

Binuclear Fluorovinyl Complexes of Iridium: Transformation of an Iridium-Bound Trifluorovinyl Group into a *trans*-[Ir–C(F)=C(F)CH₃] Moiety

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The fluorovinyl complexes [Ir₂(CF=CF₂)(CH₃)(CO)₂(μ-Cl)(dppm)₂][CF₃SO₃] (**2**) and [Ir₂(C(H)=CF₂)(CH₃)(CO)₂(μ-Br)(dppm)₂][CF₃SO₃] (**3**) are prepared by the oxidative addition of ClFC=CF₂ and BrHC=CF₂, respectively, to [Ir₂(CH₃)(CO)₂(dppm)₂][CF₃SO₃] (**1**). Both compounds have the methyl and fluorovinyl groups on different metals essentially opposite the metal–metal bond. Protonation of **2** occurs at the Ir–Ir bond to give [Ir₂(CF=CF₂)(CH₃)(CO)₂(μ-Cl)(μ-H)(dppm)₂][CF₃SO₃]₂ (**4**). Attempts to remove the chloride ligand from **2** or to replace it with hydride or methyl groups failed. Instead, the reaction of **2** with methyllithium resulted in replacement of one fluoride substituent on the trifluorovinyl group by a methyl group to give [Ir₂(CF=CFCH₃)(CH₃)(CO)₂(μ-Cl)(dppm)₂][CF₃SO₃] (**5**). The X-ray structural determination of **5** indicates that replacement of a fluoride trans to the Ir–C₂F₃ bond has occurred and that migration of the resulting methyldifluorovinyl group to the metal bearing the methyl ligand has occurred. A proposal is put forth to rationalize these observations.

Introduction

The activation of carbon–fluorine bonds is of importance from a number of perspectives. Fluorocarbons are global-warming gases,¹ having long atmospheric lifetimes,² so methods for transforming them to more innocuous substances are being sought. In addition, fluorocarbons are finding applications as agrochemicals and pharmaceuticals,³ necessitating new methods for selectively transforming or creating C–F bonds in relevant synthons. The challenges in achieving the goals of C–F activation result, in a large measure, from the strength of the C–F bond, which is the strongest single bond involving carbon.⁴ The paucity of nucleophilic substitutions of alkyl fluorides highlights the diminished reactivity of the C–F bond relative to other C–X bonds; this reaction is more than 2 orders of magnitude slower for alkyl fluorides than for alkyl chlorides.⁵

In a recent study we observed the apparent C–H and C–F activation of trifluoroethylene by the diiridium complex [Ir₂(CH₃)(CO)₂(dppm)₂][CF₃SO₃] (**1**; dppm = μ-Ph₂PCH₂PPh₂) to yield a difluorovinylidene-bridged product.⁶ However, a number of factors, including the capricious nature of the reaction (which took place over

a period of days at ambient temperature and was only observed on one occasion) and the increasing difficulty of obtaining trifluoroethylene or its synthons, have to date prevented us from studying this transformation further. Two questions that we had hoped to address in this apparent double-activation process was whether C–H or C–F activation occurred first, and what the functions of the adjacent metals might be in such a transformation. Compound **1** had previously been demonstrated to undergo double C–H activation of 1,3-butadiene,⁷ suggesting a role for adjacent metals in olefin activation.

Our inability to obtain the desired information directly from the reaction of **2** with trifluoroethylene encouraged us to seek this information indirectly. If C–H activation was the first activation step, the first species produced would be a trifluorovinyl complex, whereas initial C–F activation would yield a 2,2-difluorovinyl group. We therefore sought routes to complexes containing these fluorovinyl ligands. Several fluorovinyl complexes of transition metals are known, including a few of iridium.⁸ However, we are unaware of any binuclear complexes of iridium containing fluorovinyl groups. Our interest in binuclear complexes of fluorovinyl ligands relates to the functions of the adjacent metals in the activation of fluorocarbon ligands—a topic that seems to have been only briefly addressed in the past.⁹ Vinyl fluorides are normally quite inert;

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Table 1. Spectroscopic Data for the Compounds

compound	NMR ^{a,b}				
	$\delta(^{31}\text{P}\{^1\text{H}\})^c$	$\delta(^1\text{H})^{d,e}$	$\delta(^{19}\text{F})^f$	$\delta(^{13}\text{C}\{^1\text{H}\})^d$	IR, cm^{-1} ^{g,h}
$[\text{Ir}_2(\text{C}_2\text{F}_3)(\text{CH}_3)(\text{CO})_2(\mu\text{-Cl})\text{(dppm)}_2][\text{CF}_3\text{SO}_3]$ (2) ⁱ	-6.9 (m), -11.3 (m)	5.80 (m, 2H), 4.35 (m, 2H), 1.17 (t, 3H, $^3J_{\text{P-H}} = 5$ Hz)	-78.8 (s, 3F), -92.8 (ddt, 1F, $^4J_{\text{P-F}} = 5$ Hz, $^2J_{\text{F-F}} = 89$ Hz, $^3J_{\text{F-F}} = 37$ Hz), -126.9 (dd, 1F, $^2J_{\text{F-F}} = 89$ Hz, $^3J_{\text{F-F}} = 110$ Hz), -139.1 (dd, 1F, $^3J_{\text{F-F}} = 110, 37$ Hz)	172.5 (t, $^2J_{\text{C-P}} = 9$ Hz), 170.8 (t, $^2J_{\text{C-P}} = 11$ Hz), -24.0 (m)	2024(s), 1709 (w)
$[\text{Ir}_2(\text{C}_2\text{F}_2\text{H})(\text{CH}_3)(\text{CO})_2(\mu\text{-Br})\text{(dppm)}_2][\text{CF}_3\text{SO}_3]$ (3)	-6.8 (m), -10.3 (m)	4.93 (m, 2H), 3.76 (m, 2H), 4.62 (ddt, $^3J_{\text{H-F}} = 42$ Hz, $^3J_{\text{H-F}} = 12$ Hz, $^3J_{\text{P-H}} = 5$ Hz), 0.88 (t, 3H, $^3J_{\text{P-H}} = 5$ Hz)	-79.1 (s, 3F), -65.9 (ddt, 1F, $^2J_{\text{F-F}} = 59$ Hz, $^3J_{\text{H-F}} = 12$ Hz, $^4J_{\text{P-F}} = 5$ Hz), -84.9 (ddt, 1F, $^3J_{\text{H-F}} = 42$ Hz, $^2J_{\text{F-F}} = 59$ Hz, $^4J_{\text{P-F}} = 5$ Hz)	174.4 (t, $^2J_{\text{C-P}} = 9$ Hz), 169.5 (t, $^2J_{\text{C-P}} = 11$ Hz), -24.4 (m)	2021 (s), 1672 (w)
$[\text{Ir}_2(\text{C}_2\text{F}_3)(\text{CH}_3)(\text{CO})_2(\mu\text{-H})\text{(dppm)}_2][\text{CF}_3\text{SO}_3]_2$ (4)	-12.9 (m), -20.8 (m)	5.26 (m, 2H), 5.13 (m, 2H), 1.40 (t, 3H, $^3J_{\text{P-H}} = 6$ Hz), -13.00 (b, 1H)	-78.8 (s, 3F), -92.5 (dd, 1F, $^3J_{\text{F-F}} = 110$ Hz, $^2J_{\text{F-F}} = 86$ Hz), -122.1 (pt, 1F, $J = 100$ Hz), -133.6 (dd, $^3J_{\text{F-F}} = 110$ Hz, $^3J_{\text{F-F}} = 43$ Hz)		2021 (s), 1706 (w)
$[\text{Ir}_2(\text{C}_2\text{F}_2\text{CH}_3)(\text{CH}_3)(\text{CO})_2(\mu\text{-Cl})\text{(dppm)}_2][\text{CF}_3\text{SO}_3]$ (5)	1.2 (m), -15.7 (m)	4.08 (m, 2H), 3.44 (m, 2H), 1.22 (t, 3H, $J_{\text{F-F}} = 12$ Hz), 1.07 (t, 3H, $^3J_{\text{P-H}} = 7$ Hz)	-78.8 (s, 3F), -126 (b, 2F)	196.8 (b), 174.0 (b), 20.2 (m) -24.8 (m)	2019 (s), 1676 (w), $\nu(\text{C}=\text{C})$

^a NMR abbreviations: s = singlet, d = doublet, t = triplet, pt = pseudotriplet, m = multiplet, b = broad. ^b NMR data at 298 K in CD_2Cl_2 unless otherwise stated. ^c $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are referenced vs external 85% H_3PO_4 . ^d ^1H and ^{13}C chemical shifts are referenced vs external TMS. ^e Chemical shifts for the phenyl hydrogens are not given in the ^1H data. ^f ^{19}F chemical shifts are referenced vs external CFCl_3 . ^g IR abbreviations ($\nu(\text{CO})$ unless otherwise stated): s = strong, w = weak. ^h CH_2Cl_2 solution unless otherwise stated. ⁱ NMR data in acetone- d_6 solution.

however, examples of C–F bond cleavage reactions in the presence of nucleophiles have been reported.^{10–12} In this paper we outline our preliminary results on the preparation of fluorovinyl complexes of diiridium and on some subsequent transformations.

