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The Bridged Binding Mode as a New, Versatile Template for the Selective Activation of Carbon−Fluorine Bonds in Fluoroolefins: Activation of Trifluoroethylene

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Abstract: We report the selective activation of carbon−fluorine bonds in trifluoroethylene using the diiridium complex $[Ir_2(CH_3)(CO)_2(dppm)_2][OTf]$ (**1**). Coordination of trifluoroethylene in a bridging position between the two metals in **1** results in facile fluoride ion loss in three different ways. Attack by strong fluorophiles such as Me_3SiOTf and HOTf results in F^- removal from one of the geminal fluorines to give the *cis*-difluorovinyl-bridged product $[Ir_2(CH_3)(OTf)(CO)_2(\mu\text{-}\kappa^1{:}\eta^2\text{-}C(F){=}CFH)(dppm)_2][OTf]$. A second activation can also be accomplished by addition of excess Me_3SiOTf to give the fluorovinylidene-bridged product $[Ir_2(CH_3)(OTf)(CO)_2(\mu\text{-}C_2FH)(dppm)_2][OTf]_2$. Interestingly, activation of the trifluoroethylene-bridged precursor by water also occurs, yielding $[Ir_2(CH_3)(CO)_2(\kappa^1\text{-}C(H){=}CF_2)(\mu\text{-}OH)(dppm)_2][OTf]$, in which the lone vicinal fluorine is removed, leaving a *geminal* arrangement of fluorines in the product. A [1,2]-fluoride shift can also be induced in the trifluoroethylene-bridged precursor upon the addition of CO to give the 2,2,2-trifluoroethylidene-bridged product $[Ir_2(CH_3)(CO)_3(\mu\text{-}C(H)CF_3)(dppm)_2][CF_3SO_3]$. Addition of hydrogen to the *cis*-difluorovinyl-bridged product results in the quantitative elimination of *cis*-difluoroethylene, while its reaction with CO yields a mixture of *cis*-difluoropropene and 2,3-difluoropropene by reductive elimination of the methyl and difluorovinyl groups with an accompanying isomerization in the case of the second product. Finally, protonation of the 2,2,2-trifluoroethylidene-bridged product liberates 1,1,1-trifluoroethane, in which one hydrogen (H^+) is from the acid while the other hydrogen (H^-) is derived from activation of the methyl group.

1. Introduction

The selective activation of otherwise inert chemical bonds using metal complexes has been one of the pivotal achievements in chemistry over the past few decades,[1] presaging the use of plentiful yet unreactive substrates, such as alkanes and dinitrogen, as feedstocks for the chemical industry. Although most attention has been directed at the substantial challenges associated with the selective activation of carbon−hydrogen bonds,[2−10] particularly in unreactive alkanes, a challenge that until recently had been considered one of the “Holy Grails” of synthetic chemistry,[11] there has been significant recent interest in the activation of other inert bonds, such as carbon−carbon,[9,12,13] carbon−oxygen,[14,15] carbon−chlorine,[16,17] and nitrogen−nitrogen,[18,19] as new more efficient synthetic methodologies are sought for the generation of important molecules and for the destruction of persistent pollutants.

As is the case for studies in the activation of other carbon−heteroatom bonds, the field of carbon−fluorine bond activation is relatively new, with most concerted efforts having been expended over the past 15 years or so.[20−25] Studies in C−F bond activation are being driven in part by the important

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[‡] X-ray Crystallography Lab.

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applications of fluorocarbons in pharmaceuticals, pesticides, polymers, and refrigerants and the consequent need to develop new synthetic routes to the required fluorocarbon products.[26,27] Recent studies also indicate that chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are significant contributors to the degradation of the Earth's ozone layer and contributors as greenhouse gases, thereby necessitating investigations into methods of degrading these otherwise persistent molecules.[28−30]

Complexes involving a range of metals from across the periodic table have shown a propensity to activate carbon−fluorine bonds,[20−24] and although significant successes have been achieved in the activation of fluorinated aryl systems,[31−37] including catalytic hydrodefluorination of perfluorobenzene,[38] surprisingly little has been reported on the transition-metal-promoted activation of fluorine-containing olefins.[39−49] The main focus involving fluoroolefin activation has involved hydrodefluorination, a process in which a C−F bond is replaced by a C−H bond.[50−56] However, the main objective of this reaction has been to replace as many C−F bonds as possible with C−H bonds, and as such, selectivity has not been the main focus. In fact, only a few examples of selective C−F bond activation of fluoroolefins have been reported,[40,52,57−61] and of those, the selectivity observed has mainly differentiated between C−F bonds involving sp^2- and sp^3-hybridized carbons.[40,57,61] Braun and co-workers have shown that $[HRh(PEt_3)_3]$ can exclusively activate the sp^2-hybridized bonds of hexafluoropropene, leaving all sp^3-hybridized C−F bonds untouched, which in the presence of hydrogen gas yields 1,1,1-trifluoropropane.[57] Another study, by Jones and co-workers, has shown $Cp^*_2ZrH_2$ to be an effective reagent for the C−F bond activation of hexafluoropropene, in which the byproduct is Cp^*_2ZrHF; as a result, 6 equiv of the dihydride is necessary to activate all C−F bonds.[52] The addition of only 1 equiv results in the selectively hydrodefluorinated product 1,2,3,3,3-pentafluoropropene. This study has recently been extended to perfluorocyclobutene and perfluorocyclopentene, for which reaction of the former olefin with either $Cp^*_2ZrH_2$ or Cp^*_2ZrHF gave a mixture of single and double vinylic H/F-substituted organic products, while reaction of the latter olefin with $Cp^*_2ZrH_2$ gave single H/F substitution at both a vinylic and an aliphatic position, and Cp^*_2ZrHF again activated only the vinylic positions.[61]

Another selective transformation observed in fluoroolefin C−F bond activation is the [1,2]-fluoride shift, which has been shown to occur in a few multimetallic systems, involving trifluoroethylene,[59] tetrafluoroethylene,[62,63] and hexafluoropropene.[59] Although selectivity is not an issue in the [1,2]-fluoride shift in which a 1,2,2,2-tetrafluoroethylidene-bridged species is generated from tetrafluoroethylene, owing to its symmetry, selectivity has been observed in the case of trifluoroethylene, in which the lone vicinal fluorine is exclusively transferred, resulting in a 2,2,2-trifluoroethylidene-bridged product, and also with hexafluoropropene, in which the fluorine geminal to the trifluoromethyl group is exclusively transferred, giving a hexafluoroisopropylidene group. In all cases, the proposed mechanism involves fluoride ion abstraction to give a fluorovinyl group, followed by nucleophilic attack at the β-carbon of the fluorovinyl group by fluoride ion, giving the final [1,2]-fluoride shift product,[59,62,63] although it is not clear what species is responsible for the fluoride abstraction step.

Our strategy for effecting the facile and selective activation of C−F bonds in fluoroolefins has been to use adjacent metals that can interact with the fluoroolefins in a cooperative manner. In a bridging arrangement, the fluoroolefin can be viewed as a 1,2-dimetalated fluoroalkane, in which complete rehybridization of the olefin carbons to sp^3 has occurred, as shown for the trifluoroethylene ligand in Chart 1. In such an arrangement, each end of the bridging fluoroolefin can be viewed as a fluoroalkyl group and as such should be susceptible to fluoride ion

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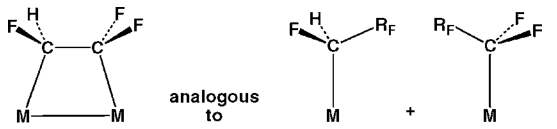
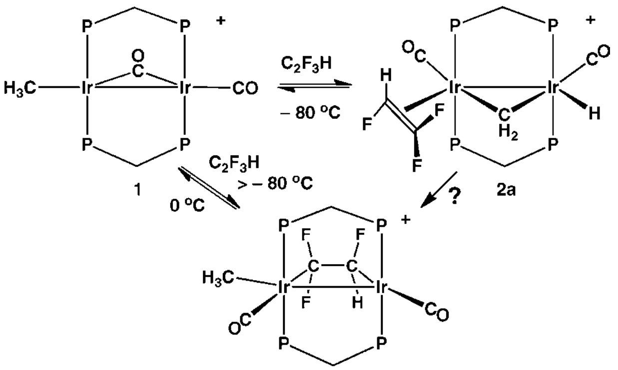
Chart 1



Scheme 1



1

2a

2

abstraction from the α-carbons, as is well documented in fluoroalkyl complexes of late transition metals.[21,50,64−67]

We have previously reported that the binuclear complex $[Ir_2(CH_3)(CO)_2(dppm)_2][OTf]$ (**1**) binds a number of fluoroolefins ($C_2H_xF_{(4-x)}$, $x = 0-4$) either in the traditional η^2-coordination mode at a single metal (ethylene, vinyl fluoride, *cis*-difluoroethylene, and 1,1-difluoroethylene) or in a bridging mode between the pair of metals (1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene). For 1,1-difluoroethylene, which can bond in both the terminal and bridging modes, we reported facile C−F bond activation at −40 °C in the bridging mode, while even at ambient temperature the terminally bound olefin was unreactive.[39,68,69] In the current report, parts of which have been previously communicated,[38] we describe a series of C−F bond activation processes involving trifluoroethylene and outline the selective functionalization of this fluoroolefin under mild conditions, yielding a number of fluorocarbon products.

2. Results

2.1. Trifluoroethylene Coordination. The diiridium complex $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**1**) reacts with trifluoroethylene at −80 °C to form the highly labile adduct $[Ir_2(H)(\eta^2\text{-}CF_2{=}CFH)(CO)_2(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2a**) in approximately 10% yield, together with starting material. Binding of the olefin in an η^2-fashion at one metal is accompanied by C−H activation of the methyl group at the adjacent metal, yielding bridging methylene and terminal hydride fragments, as outlined in Scheme 1. Owing to the low abundance of **2a**, some of the spectral parameters could not be observed. Nevertheless, substrate attack at one metal in **1** accompanied by methyl C−H activation at the adjacent metal, as proposed for **2a**, is well-precedented reactivity, having been observed with a number of olefins[69] and monodentate ligands (CO, PR_3).[70] Furthermore, the spectral parameters for these previously characterized products match well with those of **2a**, allowing us to confidently assign the structure shown.

The $^{31}P\{^1H\}$ NMR spectrum of **2a** appears as two complex, unresolved multiplets at δ −4.9 and −5.7. Although a two-resonance pattern is suggestive of an AA′BB′ spin system, the binding of the prochiral trifluoroethylene ligand, as shown, should give rise to a more complex pattern, characteristic of an ABCD spin system, by virtue of “left/right” and “top/bottom” asymmetry in **2a** (as viewed in Scheme 1). However, the complex nature of the $^{31}P\{^1H\}$ patterns suggests coincidental overlap of two sets of the four expected resonances of the ABCD spin pattern. In the ^1H NMR spectrum, only two resonances appear for the dppm methylene resonances, again presumably due to coincidental overlap involving pairs of the four expected signals, while the signals for the metal-bridged methylene group and the olefin hydrogen could not be resolved from the signals of starting materials. The hydride ligand is observed as a broad, unresolved signal at δ −12.70 that appears unaffected by ^{31}P decoupling experiments. In the $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample, the carbonyl resonances appear as broad signals at δ 187.6 and 195.2, close to the values previously noted for analogous species,[39,69,70] while in a sample derived from $^{13}CH_3$-enriched **1**, the methylene carbon appears at δ 44.2, typical of a bridging CH_2 group in related diiridium systems.[70] In addition to free trifluoroethylene and triflate ion, the ^{19}F NMR spectrum shows three distinct signals for the coordinated olefin. Two doublets appear at δ −94.4 and −97.3 for the pair of geminal fluorines, and their mutual coupling of 156.8 Hz, compared to 83 Hz geminal coupling in the free olefin, suggests significant olefin rehybridization toward sp^3.[71] The third fluoroolefin resonance appears as an unresolved multiplet at δ −220.1. In a previous study of fluoroolefin binding to **1**, this low-temperature η^2-C_2F_3H adduct was not observed,[69] although analogous adducts have been observed with ethylene,[69] allenes,[72] and 1,1-difluoroethylene.[39,69]

Warming this sample above −80 °C brings about the disappearance of **2a** and the accompanying appearance of $[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_3H)(dppm)_2][CF_3SO_3]$ (**2**), such that at −60 °C none of **2a** remains, with only **2** appearing as a product, together with unreacted **1**. The formation of **2** is slow at lower temperatures, and even at −20 °C, quantitative formation of **2** requires approximately 1 h. This product is less stable than its tetrafluoroethylene analogue,[39,69] reverting to starting materials at ambient temperature over a period of 2 h. In Scheme 1, we have indicated the possibility of direct transformation of **2a** to **2**. However, owing to the low concentration of **2a**, we cannot differentiate between this path and the path occurring via C_2F_3H dissociation and recoordination, proceeding through the precursor **1**.

