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Structure of the Decamethyl Titanocene Cation, a Metallocene with Two Agostic C−H Bonds, and Its Interaction with Fluorocarbons[†]

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Cationic transition-metal complexes find wide application as catalysts for a range of chemical transformations and in particular in the catalytic polymerization of olefins.[1] The interaction of the electron-deficient, cationic metal center with the complementary anion can greatly affect catalyst performance, and to minimize interference with the catalytically active species, anions are used with very weakly coordinating properties.[2] These counterions frequently employ fluoroorganic moieties to reduce Coulombic interactions by dissipating the negative charge and to minimize the nucleophilicity. Nevertheless, they can sometimes participate in catalyst deactivation processes.[3] We are studying the various aspects of anion coordination and activation by investigating the complexation and reactivity behavior of some simple cationic organo transition-metal complexes toward fluorinated hydrocarbons and fluorinated anions. Here we describe the salt of the "naked" Ti(III) permethyl titanocene cation $[Cp^*_2Ti][BPh_4]$ (**1**) ($Cp^* = \eta^5\text{-}C_5Me_5$), with an unprecedented structure, and its reactivity with fluorinated aromatic substrates. Results include the first structural characterization of a transition-metal η^1-fluorobenzene adduct.

The compound $[Cp^*_2Ti][BPh_4]$ (**1**) was synthesized via two routes (Scheme 1). One is the reaction of Cp^*_2TiH [4] with $[Cp_2Fe][BPh_4]$ in toluene, yielding **1**, ferrocene, and 0.5 equiv of H_2. The other is the reaction of Cp^*_2TiMe[5] with $[PhNMe_2H][BPh_4]$ in toluene, yielding **1**, free *N*,*N*-dimethylaniline, and 1 equiv of CH_4. Compound **1** cleanly reacts with THF to give the mono-THF adduct $[Cp^*_2Ti(THF)][BPh_4]$ (**2**, Scheme 1),[6] which was structurally characterized.[7] A single-crystal structure determination[8] of **1** showed that it consists of discrete $[Cp^*_2Ti]^+$ and $[BPh_4]^-$ ions without direct interionic contacts.[9] The cation (Figure 1) contains one normal η^5-Cp* ligand and one that has two methyl C−H···Ti agostic interactions, one each on two adjacent methyl groups: Ti···H(119″) = 2.16(3) Å, Ti···H(120′) = 2.20(3) Å. The agostic Cp* ligand is slipped back, resulting in Ti−C(114/115) distances that are much shorter than the other Ti−C(ring) distances. Nevertheless, the intraligand ring C−C and C(ring)−C(Me) distances are all normal for a Cp* ligand. The agostic methyl groups are bent down by 24° toward the metal center out of the Cp-plane. It is interesting to compare the structure of **1** with that of a neutral Ti complex with a tetramethyl-phenyl-substituted cyclopentadienyl ligand that has been doubly deprotonated on adjacent methyl groups, $(\eta^5\text{-}C_5Me_4Ph)[\eta^4{:}\eta^3\text{-}C_5Me_2Ph(CH_2)_2]Ti$.[10] In this compound, there is a clear elongation in the ring C−C distances connecting the "diene" and "allyl" moieties of the ligand, the $C-CH_2$ distances of 1.439(4) and 1.447(4) Å are shorter than the $C-CH_3$ distances to the agostic methyl groups in **1** (1.486(5) and 1.502(5) Å), and the $Ti-CH_2$ distances of 2.252(3) and 2.316(4) Å are much shorter than the $Ti\cdots CH_3$ distances in **1** of 2.685(5) and 2.652(4) Å. The cation in **1** adopts a bent rather than a linear metallocene geometry, in contrast to neutral titanocenes.[11] Calculations on the Cp_2M^+ (M = Sc, La) system indicated that these cationic metallocenes prefer a bent structure.[12] The bonding of the doubly agostic Cp* ligand in **1** thus far appears to be quite unique. Although **1** is highly reactive (vide infra), it is apparently reluctant to form dinitrogen complexes, unlike the neutral Ti(II) Cp^*_2Ti[13] and Ti(III) $Cp_2Ti(aryl)$[14] species. The synthesis of **1**, as described above, is performed under a nitrogen atmosphere, and cooling powdered samples under nitrogen to −196 °C does not lead to a visible color change that could indicate N_2 complexation.

