

Synthesis, Structure, and Solution Behavior of 1-Chloro-2,2-difluorovinyl Titanocene Derivatives: The First X-ray Study of a Titanium Fluorovinyl Compound and Spectroscopic Elucidation of the $[\text{Cp}_2\text{TiMe}(\eta^2\text{-CF}_2\text{=CClH})]$ Complex

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The first early-transition-metal 1-chloro-2,2-difluorovinyl complexes $[\text{Cp}_2\text{TiX}_n(\text{CCl}=\text{CF}_2)_{2-n}]$ ($\text{X} = \text{Cl}, \text{F}; n = 0, 1$) have been synthesized by the low-temperature reaction of Cp_2TiX_2 ($\text{X} = \text{Cl}, \text{F}$) with (1-chloro-2,2-difluorovinyl)lithium, generated in situ from HCFC-133a ($\text{CF}_3\text{-CH}_2\text{Cl}$) and *n*-butyllithium. The complexes have been characterized by spectroscopy and, in the case of $[\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)]$, by single crystal X-ray diffraction, making this the first structurally characterized titanium-based fluorovinyl compound. The marked solution-phase instability of these materials has been explored in an attempt to identify key characteristics that might lead to stabilized systems. To this end, syntheses of the compounds $[\text{Cp}^*_2\text{TiF}_n(\text{CF}=\text{CF}_2)_{2-n}]$ ($n = 0, 1$) and $[\text{Cp}_2\text{TiMe}(\text{CCl}=\text{CF}_2)]$ have been reported and their stabilities investigated further. In the case of $[\text{Cp}_2\text{TiMe}(\text{CCl}=\text{CF}_2)]$, this has led to the spectroscopic characterization of the π -complex $[\text{Cp}_2\text{TiMe}(\eta^2\text{-CF}_2\text{=CClH})]$ as an intermediate in the solution-phase decomposition pathway.

Introduction

The organometallic complexes of early transition metals, notably those of group 4, have played a unique role in modern chemistry, being widely used in catalysis¹ and as reagents in organic synthesis.² Moreover, titanium-based systems have long been proposed as anticancer agents,³ a role which continues to be explored, with some appreciable success.⁴ In many of these roles, the versatility of these materials is complemented by molecules containing small fluorocarbon fragments,⁵ which find extensive utility in the pharmaceutical, agrochemical, and materials industries.^{6,7} This affords the possibility that a synergy might exist in molecules

that combine both a group 4 center and a fluorocarbon fragment. Indeed, the success of this approach has been illustrated by the recent report that the compound $[\text{CpTi}(\text{NPPPh}_3)(\text{C}_6\text{H}-2,3,4,5\text{-F}_4)_2]$ is an effective catalyst for ethylene polymerization.⁸

However, investigation of this potential has long been hindered by the difficulties associated with preparing heavily fluorinated organometallic systems, particularly of early transition metals, where the electrophilic nature of the metal center results in reduced stability of the complex and a propensity for fluoride transfer to the metal.⁹ Indeed, while the past 50 years has seen expansive investigation of fluoro-organometallic chemistry, developments were initially restricted to late groups of the transition series.¹⁰ Notwithstanding, the past decade has seen a resurgence in interest in this area, resulting in several synthetic developments, including most recently the synthesis of the first titanium fluoroalkyl complexes, $[\text{Cp}_2\text{TiX}(\text{CF}_3)]$ ($\text{X} = \text{F}, \text{OTf}$).¹¹

We have previously reported the synthesis of the first group 4 trifluorovinyl complexes $[\text{Cp}_2\text{TiX}_n(\text{CF}=\text{CF}_2)_{2-n}]$

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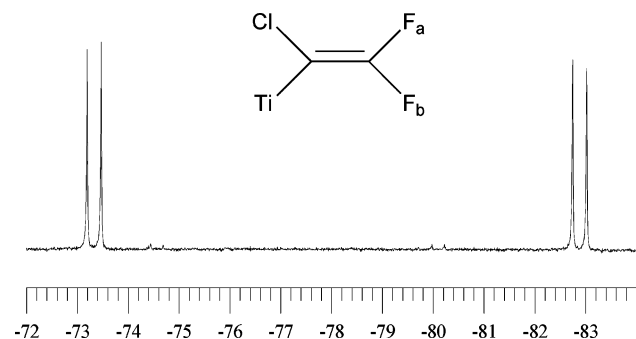


Figure 1. ^{19}F NMR spectrum of $\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)$ (**1**) and the labeling scheme adopted for 1-chloro-2,2-difluorovinyl compounds.

($\text{X} = \text{Cl}, \text{F}; n = 0, 1$),¹² via the reaction of Cp_2TiCl_2 with (trifluorovinyl)lithium, the latter being derived from 1,1,1,2-tetrafluoroethane ($\text{CF}_3\text{CH}_2\text{F}$, HFC-134a). These materials were isolated as air-stable, thermally robust solids but were found to decompose rapidly in the solution phase: a process accelerated in the zirconium analogues, which could not be isolated in a pure form. In an extension of this work, we now report the synthesis of the 1-chloro-2,2-difluorovinyl analogues $[\text{Cp}_2\text{TiX}_n(\text{CCl}=\text{CF}_2)_{2-n}]$ ($\text{X} = \text{Cl}, \text{F}; n = 0, 1$) and, significantly, the first X-ray structural study of any titanium-based fluorovinyl compound. Moreover, we describe our extended investigation into the reactivity and solution instability of both 1-chloro-2,2-difluorovinyl and trifluorovinyl derivatives and outline efforts to impart enhanced stability.