Compound **2** has been previously reported;[39,69] however, our inability to obtain some of the spectroscopic data at the time led us to incorrectly assign the orientation of the fluoroolefin

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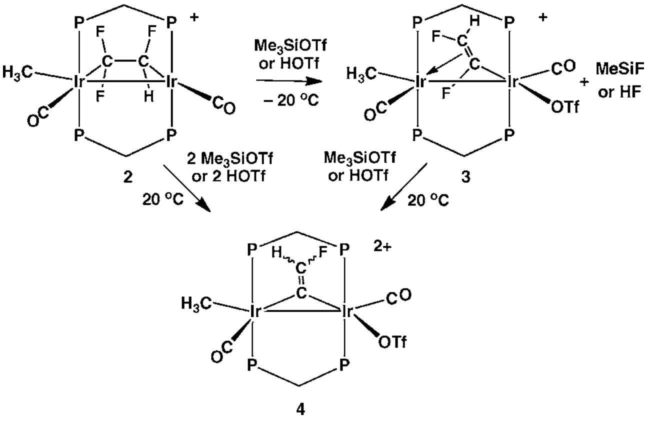
ligand, which we now, with better NMR data, can confidently assign as that shown in Scheme 1. The full spectroscopic characterization of **2**, carried out at 0 °C, is now reported.

The ^{31}P{^{1}H} NMR resonances of compound **2** appear as multiplets at δ 17.2 (1P), 14.4 (1P), and 5.1 (2P), in which two resonances are coincidentally overlapped. The lack of symmetry is consistent with the structure shown, in which there is left/right asymmetry by virtue of the differing metal environments, while the top/bottom asymmetry results from coordination of the prochiral olefin to give a chiral center at the CHF end of this unit. The ^{1}H NMR spectrum confirms the unsymmetrical nature of **2**, with the resonances for the dppm methylene protons appearing as broad multiplets at δ 3.97 (1H), 3.92 (2H), and 3.56 (1H), with coincidental overlap of the middle two resonances. The iridium-bound methyl group appears as a triplet, integrating for three protons, at δ 0.34, coupling equally to the pair of adjacent phosphorus nuclei (see Experimental Section for coupling information). Selective phosphorus decoupling experiments have shown that this moiety is coupled to the ^{31}P nuclei, giving rise to the overlapping resonances at δ 5.1 in the ^{31}P NMR spectrum. It is not surprising that the overlapping ^{31}P signals correspond to the side of the molecule in the more symmetrical environment adjacent to the CF_2 end of the olefin. The unique olefinic hydrogen appears as a broad doublet of doublets of doublets at δ 6.90, at −60 °C in the ^{1}H NMR spectrum, showing distinct coupling to all three associated fluorines. In the original report of this compound, this resonance was not identified.[69] The ^{13}C{^{1}H} NMR spectrum of a ^{13}CO-enriched sample of **2** shows two carbonyl resonances as broad multiplets at δ 185.6 and 197.2, and selective ^{31}P decoupling experiments establish that each carbonyl is bound to a different metal. In the ^{19}F NMR spectrum, three broad signals are observed at δ −53.4, −82.2, and −194.4, all of which are shifted to low field from the free ligand, the corresponding resonances of which appear at δ −100, −126, and −205, respectively. This shift to lower field, with the geminal pair having moved the farthest, is consistent with rehybridization of the associated carbons toward sp^3 and is consistent with the addition of this group across the pair of metals. A similar yet not nearly as pronounced an effect is also observed in the η^2-adduct **2a**; however, rehybridization is more pronounced in the bridging complex, and the large mutual coupling of 253.3 Hz between the two lower-field resonances is also indicative of an sp^3-hybridized $-CF_2$ group.[73] The significant decrease in the $^{3}J_{FF}$ *trans* coupling to 24.8 Hz, from the value of 115 Hz in the free ligand, further supports the bridging arrangement, in which substantial rehybrization has occurred. ^{19}F NMR experiments with selective ^{31}P decoupling have also shown that the high-field resonance at δ −194.4, assignable to the vicinal fluorine, is coupled to the ^{31}P resonances at δ 14.4 and 17.2, while the two low-field resonances at δ −53.4 and −82.2, assignable to the two geminal fluorines, are coupled to the ^{31}P resonance at δ 5.1. This suggests that the more-fluorinated end of the fluoroolefin is bound to the metal associated with the methyl group.

Such an orientation of the olefin is not that predicted on the basis of steric arguments, having the slightly more encumbered disubstituted end of the olefin bound to the more crowded metal center. However, the orientation now proposed is the electronically favored arrangement, in which the more electron-withdrawing olefin substituents are adjacent to the more electron-rich metal, having the donor methyl group attached and assuming the positive charge of the complex is localized on the other metal giving two mutually bonded Ir(II) centers.

Scheme 2



As noted above, we had anticipated that the bridged arrangement of fluoroolefin ligands and the resulting rehybridization could lead to labilization of the fluoride substituents, making carbon−fluorine bond activation feasible, so we set out to investigate the different ways in which such activation could be initiated. In what follows, we discuss the different C−F bond activation steps, followed by functionalization of the generated fluorocarbyl units to generate transformed fluorocarbons.

2.2. C−F Bond Activation. 2.2.1. Activation by Strong Lewis Acids. The reaction of **2** with either triflic acid ($HOSO_2CF_3$) or trimethylsilyl triflate ($Me_3SiOSO_2CF_3$) at −20 °C quantitatively yields the *cis*-difluorovinyl-bridged product $[Ir_2(CH_3)(OTf)(CO)_2(\mu\text{-}\kappa^1{:}\eta^2\text{-}C(F){=}CFH)(dppm)_2][CF_3SO_3]$ (**3**), as outlined in Scheme 2. This product is stable at ambient temperature, allowing for its isolation and complete characterization.

The ^{31}P{^{1}H} NMR spectrum of **3** reveals a pattern that is characteristic of an ABCD spin system having four inequivalent phosphorus nuclei, consistent with the structure shown in Scheme 2. Mutual coupling of $^{2}J_{PP} = 336.5$ Hz is observed for the resonances at δ −2.0 and −19.3, while the resonances at δ 9.5 and −3.3 display mutual coupling of 331.1 Hz; the magnitude of these $^{2}J_{PP}$ values establishes that the diphosphine units have remained *trans* at both metal centers.

In the ^{1}H NMR spectrum, the dppm methylene protons appear as three multiplets at δ 6.00 (1H), 5.52 (2H), and 4.66 (1H), in which the complex central signal corresponds to coincidental overlap of two resonances, consistent with the absence of top/bottom and front/back symmetry in the product. The iridium-bound methyl group appears as a triplet at δ 1.44, displaying equal coupling to the adjacent two phosphorus nuclei at δ −2.0 and −19.3, while the vinylic proton is identified by its distinct splitting pattern, appearing as a multiplet (dddd) at δ 5.90. The most prominent coupling is the diagnostic geminal hydrogen−fluorine coupling ($^{2}J_{HF}$) of 65.6 Hz, consistent with an approximate sp^2-hybridized $-CHF$ group.[71] The smaller coupling ($^{3}J_{HF} = 10.3$ Hz) is suggestive of a *trans* arrangement of H and the second fluorine across the olefinic bond. These couplings are consistent with those seen in the ^{19}F NMR spectrum. Selective ^{1}H{^{31}P} decoupling experiments establish that two of the additional couplings are due to the neighboring phosphorus atoms. The smaller coupling ($^{3}J_{HP} = 5.4$ Hz) arises through the η^2-interaction of the fluorovinyl framework and involves the

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(73) Dungan, C. H.; Wazer, J. R. V. *Compilation of reported ^{19}F NMR chemical shifts, 1951 to mid-1967*; Wiley-Interscience: New York, 1970.

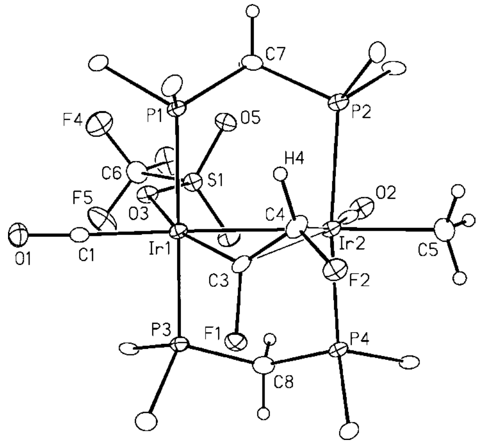

Figure 1. Perspective view of one of the two crystallographically independent $[Ir_2(CH_3)(OSO_2CF_3)(CO)_2(\mu\text{-}\kappa^1,\eta^2\text{-}CF{=}CHF)(dppm)_2]^+$ (**3**) complex ions (molecule A), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. For the phenyl groups, only the ipso carbons are shown. Relevant bond distances (Å) and angles (°) for the pair of independent molecules: Ir(1)−Ir(2) = 2.8778(7), 2.8767(7); Ir(1)−C(3) = 1.95(1), 1.93(1); Ir(2)−C(3) = 2.24(1), 2.26(1); Ir(2)−C(4) = 2.15(1), 2.22(1); C(3)−C(4) = 1.37(2), 1.39(2); F(1)−C(3) = 1.41(1), 1.38(1); F(2)−C(4) = 1.42(1), 1.38(1); Ir(1)−C(3)−F(1) = 116.1(8), 119.5(8); F(1)−C(3)−C(4) = 112.7(10), 108.3(10); F(2)−C(4)−C(3) = 116.2(11), 122.0(10).

phosphorus atom in a pseudo-*cis* arrangement, whereas the larger coupling ($^3J_{HP}$ = 16.6 Hz) is assigned to the pseudo-*trans* phosphorus again through the η^2-interaction. No coupling is observed between the vinylic proton and the two phosphorus atoms adjacent to the metal−vinyl σ-bond.

The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of **3** shows two multiplets at δ 165.9 and 172.1, consistent with a terminal arrangement of both, and selective ^{31}P decoupling establishes that each carbonyl is bound to a different metal. Furthermore, the stretches at 2053 and 2007 cm^{-1} in the IR spectrum support the terminal binding of both.

In the ^{19}F NMR spectrum, the free and the coordinated triflate ions appear at δ −79.5 and −77.7, respectively, together with two complex multiplets at δ −24.2 and −172.7 for the difluorovinyl group 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 also shows coupling of 33.2 Hz to the *cis* fluorine. Selective $^{19}F\{^{31}P\}$ 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, as the actual coupling was unresolved.

An X-ray crystallographic study of **3** confirms the geometry proposed above, as shown for one of the two independent cations in Figure 1, clearly showing the unique κ^1,η^2-bridging coordination mode of the vinyl unit and the mutually *cis* arrangement of fluorine atoms. Although $\mu\text{-}\kappa^1,\eta^2$-vinyl ligands are quite common,[74−82] we are unaware of any other examples in which this binding mode is adopted by fluorovinyl groups. The orientation shown for the bridging fluorovinyl unit clearly demonstrates why all four phosphorus, as well as all four dppm methylene protons, are rendered chemically inequivalent, as observed in the NMR experiments. The arrangement of the ancillary ligands in the complex, as proposed from the spectroscopy, is also confirmed in this X-ray study. All metrical parameters within the complex are essentially as expected. The Ir(1)−C(3) σ-vinyl linkage, at 1.95(1) and 1.93(1) Å (for the independent molecules), is typical, while the distances of the vinyl carbons to the adjacent metal (Ir(2)−C(3) = 2.24(1) and 2.26(1) Å; Ir(2)−C(4) = 2.15(1) and 2.22(1) Å) are somewhat longer for this π interaction. The vinylic C(3)−C(4) bond (1.37(2) and 1.39(2) Å) is somewhat elongated from that (*ca.* 1.34 Å) in an uncomplexed vinyl group.

