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Notes

Crystal Structure of (Pentamethylcyclopentadienyl)-(π-η^5:σ-η^1-tetramethylfulvene)titanium(III)

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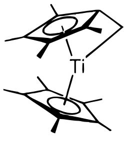
*Summary: The crystal structure of the paramagnetic derivative (pentamethylcyclopentadienyl)(tetramethylfulvene)titanium(III) (Cp*FvTi) is reported. The structural data confirm the previously surmised π-η^5:σ-η^1 bonding mode for the tetramethylfulvene ligand.*

The chemistry of organometallic bis(pentamethylcyclopentadienyl)titanium derivatives has unfolded gradually over the past 20 years. Through the pioneering work of Brintzinger *et al.*[1] and Bercaw,[2] and extensive elegant studies by Teuben *et al.*,[3,4] a clearer picture of the complex chemistry of these $Cp^*_2TiR_n$ (R = H, alkyl; $n = 0-2$) derivatives has emerged. The "deceptively simple"[3] thermal transformations of these compounds is complicated by the availability of three stable oxidation states and the paramagnetism of the Ti(II) and Ti(III) derivatives present.

Scheme 1 summarizes some of the chemistry known about these systems; the intimate details of individual steps in the scheme are understood to varying degrees of sophistication. As is readily apparent, many of the processes lead to a Ti(III) product formulated as $(C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)Ti$ (Cp*FvTi), which is one of the more thermodynamically stable compounds in this system. For example, Cp^*_2TiR derivatives are entropically unstable[5] toward elimination of RH to form Cp*FvTi, a process which occurs directly or is autocatalyzed when small amounts of Cp^*_2TiH are generated. Titanium(IV) derivatives also decompose to "tuck-in" complexes containing the Fv ligand;[6] the derivative Cp*FvTi(H) spontaneously loses H_2 upon heating to again produce Cp*FvTi. The general formulation of this species as Cp*FvTi is based on magnetic,[2] spectroscopic,[3] and thermochemical data,[6] as well as chemical derivatization.[7] While there is little doubt as to the composition of the compound, the precise details of its structure have, to our knowledge, not been reported.

We serendipitously obtained crystals of Cp*FvTi from samples of the Ti(III) tri-*n*-butylstannyl complex $Cp^*_2TiSnBu_3$. In connection with other studies,[8] we obtained this compound as a viscous purple oil via a σ-bond metathesis reaction between Cp^*_2TiR (R = H or CH_3) and tributylstannane. Attempts to purify this compound via crystallization or distillation were unsuccessful, but when crude samples (which were about 95% pure) were allowed to stand at room temperature for several weeks, crystals were deposited in the oily solid. It was presumed that these crystals were comprised of the stannyl complex; however, upon analysis it became clear that they were crystals of Cp*FvTi. Subsequent examination of the thermal stability of $Cp^*_2TiSnBu_3$ in solution revealed a propensity toward a decomposition process involving loss of Bu_3SnH ($\delta(^{119}Sn\{^1H\}) = -87.8$ ppm) and production of Cp*FvTi, which was identified by comparison to reported ^1H NMR data.[3] At elevated temperatures (>80 °C) the process is not entirely clean in that diamagnetic products are also in evidence; details of the mechanism(s) involved are not known.

A thermal ellipsoid diagram of Cp*FvTi is shown in Figure 1; listings of crystal data and selected metrical data are given in Tables 1 and 2, respectively. The molecule has C_s symmetry with the methylene group of the tetramethylfulvene ligand lying in the plane of symmetry and occupying the central ligating position of the bent metallocene equatorial plane bisecting the two π ligands. Of particular interest is whether the structural data favor one of two possible resonance forms of fulvene ligands bonded to a single transition metal, the π-η^5:σ-η^1 (ligand formal charge = −2, **A**) mode or the $\pi-\eta^6$ (formal charge = 0, **B**) formulation. Due to the paramagnetism of the compound even simple chemical shift data for the protons and carbons of the fulvene ligand are not very informative in this regard



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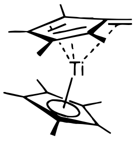

