

The first early transition metal perfluorovinyl complexes: the synthesis of $\text{Cp}_2\text{M}(\text{CF}=\text{CF}_2)_n\text{X}_{2-n}$ (Cp : $\eta^5\text{-C}_5\text{H}_5^-$; $\text{M} = \text{Ti}, \text{Zr}$; $\text{X} = \text{Cl}$ or F) and structures of $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_n\text{X}_{2-n}$ ($\text{X} = \text{Cl}, \text{F}$) via Ti K-edge EXAFS studies

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Abstract

A new route to perfluorovinyl compounds, recently reported by us, has been used to prepare the first examples of early transition metal complexes of the type $\text{Cp}_2\text{M}(\text{CF}=\text{CF}_2)_n\text{X}_{n-2}$ (Cp : $\eta^5\text{-C}_5\text{H}_5^-$; $\text{M} = \text{Ti}, \text{Zr}$; $\text{X} = \text{Cl}$ or F). These compounds are obtained in high yield from the two-stage, one-pot, reaction of HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$) with two equivalents of BuLi, followed by addition of Cp_2MX_2 ($\text{M} = \text{Ti}, \text{Zr}$, $\text{X} = \text{F}, \text{Cl}$). For two of the titanium-containing compounds Ti K-edge EXAFS data have been recorded from which distances for the titanium–carbon bond of the perfluorovinyl group of 2.033(12) and 2.050(18) Å in $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$ and $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)\text{F}$ are obtained. This is the first report of structural data for any perfluorovinyl organometallic compound, and the distances obtained are consistent with the perfluorovinyl group binding in a simple sigma fashion. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The replacement of hydrogen for fluorine in organic fragments results in moieties which are often sterically non-perturbed compared with their perprotio analogues, but which possess very different electronic properties [1,2]. These factors are reflected in significantly different physical and chemical properties for related C–H and C–F containing compounds and in no area is this more obvious than in the field of organometallic chemistry. Transition metal organometallic compounds containing fluorinated organic ligands are frequently more thermally stable than their perprotio analogues, and they often undergo quite different reactions. This is, in part, due to the very much stronger C–F bond compared with the C–H linkage. However, while there exists a large arsenal of reagents available for the introduction of alkyl and related perprotio groups onto

metal centres, this situation is not matched either in range, or stability, of reagents for the synthesis of metal–fluorocarbon species.

The introduction of the perfluorovinyl (1,1,2-trifluorovinyl) group onto metal centres is one such area where a lack of methodology has limited the number of complexes which have been synthesised. Although much attention was focused in this area in the 1960s and early 1970s there were only two practical synthetic routes. The first of these was based on the incorporation of C_2F_4 as a π -bound ligand on a coordinatively unsaturated late transition-metal centre followed by heating the $\eta^2\text{-C}_2\text{F}_4$ -containing complexes, which results in a vinylic rearrangement to generate the σ -bound $-\text{CF}=\text{CF}_2$ complexes [3]. The second method relied on generation of a perfluorovinyl lithium or Grignard reagent, usually based on bromotrifluoroethene [4]. These two routes accounted for the successful synthesis of a number of main-group and late transition metal complexes containing the perfluorovinyl ligand [5]. However, both of these methods

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have their limitations; the first is generally restricted to coordinatively unsaturated late transition metal complexes whilst the formation of Grignard and lithium reagents rely on chloro- or bromo-substituted fluorocarbon starting materials, the availability of many of which is now severely limited, at least for industrial applications, because of their impact on the ozone layer. This combination of factors has resulted, to date, in the synthesis of main-group and late transition metal perfluorovinyl compounds but no examples of early transition metal complexes.

This lack of early transition metal fluoro-organometallic complexes is unfortunate since these metals provide some of the most active organometallic centres with, in particular, the chemistry of Group 4 bis-cyclopentadienyl dihalide complexes having been widely studied because of their potential range of applications in catalysis [6], anti-cancer drugs [7] and as reagents in organic synthesis [8]. Work in this area has resulted in the production of a number of organometallic complexes with a variety of derivatised cyclopentadienyl-based ligands [9]. Although a number of alkyl-substituted complexes exist, there are relatively few alkenyl-containing titanocene complexes. Those that have been fully characterised include $\text{Cp}_2\text{TiX}(\text{C}(\text{Ph})=\text{CMe}_2)$ $\text{X} = \text{Br}$ and Cl [10], the oxygen-bridged bis-cyclopentadienyl(1,1,1,4,4,4 hexafluorobut-3-yl) compound [11] and $\text{Cp}_2^*\text{TiF}(\text{CH}=\text{CH}_2)$ [12]. The vinyl-substituted bis(pentamethylcyclopentadienyl) complexes in particular have been the subject of much recent work because of the range of reactivities and variety of novel complexes and structures that are produced, and this area has recently been reviewed [13].

We have recently reported a new route for the one-pot synthesis of perfluorovinyl-containing compounds in high yields based on the commercial CFC-replacement HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$). The high efficiency and wide-ranging nature of this method was demonstrated by the synthesis of examples of main-group and transition metal perfluorovinyl complexes [14]. Here, for the first time, we describe the synthesis of titanium(IV)- and zirconium(IV)-bis-cyclopentadienyl perfluorovinyl complexes. We also report the first structural data for perfluorovinyl-organometallic complexes via a series of Ti K-edge EXAFS studies.