2.2.2. Removal of a Second Fluoride Ion. Reaction of compound **3** with an additional equivalent of Me_3SiOTf at ambient temperature, overnight, results in C−F activation and fluoride ion removal from the α-position of the difluorovinyl group to yield the monofluorovinylidene-bridged product $[Ir_2(CH_3)(OTf)(CO)_2(\mu\text{-}C_2FH)(dppm)_2][CF_3SO_3]_2$ (**4**), as shown in Scheme 2. Compound **4** can be prepared directly from **2** by reaction with 2 equiv or more of Me_3SiOTf at ambient temperature.

The $^{31}P\{^1H\}$ spectrum of **4** shows two resonances owing to the inequivalence of the two metals. In this case, the fluorovinylidene group lies in the equatorial plane of the CO, CH_3, and OTf ligands, resulting in mirror symmetry relating the two bridging dppm ligands. The ^1H NMR spectrum shows the iridium-bound methyl group as a triplet, integrating for three protons, at the relatively downfield chemical shift of δ 2.15, and selective ^{31}P-decoupling experiments indicate that these protons couple to the pair of phosphorus nuclei at δ −5.0. The chemical shift of the fluorovinylidene proton appears as a broad doublet at δ 8.60, showing 85.6 Hz coupling to fluorine. In a ^{13}CO-enriched sample of **4**, the $^{13}C\{^1H\}$ NMR spectrum shows two broad multiplet carbonyl resonances at δ 153.4 and 176.8. Whereas the high-field carbonyl shows coupling only to the pair of phosphorus nuclei on the non-methylated metal (δ −21.0) of 11.5 Hz and is therefore presumably terminally bound to this metal, the lower-field carbonyl shows coupling to both sets of diphosphine resonances, the larger 16.6 Hz coupling to the pair of phosphorus nuclei resonating at δ −5.0, and small, unresolvable coupling to the phosphorus nuclei at δ −21.0, suggesting small $^3J_{C-P}$ coupling through the metal−metal bond. The ^{13}C-enriched methyl group displays a broad, relatively low-field singlet at δ 40.5, presumably shifted downfield due to the higher positive charge on the complex. In the ^{19}F NMR spectrum, the monofluorovinylidene group appears as a doublet at δ −107.4, having a $^2J_{HF}$ coupling of 85.6 Hz, comparable to the values seen in related fluorovinyl complexes that display geminal H−F coupling ($^2J_{HF}$).[83]

In all reactions involving fluoride ion abstraction by trimethylsilyl triflate, the resulting trimethylsilyl fluoride is obvious

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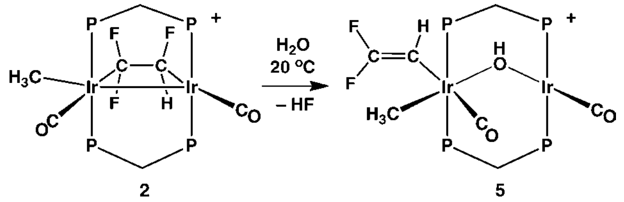
Scheme 3



in the ^{19}F NMR spectrum, displaying a distinctive resonance at δ −159.2, with coupling to the methyl protons, along with the corresponding doublet in the ^{1}H NMR at δ 0.25 ($^3J_{HF}$ = 7.5 Hz),[84,85] while in these small-scale reactions involving triflic acid, the HF produced is never directly detected, although etching of the NMR tubes occurs.

2.2.3. Activation by Water. Remarkably, compound **2** even reacts with water, leading to facile and selective C−F activation over 30 min at ambient temperature to give [Ir$_2$(CH$_3$)(κ^1-C(H)=CF$_2$)(CO)$_2$(μ-OH)(dppm)$_2$][OTf] (**5**), as outlined in Scheme 3. This reaction differs from those involving triflic acid and trimethylsilyl triflate in several ways. Replacement of the coordinated triflate in **3** by hydroxide ion leads to a hydroxide-bridged product, owing to the greater tendency of this anion to bridge, and results in the fluorovinyl group being displaced from a bridging position, as in **3**, to a terminal position in **5**. More significantly, however, activation by water has occurred with a different regiochemistry, by abstraction of the lone fluoride adjacent to hydrogen to give the 2,2-difluorovinyl product instead of a *cis*-difluorovinyl product as observed in **3**.

The ^{31}P{^{1}H} NMR spectrum of **5** appears as two resonances; while the resonance at δ 13.3 is a well resolved multiplet, the other, at δ −15.3, is a broad, unresolved multiplet due to additional coupling to one fluorine of the fluorovinyl unit.

The ^{1}H NMR signals are as expected, with the exception of the methyl peak, which appears at δ 0.39 as a *doublet* of triplets; in addition to the anticipated coupling of this group to the pair of adjacent ^{31}P nuclei, coupling of 2.5 Hz to a vinylic fluorine is also observed, as evidenced by collapse of the methyl signal to a doublet in the ^{1}H{^{31}P} experiment. The bridging hydroxide proton appears as a broad singlet at δ 1.73, the two sets of dppm methylene protons appear as multiplets at δ 3.39 and 4.44, while the vinylic proton appears at δ 4.17 as a doublet of doublet of triplets, displaying fluorine couplings of 45.4 and 13.8 Hz, assigned to *trans* and *cis* coupling, respectively. No resolvable coupling of the broad hydroxyl proton to phosphorus is observed, although the signal sharpens significantly upon broadband phosphorus decoupling.

Carbon-13 labeling of the carbonyls and the methyl group leads to three distinct resonances in the ^{13}C{^{1}H} NMR spectrum. The two carbonyl resonances at δ 174.4 (doublet of triplets) and 170.8 (triplet) indicate terminally bound groups. Each displays coupling to the pair of adjacent ^{31}P nuclei on different metals, while the former signal displays additional coupling to one of the vinylic fluorines ($^4J_{CF}$ = 12.0 Hz). The methyl carbon signal also displays coupling to the pair of adjacent phosphorus nuclei, together with coupling to one fluorine nucleus ($^2J_{CP}$ = 4.8 Hz, $^4J_{CF}$ = 4.8 Hz).

The ^{19}F NMR spectrum shows, in addition to the triflate anion, two signals appearing at δ −65.9 and −86.1 for the pair of vinylic fluorines. The downfield signal appears as a doublet of doublets, with coupling of $^2J_{FF}$ = 55.9 Hz and $^3J_{FH}$ = 13.2 Hz, while the upfield signal appears as a broad, unresolved resonance.

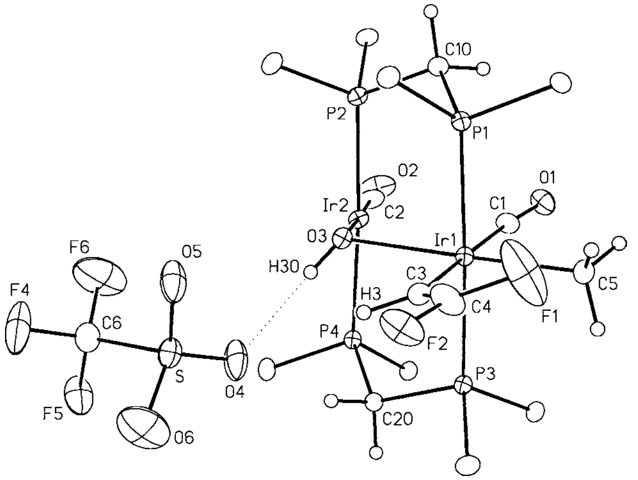


Figure 2. Perspective view of [Ir$_2$(CH$_3$)(κ^1-C(H)=CF$_2$)(CO)$_2$(μ-OH)(dppm)$_2$][OTf] (**5**), showing the atom labeling scheme. Only the ipso carbons of the dppm phenyl rings are shown, while the thermal parameters for the other atoms are as described in Figure 1. Relevant bond distances (Å) and angles (°): Ir(1)−C(3) = 2.093(3); C(3)−C(4) = 1.278(4); F(1)−C(4) = 1.311(5); F(2)−C(4) = 1.347(4); Ir(1)−C(3)−C(4) = 135.7(3); F(1)−C(4)−C(3) = 128.6(4); F(2)−C(4)−C(3) = 126.4(4); F(1)−C(4)−F(2) = 104.7(3).

An X-ray structure determination confirms the structural assignment and is shown, for the complex cation, in Figure 2. This structure has an octahedral geometry at Ir(1), consistent with an Ir(III) oxidation state, while the adjacent metal, which shares the bridging hydroxide ligand, has a square-planar geometry, characteristic of Ir(I); at 3.246(2) Å, the iridium−iridium separation is beyond bonding distance. The structure clearly confirms the geminal arrangement of the two fluorines, with the C(4)−F(1) bond (1.311(5) Å) slightly shorter than C(4)−F(2) (1.347(4) Å). We attach no chemical significance to this difference, owing to the elongated thermal ellipsoids for these atoms which may disguise a slight disorder. The C(4)−C(5) bond length of 1.278(4) Å is shorter than expected for a C−C double bond; however, this may also be a consequence of the apparent vibrational motion. We assume that the spin−spin coupling noted above between the methyl group and one fluorine nucleus results from a through-space interaction between the adjacent methyl and difluorovinyl groups, with the closest approach between F(1) and the methyl protons being 2.22 Å. A hydrogen bond is evident between the hydroxyl proton and the triflate counteranion (H(3O)−O(4) = 2.06 Å; O(3)···O(4) = 2.894(4) Å).

2.2.4. [1,2]-Fluoride Shift. Reaction of **2** with CO at −80 °C yields the expected carbonyl adduct [Ir$_2$(CH$_3$)(CO)$_3$(μ-C$_2$F$_3$H)-(dppm)$_2$][CF$_3$SO$_3$] (**6**) (Scheme 4), which like **2** displays four resonances in the ^{31}P{^{1}H} NMR spectrum; again, the large couplings between pairs of ^{31}P nuclei confirm that the phosphines have remained *trans* at the two metals.

In the ^{1}H NMR spectrum, the four methylene protons are also unique, while the methyl signal appears as a broad singlet at δ 0.72, and the unique olefinic proton appears as a doublet of doublet of doublets at δ 5.94. In this last resonance, the largest coupling of 49.7 Hz is comparable to the geminal H−F coupling observed in **2** ($^2J_{HF}$ = 34.9 Hz). The ^{13}C{^{1}H} NMR spectrum of a ^{13}CO-enriched sample shows three carbonyl resonances:

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(84) Danyluk, S. S. *J. Am. Chem. Soc.* **1964**, *86*, 4504.
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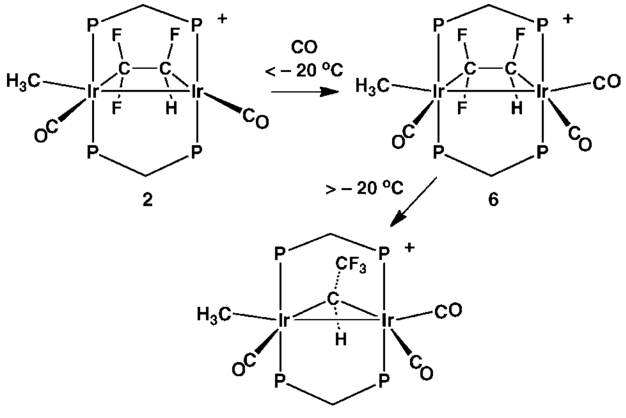
Scheme 4



two overlapping multiplets at δ 179.0 and a doublet of triplets at δ 156.3. The latter signal displays coupling to one side of the diphosphine framework (11.5 Hz) and $^3J_{CC}$ of 11.5 Hz to the ^{13}C-labeled methyl group; we suggest that this latter coupling is between the two groups opposite the Ir−Ir bond. The ^{19}F NMR spectrum shows three broad signals at δ −67.8, −81.9, and −169.8; however, no coupling could be resolved owing to their breadth.

