



Supporting Information

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Carbon-Fluorine Bond Activation in Fluoroolefins: The First Clear Documentation of Cooperative C-F Activation by Adjacent Metal Centers

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1. Experimental

General Comments. All solvents were dried (using appropriate drying agents), distilled before use and stored under dinitrogen. Deuterated solvents used for NMR experiments were freeze-pump-thaw degassed (three cycles) and stored under nitrogen or argon over molecular sieves. Reactions were carried out under argon using standard Schlenk techniques, and compounds that were obtained as solids were purified by recrystallization. Prepurified argon and nitrogen were purchased from Linde, carbon-13 enriched CO (99%) was supplied by Isotec Inc, *cis*-difluoroethylene and 1,1-difluoroethylene were supplied by Lancaster Synthesis, trifluoroethylene was supplied by SynQuest Fluorochemicals or prepared by a literature method,¹ and tetrafluoroethylene was prepared by a literature method.² All purchased gases were used as received. All other reagents were obtained from Aldrich and were used as received (unless otherwise stated). The compound $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\eta\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**), its olefin adducts, $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\eta\text{-C}_2\text{F}_4)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**2**), $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\eta\text{-C}_2\text{F}_3\text{H})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**3**), and the mixture of isomers $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\eta\text{-C}_2\text{F}_2\text{H}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**4**) and $[\text{Ir}_2(\text{CH}_3)(\eta^2\text{-C}_2\text{F}_2\text{H}_2)(\text{CO})_2(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**4a**) were prepared as previously reported.^{3,4}

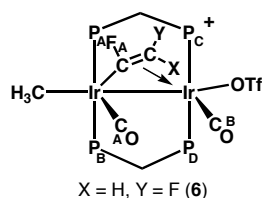
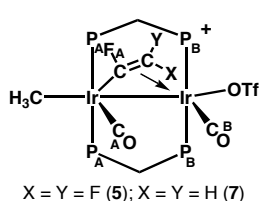
Proton NMR spectra were recorded on Varian Unity 400, 500 or 600 spectrometers, or on a Bruker AM400 spectrometer. Carbon-13 NMR spectra were recorded on Varian Unity 400 or Bruker AM300 spectrometers. Phosphorus-31 and fluorine-19 NMR spectra were recorded on Varian Unity 400 or Bruker AM400 spectrometers. Two-dimensional NMR experiments (COSY, ROESY, TOCSY and ^{13}C - ^1H HMQC) were obtained on Varian Unity 400 or 500 spectrometers. The $^{13}\text{C}\{^1\text{H}\}$ NMR data reported were acquired using the appropriate ^{13}C -labelled moiety (i.e. carbonyl or methyl) in the compound, while all IR data reported were taken from measurements on non-labelled complexes. IR spectra were obtained on a Bio-Rad RTS-60 Fourier transform infrared spectrometer, as solutions in KCl cells with 0.5-mm-window path lengths, or as solids using a Nicolet Magna 750 with a Nic-Plan infrared microscope. Mass spectrometric analyses

were performed by positive ion electrospray ionization mode using a Micromass ZabSpec Hybrid Sector-TOF. Spectral data for all compounds are given in Table S1.

Preparation of Compounds

- (a) $[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\eta^1\text{-}\eta^2\text{-C}_2\text{F}_3)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**5**). 50 mg of compound **2** (0.034 mmol) was dissolved in 7 mL of CH_2Cl_2 and cooled to -20°C . 30 μL of neat trimethylsilyl triflate ($\text{Me}_3\text{SiSO}_3\text{CF}_3$) was added dropwise and the mixture stirred at this temperature for 1 $\frac{1}{2}$ h. The resulting solution was reduced *in vacuo* to ca. 5 mL and pentane was added to precipitate a dark yellow microcrystalline compound. At temperatures above 0°C compound **5** was unstable and transformed into its isomer **8**. Isolated samples of **5** always contained substantial amounts of **8**, often with the latter as the dominant species. Characterization of **5** was by multinuclear NMR spectroscopy at -20°C . The preparation of pure **8** is described in part (d).

Below are diagrams showing the labeling for NMR-active nuclei used in Table S1 for compounds **5** – **7**.

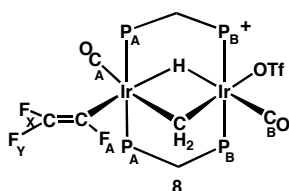


- (b) $[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\eta^1\text{-}\eta^2\text{-C}_2\text{F}_2\text{H})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**6**). 10 μL of $\text{Me}_3\text{SiSO}_3\text{CF}_3$ was added dropwise to a dichloromethane solution (5 mL) of compound **3** (50 mg, 0.037 mmol) that had been cooled to 0°C . This mixture was subsequently stirred at this temperature for $\frac{1}{2}$ h under argon. The resulting yellow-orange solution was warmed to ambient temperature, and Et_2O was added to precipitate a pale yellow microcrystalline compound **6**. The product was washed twice with 10 mL of Et_2O , the supernatant decanted, and then the solid was dried briefly under a stream of argon and then *in vacuo* (65% yield). HRMS m/z calcd for $\text{Ir}_2\text{P}_4\text{O}_5\text{C}_{56}\text{H}_{48}\text{F}_5\text{S}$ $[\text{M}]^+$: 1435.1395. Found: 1435.1391.
- (c) $[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\eta^1\text{-}\eta^2\text{-C}_2\text{FH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**7**). To a 2:1 mixture of compounds **4** and **4a** in dichloromethane at -40°C was added dropwise 30 μL of $\text{Me}_3\text{SiSO}_3\text{CF}_3$. An immediate reaction with **4** produced a yellow-orange solution