2. Results and discussion

2.1. Synthesis and characterisation

The slow addition of two equivalents of *n*-butyllithium to a diethyl ether solution of the CFC-replacement HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$) at -78°C results in the formation of the thermally unstable $\text{CF}_2=\text{CF}^-\text{Li}^+$ reagent (**1**) in good yields [14,15]. To a solution of **1**,

which contrary to previous reports [4], we have found to be stable for up to 24 h under anaerobic conditions and at low temperature, is added the Group 4 bis(cyclopentadienyl)metal dihalides dissolved in cold diethyl ether or THF. The solution is stirred and maintained at low temperature for at least 1 h before slowly being allowed to warm to room temperature (r.t.) when the formation of an off-white precipitate becomes obvious. Analysis of this material confirms it to be a mixture of lithium halides.

In all experiments, prior to working-up the reaction mixture, samples of the organic phase were withdrawn and were monitored via NMR studies to determine the extent of reaction. The ^{19}F -NMR spectra of these solutions demonstrated that the complex multiplet signals due to HFC-134a at $\delta -64.9$ and -226.5 ppm had been replaced by three sets of doublets of doublets typical of the patterns previously observed for perfluorovinyl metal complexes [16].

Although aqueous work-ups have been utilised before for late transition metal perfluorovinyl complexes [4], the use of such methods for these systems resulted in complete decomposition of the products. Instead, a large volume of hexane is added to the reaction mixture to ensure complete precipitation of the lithium salts followed by filtration under a dinitrogen atmosphere. Removal of the volatile solvent, under reduced pressure, resulted in solid products which were analytically pure. Thus, the reaction of one equivalent of perfluorovinyl lithium with Cp_2TiX_2 ($\text{X} = \text{F}, \text{Cl}$) resulted in $\text{Cp}_2\text{TiX}(\text{CF}=\text{CF}_2)$ [compound **2** $\text{X} = \text{F}$, **3** $\text{X} = \text{Cl}$] and when slightly more than two equivalents of perfluorovinyl lithium was used $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$, compound **4** was obtained. In all cases yields greater than 85% were obtained.

The ^{19}F -NMR spectrum obtained from compound **4** dissolved in CDCl_3 is shown in Fig. 1 and the data obtained for all the compounds is presented in Table 1. The fluorine NMR spectra of all the perfluorovinyl-containing complexes exhibit signals for the fluorine

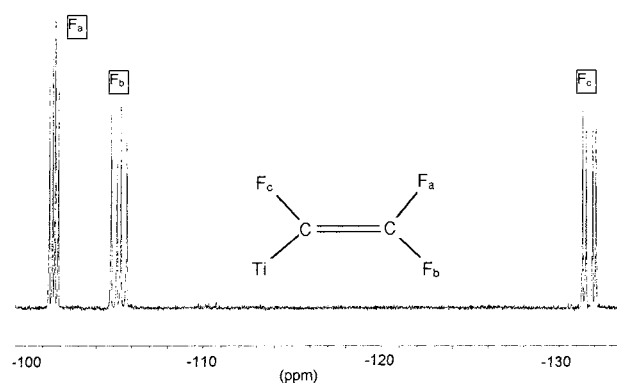


Fig. 1. ^{19}F -NMR spectrum of $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$ dissolved in CDCl_3 .

Table 1
¹⁹F-NMR data for the compounds Cp₂TiX_{2-n}(CF=CF₂)_n (X = F, Cl; n = 1, 2)

Compound	δ ¹⁹ F (ppm) ^a	$ J $ (Hz)	Assignment
Cp ₂ TiCl (CF=CF ₂)	-97.7(dd)	36(F _a , F _c), 76(F _a , F _b)	F _a
	-110.2(dd)	76(F _a , F _b), 107(F _b , F _c)	F _b
	-130.9(dd)	36(F _a , F _c), 107(F _b , F _c)	F _c
Cp ₂ TiF (CF=CF ₂)	64.3(s)	–	F
	-101.6(dd)	36(F _a , F _c), 62(F _a , F _b)	F _a
	-105.2(dd)	62(F _a , F _b), 105(F _b , F _c)	F _b
	-131.7(dd)	39(F _a , F _c), 105(F _b , F _c)	F _c
Cp ₂ Ti (CF=CF ₂) ₂	-101.8(dd)	34(F _a , F _c), 61(F _a , F _b)	F _a
	-105.0(dd)	61(F _a , F _b), 105(F _b , F _c)	F _b
	-131.9(dd)	34(F _a , F _c), 105(F _b , F _c)	F _c

^a Chemical shift values reported are for CDCl₃ solutions with respect to external CFCl₃.