Upon warming to −20 °C, compound **6** converts irreversibly to **7** over 30 min via a 1,2-fluoride shift, yielding the 2,2,2-trifluoroethylidene-bridged product shown. The ^{31}P{^{1}H} NMR spectrum of **7** again reveals four signals, indicating that all ^{31}P nuclei remain chemically inequivalent, and again the large coupling between pairs of ^{31}P nuclei indicate a *trans* dppm arrangement at both metals.

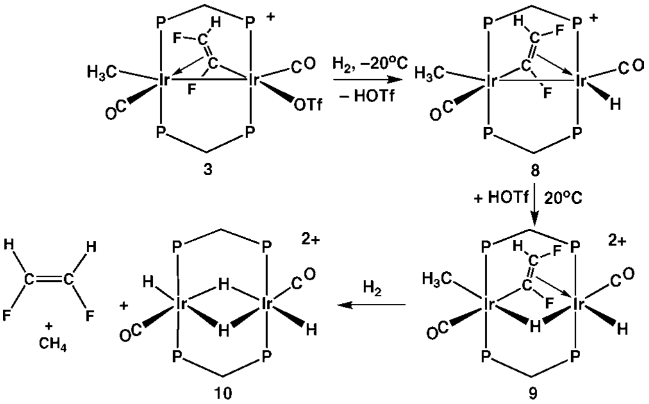
The ^{1}H NMR spectrum shows the lone proton of the bridging trifluoroethylidene group as a multiplet at δ 5.82, with coupling to the three neighboring fluorine atoms together with coupling to all four phosphorus nuclei. Upon broadband phosphorus decoupling, this signal collapses to a quartet with 17.7 Hz coupling to the three fluorines. Four unique methylene protons from the bridging diphosphines appear as multiplets at δ 5.44 (1H), 4.08 (1H), 3.88 (1H), and 3.85 (1H). Finally, the iridium-bound methyl group appears as a pseudo-triplet at δ 0.71 (3H), showing equal coupling to the two phosphorus nuclei on the same metal.

A ^{13}C{^{1}H} NMR spectrum on a non-enriched sample of **7** was obtained, showing three different signals at δ 179.7, 177.6, and 162.8, consistent with three terminal carbonyls. The terminal methyl group was also observed at δ −25.2, typical of an iridium-bound methyl group.

In the ^{19}F NMR spectrum, the free triflate counterion appears together with a doublet at δ −42.4, having a coupling constant of $^3J_{HF}$ = 17.7 Hz, corresponding to the newly formed $-CF_3$ group of the trifluoroethylidene unit.

2.3. Fluorocarbyl Group Functionalization. 2.3.1. Hydrogenolysis. The addition of H_2 to compound **3** at −20 °C gives an immediate reaction, as demonstrated by the replacement of the ^{31}P{^{1}H} NMR resonances of **3** by a new set of signals, due to the monohydride species $[Ir_2(CH_3)(H)(CO)_2(\mu\text{-}\kappa^1:\eta^2\text{-C(F)=CFH})(dppm)_2]^+$ (**8**) (Scheme 5). The appearance of **8** is accompanied by the appearance of a broad single peak at δ 12.00 in the ^{1}H NMR spectrum, consistent with the formation of triflic acid in CH_2Cl_2 (presumably stabilized by hydrogen bonding with the additional triflate ion).

Scheme 5

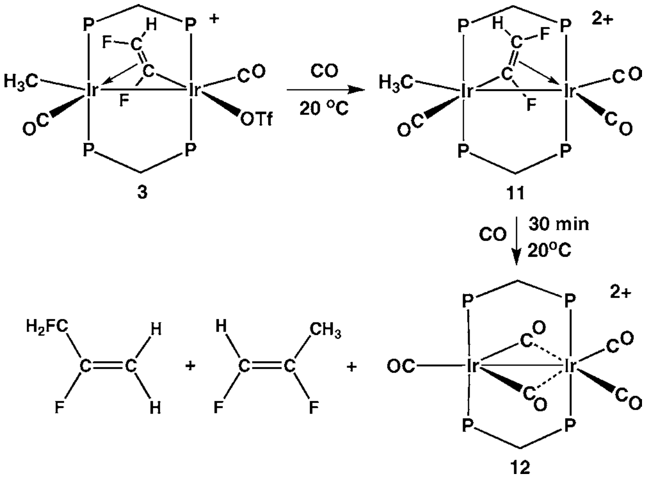


Compound **8** retains the four-resonance ^{31}P{^{1}H} NMR spectrum characteristic of chemically inequivalent environments for all phosphorus atoms, with large *trans* coupling between pairs of resonances. No evidence was observed for an initial H_2 adduct down to −80 °C; instead, facile heterolytic cleavage of H_2 results in the formation of triflic acid and the monohydride complex **8**. The new hydride resonance appears in the ^{1}H NMR spectrum at δ −6.92 as a pseudo-doublet of triplets, each showing 14.0 Hz coupling to the two adjacent phosphorus nuclei (δ −2.0 and 18.2) and 6.0 Hz coupling to the β-fluorine of the bridging difluorovinyl group. The ^{1}H NMR spectrum also shows four separate signals for the dppm methylene protons, while the methyl group appears as a pseudo-triplet at δ 1.01 ($^3J_{HP}$ = 5.0 Hz). Selective decoupling upon irradiation of the two ^{31}P resonances corresponding to one side of the diphosphine framework (δ −6.0 and 9.0) each results in a collapse of this signal to a doublet. The vinylic proton appears as a multiplet at δ 4.94, displaying two major resolvable couplings, the larger of which ($^2J_{HF}$ = 63.2 Hz) is consistent with the geminal coupling of an sp^2-hybridized C(H)F group, and the smaller of which ($^3J_{HF}$ = 14.7 Hz) is consistent with a *trans* arrangement to the other fluorine. Selective decoupling ^{1}H{^{31}P} experiments also indicate that the vinylic proton is coupled to the same two phosphorus nuclei as is the hydride, displaying 4.4 Hz coupling to the phosphorus nucleus at δ 18.2 and 18.6 Hz coupling to the phosphorus at δ −2.0. This coupling suggests that the difluorovinyl unit is η^2-bound to the non-methyl-containing iridium, indicating that it has migrated from one metal to the other in the transformation from **3**. The ^{13}C{^{1}H} NMR spectrum of a ^{13}CO- and $^{13}CH_3$-enriched sample shows two terminal carbonyl resonances at δ 179.2 and 175.5, while the methyl carbon is a broad singlet at δ −21.7.

In the ^{19}F NMR spectrum, two signals appear at δ −60.2 and −172.9; however, both are broad (*ca.* 132 and 118 Hz at half-height, respectively). ^{19}F{^{31}P} experiments result in peak sharpening of the β-fluorine when the ^{31}P resonances on the adjacent metal are decoupled, suggesting that the weak coupling observed occurs through the π-bonding interaction. No coupling is observed between the α-fluorine and the two phosphorus nuclei via the σ-bond. A similar coupling pattern was also evident in compound **3** and is suggestive of a bridging orientation of the fluorovinyl moiety.

As the temperature is raised to ambient, the resonances due to **8** are replaced by a new set of four multiplets in the ^{31}P{^{1}H} spectrum due to **9**. Concomitant with the appearance of this new species is the disappearance of the triflic acid resonance in the ^{1}H NMR spectrum and the appearance of two new hydride

Scheme 6



signals: a triplet at δ −11.00 ($^3J_{PH}$ = 12.0 Hz) and a broad, unresolved signal at δ −14.40. The methyl resonance now appears as a triplet at δ 0.80. Selective ^{31}P decoupling demonstrates that the hydride at δ −11.00 and the methyl group are coupled to different ends of the diphosphines, and so are presumably bound to different metals, while the slight sharpening of the unresolved hydride resonance at δ −14.40 upon selective and broadband ^{31}P decoupling suggests a bridging arrangement for this group. Unfortunately, the vinylic proton was not identified in the ^{1}H NMR spectrum, presumably being obscured by the dppm phenyl resonances. In a $^{13}CH_3$-enriched sample, the methyl carbon appears as a broad singlet at δ −17.9 in the $^{13}C\{^1H\}$ NMR spectrum, while a ^{13}CO-enriched sample shows two broad resonances at δ 168.2 and 160.4, suggesting terminal arrangements for these groups.

In the ^{19}F NMR spectrum the two fluorines appear as a broad multiplet at δ −87.9 and a doublet of doublets at δ −144.1. The couplings involving the latter ($^2J_{FH}$ = 60.9, $^3J_{FF}$ = 26.6 Hz) are again consistent with the *cis* arrangement of the fluorines.

Left at ambient temperature under an atmosphere of H_2, complete conversion of **9** to the previously characterized tetrahydride product, $[Ir_2(H)_2(CO)_2(\mu\text{-}H)_2(dppm)_2][CF_3SO_3]_2$ (**10**),[86] is observed over a 30 min period, resulting from hydrogenolysis and subsequent elimination of methane and *cis*-difluoroethylene, as confirmed for the latter by comparison of the ^{1}H and ^{19}F NMR spectra with that of an authentic sample.[73]

Addition of H_2 to compounds **4**, **5**, and **7** was also investigated, but no reaction was observed in these cases.

2.3.2. Reductive Elimination of Difluoropropenes. Addition of carbon monoxide to compound **3** at ambient temperature results in an immediate reaction, as demonstrated by the disappearance of its $^{31}P\{^1H\}$ NMR resonances and the corresponding appearance of a new set of signals due to the tricarbonyl compound $[Ir_2(CH_3)(CO)_3(\mu\text{-}\kappa^1{:}\eta^2\text{-}C(F){=}CFH)(dppm)_2][CF_3SO_3]_2$ (**11**), in which the triflate ion has been replaced by a carbonyl group, as shown in Scheme 6. The $^{31}P\{^1H\}$ NMR spectrum of compound **11** reveals four complex multiplets, indicative of four inequivalent phosphorus environments, like that of the precursor.

The ^{1}H NMR spectrum of **11** shows the expected four resonances for the dppm methylene protons: the methyl ligand appears as a broad triplet at δ 1.13, and the vinylic proton at δ 6.66 is identifiable by its characteristic multiplet splitting pattern, with two of the resolvable couplings being diagnostic of hydrogen−fluorine coupling. The most prominent coupling involving the fluorovinyl proton is $^2J_{HF}$, with a value of 65.2 Hz, consistent with the geminal coupling of an sp^2-hybridized −CHF group, while the smaller coupling ($^3J_{HF}$ = 15.3 Hz) confirms that the H and the other F atom are in a *trans* arrangement across the vinylic center. Selective ^{31}P-decoupling experiments demonstrate that the vinylic proton is coupling through the π-bond to two phosphorus nuclei at δ 4.0 and −18.2, suggesting that the vinyl group has again migrated to the other iridium center, as was observed in the reaction with H_2. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample shows three carbonyl resonances at δ 173.8, 167.8, and 159.0, while a $^{13}CH_3$-enriched sample shows a singlet for this group at δ −13.4. The arrangement of these ligands at both metals has been established by ^{31}P-decoupling experiments. In the ^{19}F NMR spectrum, two characteristic signals displaying fluorine−proton and fluorine−fluorine coupling are observed, the values of which again suggest a bridging orientation of the fluorovinyl moiety. The first is a broad, unresolved signal at δ −53.4, whereas the other is a higher-field signal at δ −157.8, displaying fluorine−proton coupling ($^2J_{HF}$ = 65.2 Hz), consistent with it being geminal to the vinylic proton. This signal also shows coupling of 30.9 Hz to the other fluorine, indicative of a *cis* arrangement of these atoms across the vinylic center. The absence of a ^{19}F resonance for coordinated triflate ion and the appearance of only free triflate ion confirms substitution of this group by CO.

Left under an atmosphere of CO at ambient temperature, compound **11** completely converts, within 30 min, to the previously characterized $[Ir_2(CO)_5(dppm)_2][CF_3SO_3]_2$ (**12**)[87] by reductive elimination of the mutually adjacent methyl and difluorovinyl groups to give *cis*-difluoropropene and its isomer 2,3-difluoropropene (see Scheme 6) in an approximately 1:2 ratio.