Results and Discussion

Synthesis and Characterization of (1-Chloro-2,2-difluorovinyl)titanocenes. The titanocene complexes $[\text{Cp}_2\text{TiX}(\text{CCl}=\text{CF}_2)]$ ($\text{X} = \text{Cl}$ (**1**), F (**2**)) were prepared by the low-temperature (-78°C) reaction of the appropriate titanocene dihalide, Cp_2TiX_2 ($\text{X} = \text{Cl}, \text{F}$), with 1 equiv of (1-chloro-2,2-difluorovinyl)lithium, generated in situ from HCFC-133a ($\text{CF}_3\text{CH}_2\text{Cl}$) and 2 equiv of *n*-butyllithium. Similarly, $[\text{Cp}_2\text{Ti}(\text{CCl}=\text{CF}_2)_2]$ (**3**) was obtained from the reaction of Cp_2TiCl_2 with an excess (3 equiv) of the lithium reagent, to ensure complete substitution. In all cases, the materials were obtained as analytically pure orange solids, which appear to be indefinitely stable to air and ambient moisture. It is noteworthy that while **1** and **3** can be routinely prepared in excess of 70% yield, Cp_2TiF_2 appears to be a less effective substrate, with yields of **2** rarely exceeding 30%.

In all cases, the presence of the 1-chloro-2,2-difluorovinyl group is apparent from the ^{19}F NMR spectra, which exhibit two mutually coupling doublet resonances in the regions -73 to -75 ppm and -80 to -87 ppm (Figure 1; see also Table 1), consistent with the anticipated AB spin system. The magnitude of the mutual ^{19}F – ^{19}F coupling constants (45–60 Hz) is consistent with a *geminal* interaction, though it is smaller than those observed in a series of recently reported main-group analogues (65–80 Hz),¹³ and indeed the *geminal*

Table 1. ^{19}F NMR Assignments for $[\text{Cp}_2\text{TiX}_n(\text{CCl}=\text{CF}_2)_{2-n}]$ ($n = 1$, $\text{X} = \text{Cl}$ (**1**), F (**2**); $n = 0$ (**3**))

compound	$\delta(^{19}\text{F})$	$ J/\text{Hz} $
$[\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)]$ (1)	–73.4	52.0 (F_b, F_a)
	–82.9	52.0 (F_a, F_b)
$[\text{Cp}_2\text{TiF}(\text{CCl}=\text{CF}_2)]$ (2)	171.9	24.3 (F, F_a)
	–74.3	58.0 (F_b, F_a)
	–87.6	58.0 (F_a, F_b), 24.3 (F_a, F)
$[\text{Cp}_2\text{Ti}(\text{CCl}=\text{CF}_2)_2]$ (3)	–74.6	46.5 (F_b, F_a)
	–80.2	46.5 (F_a, F_b)

interactions within $[\text{Cp}_2\text{TiX}_n(\text{CF}=\text{CF}_2)_{2-n}]$ ($\text{X} = \text{Cl}, \text{F}; n = 0, 1$) (61–76 Hz).¹²

For compound **2** an additional doublet coupling ($J = 24$ Hz) is apparent for the lower frequency resonance, arising due to interaction with the titanium-bound fluoride, which is observed as a doublet at 171.9 ppm. This affords the only means of absolute assignment for the two vinylic fluorine centers within these systems, a task previously addressed by consideration of coupling to spin-active metal/metalloid centers. In the case of group 14 systems,¹³ it has been found that the greatest magnitude interaction is to the fluorine center cis to the metalloid, which agreed with the assignments made for trifluorovinyl analogues¹⁴ and some phosphine derivatives in which a lone-pair-assisted dipolar-coupling mechanism was proposed.¹⁵ However, in the present case both dipolar and scalar mechanisms are viable and offer mutually exclusive assignments, given the accepted order of homonuclear coupling magnitudes across a vinylic system: i.e. $J_{\text{trans}} > J_{\text{gem}} > J_{\text{cis}}$. It is noted that the magnitude of the observed coupling (24 Hz) compares well with other $^4J_{\text{trans}}$ ^{19}F – ^{19}F interactions, such as that seen in $\text{Bu}_3\text{SnC}(\text{CF}_3)=\text{CF}_2$ ($J = 20$ Hz),¹⁶ and on this basis it is proposed that scalar coupling is being observed here. Thus, the lower frequency ^{19}F resonance is also assigned to the F_a nucleus for all three systems. This is also in agreement with the assignments made for $\text{Ph}_3\text{ECCl}=\text{CF}_2$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$).¹³

Further spectroscopic characterization of compounds **1–3** is limited, due to their poor solubility and instability in the solution phase. Thus, while the cyclopentadienyl units are clearly observed in both the ^1H NMR (ca. 6.5 ppm) and ^{13}C NMR spectra (ca. 120 ppm), it has proven impossible to resolve the fluorovinyl systems by ^{13}C NMR studies, the compounds decomposing during the necessarily prolonged data acquisition time. However, the presence of the fluorovinyl unit is further confirmed by infrared and Raman studies (Table 2). The C=C stretching vibration of the vinyl unit is clearly observed in the infrared spectra around 1650 cm^{-1} , while the asymmetric and symmetric C–F stretches absorb around 1250 and 1000 cm^{-1} , respectively; these data are all consistent with those reported previously for 1-chloro-2,2-difluorovinyl compounds.^{13,17} The C–Cl stretches are also observed, absorbing at ca. 830 cm^{-1}