mixture of **7** and unreacted **4a**. No change in the concentration of **4a** was noted. Upon warming to 0°C and above, compound **7** underwent rearrangements to give a number of subsequent products, the identification of which is currently being pursued.

- (d) **[Ir₂(η^1 -C₂F₃)(CF₃SO₃)(CO)₂(η -CH₂)(η -H)(dppm)₂][CF₃SO₃] (**8**). **Method a)** 50 mg of compound **2** (0.034 mmol) was dissolved in 7 mL of CH₂Cl₂ and cooled to -20°C. 30 μ L of Me₃SiSO₃CF₃ was added dropwise and the mixture stirred while allowing it to warm to room temperature over a 3 h period. The resulting solution was reduced *in vacuo* to ca. 5 mL and pentane was added to precipitate a pale yellow microcrystalline compound **8**. Isolated samples of **8** generated via this method frequently contained some proportion of compound **5** as an impurity. **Method b)** 50 mg of compound **2** (0.034 mmol) was slurried into 7 mL of benzene. 30 μ L of Me₃SiSO₃CF₃ was added dropwise and the mixture refluxed for 1h under argon. The resulting solution was cooled to 5°C in an ice-water bath to induce the precipitation of a pale yellow microcrystalline compound **8**. The clear yellow supernatant was decanted, the product was washed twice with 10 mL of pentane, and then dried briefly under a stream of argon and then *in vacuo* (68% yield). HRMS *m/z* calcd for Ir₂P₄O₅C₅₆H₄₇F₆S [M]⁺: 1453.1300. Found: 1453.1301.**

Diagram showing the labeling for Table S1 is given below.



- (e) **[Ir₂(CH₃)(CF₃SO₃)(CO)₂(η -C₂F₂)(dppm)₂][CF₃SO₃]₂ (**9**). 50 mg of compound **5** (0.031 mmol) was prepared in 7 mL of CH₂Cl₂ at 0°C. 30 μ L of Me₃SiSO₃CF₃ was added dropwise, the mixture was warmed to room temperature and stirred for 1 ½ h. The resulting yellow solution was reduced *in vacuo* to dryness and extracted into 5 mL of benzene. 20 mL of pentane was added to precipitate a pale yellow microcrystalline compound **9**. The supernatant was decanted, and the product was washed twice with 10 mL of pentane, and then dried briefly under a stream of argon and then *in vacuo* (63% yield). Anal. Calcd. for Ir₂S₃P₄F₁₁O₁₁C₅₈H₄₇: C, 40.19; H, 2.73. Found: C, 40.40; H, 3.15%.**

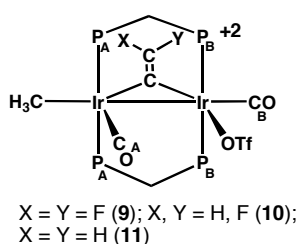
Table S1 Spectral Data for the Fluorovinyl and Fluorovinylidene Compounds^{a, b}