No spectral data were found in the literature for either *cis*-difluoropropene or 2,3-difluoropropene; thus, the identities of these fluoroolefins were established by simulation of the ^{19}F NMR spectra for these species together with their ^{1}H and ^{13}C (of a $^{13}CH_3$-enriched sample) NMR spectra. The ^{19}F NMR spectra of both isomers are shown in Figure 3, and the derived coupling constants are given in Table 1. In the case of *cis*-difluoropropene (^{19}F NMR: δ −130.3 and −166.9), the H−F geminal coupling (74.5 Hz) and the *cis* F−F coupling (9.8 Hz) are observed, establishing this arrangement. In the case in which $^{13}CH_3$-enriched precursor **3** was used, the $^1J_{CH}$ value (129.2 Hz) is typical for a methyl group, and the geminal carbon−fluorine coupling constant (24.6 Hz) is as expected.[88] This is the anticipated product of reductive elimination of the *cis*-difluorovinyl and the methyl groups.

In contrast, the appearance of 2,3-difluoropropene (^{19}F NMR: δ −109.8 and 221.4) was not anticipated and has resulted from a 1,3-hydrogen shift from the methyl group to the other end of the olefinic unit. This antarafacial transformation is presumably metal mediated. In 2,3-difluoropropene, one fluorine is now bonded to an sp^3-hybridized carbon center and displays coupling to two methyl protons ($^2J_{HF}$ = 47.5 Hz) as well as coupling to the olefinic fluorine ($^3J_{FF}$ = 30.9 Hz), both of which are

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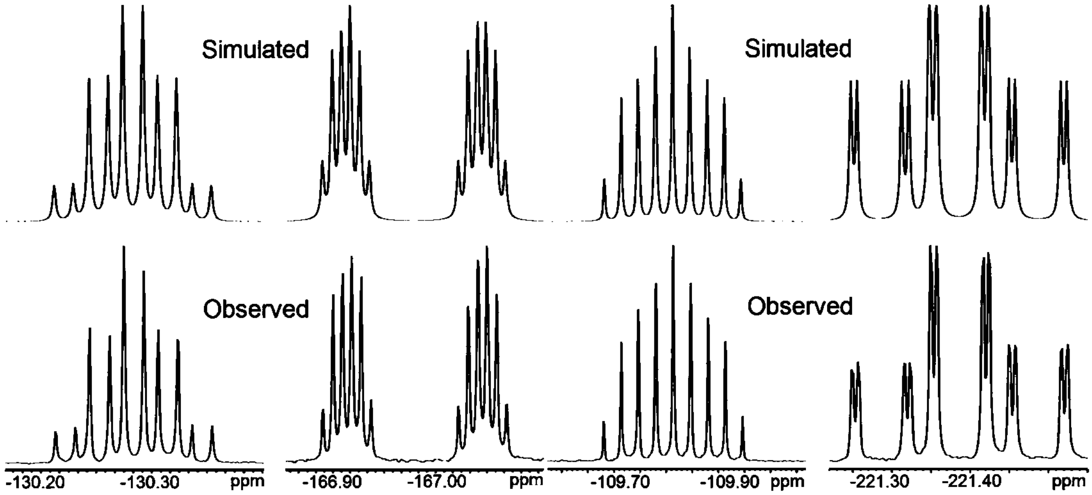
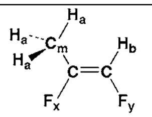
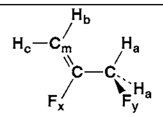


Figure 3. Observed and simulated ^{19}F NMR spectra of *cis*-difluoropropene (left two spectra) and 2,3-difluoropropene (right two spectra).

Table 1. Derived Coupling Constants for *cis*-Difluoropropene and 2,3-Difluoropropene

							
Nuclei	Coupling (Hz)	Nuclei	Coupling (Hz)	Nuclei	Coupling (Hz)	Nuclei	Coupling (Hz)
H_a-H_b	1.5	H_b-F_y	74.5	H_a-F_y	47.5	F_x-F_y	30.9
H_a-F_x	17.5	F_x-F_y	9.8	H_a-F_x	15.0	H_a-C_m	3.0
H_a-F_y	5.3	H_a-C_m	129.2	H_b-H_c	4.0	H_b-C_m	162.8
H_b-F_x	17.5	F_x-C_m	24.6	H_b-F_y	4.0	H_c-C_m	160.8
				H_b-F_x	46.0	F_y-C_m	7.2
				H_c-F_x	15.5	F_x-C_m	16.2

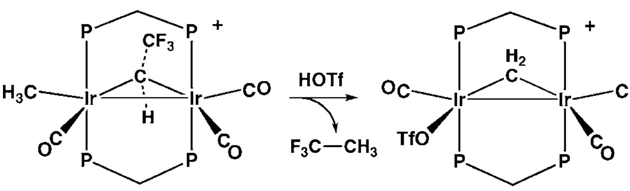
comparable to literature values for 1,2,3,3-tetrafluoropropene (*E*) ($^2J_{HF}$ = 51.29 Hz and $^3J_{FF}$ = 18.36 Hz).[89] The olefinic fluorine shows *cis*- and *trans*-proton coupling of $^3J_{HFcis}$ = 15.5 Hz and $^3J_{HFtrans}$ = 46.0 Hz, respectively, correlating with observed coupling constants for *cis*-difluoroethylene ($^3J_{HFtrans}$ = 41.8 Hz) and *trans*-difluoroethylene ($^3J_{HFcis}$ = 19.9 Hz).[90] Finally, $^1J_{CH}$ values of 162.8 and 160.8 Hz were observed in the sample prepared from $^{13}CH_3$-labeled **3** and are typical values for sp^2-hybridized centers.[91] The complete list of derived coupling constants is given in Table 1.

No reaction was observed upon the addition of CO to compounds **4**, **5**, or **7**.

2.3.3. Protonation. The reaction of **7** with triflic acid proceeds instantly at ambient temperature to yield the methylene-bridged compound $[Ir_2(OTf)(CO)_3(\mu\text{-}CH_2)(dppm)_2][OTf]$ (**13**) and 1,1,1-trifluoroethane, as shown in Scheme 7.

In the ^1H NMR spectrum, only three signals are observed (excluding the dppm phenyl protons), associated with the metal-containing product, all of which correspond to methylene groups. The first, at δ 6.57, represents that bridging the two metals and appears as a pseudo-quintet, with coupling to all four ^{31}P nuclei.

Scheme 7



7

13

Selective decoupling of each set of phosphorus signals results in collapse of this signal to a triplet, and broadband ^{31}P decoupling results in complete collapse to a singlet. Both sets of dppm methylene protons appear as multiplets at δ 5.93 and 5.48, which upon broadband ^{31}P decoupling yields an AB quartet. Confirmation of this structure was obtained through X-ray crystallography, and a representation of the cation is shown in Figure 4.

The structure of **13** is as expected; each Ir center has a distorted octahedral environment, sharing the metal−metal bond and the bridging methylene unit, which is slightly unsymmetrical (Ir(1)−C(4) = 2.037(8) Å; Ir(2)−C(4) = 2.119(8) Å) owing to the different groups (OTf, CO) in *trans* positions at the two metals. The most significant difference in the geometries at each metal results from the triflate anion coordinated on Ir(1) in place of a carbonyl at Ir(2).

In the ^{19}F NMR spectrum of the reaction mixture, the resonance for 1,1,1-trifluoroethane was observed as a quartet

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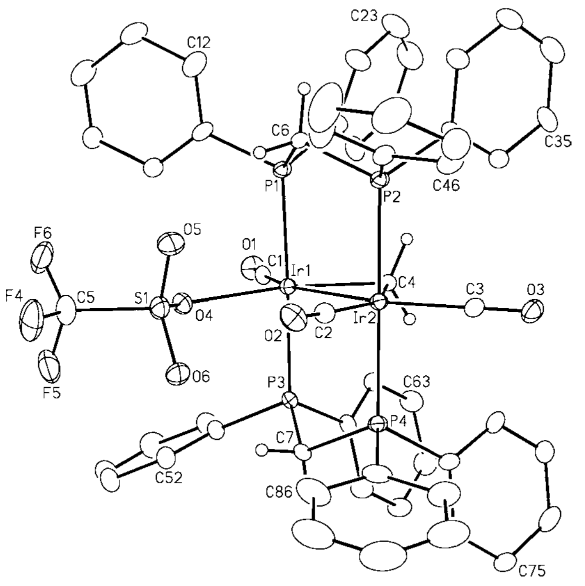

Figure 4. Perspective view of one of two crystallographically independent $[Ir_2(O_3SCF_3)(CO)_3(\mu\text{-}CH_2)(dppm)_2]^+$ (**13**) cations, showing the atom labeling scheme. Thermal parameters are as described in Figure 1. Relevant bond distances (Å) and angles (°): Ir(1)−Ir(2) = 2.8059(4), 2.7952(5); Ir(1)−C(4) = 2.037(8), 2.051(8); Ir(2)−C(4) = 2.119(8), 2.090(9); Ir(1)−C(4)−Ir(2) = 84.9(3), 84.9(4).

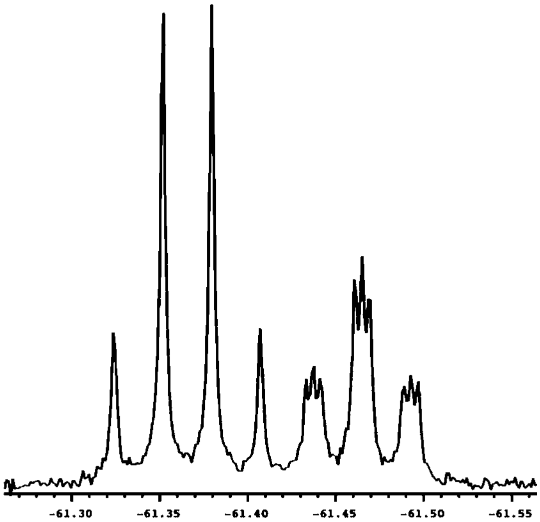

Figure 5. ^{19}F NMR spectrum of 1,1,1-trifluoroethane (left) and 1,1,1-trifluoro-2-deuterioethane.

at δ −61.4 with $^3J_{HF}$ = 13.1 Hz. Upon addition of deuterated triflic acid ($^2HOSO_2CF_3$), the resulting product is 1,1,1-trifluoro-2-deuterioethane, for which the ^{19}F NMR spectrum now appears as a 1:2:1 triplet, with additional 1.9 Hz coupling to ^2H, as shown in Figure 5, in which both isotopomers (from reaction with a mixture of HOTf and ^2HOTf) appear, establishing that the one hydrogen required in the conversion of the μ-$CHCF_3$ group to trifluoroethane comes from the acid and the other from the conversion of the Ir-bound methyl to a methylene group.

Attempts to protonate compounds **4** and **5** resulted in no reaction, while addition of triflic acid to compound **3** leads to a second C−F activation to produce **4**, as discussed above.

3. Discussion

3.1. Olefin Binding. The reaction of trifluoroethylene with $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**1**) yields two products. The kinetic product, observed in only minor amounts at −80 °C, has the olefin weakly bound in an η^2-manner to one metal. Upon warming slightly, this species immediately disappears, being replaced by a product in which the olefin bridges the pair of metals (see Scheme 1), and this product persists until approximately 0 °C, at which temperature slow reversion to starting materials occurs. Although olefin coordination to **1** in an η^2-mode is the common kinetic product for a variety of fluoroolefins,[39,68,69] the thermodynamically favored product, in which the fluoroolefin bridges the metals, is observed only for fluoroolefins having at least one pair of geminal fluorine substituents.[69] In the bridging position, the olefin can be considered as a 1,2-dimetalated alkane, in which rehybridization of the olefinic carbons from sp^2 to sp^3 has occurred, as observed in the structures of several tetrafluoroethylene-bridged species.[62,68,69] It appears that the reorganization energy[92,93] required for pyramidalization of the planar olefin is compensated for only when at least one of the olefinic carbons has two attached fluorines. This effect, in which binding of an element to fluorine is more favorable the greater the p-character of the hybrid orbitals involved,[94] is one consequence of the "*gem*-difluoro effect".[95−100] Another consequence of this effect in this study is the orientation of the bridging fluoroolefin ligand in $[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_3H)(dppm)_2][CF_3SO_3]$ (**2**), in which the difluoro-substituted end is bound to the more electron-rich metal, maximizing electron donation to this end of the olefin and its resulting pyramidalization.