nuclei of the perfluorovinyl ligand in three distinct regions δ -97 to -102, -105 to -110 and -131 to -132 ppm and each signal shows doublet of doublet coupling patterns typical of an AMX spin system. The two signals observed between -97 and -110 ppm for compounds **2–4** are assigned to the two fluorine nuclei of the terminal CF₂ group and the lower frequency resonance to the unique α -fluorine nucleus of the perfluorovinyl ligand (F_c, Fig. 1). This is in accord with previous assignments for other perfluorovinyl-containing compounds [16] in which the signals for nuclei F_a and F_b occur within a small chemical shift region whilst the signal for the F_c nucleus shows a large variation in position, ranging from -205 ppm for CF₂=CFH [17] to -138 ppm for [CpFe(CO)₂(CF=CF₂CF₃)] [18]. Assignment of the two sets of signals between δ -97 to -102 and δ -105 to -110 to F_a and F_b is made on the basis of the magnitude of the coupling constants between all the fluorine nuclei. The ¹⁹F–¹⁹F coupling constants observed in fluoroolefins are typically within the range 20–90 Hz for *gem*-coupling, 30–60 Hz for *syn*-coupling and 110–130 Hz for *anti*-coupling [17]. Although there is some overlap between the coupling constant ranges for *syn*- and *gem*-couplings the larger *anti*-coupling allows straightforward assignment of the signals observed between -105 and -110 ppm to F_b, the fluorine nucleus *anti* to F_c, and those peaks between -97 and -102 ppm to F_a. For complex **2**, Cp₂Ti(CF=CF₂)F, an additional singlet is observed in the ¹⁹F-NMR spectrum at 64.3 ppm which is assigned to the single fluoride coordinated to the titanium centre on the basis of spectra recorded for other titanium fluoride species [17]. Although it is possible to observe the ³J coupling between the cyclopentadienyl protons and the fluoride nuclei in Cp₂TiF₂ it is small (1.7 Hz [19]) and we were not able to resolve an equivalent coupling for complex **2** under similar spectroscopic conditions.

For all three compounds the proton NMR spectra exhibited a single peak between 6.4 and 6.5 ppm corresponding to the equivalent protons of the Cp rings. ¹³C-NMR spectra showed a signal within the range 116–119 ppm which is assigned to the carbons of the Cp rings. The ¹³C-NMR spectrum of a concentrated solution of Cp₂Ti(CF=CF₂)₂ dissolved in CDCl₃ also exhibits a complex multiplet at ca. 156.9 ppm, which by virtue of the number of couplings observed must be due to the two carbon nuclei of the perfluorovinyl ligand. However, it was not possible to obtain good-quality data for the perfluorovinyl part of the ¹³C-NMR spectra for the complexes due to their low solubility, the number of resonances involved and the rate of sample decomposition in common solvents, see below.

The IR spectra of the complexes are consistent with the anticipated structures and are assigned on the basis of previous vibrational spectroscopic studies of metallocene dihalides [20] and perfluorovinyl metal complexes [21]. The ν (C=C) vibrational mode of the perfluorovinyl group is assigned to the intense peak observed between 1637 and 1653 cm⁻¹ and the absorptions at ca. 1250, 1010 and 965 cm⁻¹ are assigned to the three ν (C–F) modes.

UV–vis studies of the complexes in acetonitrile solution gave rise to a number of absorptions of which those around 380–390 and 310–340 nm may be assigned to the Cp₂Ti fragment of the molecule on the basis of previous studies of Cp₂TiX₂ (X = halide) [22]. The symmetry allowed π – π^* transition of the perfluorovinyl ligand is expected around 200 nm according to the work of Lacher et al. on chloro- and fluoro-substituted ethylenes [23] and therefore, the intense peak observed at 210 nm (ϵ = 19 000 dm³ mol⁻¹ cm⁻¹) in the UV spectrum of compound **4** is assigned to this transition.

A number of attempts were made to synthesise the analogous zirconium complexes but these were always less successful. ¹⁹F-NMR spectra obtained prior to work-up procedures again showed consumption of the starting hydrofluorocarbon and the presence of new resonances which are consistent with those obtained for the titanium perfluorovinyl-containing analogues. However, the materials decomposed rapidly as the temperature of the solution was raised towards r.t. Decomposition was also evident for isolated solid products over a period of ca. 1 h. Because of this decomposition it did not prove possible to obtain satisfactory elemental analyses for any of the zirconium-containing compounds. In contrast the isolated titanium complexes are stable as solids, for example in a dry box; however, in solution they too decompose, but at varying rates. The time for complete decomposition in solution ranges from minutes to many days depending on the solvent used and the compound in question. In the hydrocarbon solvent systems that we have investigated the order

of stability for the titanium species appears to be $\text{Cp}_2\text{TiCl}(\text{CF}=\text{CF}_2) \ll \text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2 < \text{Cp}_2\text{TiF}(\text{CF}=\text{CF}_2)$ and the ultimate fate of the perfluorovinyl ligand is the generation of CF_2CFH . Interestingly, the same order of reactivity towards thermal decomposition is not observed for the perproto-vinyl analogues of the titanium and zirconium complexes, in this case the zirconium compounds are the more stable whilst $\text{Cp}_2\text{Ti}(\text{CH}=\text{CH}_2)_2$ rapidly decomposes at -30°C to ultimately generate vinylidene or metallacyclobutane complexes [24].

2.2. EXAFS studies

Because of the solution-phase decomposition of these products, it has proved impossible to obtain crystals suitable for characterisation by single-crystal X-ray diffraction methods for any of these complexes. However, we have been able to record room-temperature titanium K-edge EXAFS data for two of the perfluorovinyl-containing materials $\text{Cp}_2\text{TiF}_n(\text{CF}=\text{CF}_2)_{2-n}$ ($n = 0, 1$) milled in boron nitride. For comparison we have also recorded the EXAFS data for Cp_2TiCl_2 and Cp_2TiF_2 .

Data collection, averaging, background subtraction and modelling of the Fourier transforms of the EXAFS for Cp_2TiCl_2 , Cp_2TiF_2 and compounds **2** and **4** were carried out via standard methods [25]. The EXAFS spectra of all these compounds exhibit a small, sharp peak just below the absorption edge which may be assigned to the formally electron-dipole forbidden $1s \rightarrow 3d$ transition of the metal complex. The presence of such a feature is indicative of a non-centrosymmetric local environment such as that found in tetrahedral or pseudo-tetrahedral geometry around the central metal atom [26].

