** that is 0.34 Å shorter than in the latter compound. The bend angle of the Cp-arene ligand backbone, C(5)–C(6)–C(7), is quite acute at 95.8(3)°, and the Cp(centroid)–Ti–Ar(centroid) angle is 125.0°. The arene ring does not deviate significantly from planarity, but the bonding to the Ti atom is highly asymmetric, with Ti–C(7), Ti–C(8) and Ti–C(12) being much shorter than the Ti–C(9), –C(10) and –C(11) distances. This results in a slight lengthening of the C(7)–C(8) and C(7)–C(12) bonds relative to the other arene C–C bonds.

The formation of compound **4** is remarkable for at least two reasons: a) the reaction of a Ti$^{IV}$ cation with a Lewis acid in a halogenated solvent yields a Ti$^{III}$ halide species, and b) starting from a cation with the $[MeB(C_6F_5)_3]^-$ counterion, a product is formed with $[B(C_6F_5)_4]^-$ counterions. This indicates that the reaction involves a reduction of the

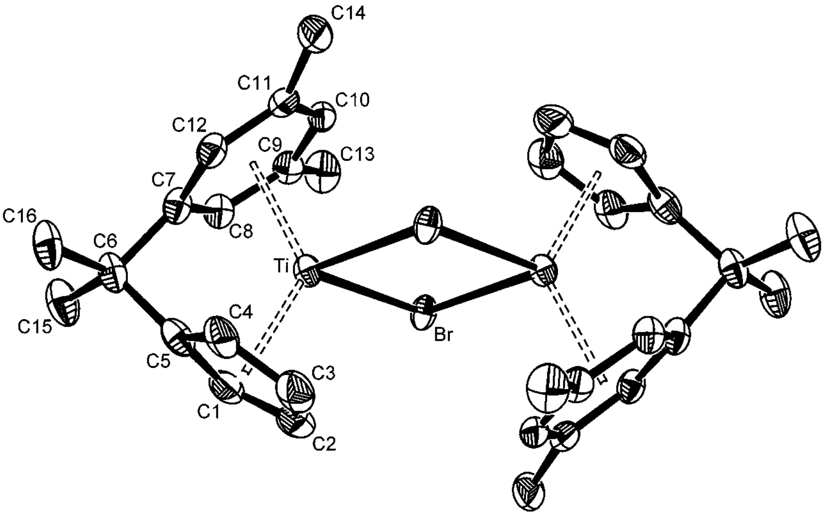

Figure 1. ORTEP diagram of the molecular structure of the cationic part of **4**; hydrogen atoms are omitted for clarity; selected interatomic distances [Å] and angles [°]: Ti–Br 2.6250(7), Ti–Br' 2.6334(7), Ti–C(1) 2.341(4), Ti–C(2) 2.410(5), Ti–C(3) 2.383(5), Ti–C(4) 2.313(4), Ti–C(5) 2.323(3), Ti–C(7) 2.379(3), Ti–C(8) 2.473(4), Ti–C(9) 2.674(4), Ti–C(10) 2.725(3), Ti–C(11) 2.713(4), Ti–C(12) 2.470(4), C(7)–C(8) 1.419(6), C(8)–C(9) 1.393(5), C(9)–C(10) 1.393(6), C(10)–C(11) 1.394(6), C(11)–C(12) 1.395(5), C(7)–C(12) 1.410(6); Br–Ti–Br' 87.90(2), Ti–Br–Ti' 92.10(2), C(5)–C(6)–C(7) 95.8(3), C(15)–C(6)–C(16) 107.6(3)

metal center, cleavage of the solvent C–Br bond, and a scrambling of the substituents on the borane/borate species. In $C_6D_5Br$ solvent, formation of $CH_3C_6D_5$ is seen (GC/MS). The isolated yield of **4** is rather low (18%) and precise reactive pathways in this transformation are, as yet, unclear, but the observations made so far are of interest. For instance, they may shed some light on the way in which $Ti^{III}$ centers can be generated by the reaction of $Ti^{IV}$ alkyls with an excess of Lewis acid activator (note that Grassi et al. use chlorobenzene as solvent for their ESR experiments with $Cp^*TiMe_3$ and Lewis acids[3b]). It also demonstrates the dynamic nature of perfluoroarylborate "weakly coordinating" anions, in which tetraarylborates may be formed from alkyltriarylborates (an interesting contrast to the aryl abstraction from the $[B(C_6F_5)_4]^-$ anion, recently reported by Bochmann et al.[13]).