3.2. C−F Activation. Our premise in this study was that, in the bridging coordination mode, the fluoroolefin, having attained sp^3 hybridization, should behave very much like a fluoroalkyl group, and as such the α-fluorine substituents should be susceptible to fluoride ion abstraction, as is well documented in late-metal fluoroalkyl complexes.[21] On the basis of this reasoning it was anticipated that fluoride ion abstraction from trifluoroethylene, in a bridging orientation, should occur readily. This has been shown to be the case, and three variations of this reactivity are observed, each of which is highly selective. The rationalization noted above also suggests that the pair of geminal fluorines, attached to the carbon that is more sp^3-like, should be more labile. Although this has been shown to be the case in the addition of the strong fluorophiles, H^+ and Me_3Si^+, this is not the case in two other modes of C−F activation, as will be discussed.

Removal of a fluoride ion from the coordinated trifluoroethylene ligand in **2**, as either HF or Me_3SiF, by reaction with either triflic acid or trimethylsilyl triflate, respectively, occurs readily at subambient temperatures, yielding the *cis*-difluorovinyl product **3** (see Scheme 2). In no case was another isomer observed. The stereoselectivity of this transformation is consistent with our ideas above that one of the geminal fluorines would be removed, and the absence of a *trans*-difluorovinyl product is in keeping with the *cis* effect,[95−100] in which the *cis*-difluorovinyl arrangement is thermodynamically favored over the *trans* arrangement, and this has been rationalized on the

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Scheme 8

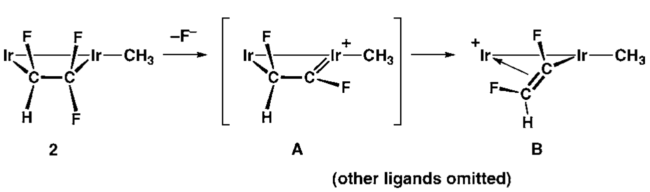
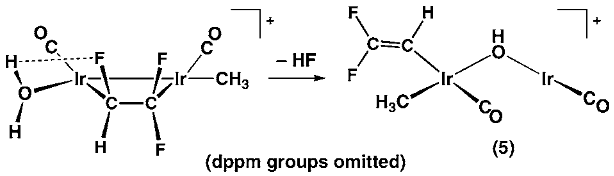


Chart 2



basis of hyperconjugation.[97,100] We propose that removal of either of the geminal fluorines yields the same transient fluorocarbene species, shown as **A** in Scheme 8 (similar to fluoride abstraction from a CF_3 ligand),[64,101] in which the metal−carbene plane bisects the HCF angle at the adjacent carbon. Rapid rearrangement of this species yields the more favorable η^2-vinyl product **B**, and migration of this fluorovinyl unit from one metal to the other gives the structure observed for **3** (see Figure 1).

Removal of a second fluoride ion, from the bridging *cis*-difluorovinyl ligand in **3**, is also possible, yielding the monofluorovinylidene-bridged product **4**. In this case, it is the fluorine on the α-carbon that is removed. Removal of this fluoride is more difficult than was removal of the first from the bridging trifluoroethylene ligand, described above, presumably because the η^2-coordination of this group results in only partial rehybridization toward sp^3, unlike the complete rehybridization in the olefin-bridged adduct **2**. Consistent with the need for metal involvement in the activation step, fluoride removal from the β-carbon of the terminally bound 2,2-difluorovinyl group in compound **5** was not observed. Only one product is observed for the fluorovinylidene-bridged species (**4**); however, we were unable to determine whether the fluorine substituent in this product is *cis* or *trans* to the methyl-bound metal.

Surprisingly, even water can be used to effect facile C−F activation of the bridging trifluoroethylene ligand, although in this case the selectivity is different from that noted above, instead yielding the *gem*-difluorovinyl product through activation of the lone vicinal C−F bond (see Scheme 3). We propose that the regioselectivity of this transformation is dictated by the position of the vacant coordination site in **2**, which lies adjacent to the "CHF" end of the fluoroolefin. Water coordination at a cationic metal center will lead to increased acidity of this group, and this has been shown to facilitate fluoride ion abstraction in fluorocarbyl ligands.[102,103] Water coordination, as shown in Chart 2, is then proposed to result in fluoride abstraction from the adjacent "CHF" group, yielding the final product **5** by movement of the resulting OH^- group to the bridging site and accompanied by a "merry-go-round" migration of the other ligands around the Ir_2 core.

The bridging trifluoroethylene arrangement in **2** is subject to a third form of C−F activation, in which fluoride migration from the "CHF" end of the fluoroolefin to the "CF_2" moiety yields a 2,2,2-trifluoroethylidene bridging unit, as diagrammed earlier in Scheme 4. This migration, which occurs instantly at ambient temperature, is initiated by carbonyl coordination at the vacant site and is presumably driven by the increase in C−F bond strengths that occurs upon increasing the fluorine substitution at carbon.[94] The transformation of a trifluoroethylene-bridged species to a trifluoroethylidene-bridged product has been proposed in a Pt_2 system,[59] although in this case the transformation was not selective, and a number of other, unidentified products also resulted. A very closely related isomerization of a bridging tetrafluoroethylene to a bridging perfluoroethylidene group has also been reported.[62,63] Neither the mechanism of this 1,2-fluoride migration nor the role played by CO addition is known.

3.3. Fluoroolefin Functionalization. Having effected the regio- and/or stereoselective activation of olefinic C−F bonds in a number of ways, as described above, we next investigated routes for the conversion of the activated products into transformed fluorocarbons.

The first route addressed was that of hydrogenolysis, in attempts to produce fluoroolefins in which one or two of the fluorines in the original trifluoroethylene have been replaced by hydrogens. This has proven to be successful in the case of the *cis*-difluorovinyl compound **3**, which under an atmosphere of hydrogen cleanly generates *cis*-difluoroethylene, together with methane, which results from accompanying hydrogenolysis of the metal−methyl bond in **3** (see Scheme 5). As a result, the stoichiometric and selective transformation of trifluoroethylene to *cis*-difluoroethylene has been achieved.

Unfortunately, under the conditions used (1 atm of H_2, ambient temperature), the 2,2-difluorovinyl species **5**, obtained in the activation of **2** by water, and the fluorovinylidene-bridged species **4**, obtained from double C−F activation of **2**, were unreactive, and no hydrogenolysis products were observed. Other ways of converting these species to the hydrogen-containing fluoroolefins will be investigated, since if this conversion were successful, the selective conversion of trifluoroethylene into *cis*-difluoroethylene, 1,1-difluoroethylene, or vinyl fluoride under the appropriate conditions could be effected.

Similarly, the 2,2,2-trifluoroethylidene-bridged product **7**, which has resulted from a 1,2-fluoride shift in the trifluoroethylene-bridged **2**, was unreactive toward H_2. This lack of reactivity is not surprising since compound **7** is coordinatively saturated. However, protonation of **7** results in facile, stoichiometric formation of 1,1,1-trifluoroethane, in which one of the hydrogens (H^+) has originated from the acid while the other (H^-) has come from the methyl ligand in **7**. Attempts to protonate the vinyl-containing products, **3** and **5**, did not succeed.

We also considered the possibility of reductive elimination of the methyl and difluorovinyl ligands in compounds **3** and **5** to generate the respective *cis*-difluoropropene and 1,1-difluoropropene. In both cases, warming of these complexes under refluxing conditions did not result in the targeted elimination products. However, we reasoned that replacement of the anionic triflate ligand in **3** by a neutral group would increase the tendency for reductive elimination by increasing the positive charge on the species. Furthermore, in the case in which the

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neutral replacement ligand was a strong π-acceptor, such as CO, which should further reduce the electron density at Ir, the tendency for reductive elimination should be further increased. In line with these ideas, triflate ion replacement by CO results in quantitative reductive elimination at ambient temperature. Although the anticipated product of reductive elimination, *cis*-difluoropropene, was obtained, it was the minor product (in a 1:2 ratio), with the major product being 2,3-difluoropropene, the result of a 1,3-hydrogen shift from the methyl ligand to the remote olefinic carbon. This conversion is favored since a fluorine that was bound to an sp^2 carbon now resides on an sp^3 carbon (rationalized by Bent's rule).[94] This antarafacial conversion is presumably metal-mediated.

4. Conclusions

Binding of trifluoroethylene in a bridging position between two metals activates it to fluoride ion abstraction under very mild conditions. This, together with previous[39,69] and ongoing work with tetrafluoroethylene and 1,1-difluoroethylene, suggests that the bridged binding mode of fluoroolefins is a general route to C−F activation. With trifluoroethylene, strong fluorophiles remove a geminal fluoride to give the *cis*-difluorovinyl product, and under marginally harsher conditions, the second of the formerly geminal fluorides can be similarly removed to yield a fluorovinylidene-bridged product. Water can also effect fluoride ion abstraction, but with a different regiochemistry, yielding a *gem*-difluorovinyl group. A third activation process is also possible upon CO addition to the trifluoroethylene adduct **2**, in which a 1,2-fluoride shift in the bridging trifluoroethylene ligand yields a 2,2,2-trifluoroethylidene-bridged product. Although some of these products are unreactive under the conditions investigated, others have been transformed under mild conditions such that the original trifluoroethylene substrate has been selectively converted into *cis*-difluoroethylene, 1,1,1-trifluoroethane, and a 1:2 mix of difluoropropenes—the latter by reductive elimination of the *cis*-difluorovinyl and methyl ligands in the complex.

This use of pairs of adjacent metals for the selective activation and subsequent conversion of fluoroolefins into a number of products represents a new strategy in carbon−fluorine bond activation.

5. Experimental Section

5.1. 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 Praxair, carbon-13-enriched CO (99%) was supplied by Isotec Inc., and trifluoroethylene was supplied by SynQuest Fluorochemicals. All purchased gases were used as received. All other reagents were obtained from Aldrich and were used as received (unless otherwise stated). The compound $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**1**) was prepared as previously reported.[70] Proton NMR spectra were recorded on Varian Unity 400 or 500 or Bruker AM400 spectrometers. Carbon-13 NMR spectra were recorded on Varian Unity 400 or 500 or Bruker AM300 spectrometers. Phosphorus-31 and fluorine-19 NMR spectra were recorded on Varian Unity 400 or 500 or Bruker AM400 spectrometers. Two-dimensional NMR experiments (COSY, NOESY and $^1H-^{13}C$ HMQC) were obtained on Varian Unity 400 or 500 spectrometers.

5.2. Preparation of Compounds. 5.2.1. $[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_3H)(dppm)_2][CF_3SO_3]$ (2). Into a brick-red solution of compound **1** (50 mg, 0.037 mmol) in 0.7 mL of CD_2Cl_2 in an NMR tube that was cooled to −20 °C in a freezer was transferred 2 mL of trifluoroethylene gas via a gastight syringe, and the subsequent reaction was investigated via multinuclear NMR spectroscopy. Upon holding the sample at −20 °C for 1.5 h, NMR spectroscopy showed quantitative conversion of **1** to compound **2**, which could be further reacted at this stage. This product was only characterized in solution, via NMR spectroscopy, since at higher temperatures loss of substrate and subsequent regeneration of starting materials occurred. ^1H NMR (CD_2Cl_2): δ 6.90 (ddd, 1H, $^2J_{HF} = 34.9$ Hz, $^3J_{HF} = 13.6$ Hz, $^3J_{HF} = 4.9$ Hz, $F_2C\text{-}CFH$), 3.97 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 3.92 (m, 2H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 3.56 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 0.34 (t, 3H, $^3J_{HP} = 6.0$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 197.2 (b, 1C, CO), 185.6 (b, 1C, CO), −8.9 (s, 1C, CH_3). ^{19}F NMR (CD_2Cl_2): δ −53.4 (m, 1F, $^2J_{FF} = 253.3$ Hz), −78.9 (s, 3F, OTf^-), −82.2 (m, 1F, $^2J_{FF} = 253.3$ Hz, $^3J_{FF} = 24.8$ Hz), −194.4 (m, 1F, $^3J_{FF} = 24.8$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.2 (dm, 1P, $^2J_{PP} = 299.4$ Hz), 14.4 (dm, 1P, $^2J_{PP} = 299.4$ Hz), 5.1 (m, 2P).