Experimental Section

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 at ambient temperature under argon using standard Schlenk techniques, and compounds that were used as solids were purified by recrystallization. Prepurified argon and nitrogen were purchased from Linde, carbon-13 enriched CO (99%) was supplied by Isotec Inc., and fluoroolefins (chlorotrifluoroethylene, iodotrifluoroethylene, and 1-bromo-2,2-difluoroethylene) were supplied by Lancaster. All gases were used as received, and all other reagents were purchased from Aldrich and were used as received. The compound $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**) was prepared as previously reported.¹³

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 and fluorine spectra were recorded on Varian Unity 400 or Bruker AM400 spectrometers. Two-dimensional NMR experiments (GCOSY, TROESY, GTOCSY, and ^{13}C – ^1H HMQC) were obtained on Varian Unity 400 or 500 spectrometers. Infrared 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. Carbonyl stretches reported are for non-isotopically enriched samples. Mass spectrometric analyses were performed by positive ion electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF. Elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 1.

Preparation of Compounds. (a) $[\text{Ir}_2(\text{C}_2\text{F}_3)(\text{CH}_3)(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**2**). A brick-red solution of $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**) (93 mg, 0.066 mmol) dissolved in 15 mL of dichloromethane was cooled to -78 °C using a dry ice/acetone bath. Excess chlorotrifluoroethylene gas was condensed onto the stirred solution, which was stirred at this temperature for 30 min, at which time the cooling bath was removed and the vessel allowed to warm to room temperature (ca. 4 h). After stirring at room temperature overnight, the yellow solution was reduced in vacuo to ca. 3 mL. Slow addition of 10 mL of Et_2O afforded a bright yellow powder. The product was washed twice with 10 mL of Et_2O , the supernatant decanted, and then the solid dried briefly under a stream of argon and then in vacuo (89% yield). Anal. Calcd for $\text{Ir}_2\text{-SCIP}_4\text{F}_6\text{O}_5\text{C}_{56}\text{H}_{14}$: C, 44.74; H, 3.18; Cl, 2.38. Found: C, 45.15; H, 3.15; 2.69. MS(ESI) $\text{P}^+ = 1341.1$.

(b) $[\text{Ir}_2(\text{C}_2\text{F}_2\text{H})(\text{CH}_3)(\text{CO})_2(\mu\text{-Br})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**3**). The procedure was the same as that described for **2** except that 1-bromo-2,2-difluoroethylene was used instead of chlorotrifluoroethylene. The yield of the orange powder was 78%. Anal. Calcd for $\text{Ir}_2\text{BrSP}_4\text{F}_5\text{O}_5\text{C}_{56}\text{H}_{48}$: C, 44.36, H, 3.19. Found: C, 44.15; H, 3.06. MS(ESI) $\text{P}^+ = 1367$.

(c) **Reaction of 1 with Iodotrifluoroethylene.** In an NMR tube, 25 mg (0.018 mmol) of **1** was dissolved in 0.7 mL of CD_2Cl_2 and cooled to -78 °C, giving a brick-red solution. Iodotrifluoroethylene (18 μL , 0.018 mmol) was added by syringe. The NMR spectra were recorded at -78 °C and at 20 deg intervals until approximately ambient temperature was reached, by which time the solution had become bright red and complete conversion to the known compound, $[\text{Ir}_2(\text{CO})_2(\mu\text{-CH}_2)(\mu\text{-I})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**6**),¹⁴ was indicated by the ^1H and ^{31}P NMR spectra. Throughout the NMR monitoring of this

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reaction the NMR spectra (^1H , ^{19}F , ^{31}P) showed only this compound, unreacted **1**, and iodotrifluoroethylene.

(d) $[\text{Ir}_2(\text{C}_2\text{F}_3)(\text{CH}_3)(\text{CO})_2(\mu\text{-H})(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (**4**). Compound **2** (48 mg, 0.032 mmol) was dissolved in 10 mL of dichloromethane, forming a yellow solution. To this was added trifluoromethanesulfonic acid (3 μL 0.034 mmol), causing the solution to lighten in color and become slightly cloudy. The mixture was stirred for 15 min and then reduced in vacuo to 5 mL. The supernatant liquid was decanted and the remaining powder washed twice with 10 mL volumes of Et_2O , leaving 37 mg (70%) of a pale yellow powder. Anal. Calcd for $\text{Ir}_2\text{ClS}_2\text{P}_4\text{F}_9\text{O}_8\text{C}_{57}\text{H}_{48}$: C, 41.75; H, 3.01. Found: C, 41.92; H, 2.82.

(e) $[\text{Ir}_2(\text{C}_2\text{F}_2\text{CH}_3)(\text{CH}_3)(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**5**). Compound **2** (29 mg, 0.020 mmol) was dissolved in 20 mL of THF, and the yellow solution was cooled in a dry ice/acetone bath to -78°C , at which time 0.1 mL of a 1.4 M solution of methyllithium in Et_2O (Aldrich) was added. The solution was stirred at this temperature for 10 min and then allowed to warm to room temperature. Stirring was continued at room temperature for a further hour, at which time the cloudy solution was transferred into another vessel that had been charged with approximately 5 g of dry Florisil. The solution was stirred over Florisil for 5 min, during which time the yellow color of the solution was discharged and the Florisil became bright yellow. The colorless supernatant was decanted, and the Florisil with adsorbed compound **5** was extracted with 10 mL of acetonitrile. The yellow extract was filtered through Celite and then reduced in vacuo to a pale yellow powder, which was found by ^{31}P NMR spectroscopy to consist of approximately 60% of **5**, with the remainder being unreacted **2**. The labeled product, $[\text{Ir}_2(\text{C}_2\text{F}_2\text{CH}_3)(^{13}\text{CH}_3)(^{13}\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**5**), was obtained by the same procedure except that $[\text{Ir}_2(^{13}\text{CH}_3)(^{13}\text{CO})(\mu\text{-}^{13}\text{CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1***) was used as the precursor. The percent of $^{13}\text{CH}_3$ enrichment in compounds **1** and **5** is essentially 100% as judged from ^1H NMR spectroscopy. All attempts to separate **5** from unreacted **2** failed, as did attempts to effect complete transformation of **2** to **5**, so elemental analyses were not obtained.

(f) **Reaction of 2 with Hydride Sources and Lewis Acids.** In a typical experiment, 40 mg of **2** was dissolved in 20 mL of THF (for reactions with hydride sources) or benzene (for reactions with Lewis acids). To this was added a solution of the test reagent (10 mg of NaBH_4 (10 equiv) in 35 mL of THF or 100 μL of 1.0 M $\text{KHB}(\text{sec-Bu})_3$ (4 equiv) in 20 mL of THF). In the case of the reaction of KH, a solution of **2** as above was added to a suspension of 2 mg of KH suspended in 15 mL of THF. In the case of the Lewis acids 40 mg of **2** in 20 mL of benzene was reacted with the test reagents (15 μL of a 2.0 M toluene solution of trimethylaluminum (1 equiv), or 3.5 μL of methyl triflate (1 equiv), or 5 μL of trimethylsilyl triflate (1 equiv), each in 20 mL of benzene, or with 10 mg of silver triflate (1 equiv) in 20 mL of acetonitrile). In all cases, progress of the reaction was assessed by pumping the mixture to dryness after 1 h and observing the ^{31}P , ^1H , and ^{19}F NMR in CD_2Cl_2 solution and, in a replicate experiment, pumping the mixture to dryness after 24 h and again running the NMR. Partial conversion to the dication **4** was observed after 1 h in the reactions with Lewis acids. From the hydride-source reactions, unreacted **2** was recovered after 24 h, accompanied by variable amounts of unidentified decomposition products.

X-ray Data Collection. Yellow crystals of $[\text{Ir}_2(\text{CF}=\text{CF}_2)(\text{Me})(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]\cdot 1.5\text{Me}_2\text{CO}$ (**2**) were obtained via slow diffusion of *n*-pentane into an acetone solution of the complex. Data were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer¹⁵ using Mo $K\alpha$ radiation at -80°C . Unit cell parameters were obtained from a least-squares refinement of the setting angles of 5737 reflections

from the data collection. The space group was determined to be $P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14]). The data were corrected for absorption through use of the SADABS procedure. See Table 2 for a summary of crystal data and X-ray data collection information.

Colorless crystals of $[\text{Ir}_2(\text{CF}=\text{CF}_2)(\text{Me})(\text{CO})_2(\mu\text{-Cl})(\mu\text{-H})(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (**4**) were obtained via slow diffusion of diethyl ether into a dichloromethane solution of the compound. Data were collected and corrected for absorption as for **2** above. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 5118 reflections from the data collection, and the space group was determined to be $P2_1/c$ (No. 14).

Yellow crystals of $[\text{Ir}_2(\text{CF}=\text{CFMe})(\text{Me})(\text{CO})(\mu\text{-Cl})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]\cdot 0.5\text{Et}_2\text{O}\cdot 0.5\text{Me}_2\text{CO}$ (**5**) were obtained via slow diffusion of diethyl ether into an acetone solution of a mixture of compounds **2** and **5**. A crystal of **5** was hand picked from a mixture of crystals of the two compounds. Redissolving the crystals afterward gave compounds **2** and **5** in the same ratio as before crystallization. Data were collected and corrected for absorption as for **2** above. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 5438 reflections from the data collection, and the space group was determined to be $C2/c$ (No. 15).

