# **ORGANOMETALLICS**

# Tandem C–F and C–H Bond Activation in Fluoroolefins Promoted by a Bis(diethylphosphino)methane-Bridged Diiridium Complex: Role of Water in the Activation Processes

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**Supporting Information** 

**ABSTRACT:** The diiridium complex  $[Ir_2(CO)_3(\mu-H)-(depm)_2]^+$  (1) reacts with vinyl fluoride, 1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene, undergoing C–F bond activation in all cases, in addition to C–H activation in the incompletely substituted fluoroolefins. Reaction of 1 with vinyl fluoride readily undergoes geminal C–F/C–H activation, resulting in the bridging vinylidene product,  $[Ir_2(H)-(CO)_3(\mu-C=CH_2)(depm)_2]^+$  (2). Compound 1 reacts with 1,1-difluoroethylene at subambient temperature to give minor amounts of  $[Ir_2(CO)_3(\kappa^1:\eta^2-C=CH)(depm)_2]^+$  (4), resulting from the loss of 2 equiv of HF from the fluoroolefin complex.



along with a mixture of two isomers of  $[Ir_2(C(F)=CH_2)(CO)_3(\mu-CF_2CH_2)(depm)_2]^+$  (5a/5b), in which 2 equiv of the olefin has been incorporated. Compound 1 also reacts with trifluoroethylene at -30 °C, giving a 1:1 mix of isomers of the trifluoroethylene-bridged species  $[Ir_2(H)(CO)_3(\mu-CFHCF_2)(depm)_2]^+$  (7a/7b), and warming this mixture above -15 °C converts both isomers to two products,  $[Ir_2(H)(CO)_3(\mu-CFHCF_2)(depm)_2]^+$  (8), in which the geminal C-F and C-H bonds in the fluoroolefin have been activated, and  $[Ir_2(H)(CO)_3(\mu-CHCF_3)(depm)_2]^+$  (9), the result of a [1,2]-fluoride shift to give the bridging 2,2,2-trifluoroethylidene moiety. Compound 9 reacts further with a second equivalent of trifluoroethylene over 12 h to produce the 2,2,2-trifluoroethylidene/*cis*-difluorovinyl complex,  $[Ir_2(C(F)=CFH)(CO)_3(\mu-CHCF_3)(depm)_2]^+$  (10). Finally, tetrafluoroethylene reacts with 1 to produce the bridged adduct,  $[Ir_2(H)(CO)_3(\mu-CF_2CF_2)(depm)_2]^+$  (11), followed by a single C-F activation to give  $[Ir_2(C(F)=CF_2)(CO)_3(depm)_2]^+$  (12). The roles of the hydride ligand and exogenous water in the C-F activation processes are discussed.

# A. INTRODUCTION

The activation of C–F bonds in fluorocarbons represents an important ongoing challenge in organometallic chemistry as new, more effective routes are sought for the removal of persistent fluorine-containing atmospheric pollutants,<sup>1,2</sup> and for the synthesis of fluorine-containing compounds, having applications as surfactants,<sup>3–5</sup> polymers,<sup>6,7</sup> pharmaceuticals,<sup>8–12</sup> and agrochemicals.<sup>13,14</sup> Transition-metal hydride complexes have been successfully utilized to effect carbon–fluorine bond activation in a range of fluorine-containing organic substrates,<sup>15–35</sup> often under very mild conditions, and in a few cases, these reactions have been shown to be catalytic.<sup>31–35</sup> In all of these transformations, the hydride ligands have been shown or proposed to fulfill a number of different roles, including elimination of HF once C–F bond activation has occurred and functionalization of the activated fragment to give a new carbon–hydrogen bond.<sup>15–35</sup>

Although the majority of C–F bond activation studies have focused on the cleavage of aromatic C–F bonds,  $^{36-47}$  there has been growing interest in the activation of olefinic C–F bonds.  $^{18-25,30,48-66}$  Varying degrees of selectivity have been observed in the hydrodefluorination of fluoroolefins using metal–hydride complexes. For example, Jones et al. have

demonstrated the efficacy of  $[Cp*_2ZrH_2]$  in the hydrodefluorination of 1,1-difluoroethylene, 1,1-difluoromethylenecyclohexane, and perfluoropropene to ethylene, methylcyclohexane, and propane, respectively,<sup>18,21,23</sup> while Whittlesey and co-workers have shown conversion of hexafluoropropene to mixtures of (Z)- and (E)-1,2,3,3,3-pentafluoropropene and 2,3,3,3-tetrafluoropropene by cis-[Ru(dmpe)<sub>2</sub>H<sub>2</sub>].<sup>19</sup> In the reactions of  $[Rh(H)(PEt_3)_3]$  with hexafluoropropene, Braun et al. found that only the olefinic C-F bonds are activated, producing 1,1,1-trifluoropropane under a hydrogen atmos-phere.<sup>20,24,30</sup> Also with late metals, Caulton and co-workers reported that the osmium-hydride complex,  $[Os(H)_3Cl$ - $(P^{i}Pr_{3})_{2}$  reacts with vinyl fluoride and 1,1-difluoroethylene to produce a variety of condition-specific products, including the carbyne complex,  $[Os(H)(F)(Cl)(\equiv CCH_3)(P^iPr_3)_2]^{22}$  while a similar complex, namely,  $[Os(H)_2(CO)(P^tBu_2Me)_2]$ , converts vinylfluoride to ethylene in the presence of a tertiary silane.<sup>25</sup>