5.2.2. $[Ir_2(H)(CO)_2(\eta^2\text{-}C_2F_3H)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (2a). Into a brick-red solution of compound **1** (50 mg, 0.037 mmol) in 0.7 mL of CD_2Cl_2 in an NMR tube that was cooled in a dry ice−acetone bath was transferred 2 mL of trifluoroethylene gas via a gastight syringe, and the subsequent reaction was investigated via multinuclear NMR spectroscopy. At −80 °C, the $^{31}P\{^1H\}$ spectrum showed the presence of small amounts of **2a** (approximately 10%), along with the resonances for the starting material (**1**). ^1H NMR (CD_2Cl_2): δ 5.23 (m, 2H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 5.02 (m, 2H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), −12.70 (b, 1H, Ir-$H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 195.2 (b, 1C, CO), 187.6 (b, 1C, CO), 44.2 (bs, 1C, $\text{-}CH_2\text{-}$). ^{19}F NMR (CD_2Cl_2): δ −79.1 (s, 3F, OTf^-), −94.4 (d, 1F, $^2J_{FF} = 156.8$ Hz), −97.3 (d, 1F, $^2J_{FF} = 156.8$ Hz), −220.1 (m, 1F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −4.9 (m, 2P), −5.7 (m, 2P).

5.2.3. $[Ir_2(CH_3)(OTf)(CO)_2(\mu\text{-}\kappa^1{:}\eta^2\text{-}C(F){=}CFH)(dppm)_2][CF_3SO_3]$ (3). Method A: 10 μL of Me_3SiOTf was added dropwise to a 10 mL dichloromethane solution of compound **2** (50 mg, 0.034 mmol) that had been cooled to −20 °C. This mixture was subsequently mixed and warmed to room temperature for 30 min. The resulting yellow-orange solution was reduced *in vacuo* to *ca.* 5 mL, and Et_2O was added to precipitate a pale yellow microcrystalline compound (**3**). The product was washed twice with 10 mL of Et_2O, the supernatant was decanted, and then the solid was dried briefly under a stream of argon and then *in vacuo*. **Method B:** 7 μL of HOTF was added to a solution of compound **2** (100 mg, 0.068 mmol) that had been cooled to −20 °C in CD_2Cl_2. The solution was mixed and slowly brought to ambient temperature. Ten milliliters of Et_2O was added to induce precipitation of a yellow microcrystalline solid, which was filtered and washed with 2 × 10 mL of Et_2O and dried under a stream of argon followed by vacuum. Crystals of compound **3** were grown via slow diffusion of pentane into a CH_2Cl_2 solution of the compound (65% yield). ^1H NMR (CD_2Cl_2): δ 6.00 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 5.90 (dddd, 1H, $^2J_{HF} = 65.6$ Hz, $^3J_{HF} = 10.3$ Hz, $^3J_{HP} = 16.6$ Hz, $^3J_{HP} = 5.4$ Hz, $\text{-}C(F){=}CFH$), 5.52 (m, 2H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 4.66 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 1.44 (t, 3H, $^3J_{HP} = 6.0$ Hz, CH_3). $^{13}C\{^1H\}$

NMR (CD_2Cl_2): δ 172.1 (b, 1C, *C*O), 165.9 (b, 1C, *C*O), −23.5 (s, 1C, *C*H_3). ^{19}F NMR (CD_2Cl_2): δ −24.2 (m, 1F, $^2J_{FF}$ = 33.2 Hz), −77.7 (s, 3F, Ir-OTf), −79.5 (s, 3F, OTf^-), −172.7 (dd, 1F, $^2J_{FH}$ = 66.4 Hz, $^3J_{FF}$ = 33.2 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 9.5 (dm, 1P, $^2J_{PP}$ = 331.1 Hz), −2.0 (dm, 1P, $^2J_{PP}$ = 336.5 Hz), −3.3 (dm, 1P, $^2J_{PP}$ = 331.1 Hz), −19.3 (dm, 1P, $^2J_{PP}$ = 336.5 Hz). IR (KBr): ν = 2053, 2007 cm^{-1} (C═O). HRMS: *m/z* calcd for $[^{193}Ir]_2P_4O_5C_{56}H_{48}F_5S$ $[M]^+$, 1437.1346; found, 1437.1367. Anal. Calcd for $Ir_2S_2P_4F_8O_8C_{57}H_{48}\cdot 0.5CH_2Cl_2$: C, 42.42; H, 3.03. Found: C, 42.37; H, 3.27.

5.2.4. $[Ir_2(CH_3)(OTf)(CO)_2(\mu\text{-}C_2FH)(dppm)_2][CF_3SO_3]_2$ (4). Method A: Compound **3**, $[Ir_2(CH_3)(OTf)(CO)_2(\mu\text{-}\kappa^1{:}\eta^2\text{-CF=CFH})(dppm)_2][CF_3SO_3]$ (50 mg, 0.032 mmol), was dissolved in 7 mL of CH_2Cl_2, to which was added dropwise 30 μL of Me_3SiOTf, and the mixture was stirred at ambient temperature overnight. **Method B:** To a sample of **3** dissolved in 0.7 mL of CH_2Cl_2 was added 15 μL of HOTf. The reaction mixture was stirred at ambient temperature overnight. In both methods, attempts to isolate the compound resulted in decomposition; therefore, **4** has only been characterized in solution (61% yield). ^{1}H NMR (CD_2Cl_2): δ 8.60 (d, 1H, $^2J_{HF}$ = 85.6 Hz, -C_2F*H*), 4.30 (m, 2H, Ph_2P-C*H_2*-PPh_2), 2.80 (m, 2H, Ph_2P-C*H_2*-PPh_2), 2.15 (t, 3H, $^3J_{HP}$ = 9.0 Hz, C*H_3*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 176.8 (bm, 1C, $^2J_{CP}$ = 16.6 Hz, *C*O), 153.4 (b, 1C, $^2J_{CP}$ = 11.5 Hz, *C*O), 40.5 (s, 1C, *C*H_3). ^{19}F NMR (CD_2Cl_2): δ −76.4 (s, 3F, Ir-OTf), −79.5 (s, 3F, OTf^-), −107.4 (d, 1F, $^2J_{FH}$ = 85.6 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −5.0 (pseudo-triplet, 2P, $^2J_{PP}$ = 23.0 Hz), −21.0 (pseudo-triplet, 2P, $^2J_{PP}$ = 23.0 Hz).

5.2.5. $[Ir_2(\kappa^1\text{-C(H)=CF}_2)(CH_3)(CO)_2(\mu\text{-OH})(dppm)_2][CF_3SO_3]$ (5). Ten microliters of freshly distilled H_2O was added to an NMR sample of compound **2** (50 mg, 0.034 mmol) in CD_2Cl_2 that had been cooled to 0 °C. The solution was slowly warmed to ambient temperature and left for 30 min. The resulting yellow-orange solution was stripped to dryness *in vacuo*, and the product was redissolved in 1 mL of THF. To the resulting solution was added pentane (10 mL) to precipitate a bright yellow microcrystalline compound (**5**). The product was washed twice with 10 mL of pentane, the supernatant was decanted, and then the solid was dried briefly under a stream of argon and then *in vacuo*. Crystals of compound **5** were grown via slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound (73% yield). ^{1}H NMR (CD_2Cl_2): δ 4.44 (m, 2H, Ph_2P-C*H_2*-PPh_2), 4.17 (ddt, 1H, $^3J_{HF}$ = 13.8 Hz, $^3J_{HF}$ = 45.4 Hz, $^3J_{HP}$ = 4.1 Hz -C(*H*)═CF_2), 3.39 (m, 2H, Ph_2P-C*H_2*-PPh_2), 1.73 (bs, 1H, -O*H*), 0.39 (dt, 3H, $^3J_{HP}$ = 6.0 Hz, $^1J_{HF}$ = 2.5 Hz, C*H_3*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 174.4 (dt, 1C, $^2J_{CP}$ = 8.3 Hz, $^4J_{CF}$ = 12.0 Hz, *C*O), 170.8 (t, 1C, $^2J_{CP}$ = 10.7 Hz, *C*O), −28.7 (dt, 1C, $^2J_{CP}$ = 4.8 Hz, $^2J_{CF}$ = 4.8 Hz, *C*H_3). ^{19}F NMR (CD_2Cl_2): δ −65.9 (dd, 1F, $^2J_{FF}$ = 55.9 Hz, $^3J_{FH}$ = 13.2 Hz), −79.5 (s, 3F, OTf^-), −86.1 (bs, 1F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 13.3 (pseudo-triplet, 2P, $^2J_{PP}$ = 9.5 Hz), −15.3 (bm, 2P). IR (KBr): ν = 1989, 1971 cm^{-1} (C═O). HRMS: *m/z* calcd for $[^{193}Ir]_2P_4O_3C_{55}H_{49}F_2$ $[M]^+$, 1305.1853; found, 1305.1883. Anal. Calcd for $Ir_2SP_4F_5O_6C_{56}H_{49}\cdot CH_2Cl_2\cdot 0.5C_4H_{10}O$: C, 44.98; H, 3.58. Found: C, 44.59; H, 3.79.

5.2.6. Reaction of 2 with CO. An NMR tube containing **2** (50 mg in 0.7 mL of CD_2Cl_2) was cooled to −80 °C, and 4 mL of CO was added via gastight syringe. The reaction was monitored by NMR spectroscopy at −60 °C, at which temperature the formation of $[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_3H)(dppm)_2][CF_3SO_3]$ (**6**) was observed. Upon warming the solution above −20 °C, the formation of a new compound, $[Ir_2(CH_3)(CO)_3(\mu\text{-C(H)(CF}_3))(dppm)_2][CF_3SO_3]$ (**7**), was observed. The conversion took approximately 30 min to proceed at −20 °C and was instantaneous at ambient temperature. To the final product was added 10 mL of ether to precipitate a yellow powder (96% yield).

Data for compound **6**. ^{1}H NMR (CD_2Cl_2): δ 5.94 (ddd, 1H, $^2J_{HF}$ = 49.7 Hz $^3J_{HF}$ = 32.3 Hz, $^3J_{HF}$ = 15.3 Hz, -C(*H*)(F)-CH_2-), 5.02 (m, 1H, Ph_2P-C*H_2*-PPh_2), 4.76 (m, 1H, Ph_2P-C*H_2*-PPh_2), 4.49 (m, 1H, Ph_2P-C*H_2*-PPh_2), 4.13 (m, 1H, Ph_2P-C*H_2*-PPh_2), 0.72 (bs, 3H, C*H_3*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 179.0 (m, 2C, *C*O), 156.3 (dt, 1C, $^2J_{CP}$ = 11.5 Hz, $^3J_{CC}$ = 11.5 Hz, *C*O), −14.8 (bs, 1C, *C*H_3). ^{19}F NMR (CD_2Cl_2): δ −67.8 (bs, 1F), −79.5 (s, 3F, OTf^-), −81.9 (bs, 1F), −169.8 (bs, 1F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −3.7 (dm, 1P, $^2J_{PP}$ = 352.1 Hz), −7.3 (dm, 1P, $^2J_{PP}$ = 352.1 Hz), −16.6 (dm, 1P, $^2J_{PP}$ = 301.8 Hz), −20.8 (dm, 1P, $^2J_{PP}$ = 301.8 Hz).

Data for compound **7**. ^{1}H NMR (CD_2Cl_2): δ 5.82 (m, 1H, $^3J_{HF}$ = 17.7 Hz, Ir-C(*H*)(CF_3)-Ir), 5.44 (m, 1H, Ph_2P-C*H_2*-PPh_2), 4.08 (m, 1H, Ph_2P-C*H_2*-PPh_2), 3.88 (m, 1H, Ph_2P-C*H_2*-PPh_2), 3.85 (m, 1H, Ph_2P-C*H_2*-PPh_2), 0.71 (t, 3H, $^3J_{HP}$ = 5.7 Hz, C*H_3*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 179.7 (m, 1C, *C*O), 177.6 (m, 1C, *C*O), 162.8 (m, 1C, *C*O), −25.2 (1C, *C*H_3). ^{19}F NMR (CD_2Cl_2): δ −42.4 (d, 3F, $^3J_{FH}$ = 17.7 Hz), −79.5 (s, 3F, OTf^-). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −9.9 (dm, $^2J_{PP}$ = 392.4 Hz, 1P), −12.6 (dm, $^2J_{PP}$ = 392.4 Hz, 1P), 15.5 (dm, $^2J_{PP}$ = 316.5 Hz, 1P), −17.2 (dm, $^2J_{PP}$ = 316.5 Hz, 1P). Anal. Calcd for $Ir_2S_2P_4F_6O_6\text{-}^{13}CC_{55}H_{49}$: C, 46.16; H, 3.33. Found: C, 45.94; H, 3.39.