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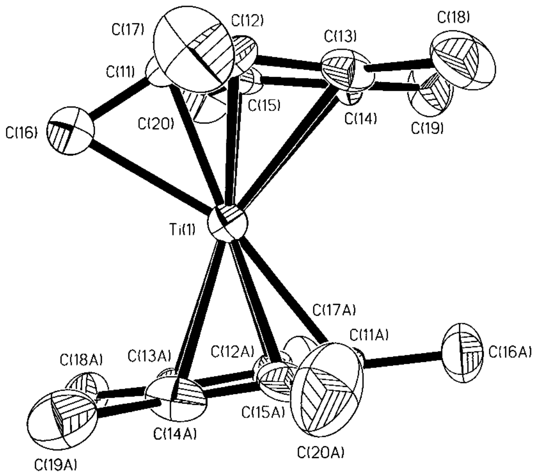

Figure 1. Thermal ellipsoid diagram (50% probability) of Cp*FvTi.

Scheme 1

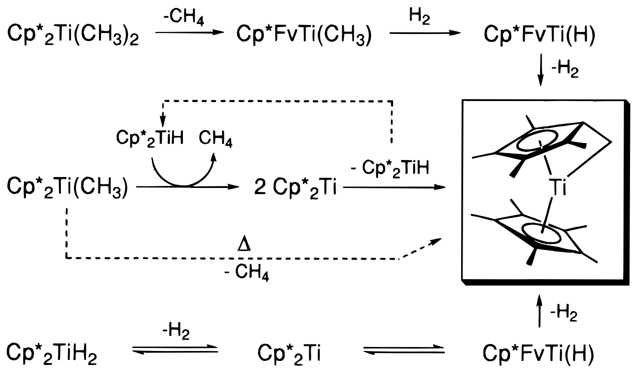

Table 1. Crystal Data and Structural Refinement Data for Cp*FvTi

formula	$C_{20}H_{29}Ti$
fw	317.33
cryst syst	monoclinic
space group	$C2/c$
a, Å	13.8225(6)
b, Å	9.7919(4)
c, Å	13.6055(6)
β, deg	103.211(1)
V, Å^3	1792.75(13)
Z	4
F(000)	684
$d_{\mathrm{ca}}3\mathrm{l}_{\mathrm{c}}$, mg mm^{-3}	1.176
μ, mm^{-1}	0.470
cryst size	0.50 × 0.50 × 0.35 mm
radiation	0.710 73 Å
θ range	2.57−24.98°
reflcns collcd	4469
indepdt reflcns	1562 ($R_{\mathrm{int}} = 0.0269$)
abs corr	semi-empirical
max and min transm	0.63306 and 0.56184
refinement method	full-matrix least-squares on F^2
data/restraints/params	1562/105/200
gof on F^2	1.043
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0328$, w$R2 = 0.0904$
R indices (all data)	$R1 = 0.0358$, w$R2 = 0.0934$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Cp*FvTi

Ti−C(11)	2.093(4)	Ti−C(11A)	2.325(4)
Ti−C(12)	2.272(8)	Ti−C(12A)	2.340(7)
Ti−C(13)	2.467(14)	Ti−C(13A)	2.36(2)
Ti−C(14)	2.465(10)	Ti−C(14A)	2.368(10)
Ti−C(15)	2.250(8)	Ti−C(15A)	2.342(8)
Ti−C(16)	2.281(14)		
C(11)−C(12)	1.433(11)	C(11A)−C(15A)	1.428(11)
C(11)−C(16)	1.437(14)	C(11A)−C(12A)	1.435(10)
C(11)−C(15)	1.455(11)	C(11A)−C(16A)	1.510(13)
C(12)−C(13)	1.413(14)	C(12A)−C(13A)	1.416(14)
C(12)−C(17)	1.543(11)	C(12A)−C(17A)	1.486(13)
C(13)−C(14)	1.431(14)	C(13A)−C(14A)	1.417(14)
C(13)−C(18)	1.517(13)	C(13A)−C(18A)	1.511(13)
C(14)−C(15)	1.475(12)	C(14A)−C(15A)	1.360(13)
C(14)−C(19)	1.527(11)	C(14A)−C(19A)	1.509(12)
C(15)−C(20)	1.518(12)	C(15A)−C(20A)	1.474(13)
C(12)−C(11)−C(16)	120.7(9)	C(11)−C(12)−C(17)	127.3(10)
C(12)−C(11)−C(15)	104.9(7)	C(11)−C(15)−C(14)	109.7(8)
C(16)−C(11)−C(15)	120.5(10)	C(11)−C(15)−C(20)	121.7(9)
C(13)−C(14)−C(15)	105.2(9)	C(14)−C(15)−C(20)	127.9(10)
C(13)−C(14)−C(19)	132.8(10)	C(12)−C(13)−C(14)	109.4(9)
C(15)−C(14)−C(19)	121.3(10)	C(12)−C(13)−C(18)	131.4(11)
C(13)−C(12)−C(11)	110.6(8)	C(14)−C(13)−C(18)	118.9(12)
C(13)−C(12)−C(17)	121.3(11)	C(11)−C(16)−Ti	63.9(5)