Structure Solution and Refinement. The structure of **2** was solved using automated Patterson location of the heavy metal atoms and structure expansion via the DIRDIF-96 program system.¹⁶ Refinement was completed using the program SHELXL-93.¹⁷ Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons. An idealized geometry was imposed upon the inversion-disordered half-occupancy solvent acetone molecule using the following restraints: $d(\text{C}(4\text{S})-\text{C}(5\text{S})) = d(\text{C}(5\text{S})-\text{C}(6\text{S})) = 1.47 \text{ \AA}$; $d(\text{O}(2\text{S})-\text{C}(5\text{S})) = 1.23 \text{ \AA}$; $d(\text{C}(4\text{S})\cdots\text{C}(6\text{S})) = 2.55 \text{ \AA}$; $d(\text{O}(2\text{S})\cdots\text{C}(4\text{S})) = d(\text{O}(2\text{S})\cdots\text{C}(6\text{S})) = 2.34 \text{ \AA}$. The final model for **2** refined to values of $R_1(F) = 0.0386$ (for 9911 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0860$ (for all 12165 independent data).

The structure of **4** was solved using direct methods (SHELXS-86¹⁸), and refinement was completed using the program SHELXL-93. Hydrogen atoms were treated as for **2** except for the hydrido ligand, which was assigned a fixed isotropic displacement parameter and idealized interatomic distances ($\text{Ir}-\text{H}(1) = \text{Ir}'-\text{H}(1) = 1.85 \text{ \AA}$; $\text{P}(1)\cdots\text{H}(1) = \text{P}(2')\cdots\text{H}(1)$ to within 0.002 \AA). The final model for **4** refined to values of $R_1(F) = 0.0387$ (for 5217 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0935$ (for all 5980 independent data).

The structure of **5** was solved using the DIRDIF-96 program system in the same manner as for **2** above. Refinement was completed using the program SHELXL-93, during which the hydrogen atoms were treated as for **2**. Idealized geometries were imposed upon one of the half-occupancy triflate ion positions and upon the half-occupancy solvent diethyl ether and acetone molecules through use of intramolecular distance restraints (fully detailed in the Supporting Information). The final model for **5** refined to values of $R_1(F) = 0.0479$ (for 9444 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1398$ (for all 12 952 independent data).

Results and Compound Characterization

The trifluorovinyl compound $[\text{Ir}_2(\text{CF}=\text{CF}_2)(\text{CH}_3)(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**2**) is readily obtained by the

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Table 2. Crystallographic Experimental Details for Compounds 2, 4, and 5

	A. Crystal Data		
	C _{60.5} H ₅₆ ClF ₆ Ir ₂ O _{6.5} P ₄ S	C ₅₇ H ₄₈ ClF ₉ Ir ₂ O ₈ P ₄ S ₂	C _{60.5} H ₅₈ ClF ₅ Ir ₂ O ₆ P ₄ S
formula	C _{60.5} H ₅₆ ClF ₆ Ir ₂ O _{6.5} P ₄ S	C ₅₇ H ₄₈ ClF ₉ Ir ₂ O ₈ P ₄ S ₂	C _{60.5} H ₅₈ ClF ₅ Ir ₂ O ₆ P ₄ S
fw	1576.84	1639.80	1551.86
cryst dimens (mm)	0.30 × 0.10 × 0.09	0.24 × 0.15 × 0.12	0.36 × 0.19 × 0.09
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (an alternate setting of <i>P</i> 2 ₁ / <i>c</i> [No. 14])	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)
unit cell params ^a			
<i>a</i> (Å)	12.2660 (8)	11.3860 (7)	29.974 (2)
<i>b</i> (Å)	32.721 (2)	11.8677 (8)	15.2663 (10)
<i>c</i> (Å)	15.4317 (10)	21.8526 (14)	27.8913 (19)
β (deg)	106.1367 (12)	97.5621 (12)	95.9674 (14)
<i>V</i> (Å ³)	5949.6 (7)	2927.2 (3)	12693.6 (15)
<i>Z</i>	4	2	8
ρ _{calcd} (g cm ⁻³)	1.760	1.860	1.624
μ (mm ⁻¹)	4.726	4.850	4.426
	B. Data Collection and Refinement Conditions		
diffractometer	Bruker PLATFORM/SMART	Bruker PLATFORM/SMART	Bruker PLATFORM/SMART
	1000 CCD	1000 CCD	1000 CCD
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)	graphite-monochromated Mo Kα (0.71073)	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	-80	-80	-80
scan type	ω scans (0.2°) (30 s exposures)	ω scans (0.2°) (25 s exposures)	ω scans (0.2°) (30 s exposures)
data collection 2θ limit (deg)	52.80	52.78	52.78
total no. of data collected	28714 (-15 ≤ <i>h</i> ≤ 14, -33 ≤ <i>k</i> ≤ 40, -19 ≤ <i>l</i> ≤ 16)	15804 (-14 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 14, -24 ≤ <i>l</i> ≤ 27)	30695 (-37 ≤ <i>h</i> ≤ 27, -19 ≤ <i>k</i> ≤ 18, -34 ≤ <i>l</i> ≤ 34)
no. of ind reflns	12 165 (<i>R</i> _{int} = 0.0434)	5980 (<i>R</i> _{int} = 0.0313)	12 952 (<i>R</i> _{int} = 0.0424)
no. of obsd reflns	9911 [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	5217 [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	9444 [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]
structure solution method	Patterson search/structure expansion (<i>DIRDIF-96</i>)	direct methods (<i>SHELXS-86</i>)	Patterson search/structure expansion (<i>DIRDIF-96</i>)
refinement method ^b	full-matrix least-squares on <i>F</i> ² (<i>SHELXL-93</i>)	full-matrix least-squares on <i>F</i> ² (<i>SHELXL-93</i>)	full-matrix least-squares on <i>F</i> ² (<i>SHELXL-93</i>)
abs corr method	empirical (<i>SADABS</i>)	empirical (<i>SADABS</i>)	empirical (<i>SADABS</i>)
range of transmn factors	0.6757–0.3313	0.5937–0.3890	0.6914–0.2987
no. of data/restraints/params	12 165 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]/6 ^c /710	5980 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]/3 ^d /384	12 952 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]/32 ^e /695
goodness-of-fit (<i>S</i>) ^f	1.044 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]	1.108 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]	1.051 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]
final <i>R</i> indices ^g			
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	0.0386	0.0387	0.0479
<i>wR</i> ₂ [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]	0.0860	0.0935	0.1398
largest diff peak and hole (e Å ⁻³)	2.115 and -1.114	1.721 and -1.411	3.319 and -1.071