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Table 2. Selected Vibrational Data for [Cp₂TiX_n(CCl=CF₂)_{2-n}] (n = 1, X = Cl (1), F (2); n = 0 (3))

compd	$\nu_{\max}/\text{cm}^{-1}$ ^a			
	C=C str	C-F asym	C-F sym	C-Cl
[Cp ₂ TiCl(CCl=CF ₂)] (1)	1688 ⁱ	1209 ⁱ	1018 ⁱ	827 ^{i,R}
[Cp ₂ TiF(CCl=CF ₂)] (2)	1649 ⁱ	1232 ⁱ	1008 ⁱ	827 ^{i,R}
[Cp ₂ Ti(CCl=CF ₂) ₂] (3)	1636 ⁱ , 1641 ^R	1201 ⁱ	952 ⁱ	829 ^{i,R}

^a The superscript R denotes that the band was observed in the Raman spectrum, and the superscript i denotes that the band was observed in the infrared spectrum.

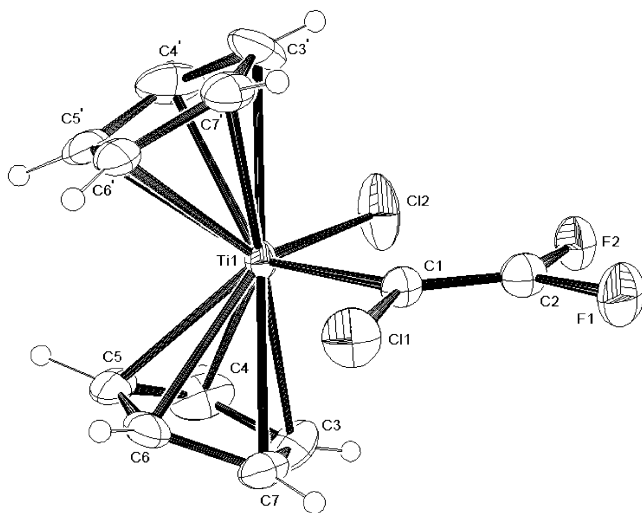


Figure 2. View of the molecular structure of [Cp₂TiCl(CCl=CF₂)] (1), with thermal ellipsoids set at the 30% probability level.

in each case, and these are also apparent as very weak bands in the Raman spectra of the neat solids. Additionally, for complex 3, a C=C stretching mode is also apparent in the Raman spectrum, affording some confirmation that similar species exist in the solution and solid phases.

Additional information was obtained for [Cp₂TiCl(CCl=CF₂)] (1) in the solid state by X-ray diffraction methods, as it proved possible to obtain X-ray-quality single crystals of this materials by the slow evaporation of a saturated hexane solution. Significantly, this constitutes the first time a titanium-bound fluorovinyl compound has been crystallographically studied and is only the second example of a titanium system with β -fluorine substituents to be so characterized, the first being [Cp₂Ti(*cis*-C(CF₃)=CH(CF₃))₂O].¹⁸ The molecular structure of 1 is illustrated in Figure 2, with selected bond distances and angles being summarized in Table 3.

Compound 1 adopts the anticipated pseudotetrahedral geometry about titanium in the solid state, with the fluorovinyl and chloride substituents occupying a plane that bisects the Cp-Ti-Cp moiety. The internal geometry of the titanocene unit is typical of other crystallographically characterized titanocenes, the Ti-C_{ring} distances lying in the range 2.378(5)–2.322(5) Å, which are comparable to those observed for Cp₂TiCl₂,¹⁹ the closest analogue of 1 with respect to electronics. The

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Cp₂TiCl(CCl=CF₂)] (1) with Estimated Standard Deviations in Parentheses

Ti1-Cl2	2.3080(18)	C1-Cl1	1.767(6)
Ti-C1	2.208(5)	C2-F1	1.332(7)
C1-C2	1.301(8)	C2-F2	1.320(7)
C12-Ti1-C1	98.41(16)	F1-C2-C1	128.0(5)
Cl1-C1-C2	112.2(4)	F2-C2-C1	124.8(6)
Ti1-C1-C2	130.6(4)	F1-C2-F1	107.2(5)
Ti1-C1-Cl1	117.2(3)		

Ti-Cl distance in 1 (2.3081(18) Å) is, however, appreciably shorter than that reported for Cp₂TiCl₂ (2.364(3) Å), consistent with the replacement of Cl with the less electronegative 1-chloro-2,2-difluorovinyl moiety. This is reflected in the Ti-C_{vinyl} linkage (2.208(5) Å), which lies in the upper range of Ti-C(sp²) distances, as revealed by a search of the Cambridge Crystallographic Database. Interestingly, this distance is also longer than those observed in the two structurally characterized examples of titanium perprotiovinyl compounds [Cp*₂Ti(CH=CH₂F)] (2.098(6) Å)²⁰ and [Cp₂Ti(CH=CH₂)(OC(CH₂)C₆H₁₁)] (2.143(4) Å).²¹