In conclusion, we have observed the formation of a cationic *ansa*-Cp-arene titanium dimethyl species, hydrocarbyl ligand scrambling on this species induced by the presence of excess Lewis acid, and a highly unusual degradation of a cationic $Ti^{IV}$ species in bromobenzene to produce a $Ti^{III}$ complex, the first structurally characterized *ansa*-Cp-arene early transition-metal derivative. These observations provide an interesting insight into the possible activation and degradation processes in titanium-based half-sandwich olefin polymerization catalysts, and we are presently studying related hemilabile monocyclopentadienyl $Ti^{IV}$ species to increase our understanding of this chemistry.

## Experimental Section

**General:** All experiments were performed under a nitrogen atmosphere with standard Schlenk and glove-box techniques. Deuterated solvents (Aldrich, Acros) were either degassed and dried over molecular sieves ($C_2D_2Cl_4$, $C_6D_5Br$, $CD_2Cl_2$) or dried over Na/K alloy and vacuum transferred before use. Dichloromethane was distilled from $P_2O_5$, $C_6H_5Br$ from Ca chips, other solvents were distilled from Na/K alloy or Na (toluene) before use. – NMR spectra were recorded on Varian Gemini 200/300, Inova 400 and Unity 500 spectrometers. The $^1$H-NMR spectra were referenced to resonances of residual protons in the deuterated solvents. Chemical shifts ($\delta$) are given relative to tetramethylsilane (downfield shifts are positive). $Li[C_5H_4CMe_2Ar]$ (Ar = 3,5-dimethylphenyl) was prepared analogously to the derivative with Ar = Ph[7] using 3,5-dimethylphenyllithium prepared in hexane from the corresponding aryl bromide and *n*BuLi. 6,6-Dimethylfulvene and 5-bromo-3-methyltoluene (Aldrich) were used as purchased.

**Preparation of ($\eta^5$-$C_5H_4CMe_2Ar$)$TiCl_3$:** To a stirred solution of $TiCl_4$ (1.0 g, 5.3 mmol) in 20 mL of dichloromethane, cooled at –40 °C, was added solid $Li[C_5H_4CMe_2Ar]$ (1.16 g, 5.3 mmol). The red suspension was warmed to room temperature and stirred for 16 h. The salts were separated by centrifugation and subsequent decanting. The solvent was removed in vacuo from the supernatant, and the resulting red-brown oil was extracted with pentane. Cooling the extract to –40 °C yielded orange crystals of the title compound. Yield: 1.28 g (3.50 mmol, 66%). – $^1$H NMR ([D$_6$]benzene): $\delta$ = 6.69 (s, 2 H, *o-H*), 6.66 (s, 1 H, *p-H*), 6.37 (ps. t, 2 H, Cp), 6.03 (ps. t, 2 H, Cp), 2.10 (s, 6 H, Ar–$CH_3$), 1.63 [s, 6 H, $C(CH_3)_2$]. – $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 158.0 (Ar $C_{ipso}$), 149.8 (Cp $C_{ipso}$), 140.2 (Ar *m-C*), 130.3 (Ar *p-C*H), 126.5 (Cp *C*H), 126.0 (Ar *o-C*H), 124.5 (Cp *C*H), 43.1 (*C*Me$_2$), 30.8 [$C(CH_3)_2$], 23.4 (Ar–$CH_3$). – $C_{16}H_{19}Cl_3Ti$ (365.6): calcd. C 52.57, H 5.24, Cl 29.09, Ti 13.10; found C 52.42, H 5.32, Cl 28.91, Ti 12.85.