Background subtraction of the averaged data for Cp_2TiCl_2 , Cp_2TiF_2 , $\text{Cp}_2\text{TiF}(\text{CF}=\text{CF}_2)$ and $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$ resulted in the EXAFS spectra shown in Fig. 2(a–d). Analysis of the primary coordination shells for the compound Cp_2TiCl_2 , as a standard, was undertaken using a model consisting of one-shell of two chlorine atoms and one-shell of ten carbon atoms. Refinement of the model resulted in $d(\text{Ti}-\text{Cl}) = 2.389(5)$ and $d(\text{Ti}-\text{C}) = 2.379(16)$ Å. Despite the widespread applications of this complex it has only been the subject of a few structural determinations, with conflicting results. An early single-crystal X-ray determination [27] reported distances to two decimal places and provided no error estimates on the derived distances of $d(\text{Ti}-\text{C})_{\text{av}} = 2.36$ and $d(\text{Ti}-\text{Cl}) = 2.37$ Å. At a similar time an electron diffraction study [28] suggested that the titanium–chlorine distance was significantly shorter (2.24 Å) than the titanium–carbon distance (2.38 Å) but again no error estimates were provided. Therefore, meaningful com-

parisons can only be made with the results of a more recent X-ray diffraction study which shows an asymmetric unit containing two titanocene dichloride molecules but with essentially similar distances for the titanium–chlorine and titanium–carbon bonds within both molecules [$d(\text{Ti}-\text{Cl})_{\text{av}} = 2.364(3)$ and $d(\text{Ti}-\text{C})_{\text{av}} = 2.370(9)$ Å] [29]. Our EXAFS results also suggest similar, but slightly longer, Ti–Cl and Ti–C distances. However, the differences are small, ca. 1% for the titanium–chlorine distance and within experimental error for the titanium–carbon shell. It is most likely that the two similar distances result in a poorer distinction of the two shells than one might normally expect and that the much smaller back-scattering contribution of the carbon atoms compared with that arising from the chlorine shell results in larger than usual uncertainties in the parameters for the carbon shell.

The Fourier transforms of the EXAFS spectra of Cp_2TiF_2 , $\text{Cp}_2\text{TiF}(\text{CF}=\text{CF}_2)$ and $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$ are shown in Fig. 2(b,c,d), and in all cases a peak at ca. 2.4 Å is observed which is assigned to shell of ten carbon atoms of the two cyclopentadienyl ligands. In the spectra of the fluoride-containing compounds (Cp_2TiF_2 and **2**) a peak is also observed at around 1.8–1.9 Å which must correspond to the Ti–F distance. Modelling of the data for Cp_2TiF_2 in this way resulted in an R-factor of 20.2% and final bond distances of $d(\text{Ti}-\text{F}) = 1.855(6)$ Å and $d(\text{Ti}-\text{C}) = 2.378(12)$ Å. For compound **2** modelling the data with two shells (1F, 10C) resulted in a titanium–fluoride bond distance of 1.812(7) Å, a Ti–C distance of 2.404(10) Å and an R-factor of 27.9%. Inclusion of a third shell (1C), corresponding to the Ti–C distance of the bound perfluorovinyl ligand, resulted, after iteration, in a drop in the R-factor to 23.1% and a Ti–C_{pfv} distance of 2.050(18) Å. The validity of including this shell is unambiguously supported by the statistical tests of Joyner et al. [30] at the 1% level. Mapping of the occupation numbers of these two shells is consistent with there being one fluoride and one perfluorovinyl ligand coordinated to the titanium metal centre, with a minimum in the R-factor corresponding to occupation numbers of 1.0 F and 1.1 C. It should, however, be noted that in general EXAFS is not particularly sensitive to occupancy levels, typically confidence limits of ± 10 –20% being accepted. Further shells were added to the model corresponding to the non-bonded Ti···F and Ti···C distances of the perfluorovinyl ligand based on geometric calculations assuming C=C and C–F bond lengths of 1.3 and 1.35 Å, respectively [31], and 120° bond angles. This resulted in a reduction in the R-factor, but not at a statistically high enough level to be included in the final model and they are, by convention [32], omitted from the parameters which are given in Table 2.