Table 3. Comparison of Metrical Parameters (Å, deg) Associated with the η^6-$C_5Me_4CH_2$ (Fv) Ligand

	Cp*FvTi	Cp*FvZrPh[a]	Cp*FvHfBz[b]	FvRuCOD[c]
Ti−C(16)	2.281(14)	2.388(7)	2.320(9)	2.323(7)
Ti−C(11)	2.093(4)	2.282(5)	2.258(8)	2.072(5)
Ti−C(12)	2.272(8)	2.444(6)	2.448(8)	2.199(5)
Ti−C(15)	2.250(8)	2.418(6)	2.412(8)	2.195(6)
Ti−C(13)	2.467(14)	2.617(6)	2.603(8)	2.341(5)
Ti−C(14)	2.465(10)	2.610(5)	2.576(8)	2.321(5)
C(11)−C(16)	1.437(14)	1.468(9)	1.453(12)	1.42(1)
C(11)−C(12)	1.433(11)	1.423(8)	1.460(11)	1.46(1)
C(11)−C(15)	1.455(11)	1.437(9)	1.396(11)	1.47(1)
C(12)−C(13)	1.413(14)	1.398(10)	1.436(11)	1.41(1)
C(14)−C(15)	1.475(12)	1.421(7)	1.410(11)	1.40(1)
C(13)−C(14)	1.431(14)	1.408(8)	1.407(11)	1.43(1)
θ[d]	35(1)	37	37	36

[a] Taken from ref 10. [b] Taken from ref 11. [c] Taken from ref 12. [d] θ defined as the tile of C(16) out of the least−squares plane of C(11)−C(15).

and key C−H coupling constant data for the methylene group are unavailable. The structural data we have obtained are thus crucial for addressing this question.

An assessment of the approximate hybridization of the metalated carbon, C(16), should be indicative of which resonance structure predominates. The C(16) methylene unit is bent out of the least-squares plane defined by C(12)−C(15) by 35(1)° toward the titanium atom, and the Ti−C(16) distance of 2.281(14) Å is close to the Ti−C(sp^3) distance of 2.231(5) Å in the related Cp*$_2$TiCH$_2$CMe$_3$.[4] The C(11)−C(16) length of 1.437(14) Å is somewhat shorter than a normal C(sp^2)−C(sp^3) carbon single bond[9] (cf. the carbon−carbon bonds between the four methyl groups of the tetramethylfulvene and the ring carbons), suggesting an order somewhat greater than 1 for this bond. The data thus points to hybridization somewhere between sp^2 and sp^3 for the C(16), but the explanation for this likely resides in the distorted environment about C(16) (C(11)−C(16)−Ti(1) = 63.9(5)°, strongly perturbed from the ideal sp^3 angle) rather than a strong contribution from the π-η^6 resonance structure in Cp*FvTi.

For comparison, selected metrical parameters for the Cp*FvTi and three other complexes containing the tetramethylfulvene ligand in a η^6-bonding arrangement are given in Table 3. Previous discussions for the closely related complexes Cp*FvZrPh[10] and Cp*FvHfCH$_2$Ph[11] have also concluded that the data found in these

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[9] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 18.