5.2.7. Reaction of 3 with H_2. Compound **3** (50 mg, 0.033 mmol) was dissolved in 0.7 mL of CD_2Cl_2 cooled to −78 °C, and 3 mL of hydrogen gas was added by a gastight syringe. No reaction was observed at this temperature; however, warming to −20 °C gave rise to a new set of peaks corresponding to $[Ir_2(CH_3)(H)(CO)_2(\mu\text{-}\kappa^1{:}\eta^2\text{-C(F)=CFH})(dppm)_2][CF_3SO_3]$ (**8**). Further warming to ambient temperature led to the formation of $[Ir_2(CH_3)(H)(CO)_2(\mu\text{-H})(\mu\text{-}\kappa^1{:}\eta^2\text{-C(F)=CFH})(dppm)_2][CF_3SO_3]_2$ (**9**), and after 30 min led to the previously characterized product $[Ir_2(\mu\text{-H})_2(H)_2(CO)_2(dppm)_2][CF_3SO_3]$ (**10**).[86]

Data for compound **8**. ^{1}H NMR (CD_2Cl_2): δ 6.38 (m, 1H, Ph_2P-C*H_2*-PPh_2), 4.94 (dddd, 1H, $^2J_{HF}$ = 63.2 Hz, $^3J_{HF}$ = 14.7 Hz, $^3J_{HP}$ = 18.6 Hz, $^3J_{HP}$ = 4.4 Hz, -C(F)═C*H*F), 4.26 (m, 1H, Ph_2P-C*H_2*-PPh_2), 3.62 (m, 1H, Ph_2P-C*H_2*-PPh_2), 3.23 (m, 1H, Ph_2P-C*H_2*-PPh_2), 1.01 (t, 3H, $^3J_{HP}$ = 5.0 Hz, C*H_3*), −6.92 (dt, 1H, $^2J_{HP}$ = 14.0 Hz, $^3J_{HF}$ = 6.0 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 179.2 (b, 1C, *C*O), 175.5 (b, 1C, *C*O), −21.7 (m, 1C, *C*H_3). ^{19}F NMR (CD_2Cl_2): δ −60.2 (m, 1F), −79.5 (s, 3F, OTf^-), −172.9 (m, 1F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.2 (m, 1P), 9.0 (m, 1P), −2.0 (m, 1P), −6.0 (m, 2P).

Data for compound **9**. ^{1}H NMR (CD_2Cl_2): δ 6.05 (m, 1H, Ph_2P-C*H_2*-PPh_2), 5.71 (m, 1H, Ph_2P-C*H_2*-PPh_2), 5.18 (m, 1H, Ph_2P-C*H_2*-PPh_2), 4.07 (m, 1H, Ph_2P-C*H_2*-PPh_2), 0.80 (t, 3H, $^3J_{HP}$ = 5.5 Hz, C*H_3*), −11.00 (t, 1H, $^2J_{HP}$ = 12.0 Hz), −14.40 (bs, 1H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 168.2 (b, 1C, *C*O), 160.4 (b, 1C, *C*O), −17.9 (bs, 1C, -*C*H_3). ^{19}F NMR (CD_2Cl_2): δ −79.5 (s, 3F, OTf^-), −87.9 (m, 1F), −144.1 (dd, 1F, $^2J_{FH}$ = 60.9 Hz, $^3J_{FF}$ = 26.6 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 16.2 (m, 1P), 1.7 (m, 1P), −1.7 (m, 1P), −13.5 (m, 2P).

5.2.8. Attempted Reactions of 4, 5, and 7 with H_2. To a solution of compound **4**, **5**, or **7** dissolved in 0.7 mL of CH_2Cl_2 was added 3 mL of H_2 via a gastight syringe. No reaction was observed in any case.

5.2.9. Reaction of 3 with CO. Fifty milligrams of compound **3** (0.032 mmol) was dissolved in 0.7 mL of CD_2Cl_2 in a J-Young tube, and 3 mL of CO gas was added by a gastight syringe. The reaction was then monitored by NMR spectroscopy.

Compound **3** instantly reacted with excess CO gas, initially resulting in the formation of $[Ir_2(CH_3)(CO)_3(\mu\text{-}\kappa^1{:}\mu^2\text{-}C_2F_2H)(dppm)_2][CF_3SO_3]_2$ (**11**) at −20 °C. Upon warming to ambient temperature, the liberation of both *cis*-difluoropropene and 2,3-difluoropropene was observed, leaving behind the previously characterized compound $[Ir_2(CO)_5(dppm)_2][CF_3SO_3]_2$ (**12**).[87] Characterization of *cis*-difluoropropene and 2,3-difluoropropene is presented in the Results section.

Data for compound **11**. ^{1}H NMR (CD_2Cl_2): δ 6.66 (m, 1H, $^2J_{HF}$ = 65.2 Hz, $^3J_{HF}$ = 15.3 Hz, -C(F)═C*H*F), 6.44 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 5.10 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 4.38 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 3.71 (m, 1H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 1.13 (t, 3H, $^3J_{HP}$ = 4.8 Hz, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 173.8 (b, 1C, *C*O), 167.8 (b, 1C, *C*O), 159.0 (b, 1C, *C*O), −13.4 (s, 1C, CH_3). ^{19}F NMR (CD_2Cl_2): δ −53.4 (bm, 1F), −79.5 (s, 3F, OTf^-), −157.8 (dd, 1F, $^2J_{FH}$ = 65.2 Hz, $^3J_{FF}$ = 30.9 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 7.4 (m, 1P), 4.0 (m, 1P), −9.4 (m, 1P), −18.2 (m, 1P).

5.2.10. Attempted Reactions of 4, 5, or 7 with CO. To a solution of compound **4**, **5**, or **7** dissolved in 0.7 mL of CH_2Cl_2 was added 3 mL of CO via a gastight syringe. No reaction was observed in any case.

5.2.11. Reaction of 7 with HOTf. A sample of **7** was dissolved in 0.7 mL of CD_2Cl_2 in an NMR tube, and 5 μL of HOTf was added, resulting in a change in color from light orange to light yellow and the formation of $[Ir_2(OTf)(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**13**). The solution was transferred to a 100 mL round-bottom flask, and 20 mL of ether was added to induce precipitation. The resulting yellow powder was further washed with ether and dried under vacuum. Spectral parameters for 1,1,1-trifluoroethane are presented in the Results section. Crystals of compound 1**3** were grown via slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound (63% yield). ^{1}H NMR (CD_2Cl_2): δ 6.57 (m, 2H, Ir-C*H*$_2$-Ir), 5.93 (m, 2H, $Ph_2P\text{-}CH_2\text{-}PPh_2$), 5.48 (m, 2H, $Ph_2P\text{-}CH_2\text{-}PPh_2$). ^{13}C{^{1}H} NMR ($CD_2Cl_2$): δ 178.3 (m, 1C, *C*O), 167.5 (t, 1C, $^2J_{CP}$ = 12.5 Hz, *C*O), 163.1 (t, 1C, $^2J_{CP}$ = 11.3 Hz, *C*O), 51.4 (quin., 1C, $^2J_{CP}$ = 5.0 Hz, Ir-*C*H$_2$-Ir). ^{19}F NMR (CD_2Cl_2): δ −77.4 (s, 3F, Ir-OTf), −79.2 (s, 3F, OTf^-). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −2.3 (pseudo-triplet, 2P, $^2J_{PP}$ = 37.7 Hz), −19.7 (pseudo-triplet, 2P, $^2J_{PP}$ = 37.7 Hz). HRMS: *m*/*z* calcd for $[^{193}Ir]_2P_4O_6C_{54}{}^{13}CH_{46}F_3S$ $[M]^+$, 1402.1204; found, 1402.1215.

5.2.12. Attempted Reactions of 4 and 5 with HOTf. A sample of **4** or **5** was dissolved in 0.7 mL of CH_2Cl_2. In both cases, an approximately 1.2-fold excess of HOTf was added via a microsyringe, resulting in no observable difference. NMR spectroscopy confirmed that no reaction had taken place in either case.

5.3. X-ray Structure Determinations. 5.3.1. General. Crystals were grown via slow diffusion of pentane into a CH_2Cl_2 solution of compound **3**, or diffusion of ether into a CH_2Cl_2 solution of the compound **5** or **13**. Data were collected using a Bruker APEX-II CCD detector/D8 diffractometer[104] with the crystals cooled to −100 °C; all data were collected using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for absorption through use of a multiscan model (TWINABS[104]) for compound **3** or through Gaussian integration from indexing of the crystal faces for compound **5** or **13**. Structures were solved using Patterson search/structure expansion (DIRDIF-2008[105]) (**3**), direct methods/structure expansion (SIR97[106]) (**5**), or direct methods (SHELXS-97[107]) (**13**). Refinements were completed using the program SHELXL-97.[107] Hydrogen atoms were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbon or oxygen atoms and were given thermal parameters 20% greater than those of their parent atoms. See Supporting Information for a listing of crystallographic experimental data.

5.3.2. Special Refinement Conditions. For compound **3**, the crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program CELL_NOW[104] (ver. 2008-2). The second twin component can be related to the first component by 180° rotation about the [1 1/8 −1/2] axis in real space and about the $[1\ 0\ \bar{1}]$ axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a SHELXL-97 HKLF 5 reflection file with the data integration program SAINT[104] (ver. 7.53A), using all reflection data (exactly overlapped, partially overlapped, and non-overlapped). The refined value of the twin fraction (SHELXL-97 BASF parameter) was 0.3377(6). Distance restraints were applied to some of the solvent CH_2Cl_2 and *n*-pentane molecules: *d*(Cl(7S)−C(4S)) = *d*(Cl(8S)−C(4S)) = 1.80(1) Å; *d*(Cl(7S)···Cl(8S)) = 2.95(1) Å; *d*(C(11S)−C(12S)) = d(C(12S)−C(13S)) = *d*(C(13S)−C(14S)) = *d*(C(14S)−C(15S)) = *d*(C(21S)−C(22S)) = *d*(C(22S)−C(23S)) = *d*(C(23S)−C(24S)) = *d*(C(24S)−C(25S)) = 1.54(1) Å; *d*(C(11S)···C(13S)) = *d*(C(12S)···C(14S)) = *d*(C(13S)···C(15S)) = *d*(C(21S)···C(23S)) = *d*(C(22S)···C(24S)) = *d*(C(23S)···C(25S)) = 2.52(1) Å.

For compound **5**, the disordered/partially occupied solvent molecules had the following distance restraints applied: for dichloromethane, C−Cl, 1.800(2) Å, Cl···Cl, 2.870(2) Å; for diethyl ether, C−C, 1.530(2) Å; C−O, 1.430(2) Å; C···O, 2.420(2) Å; C···C, 2.340(2) Å.

For compound **13**, attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent dichloromethane carbon or chlorine atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure[108] as implemented in PLATON.[109,110] A total solvent-accessible void volume of 4905 Å^3, with a total electron count of 982 (consistent with 24 molecules of solvent dichloromethane, or 1.5 molecules per formula unit of the $[Ir_2(CO)_3(CH_2)(O_3SCF_3)(dppm)_2][CF_3SO_3]$ molecule), was found in the unit cell.

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Supporting Information Available: Tables of crystallographic experimental details for **3**, **5**, and **13**; ORTEP diagrams for the complex cations of **3** and **5**, showing all non-hydrogen atoms of phenyl groups; ^{31}P and ^{19}F NMR spectra of **2**, **8**, and **11** in PDF format. Atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for **3**, **5**, and **13** in a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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