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Figure 2. Structure of the cation of **3**. Thermal ellipsoids are at 50% level. Selected bond lengths and angles: Ti(1)–F(1) = 2.151(2) Å, F(1)–C(21) = 1.402(3) Å, Ti(1)–F(1)–C(21) = 168.2(2)°.

Ti(III) complex $\text{Cp}^*[\text{C}_5\text{Me}_4\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$ with intramolecular C–F bond coordination (2.406 Å).¹⁶ The F–C distance of the coordinated fluorobenzene of 1.402(3) Å is elongated relative to the C–F distance in solid fluorobenzene, 1.364(2) Å.¹⁷ The Ti–F–C(21) angle of 168.2(2)° is very obtuse compared to the M–X–C angles in other η^1 -halobenzene transition-metal complexes (X = Br, I; 101.8–116.4°).¹⁸ The fluorobenzene in **3** appears to be relatively weakly bound and is readily displaced by more strongly coordinating ligands such as diethyl ether or THF.

The fluorobenzene adduct **3** is stable at ambient temperature in fluorobenzene solution for more than 5 days. In contrast, addition of α,α,α -trifluorotoluene to such a solution results in a rapid reaction, yielding $\text{Cp}^*_2\text{TiF}_2$ and 1,2-diphenyl-1,1,2,2-tetrafluoroethane as main products (together with products resulting from concomitant anion degradation). Thus, it appears that benzylic fluorides are much more rapidly activated by the Cp^*_2Ti cation than aryl fluorides. This has implications for the compatibility of this cation with fluorinated borate anions, as suggested by the following observations. Reaction of Cp^*_2TiMe with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ in fluorobenzene yields (after evaporation of the solvent, and washing with pentane) a brown solid that dissolves in THF-*d*₈ to give $[\text{Cp}^*_2\text{Ti}(\text{THF-}d_8)][\text{B}(\text{C}_6\text{F}_5)_4]$. No evidence was found for coordination of fluorobenzene to the metal center in $[\text{Cp}^*_2\text{Ti}][\text{B}(\text{C}_6\text{F}_5)_4]$, suggesting that in this compound the anion coordinates to the Ti center through one or two of its fluorides, without subsequent C–F activation. In contrast, reaction of Cp^*_2TiMe with $[\text{PhNMe}_2\text{H}][\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$ in fluorobenzene yields $\text{Cp}^*_2\text{TiF}_2$ as the organometallic product, similar to the reaction of **1** with α,α,α -trifluorotoluene. When the reaction was performed in neat THF-*d*₈, clean conversion to the THF adduct $[\text{Cp}^*_2\text{Ti}(\text{THF-}d_8)][\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$ was observed.

In conclusion, we have prepared a salt of the permethyl titanocene cation that exhibits unique structural features, containing a Cp^* ligand with two C–H···Ti agostic interactions. This cation reversibly coordinates the fluorine atom of fluorobenzene, but readily cleaves benzylic C–F bonds. Presently we are investigating the effect of the metal electronic configuration on the coordination and reactivity behavior of metallocene cations, aiming to increase the understanding of the properties of highly reactive electrophilic transition-metal species that are increasingly used in catalysis, and to provide more insight into possible catalyst deactivation pathways.

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Supporting Information Available: Synthesis and characterization data of the complexes described (PDF). Crystallographic data for **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Details on the structure determination of **2** can be found in the Supporting Information.
- (8) Crystal data for **1**. $\text{C}_{20}\text{H}_{30}\text{Ti} \cdot \text{C}_{24}\text{H}_{20}\text{B}$, $M_r = 637.56$, triclinic, *P*-1, $a = 13.3636(7)$ Å, $b = 15.0600(7)$ Å, $c = 17.7873(9)$ Å, $\alpha = 97.131(1)^\circ$, $\beta = 90.604(1)^\circ$, $\gamma = 91.970(1)^\circ$, $V = 3549.6(3)$ Å³, $Z = 4$, $D_c = 1.193$ g cm⁻³, $T = 100(1)$ K, $\mu(\text{Mo K}\alpha) = 0.71073$ Å. All H-atoms were located and refined freely; $wR(F^2) = 0.1265$ for 12451 reflections and 1229 parameters, $R(F) = 0.0532$ for 7628 reflections with $F_o \geq 4.0 \sigma(F_o)$. The unit cell contains two independent formula units that do not differ significantly in structure. Geometrical data given in the text pertain only to one of these units.
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- (15) Crystal data for **3**. $\text{C}_{26}\text{H}_{35}\text{FTi} \cdot \text{C}_{24}\text{H}_{20}\text{B} \cdot \text{C}_6\text{H}_5\text{F}$, $M_r = 829.79$, triclinic, *P*-1, $a = 11.992(1)$ Å, $b = 13.649(2)$ Å, $c = 14.883(1)$ Å, $\alpha = 90.95(1)^\circ$, $\beta = 109.499(8)^\circ$, $\gamma = 90.865(9)^\circ$, $V = 2295.5(4)$ Å³, $Z = 2$, $D_c = 1.200$ g cm⁻³, $T = 130(1)$ K, $\mu(\text{Mo K}\alpha) = 0.71073$ Å; $wR(F^2) = 0.1407$ for 9284 reflections and 568 parameters, $R(F) = 0.0536$ for 8148 reflections with $F_o \geq 4.0 \sigma(F_o)$.
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