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instances were more consistent with the π-η^5:σ-η^1 description for the bonding of the Fv ligand. As can be seen in Table 3, the data pertaining to the fulvene ligand in Cp*FvTi compares favorably to that in the zirconium and hafnium complexes presented. For example, the Ti−C distances follow the same trends but are systematically shorter than their counterparts in the other compounds, in some instances (for example the Ti−C(11) distance) more so than would be expected on the basis of a simple correction for differences in covalent radii between Ti(III) and Zr or Hf(IV) nuclei. This suggests that the Fv ligand in the titanium complex is bound more tightly to the metal center than in the zirconium and hafnium compounds, likely a reflection of the titanium species' higher symmetry and lower coordination number. Indeed, the trends and values for analogous parameters in the equally symmetrical ruthenium derivative FvRu(COD)[12] also included in Table 3 more closely correspond to the titanium complex data than the other group 4 derivatives.

In conclusion, we unexpectedly obtained crystals of a long known and important compound in permethyltitanocene chemistry whose precise structure has remained elusive until now. Our findings confirm previous assignments and allow for a π-η^5:σ-η^1 description of the bonding in the fulvene ligand. This is consistent with the bonding description for this ligand in other group 4 systems.

Experimental Section

Crystallization of Cp*FvTi. $Cp^*_2TiH^3$ (0.45 g, 1.41 mmol) was loaded into a round-bottomed flask and dissolved in hexanes (30 mL). A solution of Bu_3SnH (0.41 g, 1.41 mmol, Aldrich) in hexanes was added dropwise to this solution under a flow of argon at −78 °C. The mixture was warmed to room temperature, during which time it turned color from deep red to purple with evolution of gas. After the solution was stirred at room temperature for 2 h, the solvent was removed *in vacuo* leaving a viscous purple oil. ^{1}H NMR (400 MHz, C_6D_6, δ): 16.6 (30H, fwhh = 646 Hz); 1.54 (6H, br m, $SnCH_2$); 1.31 (6H, m, $SnCH_2CH_2$); 0.88 (15H, m, CH_2CH_3). The oil was stored for several weeks at room temperature in a glovebox during which time large crystals were deposited. These crystals were isolated and washed with cold hexanes (0.123 g, 26%) and identified as Cp*FvTi.

Decomposition of $Cp^*_2TiSnBu_3$. A sample of Cp^*_2-$TiSnBu_3$ was obtained as described above, and a portion was dissolved in C_6D_6. The sample was heated at 80 °C for several hours with periodic monitoring by ^{1}H and ^{119}Sn{^{1}H} NMR spectroscopy. The principle titanium-containing product was Cp*FvTi, as well as some unidentified diamagnetic species. The major tin-containing product was Bu_3SnH ($\delta = -87.7$ ppm relative to Me_4Sn at 0.0 ppm).

Structure Determination. A crystal of the compound was attached to a glass fiber and mounted on the Siemens SMART system for a data collection at 173(1) K. An initial set of cell constants was calculated from reflections harvested from three sets of 30 frames. Final cell constants were calculated from a set of 3495 of strong reflections from the actual data collection. Table 1 gives additional crystal and refinement information.

The space group *C*2/*c* was determined on the basis of systematic absences and intensity statistics.[13] However, a successful direct-methods solution could not be calculated in *C*2/*c*. Symmetry was reduced to *Cc*, which provided a solution with all non-hydrogen atoms from the *E*-map. The refinement in *Cc* provided a model that was refined as a racemic twin. The resultant occupation of the twin fragments was equivalent. The program MISSYM[14] detected an inversion center, and the *Cc* model was was transformed to *C*2/*c* to account for the additional symmetry.

The titanium atom is disordered because in space group *C*2/*c*, with $Z = 4$, the Cp* and Fv ligands lie in nearly equivalent positions. Refining as such yielded an organic fragment that was an average of the two. The Cp* and Fv ligands were also pseudosymmetric through the origin. In order to refine a unique, half-occupied molecule containing both ligands, restraints were used successfully to break the pseudosymmetry. Initially, similar distances and plane restraints were employed to guide the atoms to the proper least-squares minimum. Once this had converged, restraints for all planes except the Cp* inner ring were omitted. The model would not converge when similar bond restraints were removed; thus all bonds that were chemically similar were retained in the refinement. The total number of restraints was 105. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic ($1.2U_{iso}$ carbon for methylene $1.5U_{iso}$ carbon for methyl) displacement parameters.

All calculations were performed using SGI INDY R4400-SC or pentium computers using the SHELXTL V5.0 suite of programs.

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Supporting Information Available: Full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles for Cp*FvTi (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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