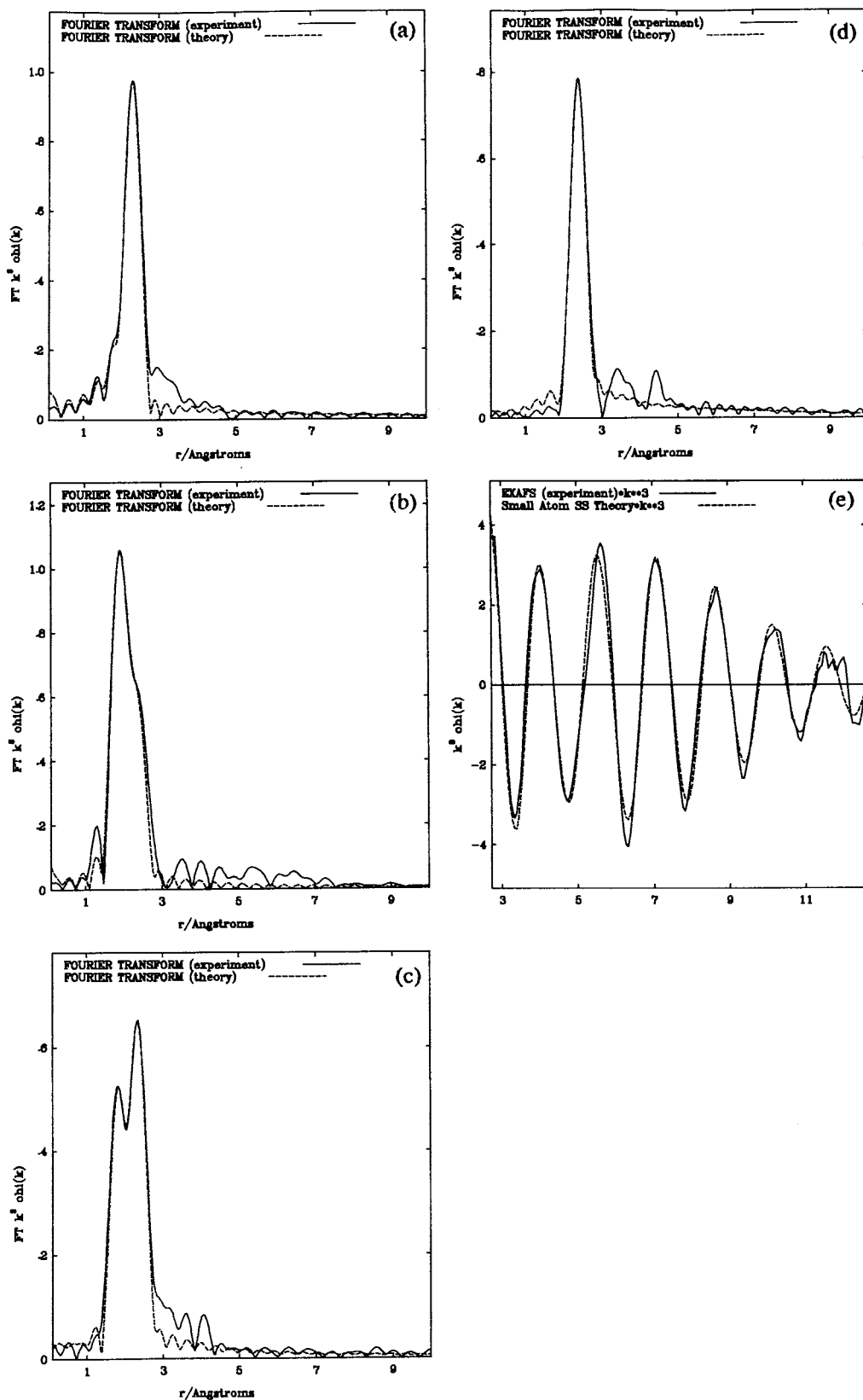


Fig. 2. The Fourier transformed EXAFS spectra (—, experimental; ---, theoretical) of (a) Cp_2TiCl_2 , (b) Cp_2TiF_2 , (c) $\text{Cp}_2\text{TiF}(\text{CF}=\text{CF}_2)$ and (d) $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$ and (e) the background subtracted Ti K-edge EXAFS spectra (—, experimental data $\times k^3$; ---, theory $\times k^3$) for $\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$ in boron nitride.

Table 2

EXAFS derived distances for the primary coordination shells of the compounds $\text{Cp}_2\text{TiX}_{2-n}(\text{CF}=\text{CF}_2)_n$ ($\text{X} = \text{F}, \text{Cl}; n = 0, 1, 2$)

Compound	Shell	Distance (Å) ^a	Debye-Waller (Å ⁻²) ^b	R-factor ^c
Cp_2TiCl_2	2.2 × Cl	2.389(5)	0.009(2)	19.7
	9.7 × C	2.379(16)	0.016(14)	
Cp_2TiF_2	2.1 × F	1.855(6)	0.006(1)	20.2
	9.7 × C	2.378(12)	0.019(2)	
$\text{Cp}_2\text{TiF}(\text{CF}=\text{CF}_2)$	1.0 × F	1.812(7)	0.001(1)	23.1
	1.1 × C	2.050(18)	0.007(7)	
	9.7 × C	2.404(10)	0.016(2)	
$\text{Cp}_2\text{Ti}(\text{CF}=\text{CF}_2)_2$	1.9 × C	2.033(12)	0.019(4)	19.0
	9.2 × C	2.416(4)	0.011(1)	

^a This work, standard deviations (2σ) are given in parentheses, systematic errors in bond distances arising from data collection and analysis procedures are estimated as ca. ± 0.02 Å.

^b Debye-Waller factor.

^c $R = [(\chi^{\text{Theory}} - \chi^{\text{Expt.}})k^3 dk / \int \chi^{\text{Expt.}} = k^3 dk] \times 100\%$, obtained after modelling of primary coordination shells only.

Modelling the Fourier transform of the EXAFS data for the bis-substituted complex **4** to a one-shell (2Cp, 10C) model resulted in an R-factor of 35.6%, whilst inclusion of a second shell containing two carbon back-scatterers corresponding to the two perfluorovinyl-carbons followed by iteration resulted in a reduction of the R-factor to 19.0% and a Ti–C_{pfv} distance of 2.033(12) Å. Once again, weaker features are observed at longer distances in the radial distribution plot and inclusion of these shells arising from the other atoms in the perfluorovinyl ligand at distances similar to those obtained from the previous compound resulted in a further reduction in the R-factor, but these parameters are not well defined and so not reported here. Fig. 2(e) shows the background subtracted k^3 weighted EXAFS data for compound **4** and its fit to the theoretically calculated k^3 EXAFS.