compounds ^c	$\delta(^{31}\text{P}\{^1\text{H}\})^d$	$\delta(^1\text{H})^{e, f}$	$\delta(^{13}\text{C}\{^1\text{H}\})^e$	$\delta(^{19}\text{F})^g$	IR cm ⁻¹
$[\text{Ir}_2(\text{CH}_3)(\text{OTf})(\text{CO})_2(\eta^1\text{-}\eta^2\text{-CF=CF}_2)(\text{dppm})_2]^+$ (5) ^h	13.0 (t, 2P _B), -8.0 (t, 2P _A) (² J _{PP} = 24 Hz)	4.5 (b, 2H, CH ₂), 3.6 (b, 2H, CH ₂), 1.4 (dt, 3H, ³ J _{HP} = 5.6 Hz, ³ J _{HF} = 6.0 Hz)	161 (b, CO _B), 178 (b, CO _A), -19	-80, -120, -131, -76 (OTf)	
$[\text{Ir}_2(\text{CH}_3)(\text{OTf})(\text{CO})_2(\eta^1\text{-}\eta^2\text{-CF=CFH})(\text{dppm})_2]^+$ (6)	9.0 (m, 1P, P _D), -2.5 (m, 2P, P _{B,C}), -19.0 (m, 1P, P _A)	6.1 (m, 1H), 6.0 (dd, 1H _X , ² J _{HF} = 65 Hz, ³ J _{HF} = 10 Hz), 5.6 (m, 1H), 5.5 (m, 1H), 4.7 (m, 1H), 1.2 (t, 3H, ³ J _{HP} = 6.0 Hz)	165 (b, CO _B), 172 (b, CO _A), -23	-23, -171, -77 (OTf)	2039 1997
$[\text{Ir}_2(\text{CH}_3)(\text{OTf})(\text{CO})_2(\eta^1\text{-}\eta^2\text{-CF=CH}_2)(\text{dppm})_2]^+$ (7) ^h	1.6 (dt, 2P _B , ³ J _{PF} = 45 Hz), -5.5 (t, 2P _A), (² J _{PP} = 18 Hz)	6.0 (d, 1H _Y , ² J _{HH} = 6 Hz), 5.4 (dd, 1H _X , ² J _{HH} = 6 Hz, ³ J _{HF} = 14 Hz), 4.3 (m, 2H), 3.1 (m, 2H), 0.2 (t, 3H, ³ J _{HP} = 5.6 Hz)	164 (d, CO _B), 172 (t, CO _A), 5	-211, -77 (OTf)	
$[\text{Ir}_2(\eta^1\text{-CF=CF}_2)(\text{OTf})(\text{CO})_2(\eta\text{-H})(\eta\text{-CH}_2)(\text{dppm})_2]^+$ (8)	-0.5 (m, 2P _B), -28.5 (m, 2P _A), (² J _{PP} = 26 Hz)	6.4 (q, ³ J _{HP} = 6.0 Hz, 2H), 5.0 (m, 4H), -12.2 (b, s, 1H)	164 (dt, CO _A), 166 (b, CO _B), 38	-92, -121, -123, -76 (OTf)	2050 1998
$[\text{Ir}_2(\text{CH}_3)(\text{OTf})(\text{CO})_2(\eta\text{-C=CF}_2)(\text{dppm})_2]^{+2}$ (9)	-6.2 (t, 2P _A), -20.6 (t, 2P _B) (² J _{PP} = 21 Hz)	4.1 (m, 2H), 2.8 (m, 2H), 1.9 (t, 3H, ³ J _{HP} = 9.0 Hz)	151 (b, CO _B), 174 (b, CO _A), 38	-69, -86, -76 (OTf)	2037 2012
$[\text{Ir}_2(\text{CH}_3)(\text{OTf})(\text{CO})_2(\eta\text{-C=CFH})(\text{dppm})_2]^{+2}$ (10)	-5.0 (t, 2P _A), -21.0 (t, 2P _B) (² J _{PP} = 23 Hz)	8.6 (d, 1H, ² J _{HF} = 85 Hz) ⁱ , 4.3 (m, 2H), 2.8 (m, 2H), 2.15 (t, 3H, ³ J _{HP} = 9.0 Hz)	153 (t, CO _B), 176 (b, CO _A), 41	-107, -76 (OTf)	2048 2005
$[\text{Ir}_2(\text{CH}_3)(\text{OTf})(\text{CO})_2(\eta\text{-C=CH}_2)(\text{dppm})_2]^{+2}$ (11) ^h	-10.0 (t, 2P _B), -20.0 (t, 2P _A), (² J _{PP} = 17 Hz)	6.01 (s, 1H) ⁱ , 5.99 (s, 1H) ⁱ , 4.1 (m, 2H), 2.9 (m, 2H), 1.25 (t, 3H, ³ J _{HP} = 4.9 Hz)	164 (b, CO _B), 170 (b, CO _A), 0.2	-77 (OTf)	

^a NMR abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. ^b NMR data CD₂Cl₂ unless otherwise stated. ^c In all cases trifluoromethanesulfonate is the accompanying anion. ^d ³¹P{¹H} chemical shifts are referenced vs. external 85% H₃PO₄. ^e ¹H and ¹³C chemical shifts are referenced vs. external TMS. ^f Chemical shifts for the phenyl hydrogens are not given in the ¹H data. ^g Free anion (CF₃SO₃⁻) resonance occurs at -79 ppm in the ¹⁹F spectrum. For a detailed discussion of the coupling within the fluorovinyl ligands, see the Additional Characterization Information in Section 2. ^h Low temperature species. ⁱ Vinylidene protons. Assignment as H_X or H_Y has not been made.

Surprisingly, mass spectrometric analysis did not yield the expected dicationic species, but instead gave a monocationic species that was consistent with the formulation $\text{Ir}_2\text{P}_4\text{O}_3\text{C}_{55}\text{H}_{47}\text{F}_2$, which could have arisen from triflate replacement by a water molecule in the mass spectrometer, followed by loss of two protons. Such transformations of highly charged complexes have been reported.⁵ HRMS m/z calcd for $\text{Ir}_2\text{P}_4\text{O}_3\text{C}_{55}\text{H}_{47}\text{F}_2$ $[\text{M}^{+3} + \text{H}_2\text{O} - 2\text{H}^+]^+$: 1303.1703. Found: 1303.1714.