**Preparation of ($\eta^5$-$C_5H_4CMe_2Ar$)$TiMe_3$ (1):** To a solution of ($C_5H_4CMe_2Ar$)$TiCl_3$ (0.95 g, 2.6 mmol) in 15 mL of benzene was added $Me_2Mg(dioxane)_{0.5}$ (1.86 g, 4.0 mmol). The suspension was stirred at ambient temperature while the color changed gradually from red to yellow. The mixture was centrifuged and the salts were separated by decantation. The solvent was removed in vacuo, and the residue extracted with pentane. Evaporation of the solvent yielded **1** as a yellow oil that solidified on standing. The compound is very soluble in pentane, but may be crystallized from this solvent at low temperature to yield analytically pure material. – $^1$H NMR ([D$_6$]benzene): $\delta$ = 6.94 (s, 2 H, *o-H*), 6.69 (s, 1 H, *p-H*), 5.95 (ps. t, 2 H, Cp), 5.81 (ps. t, 2 H, Cp), 2.15 (s, 6 H, Ar–$CH_3$), 1.45 [s, 6 H, $C(CH_3)_2$], 1.31 (s, 9 H, Ti–$CH_3$) . – $^{13}$C NMR ([D$_6$]benzene): $\delta$ = 150.3 (s, Ar $C_{ipso}$), 144.7 (s, Cp $C_{ipso}$), 137.4 (s, Ar *m-C*), 129 (Ar *p-C*H, part. overlapped by solvent), 124.3 (d, $J_{CH}$ = 149 Hz, Ar *o-C*H), 114.0 (d, $J_{CH}$ = 167 Hz, Cp *C*H), 109.5 (d, $J_{CH}$ = 171 Hz, Cp *C*H), 63.0 (q, $J_{CH}$ = 120 Hz, Ti-$CH_3$), 39.7 (s, *C*Me$_2$), 29.6 [q, $J_{CH}$ = 132 Hz, $C(CH_3)_2$], 21.6 (q, $J_{CH}$ = 121 Hz, Ar–$CH_3$). – $C_{19}H_{28}Ti$ (304.3): calcd. C 74.99, H 9.27, Ti 15.73; found C 74.80, H 9.29, Ti 15.50.

**Generation of [($\eta^5$,$\eta^6$-$C_5H_4CMe_2Ar$)$TiMe_2$][$MeB(C_6F_5)_3$] (2):** A solution of **1** (13.5 mg, 44.3 μmol) in 0.25 mL of $C_2D_2Cl_4$ was added to a solution of $B(C_6F_5)_3$ (22.7 mg, 44.3 μmol) in 0.25 mL of $C_2D_2Cl_4$ to give a deep red solution of **2**. The reaction proceeds in a similar fashion in $C_6D_5Br$ solvent. – $^1$H NMR ($C_6D_5Br$): $\delta$ = 7.02 (s, 1 H, *p-H*), 6.74 (ps. t, 2 H, Cp), 5.91 (s, 2 H, *o-H*), 5.15 (ps. t, 2 H, Cp), 2.10 (s, 6 H, Ar–$CH_3$), 1.07 [6 H, $C(CH_3)_2$, + 3 H B–$CH_3$], 0.34 (s, 6 H, Ti–$CH_3$). – $^{13}$C NMR ($C_2D_2Cl_4$, –40 °C): $\delta$ = 155.2 (s, Ar $C_{ipso}$), 151.2 (d, $J_{CF}$ = 236 Hz, *o-C*F), 140.3 (d, $J_{CF}$ = 236 Hz, *p-C*F), 139.2 (d, $J_{CF}$ = 236 Hz, *m-C*F), 138.0 (s, Cp $C_{ipso}$), 135.3 (d, $J_{CH}$ = 166 Hz, Ar *p-C*H), 131.4 (br, $C_6F_5$ $C_{ipso}$), 128.2 (d, $J_{CH}$ = 186 Hz, Ar *o-C*H), 125.3 (d, $J_{CH}$ = 166 Hz, Cp *C*H), 123.4 (s, Ar *m-C*), 115.9 (d, $J_{CH}$ = 172 Hz, Cp *C*H), 74.4 (q, $J_{CH}$ = 126 Hz, Ti–$CH_3$), 43.9 (s, *C*Me$_2$), 25.8 [q, $J_{CH}$ = 130 Hz, $C(CH_3)_2$], 21.6 (q, $J_{CH}$ = 126 Hz, Ar–$CH_3$), 13.5 (br, B–$CH_3$). – $^{19}$F NMR ($C_2D_2Cl_4$): $\delta$ = –132.8 (*o-F*), –164.1 (*p-F*), –166.7 (*m-F*).

**Reaction of 2 with [D$_8$]THF:** To a deep red solution of **2** in $C_6D_5Br$, prepared as described above, was added a drop of [D$_8$]THF, resulting in a red solution of [($\eta^5$-$C_5H_4CMe_2Ar$)$TiMe_2(THF)_n$][$MeB(C_6F_5)_3$]. – $^1$H NMR ($C_6D_5Br$/[D$_8$]THF): $\delta$ = 6.72 (s, 2 H, *o-H*), 6.66 (s, 1 H, *p-H*), 6.14 (ps. t, 2 H, Cp), 6.04 (ps. t, 2 H, Cp), 2.14 (s, 6 H, Ar–$CH_3$), 1.37 [6 H, $C(CH_3)_2$ + 6 H, Ti–$CH_3$], 1.04 (br, 3 H, B–$CH_3$).