There are relatively few data with which to directly compare these distances. The Ti–F and Ti–C distances are consistent with those observed in related, structurally characterised, L_2TiF_2 systems. For example when $\text{L} = (\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3))$ [33] and $\text{L} = (\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)$ [34] $d(\text{Ti}-\text{F}) = 1.832(2)$ and $1.855(1)$ Å and the average Ti–C distance in $(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)_2\text{TiF}_2$ is $2.407(3)$ Å. There is, however, no published structural work for any metal-bound perfluorovinyl group and only one crystal structure for a metal-perhalovinyl compound [3,4,7,8 tetramethyl-1,10-phenanthroline-*N,N'*-(bis(trichlorovinyl))-mercury] [35], but this does not allow for meaningful comparison. We have recently obtained crystallographic data for some complexes containing perfluorovinyl-phosphorus(III) ligands. For *cis*-platinum(II) complexes containing $\text{PPh}_2(\text{CF}=\text{CF}_2)$ [36] we find an average P–

C_{pfv} distance of 1.808(12) Å which is essentially the same as that found for the P–C_{vinyl} distance [1.807(8) Å] recorded for the analogous complexes containing $\text{PPh}_2(\text{CH}=\text{CH}_2)$ [37]. For the two structurally characterised examples of titanium perproton-vinyl complexes ($\text{Cp}_2\text{Ti}(\text{CH}=\text{CH}_2)(\text{OC}(\text{CH}_2)\text{C}_6\text{H}_{11})$ and $\text{Cp}_2^*\text{Ti}(\text{CH}=\text{CH}_2)\text{F}$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) the Ti–C_{vinyl} distances are 2.143(4) and 2.098(6) Å, respectively [38,39]. The EXAFS-derived titanium–perfluorovinylcarbon bond lengths determined for compounds **2** [2.050(18) Å] and **4** [2.033(12) Å] are similar and both are slightly shorter (ca. 4% compared with $\text{Cp}_2^*\text{Ti}(\text{CH}=\text{CH}_2)\text{F}$) than those observed for the related vinyl complexes.

These two Ti–C_{pfv} distances represent the first reported estimates of this parameter for any metal-bound perfluorovinyl complex. We note that in both cases the obtained distances are similar to 2.03 Å, the sum of the covalent radii for Ti(IV) (1.36 Å) and sp² hybridised carbon (0.67 Å) [40]. This suggests that the perfluorovinyl group is bound in a simple σ -fashion and that there is no obvious π -delocalisation even though the metal is electron poor. This, however, is not surprising since there is also no evidence for π -donation in the $\text{Cp}_2^*\text{TiF}(\text{CH}=\text{CH}_2)$ system [$d(\text{Ti}-\text{C}_{\text{vinyl}}) = 2.099$ Å] despite the vinyl ligand presumably being a better potential π -donor than the fluorinated analogue.

3. Experimental

HFC-134a (ICI Klea), butyllithium (2.5 M in hexane, Aldrich), titanocenedichloride (Lancaster Synthesis) were used as supplied after verification of purity using spectroscopic methods. Diethyl ether (BDH) and THF (BDH) were dried by standing over sodium wire for ca. 1 day and subsequently refluxed over sodium/benzophenone under a dinitrogen atmosphere. Hexane (Cannon Scientific) was stored over sodium wire prior to use. Fluorine and proton NMR spectra were recorded on solutions of samples on a Bruker AC200 instrument at 188.3 and 200.2 MHz and referenced against CFCl_3 and TMS, respectively, using the high-frequency-positive convention. ¹³C-NMR spectra were recorded on a Bruker AC300 machine at 75.47 MHz and referenced against TMS. Elemental analyses were performed by the analytical service in the Department. IR spectra were recorded on a Nicolet PC5 instrument and mass spectra were recorded by the Michael Barber Mass Spectrometry centre, UMIST. All reactions were carried out under anaerobic and anhydrous conditions. All glassware was flame dried prior to use, and moisture sensitive reagents were handled under an argon atmosphere in a dry-box (Belle Technology, UK). All recorded reaction temperatures are uncorrected internal temperatures.

3.1. Preparation of bis(cyclopentadienyl)titaniumdifluoride

This was prepared based on literature methods [4] by reacting sodium fluoride (1.68 g, 40.00 mmol) dissolved in water (15 ml) with a suspension of bis-(cyclopentadienyl) titanium dichloride (5.00 g, 20.00 mmol) dissolved in 100 ml of water in a single neck round bottom flask. The reaction is vigorously stirred for 3 h yielding a yellow solid, which is subsequently filtered and dried overnight.