Diagram for the labeling of compounds **9** – **11** in Table S1 is given below:



(a) **$[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\square\text{-C}_2\text{FH})(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (**10**)**. 50 mg of compound **6** (0.032 mmol) was dissolved in 7 mL of CH_2Cl_2 , 30 μL of $\text{Me}_3\text{SiSO}_3\text{CF}_3$ was added dropwise and the mixture stirred at ambient temperature for 1 ½ h. The resulting yellow solution was reduced *in vacuo* to ca. 5 mL and pentane was added to precipitate a pale yellow microcrystalline compound **10**. After isolation, the product was washed twice with 10 mL of pentane, and then dried briefly under a stream of argon and then *in vacuo* (61% yield). Anal. Calcd. for $\text{Ir}_2\text{S}_3\text{P}_4\text{F}_{10}\text{O}_{11}\text{C}_{58}\text{H}_{48}$: C, 40.61; H, 2.82. Found: C, 40.28; H, 3.18%. Suitable HRMS data were not obtained on this compound, however the LRMS mass spectrum of **10** shows a parent ion at 1285 dalton with the correct isotope pattern for the analogous type of species found with compound **9**, m/z calcd for $\text{Ir}_2\text{P}_4\text{O}_3\text{C}_{55}\text{H}_{48}\text{F}$ $[\text{M}^{+3} + \text{H}_2\text{O} - 2\text{H}^+]^+$: 1285.1703.

(b) **$[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\square\text{-C}_2\text{H}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (**11**)**. 30 μL of $\text{Me}_3\text{SiSO}_3\text{CF}_3$ was added dropwise to a 1:1 mixture of compounds **7** and **4a** (*vide supra*) and the mixture left at 0°C for 1 h. Upon warming the resulting yellow solution of **11** and **4a** to ambient temperature, subsequent transformations of **11** into unidentified products occurred so characterization of this product was based on multinuclear NMR at -20°C.

Addition of Hydrogen to Fluorovinyl Complexes

In a typical experiment, 50 mg (~0.033 mmol) of the fluorovinyl complex, was dissolved in 0.7 mL of CD_2Cl_2 in an NMR tube at -78°C. To this solution was slowly added between 1

and 5 equivalents (0.5 mL to 2.5 mL) of gaseous hydrogen by means of a gas-tight syringe. NMR spectra (^{31}P , ^1H , ^{13}C and ^{19}F) were recorded from -80°C to ambient temperature at 20°C intervals, and followed over a 24 h period. NMR spectroscopy has been used in the characterization of all products generated from the reaction of hydrogen with the fluorovinyl complexes (**6** and **8**, respectively), along with the final common product in both instances, the previously isolated tetrahydride complex $[\text{Ir}_2(\text{H})_2(\text{CO})_2(\mu\text{-H})_2(\text{dppm})_2]^{+2}$, which has been further characterized by X-ray crystallography.⁶ Identification of the fluoroolefin products generated was established by spectral comparison to the known compounds.⁷ When a sample of compound **8** was left overnight under an atmosphere of H_2 , trifluoroethylene was produced quantitatively as the only fluorinated organic compound (other than CF_3SO_3^-) observed in the ^{19}F NMR spectrum. In the case of **6**, both *cis*-difluoroethylene and *cis*-difluoropropene were observed as the major ^{19}F -containing products in the ^{19}F NMR spectrum, in approximately a 2:1 ratio. The only other fluorine-containing product displayed two fluorine resonances and was present in between 10 and 15% yield. This unidentified species was not the hydrogenation product of either of the two olefins observed, as judged by a comparison of the ^{19}F NMR spectrum with those of the authentic samples.

Addition of Carbon Monoxide to Fluorovinyl Complexes

In a typical experiment, 50 mg (~ 0.033 mmol) of the fluorovinyl complex, was dissolved in 0.7 mL of CD_2Cl_2 in an NMR tube at -78°C . To this solution was slowly added between 1 and 5 equivalents of gaseous carbon monoxide by means of a gas-tight syringe. NMR spectra (^{31}P , ^1H , ^{13}C and ^{19}F) were recorded from -80°C to ambient temperature at 20°C intervals, and followed over a 24 h period. NMR spectroscopy has been used in the characterization of all products generated from the reaction of CO with the fluorovinyl complexes (**6** and **7**, respectively), along with the final common product in both instances, the previously isolated pentacarbonyl complex $[\text{Ir}_2(\text{CO})_4(\mu\text{-CO})(\text{dppm})_2]^{+2}$. Identification of the fluoroolefin products generated was established by spectral comparison to the known compounds.⁷ When a sample of compound **6** was left overnight under an atmosphere of CO, *cis*-difluoropropene was produced in quantitative yields as the only fluorinated organic compound (other than CF_3SO_3^-) observed in the ^{19}F NMR spectrum, while in the case of compound **7**, 2-fluoropropene was the exclusive ^{19}F -containing product.