**Reaction of 2 with $B(C_6F_5)_3$:** In an NMR tube with a Teflon (Young) valve, a solution of **2** was prepared as described above, but using two equivalents of $B(C_6F_5)_3$ per Ti. The tube was allowed to stand at ambient temperature, and was monitored at regular intervals by $^1$H and $^{19}$F NMR. After 24 h all of **2** had disappeared, giving **3** and $MeB(C_6F_5)_2$.

**3:** $^1$H NMR ($C_6D_5Br$, –30 °C): $\delta$ = 6.85 and 6.80 (br, 1 H each, Cp), 6.71 (s, 1 H, *p*-H), 5.96 and 5.74 (s, 1 H each, *o-H*), 5.66 and 5.53 (br, 1 H each, Cp), 2.11 and 1.38 (s, 3 H each, Ar–$CH_3$), 1.13–1.09 [total 9 H, $C(CH_3)_2$ + Ti–$CH_3$]. – $^{13}C\{^1H\}$ NMR ($C_6D_5Br$, –30 °C): $\delta$ = 102.7 (t, $^3J_{CF}$ = 7.3 Hz, Ti–$CH_3$), 40.5 [*C*($CH_3)_2$], 22.2 [$C(CH_3)_2$], 20.2, 21.0 (Ar–$CH_3$), aromatic resonances poorly resolved. – $^{19}$F NMR ($C_6D_5Br$, –30 °C): $\delta$ = –114.3 (*o*-F, Ti–Ar), –

132.9 (*o*-F, B–Ar), –149.9 (*p*-F, Ti–Ar), –159.5 (*m*-F, Ti–Ar), –164.7 (*p*-F, B–Ar), –167.3 (*m*-F, B–Ar).

**$MeB(C_6F_5)_2$:** $^1H$ NMR ($C_6D_5Br$, 20 °C): $\delta = 1.52$ (quint., $^5J_{HF} = 2$ Hz, B–Me). – $^{19}F$ NMR ($C_6D_5Br$, –30 °C): $\delta = -129.9$ (*o*-F), –147.5 (*p*-F), –161.5 (*m*-F).

**Formation of $\{[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ar)Ti(\mu\text{-}Br)]_2\}[B(C_6F_5)_4]_2$ (4):** A solution of **1** (0.120 g, 0.39 mmol) in 5 mL of bromobenzene was added to $B(C_6F_5)_3$ (0.40 g, 0.78 mmol). Over a period of 3 weeks at ambient temperature green-brown crystals separated from the solution. The supernatant was decanted and the crystals rinsed twice with 10 mL of pentane. Yield: 0.070 g (34 µmol, 18%) of analytically pure **4**. – $C_{80}H_{38}B_2Br_2F_{40}Ti_2$ (2036.3): calcd. C 47.19, H 1.88, Ti 4.70; found C 47.03, H 2.22, Ti 4.58.

**Crystal Structure Analysis of 4:** Enraf–Nonius CAD4-F diffractometer, Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å), $T = 130$ K; monoclinic, $P2_1/n$, $a = 13.616(2)$, $b = 16.014(1)$, $c = 17.702(2)$ Å, $\beta = 109.01(1)$, $V = 3649.4(7)$ Å$^3$, $Z = 2$, $D_x = 1.853$ g cm$^{-3}$, $\mu = 14.7$ cm$^{-1}$. The structure was solved by direct methods. A final refinement on $F^2$ converged at $wR(F^2) = 0.1143$ for 7118 reflections with $F_o^2 \geq 0$ and $R(F) = 0.0415$ for 5390 reflections with $F_o \geq 4\sigma(F_o)$ and 644 parameters.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135683. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

**Note Added in Proof (February 28, 2000):** During the processing of this contribution a paper was published describing the generation and NMR-spectroscopic characterization (in $CD_2Cl_2$ solvent at –60 °C) of the cation $[\eta^5,\eta^6\text{-}C_5H_4CMe_2Ph)TiMe_2]^+$.[14]

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