3.2. Fluoro(perfluorovinyl)bis(η^5 -cyclopentadienyl)-titanium(IV) **2**

A 1 l 3-neck flask held at -80°C is equipped with a magnetic stirrer, a rubber septum and a silicon oil bubbler and maintained under a positive flow of dinitrogen gas. The flask is charged with pre-cooled diethyl ether (200 ml, -50°C) and liquid HFC 134a (0.20 cm³, 2.32 mmol) in diethyl ether (50 ml, -80°C) is added. Butyllithium (2.5 M in hexane, 1.85 cm³, 4.63 mmol) was added slowly to the stirred solution over a 0.5 h period. Once addition of the BuLi is complete the reaction temperature is maintained between -55 and -80°C for 2 h to ensure generation of $\text{CF}_2=\text{CF}-\text{Li}^+$. The reaction mixture temperature is lowered to -110°C and bis-cyclopentadienyl titanium difluoride (0.50 g, 2.32 mmol), dissolved in THF (200 ml, -80°C), is added slowly. The reaction is left to warm to -35°C over a period of a few hours and then allowed to attain r.t. by removal of the slush bath. The solvent volume is reduced in vacuo to half and hexane (300 ml) is added, resulting in the precipitation of lithium salts, from the organic phase. The mixture is allowed to settle before being carefully filtered through a No. 4 sinter under a dinitrogen atmosphere. The solvent is then removed in vacuo to leave a pastel orange solid which is subsequently washed with hexane (4×10 cm³), and dried under vacuum for 30 min to afford **2** as a yellow–orange coloured material Yield 0.56 g, 88%. m.p. (uncorrected) 135(dec.) $^\circ\text{C}$. (Found: C, 50.5; H, 4.1; F, 25.2%. $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CF}=\text{CF}_2)\text{F}$ requires: C, 51.8; H, 3.6; F, 27.3%). $\delta\text{C}\{^1\text{H}\}$ (CDCl_3), 119.0 [m, C_5H_5]; $\nu_{\text{max}}/\text{cm}^{-1}$ 1637 (C=C), 1636, 1233, 1009, 962, 827 (nujol mull); m/z (CI NH_4^+) 276 ($[\text{M}-2\text{H}]^+$, 100%), 259 (10%, $[\text{M}-\text{F}]^+$), 195 (20, $[\text{M}-2\text{H}-\text{C}_2\text{F}_3]^+$); UV–vis $\lambda_{\text{max}}/\text{nm}$ (MeCN) 462, 378, 312, 243 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 650, 1750, 3950 and 14 800).

3.3. Chloro(perfluorovinyl)bis(η^5 -cyclopentadienyl)-titanium(IV) **3**

Compound **3** was prepared using a similar preparative method to that for **2**. BuLi 2.5 M (6.44 cm³, 16.08 mmol) is added to a solution of HFC 134a (0.68 cm³,

8.04 mmol) in diethyl ether (180 ml, -80°C). After ca. 2 h Cp_2TiCl_2 (2.00 g, 8.04 mmol), dissolved in THF (250 ml, -80°C), is added slowly to the reaction mixture which is held at -110°C . After the reaction is complete it is worked up as previously described resulting in a red–orange coloured material. Yield 2.05 g, 87%. m.p. (uncorrected) 150(dec.) $^\circ\text{C}$. $\delta\text{C}\{^1\text{H}\}$ (CDCl_3), 116.5 [m, C_5H_5]; $\nu_{\text{max}}/\text{cm}^{-1}$ 1653 (C=C), 1653, 1234, 1005, 966, 819 (nujol mull); m/z (CI NH_4^+) 312 ($[\text{M}+\text{NH}_4]^+$, 5%), 213 (100, $[\text{M}-\text{C}_2\text{F}_3]^+$), 197 (35, $[\text{M}-\text{C}_2\text{F}_2\text{Cl}]^+$); UV–vis $\lambda_{\text{max}}/\text{nm}$ (MeCN) 389, 248 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 3550 and 16 550).

3.4. Bis(perfluorovinyl)bis(η^5 -cyclopentadienyl)titanium(IV) **4**

In a similar procedure to that outlined for compound **2**, to cold liquid HFC 134a (4.06 cm³, 48.19 mmol) in hexane (400 ml) is added butyllithium (2.5 M in hexane, 38.55 cm³, 96.33 mmol) over a 0.5 h period. After 2 h the temperature of the reaction mixture is lowered to -110°C and bis-cyclopentadienyl titanium dichloride (4.00 g, 16.06 mmol), dissolved in THF (400 ml, -80°C), is added slowly. After warming to r.t. the solvent volume is reduced and hexane is added. The mixture is filtered under a dinitrogen atmosphere and the volatile organic solvents are removed in vacuo. The orange solid is washed with hexane (4×10 cm³), and dried under vacuum for 30 min. to afford **4** as a light orange coloured material. Yield 4.8 g, 88%, m.p. (uncorrected) 131 $^\circ\text{C}$.

(Found: C, 49.2; H, 3.2; F, 33.5; Ti, 14.4%. $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CF}=\text{CF}_2)_2$ requires: C, 49.4; H, 2.9; F, 33.5; Ti, 14.1%). $\delta\text{H}(\text{CDCl}_3)$, 6.40 (s, C_5H_5); $\delta\text{C}\{^1\text{H}\}$ (CDCl_3), 156.9 [m, $\text{CF}=\text{CF}_2$], 118.1 [m, C_5H_5]; $\nu_{\text{max}}/\text{cm}^{-1}$ (nujol mull) 1637, (C=C), 1262, 1009, 966 (C–F); m/z (CI NH_4^+) 358 ($[\text{M}+\text{NH}_4]^+$, 30%), 276 (100, $[\text{M}+\text{NH}_4-\text{C}_2\text{F}_3]^+$), 214 (70, $[\text{M}+\text{NH}_4-\text{C}_4\text{F}_5]^+$); UV–vis $\lambda_{\text{max}}/\text{nm}$ (MeCN) 468, 394, 344, 235(sh), 210 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 1075, 2065, 1830, 15 100 and 19 000).