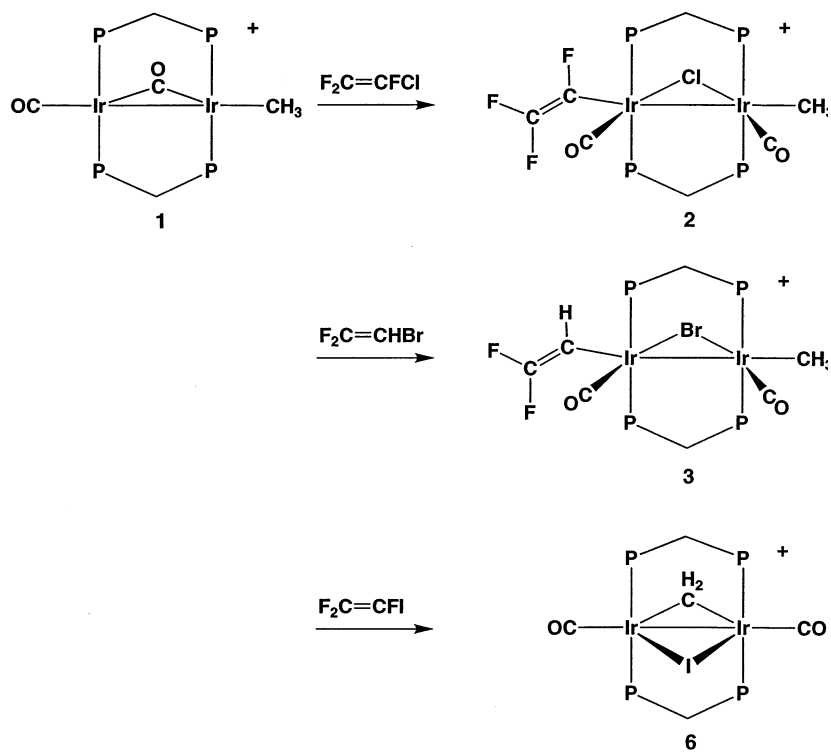
^a Obtained from least-squares refinement of 5737 centered reflections for compound **2**, 5118 reflections for **4**, and 5438 reflections for **5**. ^b Refinement on *F*_o² for all reflections (all of these having *F*_o² ≥ -3σ(*F*_o²)). Weighted *R*-factors *wR*₂ and all goodnesses of fit *S* are based on *F*_o²; conventional *R*-factors *R*₁ are based on *F*_o, with *F*_o set to zero for negative *F*_o². The observed criterion of *F*_o² > 2σ(*F*_o²) is used only for calculating *R*₁ and is not relevant to the choice of reflections for refinement. *R*-factors based on *F*_o² are statistically about twice as large as those based on *F*_o, and *R*-factors based on ALL data will be even larger. ^c An idealized geometry was imposed upon the inversion-disordered half-occupancy solvent acetone molecule using the following restraints: *d*(C(4S)–C(5S)) = *d*(C(5S)–C(6S)) = 1.47 Å; *d*(O(2S)–C(5S)) = 1.23 Å; *d*(C(4S)–C(6S)) = 2.55 Å; *d*(O(2S)–C(4S)) = *d*(O(2S)–C(6S)) = 2.34 Å. ^d An idealized geometry was imposed upon the hydrido ligand by fixing the Ir–H(1) and Ir'–H(1) distances to equal 1.85 Å and by constraining the P(1)–H(1) and P(2)–H(1) distances to be equal (to within 0.002 Å). ^e One of the half-occupancy triflate ion positions was found to be disordered about a crystallographic 2-fold axis, leading to employment of the following restraints: *d*(S(2)–C(92)) = 1.80 Å; *d*(S(2)–O(94)) = *d*(S(2)–O(95)) = *d*(S(2)–O(96)) = 1.45 Å; *d*(F(94)–C(92)) = *d*(F(95)–C(92)) = *d*(F(96)–C(92)) = 1.35 Å; *d*(F(94)–F(95)) = *d*(F(94)–F(96)) = *d*(F(95)–F(96)) = 2.20 Å; *d*(O(94)–O(95)) = *d*(O(94)–O(96)) = *d*(O(95)–O(96)) = 2.37 Å; *d*(F(94)–O(95)) = *d*(F(94)–O(96)) = *d*(F(95)–O(94)) = *d*(F(95)–O(96)) = *d*(F(96)–O(94)) = *d*(F(96)–O(95)) = 3.04 Å. Distances were also assigned idealized values for the half-occupancy solvent diethyl ether (*d*(O(1S)–C(1S)) = *d*(O(1S)–C(3S)) = 1.43 Å; *d*(C(1S)–C(2S)) = *d*(C(3S)–C(4S)) = 1.54 Å; *d*(O(1S)–C(2S)) = *d*(O(1S)–C(4S)) = 2.43 Å; *d*(C(1S)–C(3S)) = 2.34 Å) and acetone (*d*(O(2S)–C(6S)) = 1.20 Å; *d*(C(5S)–C(6S)) = *d*(C(6S)–C(7S)) = 1.54 Å; *d*(O(2S)–C(5S)) = *d*(O(2S)–C(7S)) = 2.38 Å; *d*(C(5S)–C(7S)) = 2.67 Å) molecules. ^f *S* = [Σ*w*(*F*_o² - *F*_c²)/(*n* - *p*)]^{1/2} (*n* = number of data; *p* = number of parameters varied; *w* = [σ²(*F*_o²) + (*AP*)² + (*BP*)²]⁻¹ where *P* = [Max(*F*_o², 0) + 2*F*_c²]/3). For compound **2**, *A* = 0.0381, *B* = 6.2180; for **4**, *A* = 0.0378, *B* = 13.5695; for **5**, *A* = 0.0670, *B* = 151.3170. ^g *R*₁ = Σ||*F*_o|| - ||*F*_c||/Σ||*F*_o||; *wR*₂ = [Σ*w*(*F*_o² - *F*_c²)/Σ*w*(*F*_o⁴)]^{1/2}.

oxidative addition of the C–Cl bond of chlorotrifluoroethylene to [Ir₂(CH₃)(CO)(μ-CO)(dppm)₂][CF₃SO₃] (**1**), as shown in Scheme 1. Attempts to detect intermediates in this transformation, such as a chlorotrifluoroethylene adduct, were not successful. At -80 °C no reaction between **1** and ClFC=CF₂ was observed over a 2 h period by NMR, whereas warming to ambient temperature resulted in the slow but complete conversion to **2** overnight (ca. 18 h). At intermediate temperatures the only species observed were the reactants and product in varying amounts.

The ³¹P{¹H} NMR spectrum of **2** shows the characteristic, second-order multiplets at -6.9 and -11.3 ppm,

belonging to an AA'BB' spin system. In the ¹H NMR spectrum the methylene protons of the dppm ligands appear normal and the methyl group appears as a triplet at 1.17 ppm, with coupling of 5 Hz to the two adjacent ³¹P nuclei on one iridium. The ¹³C{¹H} NMR spectrum of the ¹³C-enriched [Ir₂(C₂F₃)(¹³CH₃)(¹³CO)₂-(μ-Cl)(dppm)₂][CF₃SO₃] (**2**^{*}) displays resonances typical of terminally bound Ir-carbonyls (172.5, 170.8 ppm) and a high-field resonance at -24.0 ppm corresponding to the methylene group. In the ¹⁹F NMR spectrum the three trifluorovinyl fluorines appear at -92.8, -126.9, and -139.1 ppm, in the normal range for fluorines attached to sp²-hybridized carbon atoms.¹⁹ The assignment of the

Scheme 1



^{19}F spectrum is aided by comparisons to other trifluorovinyl groups in which the coupling between geminal fluorines ($^2J_{\text{FF}}$) is found in the range 75–107 Hz. For example, in trifluoroethylene and chlorotrifluoroethylene $^2J_{\text{FF}} = 87$ and 76 Hz, respectively, while in a series of trifluorovinyl complexes $[\text{M}(\text{X})(\text{Y})(\text{P}(\text{Et}_3)_2)_2]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{X} = \text{C}_2\text{F}_3$; $\text{Y} = \text{C}_2\text{F}_3, \text{Br}$),²⁰ *cis*- $[\text{Pt}(\text{CF}=\text{CF}_2)_2(\text{PPh}_3)_2]$, and *cis*- $[\text{PtCl}(\text{CF}=\text{CF}_2)(\text{P}(\text{Bu}_3)_2)_2]$ ²¹ values near 100 Hz have been reported. For the aforementioned compounds *cis* coupling ($^3J_{\text{FF}}$)_{cis} is in the range 32–40 Hz, whereas *trans* coupling ($^3J_{\text{FF}}$)_{trans} between 101 and 120 Hz is observed. On the basis of the coupling constants, the two ^{19}F resonances of **2** at -92.8 and -126.9 ppm are assigned to the geminal fluorines on the β -carbon, having a mutual coupling of 89 Hz. The former signal appears as a doublet of doublets of triplets and is assigned as *cis* to the lone fluorine on the α carbon (at -139.1 ppm) on the basis of the 37 Hz coupling between the two. The triplet coupling (5 Hz) of this β -fluorine results from four-bond coupling with the ^{31}P nuclei that are bound to the same metal as the C_2F_3 ligand. Neither of the other two fluorines shows coupling to the ^{31}P nuclei. The two mutually *trans* fluorines show mutual coupling of 110 Hz.

The structure proposed for **2** has been confirmed by an X-ray structure determination, as shown for the complex cation in Figure 1. Selected bond lengths and angles are given in Table 3. Compound **2** has an unsymmetrical A-frame structure in which the chloro ligand bridges the metals in an essentially symmetrical manner. One carbonyl on each metal lies approximately

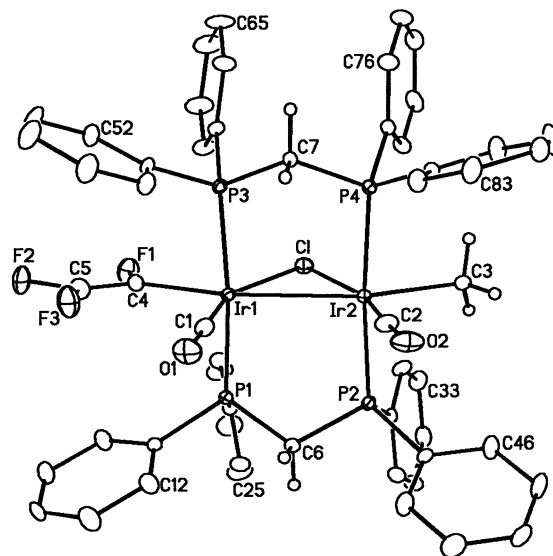


Figure 1. Perspective view of the $[\text{Ir}_2(\text{CF}=\text{CF}_2)(\text{CH}_3)(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2]^+$ cation of complex **2** showing the atom-labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The methylene and methyl hydrogens are shown with arbitrarily small thermal parameters, while the phenyl hydrogens are not shown.

opposite the Ir–Cl bonds, while the methyl and trifluorovinyl groups occupy positions on each metal opposite the metal–metal bond, but bent slightly toward the bridging chloride ligand ($\text{Ir}(1)\text{--Ir}(2)\text{--C}(3) = 156.8(2)^\circ$, $\text{Ir}(2)\text{--Ir}(1)\text{--C}(4) = 165.7(2)^\circ$). The Ir–Ir separation ($2.8116(3)$ Å) is consistent with a single bond and is noticeably shorter than the intraligand P–P separations ($\text{P}(1)\text{--P}(2) = 3.026(2)$ Å, $\text{P}(3)\text{--P}(4) = 3.033(2)$ Å), consistent with a bonding interaction between the two metals. Both C–F distances on the β -carbon ($\text{C}(5)\text{--F}(2)$