The fluorovinyl unit of 1 is remarkable in exhibiting a C=C linkage (1.301(8) Å) of length comparable to the typical C(sp²)=C(sp²) distance (1.299 Å)²² and, indeed, to those observed in both C₂H₄ (1.3142(3) Å)²³ and C₂F₄ (1.311(3) Å).²⁴ Only in the group 14 systems Ph₃E(CCl=CF₂) (E = Ge, Sn) has such close agreement been previously noted,¹³ most chlorodifluorovinyl, and indeed trifluorovinyl, analogues exhibiting a markedly shortened C=C linkage (e.g.: HgCl(CCl=CF₂), 1.23(5) Å; *trans*-[Pd(CCl=CF₂)₂(PBu₃)₂], 1.26(2) Å; [(Ph₃P)Au(CCl=CF₂)]₂, 1.281(15) Å;¹⁷ Ph₃E(CF=CF₂), 1.230(8) Å (E = Ge), 1.259(12) Å (E = Sn), 1.21(2) Å (E = Pb)¹⁴). This foreshortening has previously been attributed, in part, to libration effects, which become more significant with increasing mass of the metalloid fragment.

The C-Cl distance in 1 (1.766(6) Å) is somewhat longer than the averaged C(sp²)-Cl value (1.734 Å),²² as has been noted previously,¹⁷ though this constitutes one of the more extreme examples. In contrast, variation between the two β -C-F distances, another commonly observed feature in fluorovinyl structures, is in this instance negligible; indeed, only for Ph₃Ge(CCl=CF₂) has a smaller variation been noted.¹³ It is, however, significant that the C-F linkage *cis* to the metal is in this case the shorter one, this seemingly being an emerging pattern within structurally characterized 1-chloro-2,2-difluorovinyl systems.¹³

In the extended structure, molecules of 1 align in files through the crystal, such that the fluorovinyl units bridge the cyclopentadienyl rings of the leading molecule via weak H \cdots F interactions ($d(\text{H5}\cdots\text{F1}) = 2.56$ Å), which constrain the molecules to adopt alternating orienta-

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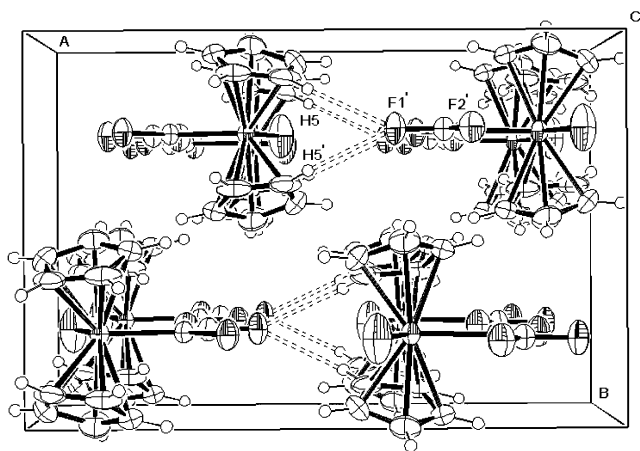


Figure 3. Molecular packing of $[\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)]$ (**1**), projected along the a direction, with $\text{H5}\cdots\text{F1}$ interactions illustrated.

tions. Adjacent files are held together in comparable fashion ($d(\text{H6}\cdots\text{F2}) = 2.54 \text{ \AA}$), forming sheets in the ac plane, which associate in head-to-tail fashion along b (Figure 3), by π -stacking between alternate vinyl and cyclopentadienyl functions.

Solution Studies. In common with the analogous trifluorovinyl systems, the titanocenes **1–3** exhibit a propensity for decomposition in the solution phase, which results in complete loss of the fluorovinyl group with formation of intractable byproducts. This process has been studied in a range of hydrocarbon and non-hydrocarbon solvents, which reveal comparable behavior throughout. Thus, the order of stability is $[\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)]$ (**1**) \ll $[\text{Cp}_2\text{Ti}(\text{CCl}=\text{CF}_2)_2]$ (**2**) $<$ $[\text{Cp}_2\text{TiF}(\text{CCl}=\text{CF}_2)]$ (**3**), decomposition of **1** being complete within 2 days, while **3** persists in solution for up to 1 week. Significantly, while this is the same order of stability noted for the trifluorovinyl systems,¹² compounds **1–3** are appreciably longer lived than their perfluorinated analogues, the most stable of which, $[\text{Cp}_2\text{TiF}(\text{CF}=\text{CF}_2)]$, fully decomposes within 2 days.

The mechanism of decomposition of both chlorodifluorovinyl and trifluorovinyl titanocenes remains unclear, though the process has been studied in several complementary solvent systems. Thus, samples of **1–3**, and the trifluorovinyl analogues, were dissolved in hexane, CCl_4 , CHCl_3 , CDCl_3 , CFCl_3 , perfluorodecalin, CS_2 , and SO_2 both in the absence of air and in the presence of D_2O or H_2O and the decomposition process monitored by ^{19}F NMR spectroscopy. In every case, gradual loss of the metal-bound fluorovinyl group was observed, concomitant with the appearance of resonances due to either $\text{CF}_2=\text{CClH}$ ($\delta_{\text{F}} -86.3$ (dd, $J_{\text{FF}} = 38.5$, $J_{\text{HF}} = 17$ Hz), -90.8 (d, $J_{\text{HF}} = 38.5$ Hz)) or $\text{CF}_2=\text{CFH}$ ($\delta_{\text{F}} -99.0$ (ddd, $J_{\text{FF}} = 87.0$, 37.2 , $J_{\text{HF}} = 13$ Hz), -126.0 (dd, $J_{\text{FF}} = 116.0$, 87.0 Hz); -205.0 (ddd, $J_{\text{FF}} = 116.0$, 32.5 , $J_{\text{HF}} = 70$ Hz)), respectively. Interestingly, the rates of decomposition appear unaffected by either the choice of solvent or the presence of moisture, suggesting the mechanism to be independent of these factors. Indeed, the consistent formation, in quantity, of the hydrofluoroalkene byproducts, even when dissolved in non-hydrocarbon solvents, suggests that the solvent is not the source of protons in this case.