3.5. Bis(perfluorovinyl)bis(η^5 -cyclopentadienyl)-zirconium(IV) **5**

A preparative route similar to that for **2** outlined above was used. BuLi (2.5 M, 20.0 cm³, 0.050 mol) is added to a solution of HFC 134a (2.16 cm³, 0.026 mol) in diethyl ether (180 cm³, -80°C). After ca. 5 h Cp_2ZrCl_2 (3.00 g, 0.010 mol) dissolved in THF (25 cm³, -80°C) is added slowly to the reaction mixture which is held at -110°C . The reaction is left to warm slowly to -35°C and then allowed to attain r.t. by removing the slush bath. The solvent volume is reduced in vacuo by 80 ml and hexane (100 cm³) is added which results in the separation of dark polymeric material and precipi-

tation of the lithium salts. The mixture is allowed to settle before being filtered through a No. 4 sinter under a dinitrogen atmosphere. The solvent is then removed in vacuo to leave an oily brown residue. A light brown precipitate is extracted by washing with $2 \times 20 \text{ cm}^3$ of hexane followed by filtration under a dinitrogen atmosphere. Yield 1.45 g, 38%, m.p. (uncorrected) 131°C , dec. $\delta\text{F}(\text{CDCl}_3)$, -92.3 [1F, dd, $J(\text{FF})$ 34.4, 80.7 Hz, $\text{CF}=\text{CFF}$], -115.4 [1F, dd, $J(\text{FF})$ 80.7, 105.9 Hz, $\text{CF}=\text{CFF}$], -161.6 [1F, dd, $J(\text{FF})$ 34.4, 105.9 Hz, $\text{CF}=\text{CF}_2$]; $\delta\text{H}(\text{CDCl}_3)$, 6.4 [s, C_5H_5]; $\delta\text{C}\{^1\text{H}\}$ (CDCl_3), 111.0 [m, C_5H_5]; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr disc) 3100 (C–H), 1665 (C=C), 1233, 1015, 968 (C–F).

3.6. Chloro(perfluorovinyl)bis(η^5 -cyclopentadienyl)-zirconium(IV) **6**

A similar preparative method to that for compound **2** was used. BuLi (2.5 M, 9.50 cm^3 , 0.024 mol) is added to a solution of HFC 134a (1.0 cm^3 , 0.012 mol) in diethyl ether (200 cm^3 , -80°C). After ca. 5h Cp_2ZrCl_2 (3.51 g, 0.012 mol) dissolved in THF (50 cm^3 , -80°C) is added to the reaction mixture which is held at -110°C . The reaction is slowly allowed to warm to r.t. overnight and then worked up as described previously. 1.26 g, 31% m.p. (uncorrected) 150°C dec. $\delta\text{F}(\text{CDCl}_3)$, -97.65 [1F, dd, $J(\text{FF})$ 36 Hz, $J(\text{FF})$ 76 Hz, $\text{CF}=\text{CFF}$], -110.2 [1F, dd, $J(\text{FF})$ 76 Hz, $J(\text{FF})$ 107 Hz, $\text{CF}=\text{CFF}$], -130.9 [1F, dd, $J(\text{FF})$ 107 Hz, $J(\text{FF})$ 36 Hz, $\text{CF}=\text{CF}_2$]; $\delta\text{H}(\text{CDCl}_3)$, 6.3 [s, C_5H_5]; $\delta\text{C}\{^1\text{H}\}$ (CDCl_3), 114.0 [m, C_5H_5]; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr disc) 3105 (C–H), 1667 (C=C), 1232, 1013, 966 (C–F).

3.7. EXAFS measurements

The EXAFS studies were carried out on solids ground with boron nitride (Aldrich) and packed into a 1 mm thick aluminium spacer and held in place using sticky tape. The Ti K-edge transmission spectra were recorded at the Daresbury Synchrotron Radiation Source, UK, operating at 2 GeV (ca. 3.2×10^{-10} J) with an average operating current of 210 mA on station 9.2 using Si(220) monochromator offset to 50% of the rocking curve for harmonic rejection. Four data sets were collected in k -space for each sample and averaged to improve the signal-to-noise ratio. No sample decomposition was detected during the experiment. Background subtraction of the data was performed using the program EX [41]. A second-order polynomial was fitted to the pre-edge region and this was subtracted from the spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using a high-order polynomial and the optimal fit judged by minimising the intensity of chemically insignificant peaks at low r in the Fourier transform. Because the number, and more particularly the atomic

number, of backscattering atoms around the titanium centre are relatively low the amount of backscattering is small and the data has a poor signal to noise ratio at high k -values, even after averaging a number of data-sets; for this reason modelling of the data was typically confined to the region $k = 3.5$ to $k = 12.5$. Modelling of the background subtracted k^3 -weighted EXAFS used curved-wave theory with phase shifts calculated using the default ab initio method of the program EXCURVE [42]. The refinement process involved iteration of the distances and Debye–Waller factors for each shell as well as the Fermi energy difference (E_f) against the background subtracted data. After the lowest R-factor was obtained in this way the shell occupation numbers were iterated against the shell radii and E_f value. During modelling all shells were tested for statistical significance according to the usual methods [30] and only those that passed at the 95% confidence limits, or better, are included.

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