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Table 3. Selected Interatomic Distances and Angles for Compound 2

(a) Distances (Å)							
Ir(1)	Ir(2)	2.8116(3)	P(1)	C(6)	1.822(5)		
Ir(1)	Cl	2.416(1)	P(2)	C(6)	1.821(5)		
Ir(1)	P(1)	2.350(1)	P(3)	C(7)	1.817(5)		
Ir(1)	P(3)	2.353(1)	P(3)	P(4)	3.033(2) ^a		
Ir(1)	C(1)	1.863(7)	P(4)	C(7)	1.823(5)		
Ir(1)	C(4)	2.090(6)	F(1)	C(4)	1.376(7)		
Ir(2)	Cl	2.449(1)	F(2)	C(5)	1.351(8)		
Ir(2)	P(2)	2.353(1)	F(3)	C(5)	1.337(8)		
Ir(2)	P(4)	2.346(1)	O(1)	C(1)	1.143(7)		
Ir(2)	C(2)	1.809(6)	O(2)	C(2)	1.142(7)		
Ir(2)	C(3)	2.182(6)	C(4)	C(5)	1.298(9)		
P(1)	P(2)	3.026(2) ^a					
(b) Angles (deg)							
Ir(2)	Ir(1)	Cl	55.24(3)	Cl	Ir(2)	C(3)	102.7(2)
Ir(2)	Ir(1)	P(1)	92.95(3)	P(2)	Ir(2)	P(4)	174.66(5)
Ir(2)	Ir(1)	P(3)	92.60(3)	P(2)	Ir(2)	C(2)	87.6(2)
Ir(2)	Ir(1)	C(1)	96.7(2)	P(2)	Ir(2)	C(4)	89.6(2)
Ir(2)	Ir(1)	C(4)	165.7(2)	P(4)	Ir(2)	C(2)	89.1(2)
Cl	Ir(1)	P(1)	90.69(5)	P(4)	Ir(2)	C(3)	86.6(2)
Cl	Ir(1)	P(3)	91.23(5)	C(2)	Ir(2)	C(3)	94.9(3)
Cl	Ir(1)	C(1)	151.9(2)	Ir(1)	Cl	Ir(2)	70.62(4)
Cl	Ir(1)	C(4)	110.6(2)	Ir(1)	P(1)	C(6)	110.0(2)
P(1)	Ir(1)	P(3)	174.25(5)	Ir(2)	P(2)	C(6)	112.1(2)
P(1)	Ir(1)	C(1)	88.9(2)	Ir(1)	P(3)	C(7)	111.8(17)
P(1)	Ir(1)	C(4)	88.6(2)	Ir(2)	P(4)	C(7)	111.6(2)
P(3)	Ir(1)	C(1)	92.0(2)	Ir(1)	C(1)	O(1)	177.0(6)
P(3)	Ir(1)	C(4)	85.7(2)	Ir(2)	C(2)	O(2)	174.9(7)
C(1)	Ir(1)	C(4)	97.5(3)	Ir(1)	C(4)	F(1)	121.4(4)
Ir(1)	Ir(2)	Cl	54.14(3)	Ir(1)	C(4)	C(5)	127.7(5)
Ir(1)	Ir(2)	P(2)	92.19(3)	F(1)	C(4)	C(5)	110.7(5)
Ir(1)	Ir(2)	P(4)	92.80(3)	F(2)	C(5)	F(3)	106.8(6)
Ir(1)	Ir(2)	C(2)	108.2(2)	F(2)	C(5)	C(4)	127.5(7)
Ir(1)	Ir(2)	C(3)	156.8(2)	F(3)	C(5)	C(4)	125.5(6)
Cl	Ir(2)	P(2)	93.42(5)	P(1)	C(6)	P(2)	112.4(3)
Cl	Ir(2)	P(4)	91.06(5)	P(3)	C(7)	P(4)	112.8(3)
Cl	Ir(2)	C(2)	162.3(2)				

^a Nonbonded distance.

= 1.351(8) Å, C(5)–F(3) = 1.337(8) Å) are somewhat shorter than C(4)–F(1) of 1.376(7) Å; the shortening of C–F bonds as the number of fluorines on a carbon is increased has previously been noted.²² Metal–fluoro-carbon bonds are also generally observed to be shorter and stronger than those involving nonfluorinated hydrocarbons,²³ and the same is observed in **2**, in which the Ir(1)–C(4) bond (2.090(6) Å) is significantly shorter than Ir(2)–C(3) (2.182(6) Å). Although some of this difference results from the different hybridizations of the trifluorovinyl and methyl carbons ($r(sp^2) = 0.74$ Å; $r(sp^3) = 0.77$ Å), some shortening certainly must be due to fluorine substituents on the former. However, the Ir(1)–C₂F₃ bond is not substantially different than related Rh–vinyl distances in the isopropenyl and trimethylvinyl compounds [RhOs(C(CH₃)=CH₂)(CO)₃(dppm)₂] and [RhOs(C(CH₃)=C(CH₃)₂(CH₃)(CO)₃(dppm)₂][CF₃SO₃] (2.04(2) and 1.955(5) Å, respectively)²⁴ and is also comparable to the Ir–vinyl distances (2.0(2)–2.13(1) Å) in [Ir₂Cl₂(CR=CHR)₂(CO)₂(dppm)₂]²⁵ and Ir₂ClH(CR=CHR)(CO)₂(μ-H)(dppm)₂[BF₄]²⁶ (R = CO₂Me). The olefinic C(4)–C(5) separation (1.298(9) Å) is consistent

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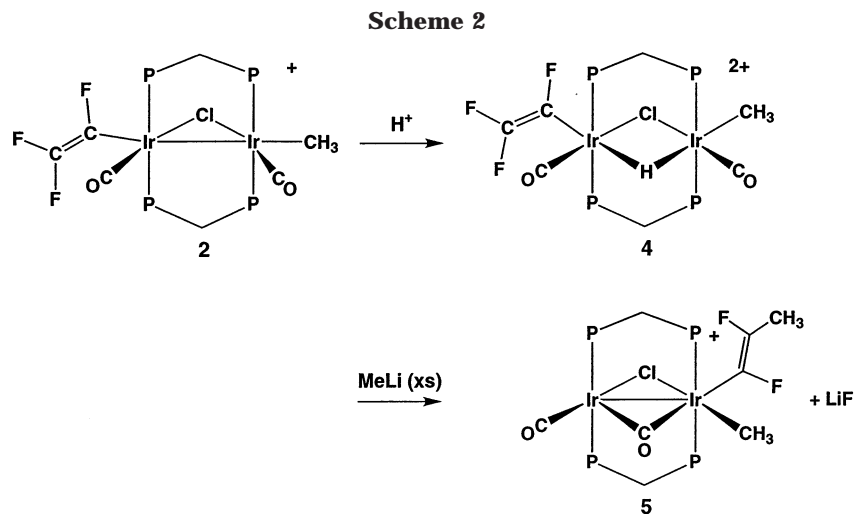
with a C=C double bond, although is somewhat shorter than for nonfluorinated olefins.²⁷

An analogous 2,2-difluorovinyl complex, [Ir₂(CH=CF₂)(CH₃)(CO)₂(μ-Br)(dppm)₂][CF₃SO₃] (**3**), is prepared, much as is **2**, by the oxidative addition of 1-bromo-2,2-difluoroethylene to **1** (see Scheme 1). This reaction occurs more readily than that involving **1** and chlorotrifluoroethylene, with small amounts of **3** being detected by NMR even at –80 °C, and the reaction proceeding to completion within 1 h at ambient temperature. This is in accord with the expectation of more facile C–Br oxidative addition to an electron-rich transition metal compared to addition of a C–Cl bond.²⁸ Spectroscopically, compound **3** is quite comparable to **2**; in particular, their ³¹P{¹H} NMR spectra are very similar (see Table 1). The methyl protons of **3** again appear as a triplet (³J_{PH} = 5 Hz) at typically high field (0.88 ppm), and the hydrogen of the difluorovinyl ligand, at 4.62 ppm, shows 42 Hz coupling to the trans fluorine (at –84.9 ppm) and 12 Hz to the cis fluorine (at –65.9 ppm). This vinyl hydrogen also displays coupling (5 Hz) to the adjacent pair of ³¹P nuclei. In the ¹⁹F NMR spectrum, both fluorines display coupling of 59 Hz, significantly less than the geminal coupling observed in **2**. Smaller geminal coupling has previously been observed when a fluorine on the adjacent α-carbon has been replaced by a less electronegative group.²⁹ Attempts to prepare the fluoro-bridged analogue of **3**, which would be related to a presumed C–F bond-activation product of trifluoroethylene, by bromide replacement in **3** using KF/18-crown-6 in THF gave no reaction overnight. Similarly, the reaction of **3** with AgF in THF gave only decomposition products.