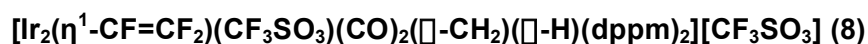
2. Additional Information on Compound Characterization

Explanations below are given as additional support for the structural assignments on all reported compounds, particularly regarding the fluorocarbyl ligands.

[Ir₂(CH₃)(CF₃SO₃)(CO)₂(η - η ¹: η ²-C₂F₃)(dppm)₂][CF₃SO₃] (5)

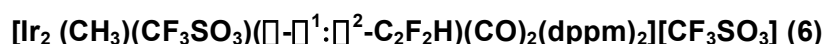
The ¹³C{¹H} NMR spectrum of a ¹³CO-enriched sample of **5** shows two broad multiplet carbonyl resonances at 161 ppm and 178 ppm. The lower-field shift of the latter suggests that this carbonyl (CO_A) approaches the second metal, possibly even interacting with it weakly in a semi-bridging arrangement.⁸ This arrangement is confirmed through the ¹³C{¹H, ³¹P} NMR spectrum in which the terminal carbonyl at 161 ppm (CO_B) shows unresolved coupling only to the pair of phosphorus nuclei (P_B) on the non-methylated metal (13.0 ppm), while the down-field signal at 178 ppm shows unresolved coupling to both sets of phosphine resonances as demonstrated by sharpening of the signals upon selective ³¹P decoupling experiments. Both carbonyls are also coupled to different fluorine atoms in the complex; the lower-field shift is coupled through the σ bond to the fluorine on the α carbon (-131 ppm), while the higher-field signal couples through the π bond to one of the geminal fluorines (-120 ppm), again helping to establish the bridging orientation of the perfluorovinyl moiety. The ¹³CH₃-enriched methyl group displays a broad high-field doublet at -19 ppm, arising from another long-range coupling to a single fluorine (⁴J_{CF} = 13.0 Hz) at -120 ppm.

The resulting trifluorovinyl group of **5** appears in the ¹⁹F NMR spectrum as three new signals, at -80 ppm, -120 ppm and -131 ppm, consistent with the general chemical shifts expected for a trifluorovinyl moiety. The two lower-field resonances show mutual coupling of 85 Hz, which is consistent with the geminal coupling of an sp² hybridized CF₂ group.⁹ Coupling of the two high-field resonances is 100 Hz, which suggests a trans arrangement of these two fluorines: the lower than usual coupling value is consistent with the presence of a π interaction of the vinyl group with the second metal. Finally, the cis orientation of the remaining pair is confirmed through their mutual coupling of 20 Hz, which is also diminished relative to that of a terminal arrangement, suggesting the presence of a bridging perfluorovinyl moiety in the molecule. Other couplings between the fluorine atoms and other active nuclei in the fully ¹³C-labelled compound (noted above) have confirmed the assignment of the orientation of the perfluorovinyl group as bridging. Also in the ¹⁹F NMR spectrum, the Me₃SiF that is generated in the above transformation of **2** to **5** appears as a characteristic signal at -159 ppm, along with two clearly separated signals at -76 ppm and -79 ppm, each integrating for three fluorines, corresponding to the coordinated and free triflate counterions, respectively.



We have not yet established the detailed mechanism of the rearrangement of **5** to **8**, which gives rise to hydride and methylene groups on opposite faces of the complex; however, it seems to occur by a deprotonation/reprotonation sequence as evidenced by the observation of free triflic acid at intermediate times, appearing at approximately 12 ppm in the ^1H NMR spectrum.

Again the ^{19}F NMR spectrum shows the characteristic signals and couplings of a perfluorovinyl group; however now the orientation is clearly terminal. Three new signals, all doublets of doublets, appear at -92 ppm, -121 ppm and -123 ppm. Consistently, the two lower field signals again show mutual geminal coupling of 90 Hz, while the two higher-field signals display the normal 115 Hz coupling of two fluorine atoms in a trans arrangement. The remaining pair also show mutual cis coupling of 40 Hz to one another. Another sharp singlet, in addition to that seen at -79 ppm for the free triflate counterion, is also observed in the ^{19}F NMR spectrum at -76 ppm which is consistent with a coordinated triflate ion.¹⁰ The proposed geometry has been confirmed by an X-ray structure determination, as shown in Part 3.



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** reveals a pattern that is characteristic of an ABCD spin system, indicating four inequivalent phosphorus environments. Signals are present at 9.0 ppm (1P), -2.5 ppm (2P) and -19.0 ppm (1P), each appearing as a complex multiplet showing some mutual coupling to its neighbors. Two distinct magnitudes of $^2J_{\text{PP}}$ couplings are apparent, with the smaller, more typical, $^2J_{\text{PP}}$ couplings of the diphosphine groups, consistent with the absence of lateral symmetry within the molecule, while the much larger coupling (~320 Hz) is between nonequivalent phosphorus atoms oriented in a trans arrangement across the metals, indicative of a lack of top/bottom symmetry. Accidental superposition of the signals from two inequivalent phosphorus nuclei accounts for the appearance of only three resonances, the central one of which is of double intensity. In the ^1H NMR spectrum the dppm methylene protons appear as four separate multiplets at 6.1 ppm (1H), 5.6 ppm (1H), 5.5 ppm (1H) and 4.7 ppm (1H) with characteristic 14 Hz coupling to phosphorus. The vinylic proton is identifiable in the ^1H -NMR spectrum by its distinct splitting pattern, which appears as a multiplet (dddd) at 6.0 ppm with all of the couplings resolvable. The first and most prominent coupling is the diagnostic hydrogen-fluorine coupling ($^2J_{\text{HF}}$), with a value of 65 Hz, consistent with the geminal coupling of an sp^2 hybridized -C(H)F group.¹¹ The smaller coupling ($^3J_{\text{HF}} = 10$ Hz) is consistent with the H and