Quantitative ^{19}F NMR studies of the decomposition of $[\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2]$ in CDCl_3 , in a sealed system with

Table 4. ^{19}F NMR Data for $[\text{Cp}^*_2\text{Ti}(\text{CCl}=\text{CF}_2)_2]$ (**4**) and $[\text{Cp}^*_2\text{TiF}(\text{CCl}=\text{CF}_2)]$ (**5**)

compd	$\delta(^{19}\text{F})$	J/Hz
$[\text{Cp}^*_2\text{Ti}(\text{CF}=\text{CF}_2)_2]$ (4)	-99.0	35.5 (F_a, F_c), 90.0 (F_a, F_b)
	-118.3	90.0 (F_a, F_b), 105.0 (F_b, F_c)
	-154.5	35.5 (F_a, F_c), 105.0 (F_b, F_c)
$[\text{Cp}^*_2\text{TiF}(\text{CF}=\text{CF}_2)]$ (5)	154.3	10.0 (F, F_c), 32.0 (F, F_b)
	-98.4	36.0 (F_a, F_c), 98.0 (F_a, F_b)
	-123.8	32.0 (F, F_b), 98.0 (F_a, F_b), 105.0 (F_b, F_c)
	-87.6	10.0 (F, F_c), 36.0 (F_a, F_c), 105.0 (F_b, F_c)

hexafluorobenzene as an internal standard, reveal that at least 30% of the fluorovinyl units are lost as $\text{CF}_2=\text{CFH}$, further precluding the involvement of trace amounts of occluded solvent. The fate of the remaining fluorocarbon, and titanocene, fragments is presumably the solid residue, which progressively drops from solution during decomposition. Microanalytical data for this material reveal the presence of appreciable quantities of titanium ($\sim 16\%$), carbon ($\sim 40\%$), hydrogen ($\sim 4\%$), and variable quantities of fluorine (2–20%) in each case, with ca. 20% chlorine for **1–3**. Identification of these residues has, however, proven impossible, the ^1H NMR spectra revealing a complex mixture of materials, and their low solubility precludes acquisition of informative ^{13}C NMR spectra. Notwithstanding, ^1H NMR studies reveal the loss of the symmetrical bis(cyclopentadienyl)-titanium fragment, the previously observed singlet being replaced with several complex multiplets in the range 6.7–6.5 ppm; this supports the observations that the hydrofluoroalkene decomposition products arise from proton abstraction from the cyclopentadienyl rings. Significantly, the ^{19}F NMR spectra reveal an apparent absence of any other fluorocarbons, resonances observed in the region 110–120 ppm being more consistent with titanium fluorides.²⁵

Stabilized Derivatives. In view of the noted instability of both the 1-chloro-2,2-difluorovinyl and trifluorovinyl titanocenes, we have sought to develop more stable systems through modification of the ancillary ligands. Thus, the reaction of excess (trifluorovinyl)-lithium with $\text{Cp}^*_2\text{TiCl}_2$ was explored and resulted after workup in isolation of a small quantity of a deep purple solid. The ^1H NMR spectrum indicates the presence of several species, apparently based upon the bis(pentamethylcyclopentadienyl)titanium fragment, the predominant component being $\text{Cp}^*_2\text{TiCl}_2$ ($\delta_{\text{H}} 2.04$); indeed, ^{19}F NMR studies revealed only trace amounts of fluorinated products. Notwithstanding, study of a saturated sample allowed for identification of two distinct trifluorovinyl-containing species, characterized by doublet of doublet based resonances in the regions 95–105, 115–125, and 155–160 ppm (Table 4), the major set of which has been arbitrarily assigned to the bis-substituted system $[\text{Cp}^*_2\text{Ti}(\text{CF}=\text{CF}_2)_2]$ (**4**). The trace resonances exhibit additional doublet multiplicity, apparently due to coupling with a single titanium-bound fluoride, which is observed as a doublet of doublets at 154.3 ppm. This would suggest partial fluorination of the substrate to afford $[\text{Cp}^*_2\text{TiF}(\text{CF}=\text{CF}_2)]$ (**5**), though whether this

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arises during synthesis or as a result of partial decomposition remains unclear. However, it is significant that both **4** and **5** appear indefinitely stable in solution, the observed resonances persisting for periods of several weeks, and there is no evidence for generation of $\text{CF}_2=\text{CFH}$. Unfortunately, the low yields and poor solubility of the products precluded further extended study.