In an attempt to generate the iodo-bridged, trifluorovinyl analogue of **2**, the reaction between **1** and iodotrifluoroethylene was attempted. However, instead of a simple oxidative-addition reaction paralleling the formation of **2** and **3**, the only product obtained is the iodo- and methylene-bridged product [Ir₂(CO)₂(μ-I)(μ-CH₂)(dppm)₂][CF₃SO₃] (**6**), shown in Scheme 1. This product, previously prepared by a different route and characterized in this group,¹⁴ displays a singlet at –7.9 ppm in the ³¹P{¹H} NMR spectrum and a quintet (³J_{PH} = 8.3 Hz) for the protons of the bridging methylene group at 10.0 ppm in the ¹H NMR spectrum. The other presumed product in the reaction, trifluoroethylene, was not detected by ¹⁹F NMR spectroscopy. The bridging methylene group of this product is established as originating from the methyl group of **1** by labeling experiments. Therefore, starting with ¹³CH₃-labeled **1** gives a product having a μ-¹³CH₂ group; no trace of unlabeled product is detected by ¹H NMR spectroscopy.

Attempts to replace the bridging chloro ligand in **2** with either hydride or alkyl groups have met with failure. Compound **2** was unreactive to NaBH₄, KH, or KHB(sec-Bu)₃ in THF at ambient temperature and was also unreactive to the Lewis acids trimethylaluminum, methyltriflate, and trimethylsilyl triflate. In all cases **2** was recovered, as the sole or major product, although

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in the attempted reactions of the Lewis acids, varying amounts of a hydride species was recovered. This hydride product, the complex cation of which was identified as $[Ir_2(CF=CF_2)(CH_3)(CO)_2(\mu-H)(\mu-Cl)(dppm)_2]^{2+}$, presumably results from hydrolysis of the Lewis acid by adventitious water and subsequent protonation of **2**; this species was subsequently generated quantitatively by reaction of **2** with triflic acid to give $[Ir_2(CF=CF_2)(CH_3)(CO)_2(\mu-H)(\mu-Cl)(dppm)_2][CF_3SO_3]_2$ (**4**) (see Scheme 2). Spectroscopically, compound **4** bears a strong resemblance to **2**, and in particular the ^{19}F NMR spectrum displays similar chemical shifts and coupling constants for the trifluorovinyl group in both compounds (see Table 1). The 1H NMR spectrum shows the methyl group as a triplet at 1.40 ppm ($^3J_{PH} = 6$ Hz), and the hydride ligand appears as a broad unresolved resonance at -13.00 ppm; the breadth of the hydride resonance presumably results from coupling to all four phosphorus nuclei, suggesting a bridging arrangement, which has been confirmed by ^{31}P -decoupling experiments. This structural assignment has been confirmed by an X-ray determination, and the final structure of the cation is shown in Figure 2, with selected bond lengths and angles given in Table 4. The molecule was found to be disordered about an inversion center, meaning that the trifluorovinyl group and C(2)O(2) are superimposed at 50% occupancy, as are the methyl group and C(1)O(1) as well as Cl and H(1); nevertheless, the non-hydrogen atoms are readily resolved, and least-squares refinement proceeded satisfactorily. Although, the disorder precludes unambiguous location of the hydride ligand, its position bridging the metals is supported by the substantial lengthening of the Ir–Ir bond from 2.8116(3) Å in **2** to 3.0315(5) Å in **4**. Also consistent with the bridging location of the hydride ligand is the opening up of the pocket between the carbonyls on protonation. As a consequence, the Ir–Ir–CO angles in **2** ($96.7(2)^\circ$, $108.2(2)^\circ$) have increased substantially to $124.7(5)^\circ$ and $128.7(5)^\circ$ in **4**. Both effects are well documented in hydride-bridged metal–carbonyl clusters.³⁰ Although the observed disorder would normally preclude a discussion of bond lengths, the parameters involving the trifluorovinyl group give us confidence that our disordered model accounts accurately for the atom positions.

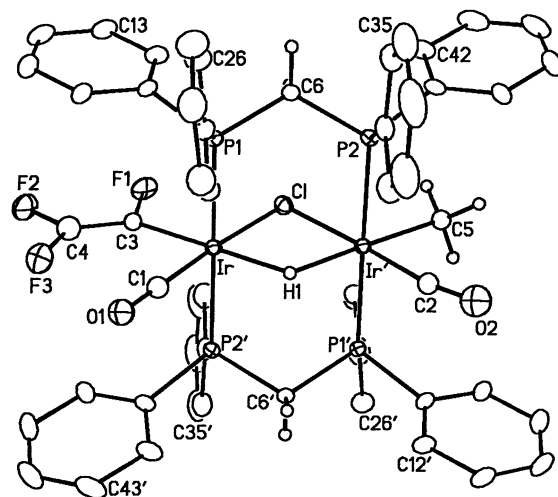


Figure 2. Perspective view of the $[Ir_2(CF=CF_2)(CH_3)(CO)_2(\mu-H)(\mu-Cl)(dppm)_2]^{2+}$ cation of complex **4** showing the atom-labeling scheme. The bridging hydride ligand was not located in the X-ray study. Thermal parameters are as described for Figure 1. Only one of the disordered molecules is shown. For an explanation of the disorder see the text.

The C–F bond lengths in compound **4** agree well with those of **2** and show the same trend ($C_\alpha-F > C_\beta-F$). In the geometry shown, both the trifluorovinyl and methyl groups are opposite the bridging hydride ligand and might be expected to show somewhat elongated metal–carbon bonds owing to the high trans influence of the hydride ligand.³¹ However, both of these bonds in **4** (Ir–C(3) = 2.02(1) Å, Ir'–C(5) = 2.15(1) Å) are actually somewhat *shorter* than the corresponding distances in **2** (2.090(6), 2.182(6) Å). It should be recalled however that metal–metal bonds can also display a significant trans influence,³² which in these compounds appears to exceed that of the bridging hydride ligand. It may also be that the methyl and trifluorovinyl ligands in **2** are exerting a trans influence on each other via the metal–

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Table 4. Selected Interatomic Distances and Angles for Compound 4

(a) Distances (Å)							
Ir	Ir'	3.0315(5) ^a	Ir'	H(1)	1.85 ^b		
Ir	Cl	2.318(3)	P(1)	P(2)	3.051(2) ^c		
Ir	P(1)	2.372(1)	P(1)	C(6)	1.818(6)		
Ir	P(2')	2.381(1)	P(2)	C(6)	1.834(6)		
Ir	C(1)	1.90(1)	F(1)	C(3)	1.39(2)		
Ir	C(3)	2.02(1)	F(2)	C(4)	1.29(2)		
Ir	H(1)	1.85 ^b	F(3)	C(4)	1.34(2)		
Ir'	Cl	2.369(3)	O(1)	C(1)	1.11(2)		
Ir'	C(2)	1.89(2)	O(2)	C(2)	1.09(2)		
Ir'	C(5)	2.15(1)	C(3)	C(4)	1.33(2)		
(b) Angles (deg)							
Ir'	Ir	Cl	50.45(8)	Cl	Ir'	P(2)	89.65(8)
Ir'	Ir	P(1)	89.48(4)	Cl	Ir'	C(2)	177.6(5)
Ir'	Ir	P(2')	90.98(4)	Cl	Ir'	C(5)	94.8(4)
Ir'	Ir	C(1)	124.7(5)	Cl	Ir'	H(1)	84.0 ^d
Ir'	Ir	C(3)	145.9(4)	P(1')	Ir'	C(2)	88.1(4)
Ir'	Ir	H(1)	35.0 ^d	P(1')	Ir'	C(5)	88.9(4)
Cl	Ir	P(1)	88.20(8)	P(1')	Ir'	H(1)	88.6 ^d
Cl	Ir	P(2')	91.64(8)	P(2)	Ir'	C(2)	91.1(4)
Cl	Ir	C(1)	175.1(5)	P(2)	Ir'	C(5)	91.1(4)
Cl	Ir	C(3)	95.4(4)	P(2)	Ir'	H(1)	91.4 ^d
Cl	Ir	H(1)	85.4 ^d	C(2)	Ir'	C(5)	87.5(6)
P(1)	Ir	P(2')	179.25(5)	C(2)	Ir'	H(1)	93.7 ^d
P(1)	Ir	C(1)	91.7(4)	C(5)	Ir'	H(1)	110.0 ^d
P(1)	Ir	C(3)	89.5(4)	Ir	Cl	Ir'	80.58(9)
P(1)	Ir	H(1)	90.5 ^d	Ir	P(1)	C(6)	111.5(2)
P(2')	Ir	C(1)	88.6(4)	Ir'	P(2)	C(6)	109.4(2)
P(2')	Ir	C(3)	89.8(4)	Ir	C(1)	O(1)	177(1)
P(2')	Ir	H(1)	90.2 ^d	Ir'	C(2)	O(2)	166(2)
C(1)	Ir	C(3)	89.5(6)	Ir	C(3)	F(1)	116(1)
C(1)	Ir	H(1)	89.7 ^d	Ir	C(3)	C(4)	137(1)
C(3)	Ir	H(1)	179.2 ^d	F(1)	C(3)	C(4)	106(1)
Ir	Ir'	Cl	48.97(7)	F(2)	C(4)	F(3)	110(1)
Ir	Ir'	C(2)	128.7(5)	F(2)	C(4)	C(3)	130(2)
Ir	Ir'	C(5)	143.7(4)	F(3)	C(4)	C(3)	120(1)
Ir	Ir'	H(1)	35.0 ^d	P(1)	C(6)	P(2)	113.3(3)
Cl	Ir'	P(1')	91.10(8)	Ir	H(1)	Ir'	110.0 ^d

^a Primed atoms are related to unprimed ones via the crystallographic inversion center (0, 0, 0). ^b Distance fixed during refinement. ^c Nonbonded distance. ^d Angle includes Ir–H distances fixed during refinement.

metal bond. The transmission of electronic effects from one metal to another in binuclear complexes has been observed.³³ All other parameters within the complex are as expected.