the other F atom being in a trans arrangement across the vinylic center. These couplings are consistent with those seen in the ^{19}F NMR spectrum (*vide infra*). Selective $^1\text{H}\{^{31}\text{P}\}$ decoupling experiments have established that two of the couplings apparent in the ^1H NMR resonance of the fluorovinyl moiety are due to the neighboring phosphorus atoms. The first coupling is small (5 Hz) and corresponds to a cis arrangement between the vinylic proton and one phosphorus atom, whereas the larger coupling ($^3J_{\text{HP}}=18$ Hz) is consistent with a trans orientation between the vinylic proton and the opposite phosphorus atom. This difference in coupling constants further indicates a loss of top/bottom symmetry, and suggests that the vinyl moiety is positioned in a bridging arrangement across the bimetallic core.

In the ^{19}F NMR spectrum there are three characteristic signals along with that of the triflate counterion at -79 ppm. The first is a sharp singlet at -77 ppm, integrating for three fluorines, and is assigned to the coordinated triflate ion. The other two signals, at -23 and -171 ppm, consist of complex doublets displaying fluorine-phosphorus, fluorine-proton, and fluorine-fluorine coupling. The fluorine-proton coupling is consistent with that described above, with the higher field signal corresponding to the geminal partner to the proton. This signal shows mutual coupling of 35 Hz to the other fluorine, consistent with a cis arrangement of these atoms across the vinylic center. Selective $^{19}\text{F}\{^{31}\text{P}\}$ decoupling experiments have established that both fluorine atoms couple to ^{31}P nuclei on different ends of the framework; however, only peak sharpening was observable and the actual magnitudes of the coupling were undeterminable. Diminished coupling through the π component of the vinyl center, compared that of an η^1 -fluorovinyl moiety, again helps to establish this as a bridging vinyl species (*vide supra*).

$[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\eta^2\text{-C}_2\text{FH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (7)

The reaction of a 2:1 mixture of isomers **4** and **4a** with $\text{Me}_3\text{SiSO}_3\text{CF}_3$ at -20°C results in the C-F activation of complex **4**, as demonstrated by the disappearance of its associated signals and the concomitant appearance of a new set of resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, corresponding to compound **7**. Isomer **4a** remains unchanged, although liberation of the free olefin occurs at temperatures above 0°C . The instability of **7** at temperatures above 0°C has limited our characterization of this product to solution NMR.

The vinylic protons are identifiable in the ^1H -NMR spectrum by their characteristic coupling pattern, in which they appear as mutually coupled doublets at 6.0 ppm and a 5.4 ppm, with the latter having an additional splitting of 14 Hz ($^3J_{\text{HF}}$), due to the trans arrangement across

the vinylic center. A gCOSY NMR experiment also confirms the correlation between the vinylic protons.

In the ^{19}F NMR spectrum, the single fluorovinyl resonance at -211 ppm, appears as a triplet, displaying the same 45 Hz coupling to phosphorus as observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Selective decoupling confirms this relationship, although interestingly, this coupling is not to the set of phosphorus nuclei adjacent to the σ -vinyl moiety, but is to the ^{31}P nuclei that are bound to the metal which interacts with the fluorovinyl group via the π -interaction. Further, in the ^{13}C -labelled complex (**7***), this fluorine also displays a strong coupling to a carbonyl that correlates to the distal set of ^{31}P nuclei, as seen with compound **5**. This further suggests the perfluorovinyl group allows coupling through the π -component when the moiety is in a bridged orientation. ^{19}F NMR spectroscopy also confirms the coordinated triflate counterion at -77 ppm and again shows Me_3SiF as a product of the reaction with a characteristic splitting pattern at -159 ppm.

$[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\pi\text{-C}_2\text{F}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (9**)**

The ^{13}C NMR spectrum of a ^{13}CO -enriched sample of **9** shows two broad multiplet carbonyl resonances at 151 ppm and 174 ppm. The high-field carbonyl resonance (CO_B), which lies at significantly higher field than those in other compounds, is suggested to be in the site opposite the metal-metal bond in a position remote from the adjacent metal. Such positioning has been previously associated with the high-field shifts.⁸

The difluorovinylidene group appears in the ^{19}F NMR spectrum as two new doublet signals, at -69 ppm and -86 ppm, with mutual coupling of 97 Hz, consistent with the geminal coupling seen in a previously crystallographically established di-iron complex.¹² Again, in the ^{19}F NMR spectrum there is evidence for the coordinated triflate ion, at -76 ppm, along with that of the triflate counterions at -79 ppm, along with a characteristic signal at -159 ppm corresponding to the Me_3SiF that is generated in the above transformation.