We have also sought to explore the influence of the spectator ligand in the mono-fluorovinyl systems, with the preparation of a range of alkyl-substituted derivatives. These were obtained by the addition, at -78°C , of RLi ($\text{R} = n\text{-Bu, Me}$) to the mono(fluorovinyl) complexes $[\text{Cp}_2\text{TiCl}(\text{CX}=\text{CF}_2)]$ ($\text{X} = \text{F, Cl}$), which were generated in situ. Workup typically afforded the products as viscous oils, for which, in each case, a unique set of fluorovinyl resonances was apparent in the ^{19}F NMR spectra. Isolation of the pure product was not generally possible. However, the complex $[\text{Cp}_2\text{TiMe}(\text{CCl}=\text{CF}_2)]$ (**6**) was obtained as a solid, in excess of 75% yield, the composition of which was verified by microanalytical data. Moreover, substitution of the titanium-bound chloride by methyl, as opposed to addition-elimination at the fluorovinyl moiety, was verified by spectroscopic data. The infrared spectrum indicated the presence of both symmetric and asymmetric C–F modes ($1153, 1024\text{ cm}^{-1}$) and the characteristic C–Cl band (819 cm^{-1}). The ^{19}F NMR of **6** exhibits two sets of mutually coupling doublet-based resonances at -77.9 and -82.5 ppm ($J_{\text{FF}} = 75.3\text{ Hz}$), the higher frequency of which exhibits further quartet multiplicity ($J_{\text{HF}} = 1.9\text{ Hz}$), presumably due to coupling with the titanium-bound methyl group. Indeed, a comparable coupling is observed for the methyl resonance in the ^1H NMR spectrum ($\delta_{\text{H}} 1.6, 3\text{H}$), which integrates consistently with the sole cyclopentadienyl resonance ($\delta_{\text{H}} 6.4, 10\text{H}$). It is interesting that coupling with the ancillary ligand is observed for the higher frequency ^{19}F resonance, this being in contrast to the case outlined for $[\text{Cp}_2\text{TiF}(\text{CF}=\text{CF}_2)]$ (**2**). Given the minimal effect upon the fluorine resonant frequency anticipated by substituting Ti–F with Ti–Me, this would suggest differing mechanisms for the two cases. Indeed, spatially the methyl function is more predisposed to a dipolar interaction than is the case for F, and it possesses a reduced propensity for a scalar (5J) mechanism. However, neither mechanism has yet been proven for **6**.

In common with the titanocene derivatives **1–3**, acquisition of ^{13}C NMR data for **6** has proven impracticable, due to poor solubility and instability in the solution phase. Indeed, the ^{19}F NMR resonances associated with **6** are absent from solutions after 2 days; however, in contrast to previous examples, liberation of $\text{CF}_2=\text{CClH}$ is not immediately observed. Instead, **6** preferentially gives way to a “metastable” intermediate (**7**), characterized by two distinctive ^{19}F NMR resonances at -89.9 (ddq, $J = 50.0, 3.0, 2.5\text{ Hz}$) and -93.5 ppm (ddq, $J = 50.0, 25.3, 2.6\text{ Hz}$) and proton resonances at 4.2 (1H, dqd, $J = 25.3, 7.0, 2.5\text{ Hz}$) and 1.6 ppm (3H, ddd, $J = 7.0, 3.0, 2.6\text{ Hz}$); the presence of the Cp fragments is confirmed by a resonance at 6.6 ppm (10H, s). This species undergoes slow decomposition, with gradual formation of $\text{CF}_2=\text{CClH}$, but persists for up to 2 weeks. Generation of **7** is, however, not quantitative; in common with **1–3**, several cyclopentadienyl-contain-

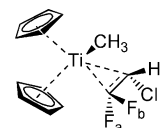


Figure 4. Proposed structure of “metastable” intermediate **7**.

Table 5. Assignment of NMR Data for “Metastable” Intermediate **7**

δ	multi- plicity	$ J /\text{Hz}$	assignt
-89.9	dqd	50.0 (F_a, F_b), 3.0 (F_a, H_a), 2.5 (F_a, H_b)	F_a
-93.5	ddq	50.0 (F_a, F_b), 25.3 (F_b, H_b), 2.6 (F_b, H_a)	F_b
1.6	ddd	7.0 (H_a, H_b), 3.0 (F_a, H_a), 2.6 (F_b, H_a)	H_a
4.2	dqd	25.3 (F_b, F_b), 7.0 (H_a, H_b), 2.5 (F_a, H_b)	H_b

ing species are apparent from the ^1H NMR spectrum ($6.7\text{--}6.5\text{ ppm}$) and the presence of titanium-bound fluoride is inferred from two singlet resonances in the ^{19}F NMR spectrum ($\delta_{\text{F}} 112.6$ and 112).

Isolation and unequivocal identification of **7** have thus far proven impracticable. However, the observed NMR data would seem consistent with a complex in which a $\text{CF}_2=\text{CClH}$ moiety is π -bound to a Cp_2TiMe fragment (Figure 4, Table 5). There are two F–H coupling constants (25.3 and 2.5 Hz); the larger value, although uncharacteristically large for a normal α, β -alkenic coupling constant, is consistent with partial pyramidalization of the $\text{CF}_2=\text{CClH}$ unit, as is commonly observed of π -bound fluoroalkenes. By extrapolation of the anticipated Karplus behavior in the fully pyramidalized system, this coupling is assigned to $\text{F}_b\text{--H}_b$ (cis), while the smaller interaction (2.5 Hz) is derived from $\text{F}_a\text{--H}_b$. Thus, the higher frequency resonance is assigned to F_a and the lower one to F_b ; this is consistent with the assignment for free $\text{CF}_2=\text{CClH}$. The additional couplings to each alkenic resonance are assigned to interaction with the titanium-bound methyl group, verifying the integrity of the Cp_2TiMe unit.