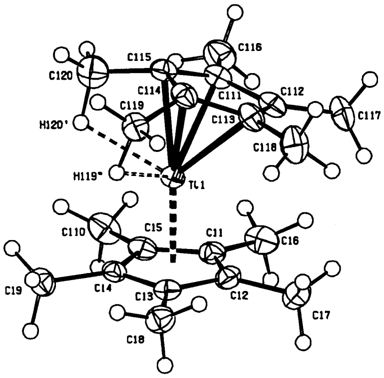
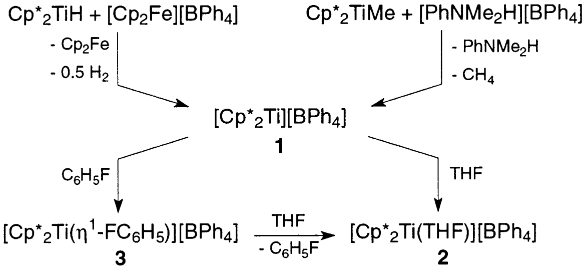


Figure 1. Structure of the cation of **1**. Thermal ellipsoids are at 50% level. Selected bond lengths: Ti(1)−C(111) = 2.352(3) Å, Ti(1)−C(112) = 2.471(3) Å, Ti(1)−C(113) = 2.353(3) Å, Ti(1)−C(114) = 2.159(3) Å, Ti(1)−C(115) = 2.167(3) Å.

Scheme 1



When dissolved or generated in fluorobenzene, **1** forms a green fluorobenzene adduct $[Cp^*_2Ti(\eta^1\text{-}FC_6H_5)][BPh_4]$ (**3**, Scheme 1) that was structurally characterized.[15] Its structure (Figure 2) reveals a normal bent metallocene geometry and η^1-coordination of the fluorobenzene to the metal via the fluorine atom. The Ti−F bond of 2.151(2) Å is relatively short compared to that in the zwitterionic

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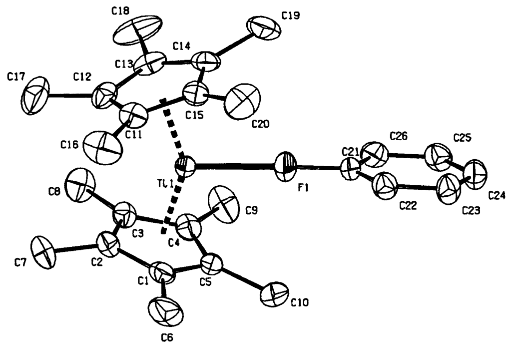

Figure 2. Structure of the cation of **3**. Thermal ellipsoids are at 50% level. Selected bond lengths and angles: Ti(1)−F(1) = 2.151(2) Å, F(1)−C(21) = 1.402(3) Å, Ti(1)−F(1)−C(21) = 168.2(2)°.

Ti(III) complex $Cp^*[C_5Me_4CH_2B(C_6F_5)_3]Ti$ 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 $Cp^*_2TiF_2$ 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 $[PhNMe_2H][B(C_6F_5)_4]$ in fluorobenzene yields (after evaporation of the solvent, and washing with pentane) a brown solid that dissolves in THF-d_8 to give $[Cp^*_2Ti(THF\text{-}d_8)][B(C_6F_5)_4]$. No evidence was found for coordination of fluorobenzene to the metal center in $[Cp^*_2Ti][B(C_6F_5)_4]$, 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 $[PhNMe_2H][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ in fluorobenzene yields $Cp^*_2TiF_2$ 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 $[Cp^*_2Ti(THF\text{-}d_8)][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ 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**. $C_{20}H_{30}Ti.\ C_{24}H_{20}B$, $M_r = 637.56$, triclinic, P-1, $a = 13.3636(7)$ Å, $b = 15.0600(7)$ Å, $c = 17.7873(9)$ Å, $\alpha = 97.131(1)°$, $\beta = 90.604(1)°$, $\gamma = 91.970(1)°$, V = 3549.6(3) Å^3, $Z = 4$, $D_c = 1.193$ g cm^{-3}, $T = 100(1)$ K, μ(Mo Kα) = 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**. $C_{26}H_{35}FTi{\cdot}C_{24}H_{20}B{\cdot}C_6H_5F$, $M_r = 829.79$, triclinic, P-1, $a = 11.992(1)$ Å, $b = 13.649(2)$ Å, $c = 14.883(1)$ Å, $\alpha = 90.95(1)°$, $\beta = 109.499(8)°$, $\gamma = 90.865(9)°$, $V = 2295.5(4)$ Å3, $Z = 2$, $D_c = 1.200$ g cm^{-3}, $T = 130(1)$ K, μ(Mo Kα) = 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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