$[\text{Ir}_2(\text{CH}_3)(\text{CF}_3\text{SO}_3)(\text{CO})_2(\pi\text{-C}_2\text{FH})(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (10**)**

The vinylidene proton appears as a doublet at 8.6 ppm in the ^1H -NMR spectrum, displaying 85 Hz coupling to the fluorine in the geminal site. In the ^{19}F -NMR spectrum, this fluorine appears, also as a doublet, at -107 ppm, with complementary coupling to the geminal proton. Also in the ^{19}F -NMR spectrum, the resonances for the free and coordinated triflate ion and for the Me_3SiF appear as usual. The ^{13}C -NMR resonances for the carbonyls are close to those of **9**.

[Ir₂(CH₃)(CF₃SO₃)(CO)₂(η -C₂H₂)(dppm)₂][CF₃SO₃]₂ (11**)**

The vinylidene protons appear as two relatively broad singlets, which integrate for one proton each, at 5.99 ppm and 6.01 ppm. The lack of resolvable coupling between the pair of vinylidene protons is typical for such an arrangement. The ¹³C{¹H} NMR spectrum of a ¹³CO enriched sample of **11** shows two broad multiplet carbonyl resonances at 164 ppm and 170 ppm, both of which couple to different sets of phosphines. The lower-field shift of the latter suggests that this carbonyl may interact weakly with the second metal, in a semi-bridging arrangement, however no sharpening of the signals was observed upon ³¹P decoupling.

3. X-ray Crystallography. Structure of [Ir₂(η ¹-CF=CF₂)(CF₃SO₃)(CO)₂(η -CH₂)(η -H)-(dppm)₂][CF₃SO₃] \cdot 3CH₂Cl₂ (8** \cdot 3CH₂Cl₂)**

Pale yellow crystals of **8** \cdot 3CH₂Cl₂ were obtained via slow diffusion of Et₂O into a CH₂Cl₂ solution of compound **8**. Crystallographic data: formula C_{59.6}H_{52.6}Cl₆F_{7.8}Ir₂O_{8.4}P₄S₂, MW 1836.52, orthorhombic, *Pca*2₁ (No. 29), *a* = 24.274(2) Å, *b* = 11.9330(12) Å, *c* = 23.325(2) Å, *Z* = 4, *V* = 6756.2(12) Å³, *r*_{calcd} = 1.806 g cm⁻³, Bruker SMART 1000 CCD detector/PLATFORM diffractometer,¹³ *T* = -80°C, Mo K α radiation (*l* = 0.71073 Å), *m* = 4.403 mm⁻¹, 47527 total data (2 θ _{max} = 52.80°), 13819 unique data (*R*_{int} = 0.0513), structure solution: direct methods (*SHELXS*-86¹⁴), refinement on *F*² (*SHELXL*-93¹⁵), hydrogen atoms (except for the hydrido ligand H(1A) [vide infra]) generated from sp² or sp³ geometries of their attached carbon atoms with thermal parameters 20% greater than those of the attached carbons, absorption correction: multi-scan (*SADABS*), range of transmission factors 0.6672–0.3160, Flack absolute structure parameter¹⁶ 0.014(6), 478 parameters varied, 22 restraints (vide infra), GoF(*F*²) (all independent data) = 1.006, *R*₁(*F*) = 0.0348 (12270 data with *F*_o² \geq 2*s*(*F*_o²)) and *wR*₂(*F*²) = 0.0848 (all independent data). Attempts to refine the atoms of the trifluorovinyl group with occupancy factors of 100% were unsuccessful, as were efforts to locate and refine the bridging hydrido group. The location and intensity of electron density peaks in the neighborhood of the trifluorovinyl group suggested disorder with a terminal carbonyl ligand, and our final model shows that **8** had cocrystallized with [Ir₂(CF₃SO₃)(CO)₃(*m*-CH₂)(dppm)₂][CF₃SO₃] in 60:40 ratio. This latter compound has apparently resulted from loss of trifluoroethylene from the title species during crystallization, accompanied by scavenging of carbon monoxide from additional decomposition product(s). Views of the two disordered molecules together with their