The mechanism by which **7** arises remains elusive, though it would seem to result in reduction of the titanium center to Ti(III), a fact supported by apparent broadening of the NMR spectra and more consistent with the suggested pyramidalization at the alkene. In combination with consideration of the solution studies of **1–3** (vide supra) and **6**, which indicate several decomposition residues, this would seem to suggest a bimolecular process, leading to slippage of the alkene with concomitant abstraction of hydrogen from an adjacent cyclopentadienyl unit. That intermediates comparable to **7** are not observed in the decomposition of **1–3**, or indeed the trifluorovinyl analogues, can be attributed to the presence in these systems of an electron-withdrawing ancillary ligand, capable of diminishing the π -donor capacity of the titanium fragment. In contrast, the +I influence of the methyl group of **7** enhances π -donation, which would be expected to slow the rate of dissociation of the fluoroalkene.

Conclusions

We have reported the high-yielding synthesis of the first examples of early-transition-metal 1-chloro-2,2-difluorovinyl compounds: the titanocene derivatives $[\text{Cp}_2\text{TiX}_n(\text{CCl}=\text{CF}_2)_{2-n}]$ ($\text{X} = \text{Cl, F}, n = 0, 1$). These materials have been characterized by spectroscopy and,

in the case of $[\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)]$, by single-crystal X-ray diffraction. This is the first crystallographically studied group 4 fluorovinyl compound and only the second group 4 compound containing β -fluorine atoms to be so characterized. We have also reported that, in common with their trifluorovinyl analogues, the titanocene derivatives decompose rapidly in numerous common solvents, via a mechanism involving loss of the fluorovinyl moiety as the hydrofluoroalkene. In seeking to reduce this decomposition, we have outlined the preparation, albeit in low yields, of $[\text{Cp}^*_2\text{TiF}_n(\text{CF}=\text{CF}_2)_{2-n}]$ ($n = 0, 1$) and the isolation in quantity of the novel alkyl-containing compound $[\text{Cp}_2\text{TiMe}(\text{CCl}=\text{CF}_2)]$. Significantly, during solution-phase studies of $[\text{Cp}_2\text{TiMe}(\text{CCl}=\text{CF}_2)]$ we have observed what we believe to be a key intermediate in the decomposition process, which, on the basis of spectroscopic findings, we suggest is $[\text{Cp}_2\text{Ti}(\text{Me})(\eta^2\text{-CF}_2=\text{CClH})]$. This is the first such evidence for a metal-bound $\eta^2\text{-CF}_2\text{CClH}$ unit in early-transition-metal chemistry.

Experimental Section

General Methods. Reactions were performed under anaerobic conditions in flame-dried glassware, with moisture-sensitive reagents being handled under an argon atmosphere in a drybox (Belle Technologies). Diethyl ether and THF were dried over sodium wire for ca. 1 day prior to use. The compounds $\text{CF}_3\text{CH}_2\text{Cl}$, $\text{CF}_3\text{CH}_2\text{F}$ (Ineos Fluor), $n\text{-BuLi}$ (2.5 M in hexane), MeLi (1.6 M in ether) (Acros), Cp_2TiCl_2 , and $\text{Cp}^*_2\text{-TiCl}_2$ (Lancaster) were used as supplied, after spectroscopic verification of purity. The compounds $[\text{Cp}_2\text{TiX}_n(\text{CF}=\text{CF}_2)_{2-n}]$ ($X = \text{Cl, F, } n = 0, 1$)¹² and Cp_2TiF_2 ^{12,26} were prepared as previously described. NMR spectra were recorded on Bruker DPX200 (¹⁹F, 188.310 MHz referenced to external CFCl_3) and DPX400 (¹³C and Dept-135, 100.555 MHz; ¹H, 400.4 MHz; referenced to external SiMe_4) spectrometers. All NMR spectra were recorded of CDCl_3 solutions, and resonances are reported using the high-frequency positive convention. Infrared spectra were recorded of chloroform solutions between KBr plates on a Nicolet Nexus FTIR/Raman spectrometer; Raman spectra were recorded of the neat solids. Elemental analyses were performed by the departmental microanalytical service.

Preparation of $[\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)]$ (1). To a three-necked round-bottomed flask, equipped with nitrogen inlet/outlet and magnetic stirrer, maintained at -78°C , were added diethyl ether (70 cm^3) and $\text{CF}_3\text{CH}_2\text{Cl}$ (0.28 cm^3 , 3.28 mmol). BuLi (2.6 cm^3 , 6.5 mmol) was added at such a rate as to maintain the low temperature. The mixture was stirred for 2 h to ensure complete generation of the (1-chloro-2,2-difluorovinyl)lithium reagent. After this time, Cp_2TiCl_2 (0.801 g, 3.22 mmol) dissolved in THF (35 cm^3) was added dropwise, and then the mixture was stirred at -60°C overnight. After being allowed to attain ambient temperature, the reaction mixture was worked up by the addition of hexane, the settled mixture quickly filtered through Celite, and the solvent removed by rotary evaporation to afford the title compound as a vivid orange solid. Yield: 0.741 g, 73.9%. Mp: 120°C dec. Anal. Found: C, 46.3; H, 3.4; Cl, 22.6. Calcd for $\text{Cp}_2\text{TiCl}(\text{CCl}=\text{CF}_2)$: C, 46.4; H, 3.2; Cl, 22.8. For δ_{F} , see Table 1. δ_{H} 6.50 (s, C_5H_5). For $\nu_{\text{max}}/\text{cm}^{-1}$, see Table 2.