Attempts to replace the chloro ligand in **2** by a methyl group by reaction with methyllithium also did not succeed, although in this case a reaction did occur. In the presence of a 7-fold excess of methyllithium, 65% conversion to a new product, **5**, occurred (Scheme 2). However, NMR studies demonstrated that chloride replacement did not occur; instead, replacement of one fluorine on the trifluorovinyl group by a methyl group occurred, yielding $[\text{Ir}_2(\text{CF}=\text{CFMe})(\text{CH}_3)(\text{CO})(\mu\text{-Cl})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**5**). The ¹H NMR spectrum of **5** shows two methyl resonances. The signal at 1.22 ppm appears as a pseudo triplet and is assigned to the methyl group on the vinyl ligand, in which the coupling to both fluorine nuclei is essentially the same ($J_{\text{FH}} \approx 12$ Hz), whereas the higher-field resonance at 1.07 ppm is due to the methyl that is bound to one metal, showing coupling to two adjacent ³¹P nuclei. Surprisingly, the

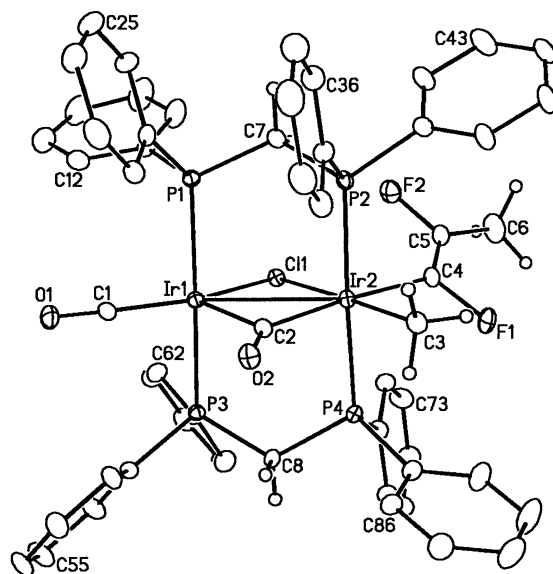


Figure 3. Perspective view of the $[\text{Ir}_2(\text{CF}=\text{C}(\text{F})\text{CH}_3)(\text{CH}_3)(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2]^+$ cation of complex **5** showing the atom-labeling scheme. Thermal parameters are as described for Figure 1.

two chemically inequivalent fluorine atoms of the methyl difluorovinyl group resonate at approximately the same chemical shift as a broad unresolved signal at -126 ppm, and this signal integrates well compared to that of the triflate anion. The ¹³C{¹H} NMR and the IR spectra are consistent with one terminal and one bridging carbonyl ligand. To establish which methyl group in **5** results from the Ir-bound methyl group in the precursor and which is obtained from methyl-lithium, the ¹³C-enriched precursor $[\text{Ir}_2(\text{CF}=\text{CF}_2)(^{13}\text{CH}_3)(^{13}\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ was reacted with unenriched MeLi. The product had the ¹³CH₃ group exclusively on iridium, with no significant ¹³CH₃ enrichment of the methyl difluorovinyl group. Clearly, the iridium-bound methyl group remains on the metals, while replacement of a fluoride is effected by MeLi. In the ¹³C{¹H} NMR spectrum of this ¹³CH₃-enriched sample the iridium-bound methyl signal appears at -24.8 ppm, while that for the vinylic methyl group is at lower field (20.2 ppm) and is very weak since no enrichment occurred at this site (observation of the ¹³C signal for the vinyl-substituted methyl group required overnight data acquisition). Both signals are broad and unresolved, so coupling to ³¹P or ¹⁹F nuclei cannot be determined.

Although spectroscopy clearly establishes the formation of a methyl difluorovinyl group in **5**, it did not enable us to establish the geometry of this group or the relative positions of the methyl and vinyl ligands. However, these details were established by an X-ray structural determination of **5**, which is shown for the cation in Figure 3. Relevant bond lengths and angles are given in Table 5. Two details immediately stand out in the structure of **5**; first, the methyl and methyl difluorovinyl groups are mutually *cis* on the same metal, and second, fluoride substitution has occurred *trans* to the Ir–vinyl bond to give the *trans* isomer of the methyl difluorovinyl group. The Ir–Ir distance (2.9603(4) Å) is substantially longer than a normal single bond (cf. 2.8116(3) Å in **2**),

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Table 5. Selected Interatomic Distances and Angles for Compound 5

(a) Distances (Å)							
Ir(1)	Ir(2)	2.9603(4)	P(1)	P(2)	3.057(3) ^a		
Ir(1)	Cl(1)	2.401(2)	P(1)	C(7)	1.828(8)		
Ir(1)	P(1)	2.358(2)	P(2)	C(7)	1.840(9)		
Ir(1)	P(3)	2.349(2)	P(3)	P(4)	3.133(3) ^a		
Ir(1)	C(1)	1.834(8)	P(3)	C(8)	1.818(8)		
Ir(1)	C(2)	2.116(8)	P(4)	C(8)	1.829(8)		
Ir(2)	Cl(1)	2.552(2)	F(1)	C(4)	1.40(1)		
Ir(2)	P(2)	2.358(2)	F(2)	C(5)	1.39(1)		
Ir(2)	P(4)	2.361(2)	O(1)	C(1)	1.14(1)		
Ir(2)	C(2)	2.083(8)	O(2)	C(2)	1.158(9)		
Ir(2)	C(3)	2.099(8)	C(4)	C(5)	1.30(1)		
Ir(2)	C(4)	2.066(8)	C(5)	C(6)	1.48(1)		
(b) Angles (deg)							
Ir(2)	Ir(1)	Cl(1)	55.68(5)	P(2)	Ir(2)	C(2)	92.8(2)
Ir(2)	Ir(1)	P(1)	91.05(5)	P(2)	Ir(2)	C(3)	89.2(2)
Ir(2)	Ir(1)	P(3)	92.19(5)	P(2)	Ir(2)	C(4)	89.0(2)
Ir(2)	Ir(1)	C(1)	147.8(2)	P(4)	Ir(2)	C(2)	88.3(2)
Ir(2)	Ir(1)	C(2)	44.7(2)	P(4)	Ir(2)	C(3)	88.7(2)
Cl(1)	Ir(1)	P(1)	84.70(7)	P(4)	Ir(2)	C(4)	89.6(2)
Cl(1)	Ir(1)	P(3)	87.25(7)	C(2)	Ir(2)	C(3)	86.8(3)
Cl(1)	Ir(1)	C(1)	156.5(3)	C(2)	Ir(2)	C(4)	174.1(3)
Cl(1)	Ir(1)	C(2)	100.0(2)	C(3)	Ir(2)	C(4)	87.6(3)
P(1)	Ir(1)	P(3)	167.60(7)	Ir(1)	Cl(1)	Ir(2)	73.33(5)
P(1)	Ir(1)	C(1)	92.6(3)	Ir(1)	P(1)	C(7)	112.9(3)
P(1)	Ir(1)	C(2)	101.6(2)	Ir(2)	P(2)	C(7)	108.4(3)
P(3)	Ir(1)	C(1)	91.0(3)	Ir(1)	P(3)	C(8)	111.2(3)
P(3)	Ir(1)	C(2)	89.1(2)	Ir(2)	P(4)	C(8)	111.1(3)
C(1)	Ir(1)	C(2)	103.4(3)	Ir(1)	C(1)	O(1)	177.6(7)
Ir(1)	Ir(2)	Cl(1)	50.99(4)	Ir(1)	C(2)	Ir(2)	89.7(3)
Ir(1)	Ir(2)	P(2)	90.36(5)	Ir(1)	C(2)	O(2)	128.5(6)
Ir(1)	Ir(2)	P(4)	92.02(5)	Ir(2)	C(2)	O(2)	141.5(7)
Ir(1)	Ir(2)	C(2)	45.6(2)	Ir(2)	C(4)	F(1)	115.7(6)
Ir(1)	Ir(2)	C(3)	132.4(2)	Ir(2)	C(4)	C(5)	132.3(7)
Ir(1)	Ir(2)	C(4)	140.0(2)	F(1)	C(4)	C(5)	111.6(7)
Cl(1)	Ir(2)	P(2)	93.87(7)	F(2)	C(5)	C(4)	117.1(7)
Cl(4)	Ir(2)	P(4)	88.17(6)	F(2)	C(5)	C(6)	111.4(8)
Cl(1)	Ir(2)	C(2)	96.3(2)	C(4)	C(5)	C(6)	131.4(9)
Cl(1)	Ir(2)	C(3)	175.5(2)	P(1)	C(7)	P(2)	113.0(4)
Cl(1)	Ir(2)	C(4)	89.2(2)	P(3)	C(8)	P(4)	118.4(4)
P(2)	Ir(2)	P(4)	177.52(7)				

^a Nonbonded distance.

but is compressed compared to nonbonded distances in comparable compounds, for which separations are usually substantially greater than 3 Å. This Ir(1)–Ir(2) separation is also less than the nonbonded intraligand P(1)–P(2) and P(3)–P(4) separations of 3.057(3) and 3.133(3), respectively, indicating some compression along the metal–metal axis. The bonding can therefore be considered in terms of two extremes. In the first scenario the metals are nonbonded and the bridging carbonyl is semibridging, in which it is primarily bound to Ir(2) while simultaneously functioning as a π -acceptor from Ir(1). This view is consistent with the long Ir(1)–Ir(2) separation noted and with the unsymmetrical geometry of the bridging carbonyl (Ir(2)–C(2) = 2.083(8) Å, Ir(1)–C(2) = 2.116(8) Å; Ir(2)–C(2)–O(2) = 141.5(7)°, Ir(1)–C(2)–O(2) = 128.5(6)°), which is more linear with respect to the metal to which it is more strongly bound. In the second extreme a symmetrically bridging carbonyl would be accompanied by an Ir–Ir bond. The observed structure is probably best described as lying somewhere between the two extremes. In the former description the geometry about Ir(2) is octahedral, while that about Ir(1) is tetragonal pyramidal, having the weaker π -interaction to the semibridging carbonyl in the apical site.