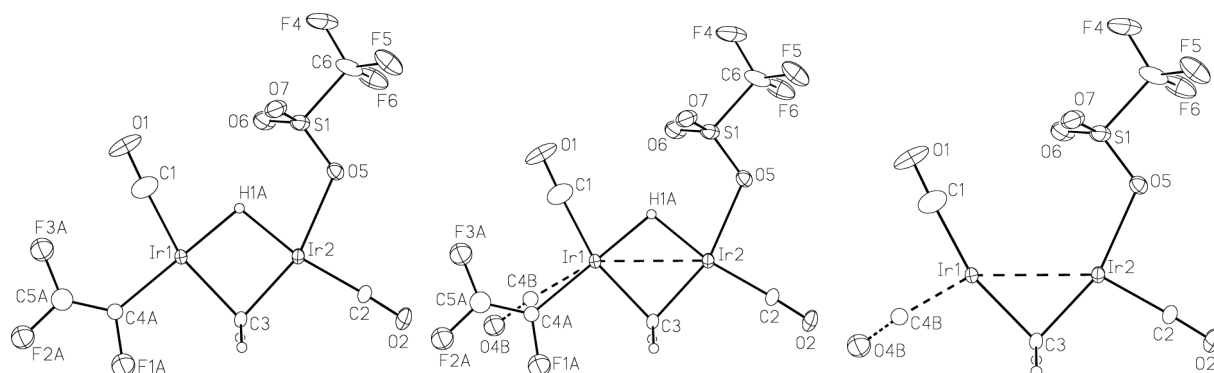
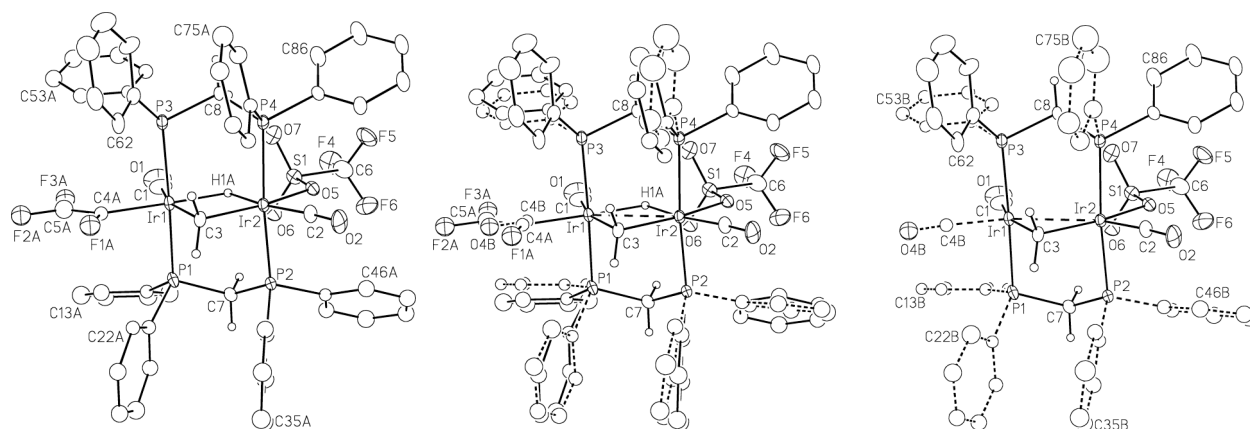
superimposed structures are shown in Figure S1. Analogous views showing only the ligands in the equatorial plane (dppm ligands omitted) are shown in Figure S2.

In the compound of interest, the trifluorovinyl C–F distances were constrained to be equal and the fluorines were refined with a common isotropic displacement parameter. The iridium-bound carbons of the trifluorovinyl and carbonyl groups (C(4A) and C(4B)) were refined with a common isotropic displacement parameter, as were the terminal trifluorovinyl (CF=C_{F2}) carbon (C(5A)) and the carbonyl oxygen (O(4B)). Distances involving the carbonyl group were fixed: Ir(1)–C(4B) = 1.88 Å; C(4B)–O(4B) = 1.13 Å; Ir(1)–O(4B) = 3.01 Å. The hydrido ligand H(1A) of the major (60%) conformer was not located, but its presence was established via spectroscopic methods. The Ir(1)–H(1A) and Ir(2)–H(1A) distances were fixed at 1.85 Å, and the Ir(1), Ir(2), C(3), and H(1A) atoms were constrained to be coplanar (i.e. by limiting to no more than 0.01 Å³ the volume of the tetrahedron formed by these four atoms).

The triflate ion was disordered in an 80:20 distribution of positions. While the atoms of the major conformer were refined with anisotropic displacement parameters and no geometric restraints, the atoms of the minor conformer were given a common isotropic displacement parameter, and the following fixed distances were used: S–C = 1.80 Å; S–O = 1.45 Å; C–F = 1.35 Å; F–F = 2.20 Å; O–O = 2.37 Å.

Attempts to refine peaks of residual electron density as solvent dichloromethane carbon or chlorine atoms were unsuccessful. The data were corrected for disordered electron density through use of the *SQUEEZE* procedure¹⁷ as implemented in *PLATON*.¹⁸ A total solvent-accessible void volume of 1312.1 Å³ with a total electron count of 506 (consistent with twelve molecules of solvent dichloromethane, or three molecules per formula unit of the complex molecule) was found in the unit cell.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 620865, and may be retrieved free of charge via the World Wide Web at <http://www.ccdc.cam.ac.uk/products/csd/request/>.



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