$[\text{Cp}_2\text{TiF}(\text{CCl}=\text{CF}_2)]$ (2). The synthesis was carried out as for **1**, using $\text{CF}_3\text{CH}_2\text{Cl}$ (0.29 cm^3 , 3.40 mmol), $n\text{-BuLi}$ (2.7 cm^3 , 6.75 mmol), and Cp_2TiF_2 (0.735 g, 3.40 mmol). Workup afforded **2** as an orange solid. Yield: 0.260 g, 26.2%. Mp: 84°C dec. Anal. Found: C, 48.5; H, 3.6; F, 19.5. Calcd for $\text{Cp}_2\text{-TiF}(\text{CCl}=\text{CF}_2)$: C, 48.9; H, 3.4; F, 19.4. For δ_{F} , see Table 1. δ_{H} 6.40 (s, C_5H_5). For $\nu_{\text{max}}/\text{cm}^{-1}$, see Table 2.

$[\text{Cp}_2\text{Ti}(\text{CCl}=\text{CF}_2)_2]$ (3). The synthesis was carried out as for **1**, using $\text{CF}_3\text{CH}_2\text{Cl}$ (1.37 cm^3 , 16.06 mmol), $n\text{-BuLi}$ (12.8 cm^3 , 32.00 mmol), and Cp_2TiCl_2 (1.335 g, 5.36 mmol). Workup afforded **3** as an orange-red solid. Yield: 1.364 g, 74.8%. Mp: 123°C . Anal. Found: C, 48.5; H, 3.6; F, 19.5. Calcd for $\text{Cp}_2\text{-TiF}(\text{CCl}=\text{CF}_2)$: C, 48.9; H, 3.4; F, 19.4. For δ_{F} , see Table 1. δ_{H} 6.50 (s, C_5H_5). For $\nu_{\text{max}}/\text{cm}^{-1}$, see Table 2.

Synthesis of $[\text{Cp}^*_2\text{TiF}_n(\text{CF}=\text{CF}_2)_{2-n}]$ ($n = 0$ (4), $n = 1$ (5)). (Trifluorovinyl)lithium ($\text{LiCF}=\text{CF}_2$) was prepared from $\text{CF}_3\text{CH}_2\text{F}$ (0.525 cm^3 , 6.23 mmol) and $n\text{-BuLi}$ (5.0 cm^3 , 12.50 mmol), as previously described.¹² Addition of $\text{Cp}^*_2\text{TiCl}_2$ (0.810 g, 2.08 mmol) as a solution in THF (70 cm^3), followed by standard workup afforded a deep purple solid. For δ_{F} , see Table 4.

Preparation of $[\text{Cp}_2\text{TiMe}(\text{CCl}=\text{CF}_2)]$ (6). Compound **1** was prepared in situ from $\text{CF}_3\text{CH}_2\text{Cl}$ (0.27 cm^3 , 3.11 mmol), $n\text{-BuLi}$ (2.5 cm^3 , 6.25 mmol), and Cp_2TiCl_2 (0.773 g, 3.10 mmol). After the mixture was stirred overnight, MeLi (2.0 cm^3 , 3.20 mmol) was added and then the mixture was allowed to slowly attain ambient temperature. Standard workup afforded **6** as a deep red oil, which was dried in vacuo to afford a crystalline solid. Yield: 0.693 g, 76.9%. Mp: 102°C . Anal. Found: C, 53.4; H, 4.8; Cl, 12.0. Calcd for $\text{Cp}_2\text{TiMe}(\text{CCl}=\text{CF}_2)$: C, 53.7; H, 4.5; Cl, 12.2. δ_{F} -78 (dq, $J_{\text{FF}} = 75.3$ Hz, $J_{\text{HF}} = 2$ Hz), -82.5 (d, $J_{\text{FF}} = 75.3$ Hz). δ_{H} 6.13 (10H, s, C_5H_5), 1.55 (3H, t, $J = 2.0$ Hz, Me). $\nu_{\text{max}}/\text{cm}^{-1}$ 1678 (C=C str), 1153 (C-F sym), 1024 (C-F asym), 819.61 (C-Cl str).

X-ray Crystallography. Single crystals of **1** were obtained by the slow evaporation of a saturated hexane solution. Data were recorded on a Nonius MACH-3 four-circle diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 73 Å), at 150(2) K; the structure was solved by direct methods and subjected to full-matrix least-squares refinement on F^2 using the SHELX-97²⁷ program. Absorption corrections were by the multiscan method using the SORTAV program. All non-hydrogen atoms were refined with anisotropic thermal parameters, while hydrogen atoms were fixed in idealized positions. Molecular representations shown in the figures were generated using ORTEP 3 for Windows.²⁸

Crystal data: $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{F}_2\text{Ti}$, M_r 311.00, orthorhombic, $Pnma$ (No. 62), $a = 15.927(3)$ Å, $b = 10.5590(17)$ Å, $c = 7.1439(10)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 1201.4(3)$ Å³, $Z = 4$, $D = 1.719$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 1.153$ mm^{-1} , crystal size $0.10 \times 0.10 \times 0.30$ mm, 2148 data ($\theta = 2.6\text{--}25.0^\circ$), $F(000) = 624$, R1, wR2 ($I > 2\sigma(I)$) = 0.0449, 0.1007, largest difference peak and hole 0.63, -0.64 .

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Supporting Information Available: For the single-crystal structure determination, tables of crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles and packing diagrams; data are also available as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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