Both the Ir–vinyl and Ir–methyl bonds in **5** (2.066(8), 2.099(8) Å, respectively) are shorter than the analogous distances in **2** (2.090(6), 2.182(6) Å), probably reflecting the movement of these groups away from their locations in **2** opposite the Ir–Ir bond (recall our argument earlier about the high trans influence of this bond). In **5** the trans influence of the methyl group appears responsible for the significantly longer Ir(2)–Cl(1) bond compared to Ir(1)–Cl(1) (2.552(2) vs 2.401(2) Å). Within the methyldifluorovinyl group, both C–F bonds are essentially identical, and consistent with earlier arguments, removal of a fluorine substituent from **2** has resulted in a lengthening of the remaining C–F bond on the β -carbon.

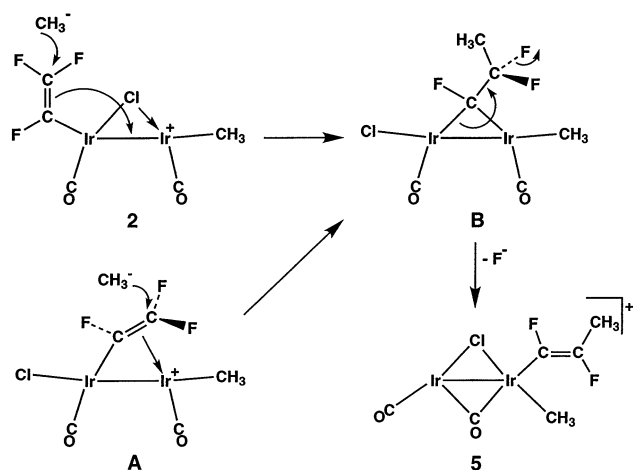
Discussion

As noted earlier, our one-time observation that geminal C–H and C–F activation of trifluoroethylene by the diiridium complex **1** yielded a difluorovinylidene group⁶ prompted us to investigate related trifluorovinyl and 2,2-difluorovinyl complexes in order to gain information on the order of C–H vs C–F activation in partially fluorinated olefins. If C–H activation of trifluoroethylene occurred first, we were interested in determining how the adjacent metals effected subsequent C–F activation of the resulting trifluorovinyl group. Similarly, if C–F activation was first, the resulting 2,2-difluorovinyl group would yield a difluorovinylidene group by subsequent C–H activation.

The targeted trifluorovinyl and 2,2-difluorovinyl complexes [Ir₂(R)(CH₃)(CO)₂(μ -X)(dppm)₂][CF₃SO₃] (R = FC=CF₂, X = Cl (**2**); R = HC=CF₂, X = Br (**3**)) were readily prepared by the oxidative addition of ClFC=CF₂ and BrHC=CF₂, respectively, to [Ir₂(CH₃)(CO)(μ -CO)(dppm)₂][CF₃SO₃] (**1**). The structure of both species has the fluorovinyl and the methyl groups on the outside of the complex, essentially opposite the metal–metal bond. Unfortunately, this is not a suitable position for activation of the fluorovinyl substrates by the adjacent metal, and attempts to induce such activation in these halide-bridged species, under refluxing conditions (CH₂Cl₂ or THF solvent), failed. Attempts to substitute the bridging chloride ligand in **2** by hydride, to give a species analogous to that proposed in an initial C–H activation of trifluoroethylene, failed with a number of hydride sources. Furthermore, attempts to remove the chloride ligand using Lewis acids such as (CH₃)₃SiOSO₂CF₃ also failed. The only reaction observed in these cases was protonation of **2**, by the acids derived from hydrolysis of the Lewis acid by adventitious water. It is noteworthy that protonation of **2** did not result in subsequent reductive elimination of either methane or trifluoroethylene. However, protonation at the metal–metal bond, as observed, leaves the hydride trans to both organic ligands and unable to readily eliminate. Given the facile protonation of **2**, it is perhaps surprising that analogous methylation by methyl triflate did not occur, although we have previously observed that similar cationic species can be basic enough to be protonated, yet remain unreactive to the weaker electrophile, methyl triflate. Attempts to effect removal of the chloride ion in **2** by reaction with silver triflate resulted in decomposition.

In an attempt to replace the bridging chloride ligand in **2** by a methyl group using methyllithium, one of the

Scheme 3



fluorines on the trifluorovinyl group was instead replaced. We were initially surprised that replacement of an olefin-bound fluorine was preferred to replacement of the metal-bound chlorine and were also subsequently surprised by the stereoselective replacement of the fluorine trans to iridium and by the final geometry of the complex in which both the methyl difluorovinyl group and the methyl ligand are mutually cis on the same metal. Clearly transfer of either the methyl or the vinyl group from one metal to the other has occurred.

Substitution on vinyl fluorides by strong nucleophiles has been reported to proceed by an addition–elimination sequence to give the substituted vinyl derivative.³⁴ It is reasonable to expect nucleophilic attack to occur at the β -carbon, which should be more electrophilic as a consequence of the two fluorine substituents. The transfer of the vinyl group in **2** to the metal bearing the methyl group in **5** suggests a bridging arrangement for this vinylic group at some stage. We therefore suggest that nucleophilic attack is accompanied by movement of the resulting fragment to the bridging site, yielding a trifluoroalkylidene-bridged species (**B**) as shown in Scheme 3 (dppm ligands are omitted for clarity). Analogous fluoroalkylidene-bridged species have been reported.⁹ Subsequent loss of fluoride ion as LiF (evidenced by the cloudy solution), with movement of the new methyl-substituted vinyl group to the second metal, would yield the observed product (**5**) as shown. Alternately, nucleophilic attack on a putative trifluorovinyl-bridged intermediate (**A**) would yield the same fluoroalkylidene-bridged species (**B**). Although bridging vinyl groups have not been observed in the chemistry reported herein, binuclear complexes containing such groups are well documented.³⁵ Consequently, an intermediate such as **A** cannot be ruled out in the transfor-

mation of **2** to **5**. This scheme does not explain the trans arrangement of substituents on the vinyl group; however, we note that other related substitutions on fluorovinyl groups also gave trans products.^{10,11,12b} This may result from steric factors favoring a trans arrangement of the bulkier methyl and metal substituents. It is also possible that the transformation of **2** to **5** occurs by migration of the methyl group to the metal bearing the fluorovinyl ligand, rather than by the mechanism described above. However, we rule this out since such a product would have the positions of these two groups reversed in the final product.

The mutually cis arrangement of methyl and vinyl ligands on the same metal suggests the possibility of reductive elimination of *trans*-2,3-difluoro-2-butene generating the known³⁶ A-frame complex cation $[\text{Ir}_2(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2]^+$. Certainly, the reductive elimination involving unsaturated substrates is known to be more facile than that involving saturated substrates.³⁷ This has not been achieved under relatively mild conditions (refluxing CH_2Cl_2), presumably reflecting the strong Ir–fluorovinyl bond,²³ but attempts will be made to promote reductive elimination through the use of oxidizing agents.³⁸

Conclusions

Although binuclear complexes containing the trifluorovinyl and 2,2-difluorovinyl ligands have been synthesized, attempts to activate the C–F and C–H bonds on the α -carbons of these ligands by the adjacent metal have failed. Certainly one factor inhibiting the targeted activation steps is the location of the fluorovinyl groups on the outside of the respective complexes, in a position remote from the adjacent metal. Attempts to replace or remove the bridging chloride ligand in **2** in attempts to bring the trifluorovinyl group toward the bridging site have failed. Subsequent studies will be aimed at related complexes in which halide removal or replacement can be achieved in order to probe the functions of adjacent metals in the activation of fluorocarbyl groups.

We have discovered that the fluorine atom trans to Ir in the trifluorovinyl complex **2** can be selectively replaced by a methyl group, and we propose that this occurs via a fluoroalkylidene-bridged intermediate.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support of this research and NSERC for funding the PLATFORM/SMART 1000 CCD diffractometer. M.C. thanks the University of Alberta and the Killam Trusts for a Killam Annual Research Professorship and acknowledges Professor Jeff Stryker for helpful discussions.

Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compounds **2**, **4**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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