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Scheme 1



Our approach in bringing about C–F activation in fluoroolefins has involved the use of pairs of metals for the cooperative and selective activation of these substrates. The bridging fluoroolefins in  $[Ir_2(CH_3)(CO)_2(\mu\text{-olefin})(dppm)_2]^+$  $(dppm = \mu\text{-Ph}_2PCH_2PPh_2; olefin = C_2F_4, C_2F_3H, or 1,1 <math>C_2F_2H_2$ ) undergo facile fluoride-ion abstraction by Lewis or Brønsted acids, including water,<sup>67–69</sup> and in one exceptional case, the activation of 1,1-difluoroethylene was promoted under a CO atmosphere, leading to complete dehydrofluorination of this group.<sup>69</sup> Following C–F bond activation in these fluoroolefins, a series of C–C and C–H bond-forming reactions have allowed the conversion of tetrafluoroethylene to trifluoroethylene; the conversion of trifluoroethylene into *cis*difluoroethylene, 1,2-difluoropropene, 2,3-difluoropropene, and 1,1,1-trifluoroethane; and the conversion of 1,1-difluoroethylene to 2-fluoropropene.<sup>68,69</sup>

In an attempt to extend the scope of cooperative C–F activation by binuclear complexes, we have made two key modifications. First, we have replaced the bridging dppm groups by the smaller, more basic depm (bis-(diethylphosphino)methane,  $Et_2PCH_2PEt_2$ ), in order to improve access of the fluoroolefins to the metals and to utilize the ligand basicity as an aid in stabilizing the cationic products of fluoride-ion removal. In addition, we have replaced the methyl ligand in the above complex by a hydride ligand in order to determine what role this ligand might play in the C–F activation process and in the replacement of fluorines in fluoroolefin substrates. The initial results of this study are reported herein.

### **B. RESULTS**

i. Activation of Vinyl Fluoride. The reaction of  $[Ir_{2}(CO)_{3}(\mu-H)(depm)_{2}][BAr^{F}_{4}] (BAr^{F}_{4} = [B(3,5 (CF_3)_2C_6H_3)_4$  (1) with vinyl fluoride at ambient temperature results in the formation of  $[Ir_2(H)(CO)_3(\mu-C=CH_2) (depm)_2$  [BAr<sup>F</sup><sub>4</sub>] (2) and [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -H)( $\mu$ -C=CHF)- $(depm)_2$  [BAr<sup>F</sup><sub>4</sub>] (3) in an approximate 20:1 ratio after 30 min, as shown in Scheme 1. The major product, compound 2, a vinylidene-bridged compound, is the apparent result of simultaneous C-F and C-H activation of the geminal hydrogen/fluorine pair in vinyl fluoride, while the minor product 3, a fluorovinylidene compound, is the result of double C-H activation of the geminal hydrogens, accompanied by CO loss. Repeating the reaction of 1 with vinyl fluoride in the presence of trimethylamine-N-oxide (TMNO) results in the exclusive formation of 3 after 10 min, indicating that CO loss is the rate-determining step in the double geminal C-H bond activation process, whereas performing the reaction in the presence of added water (ca. 5 equiv) results in the exclusive formation of 2, again in only 10 min, indicating that water is involved in the C-F activation pathway. Much of the chemistry reported herein was carried out using the [BAr<sup>F</sup><sub>4</sub>]<sup>-</sup> anion since it gave the best results for obtaining solid samples. However, as

noted in the Experimental Section, even with this anion, we were often unsuccessful in obtaining solid samples; our inability to obtain crystalline samples remains one of the disadvantages of depm in this study.

Compound 2 displays two multiplets (appearing as pseudotriplets) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at  $\delta$  -8.1 and -16.9, consistent with the chemical inequivalence of the metal centers and the resulting inequivalence of the different ends of the bridging diphosphines. The <sup>1</sup>H NMR spectrum shows two vinylidene protons as singlets at  $\delta$  6.33 and 6.29, two multiplets corresponding to the methylene groups linking the two PEt<sub>2</sub> moieties of each depm ligand at  $\delta$  2.71 and 2.09, an upfield triplet at  $\delta$  –11.95 with coupling to the pair of neighboring phosphines  $({}^{2}J_{HP} = 16.2 \text{ Hz})$ , and the ethyl resonances in their expected positions (all having the appropriate integrations). The <sup>1</sup>H NMR spectrum also displays a broad singlet at  $\delta$  12.0, indicating the formation of solvated HF as a byproduct, which also appears in the  $^{19}\mathrm{F}$  NMR spectrum as a broad singlet at  $\delta$ -160; both signals are sufficiently broad (ca. 220 Hz at half height) to mask the H-F coupling, which can vary between 120 and 520 Hz, depending upon the solution species present.<sup>70–72</sup> The <sup>13</sup>C $\{^{1}H\}$  NMR spectrum of 2 displays three equal intensity carbonyl resonances at  $\delta$  179.3, 179.0, and 164.8, all appearing as triplets owing to coupling to the adjacent pairs of <sup>31</sup>P nuclei, and selective <sup>31</sup>P decoupling experiments establish that the hydride and the carbonyl at  $\delta$  179.0 are on one metal with the remaining pair of carbonyls bound to the other metal.

An X-ray structure determination of compound 2, shown for the complex cation in Figure 1, is fully consistent with the structure proposed based upon NMR spectroscopy. The Ir(1)– Ir(2) separation of 2.7960(4) Å confirms a metal–metal interaction, while the bridging vinylidene displays a C(4)–C(5)distance (1.330(4) Å) consistent with a double bond, and is unsymmetrically bridged, being closer to Ir(1) than to Ir(2)(2.031(3) versus 2.126(3) Å), presumably a result of greater crowding at the metal having two carbonyls attached (Ir(2)).

Attempts to investigate the possible role of the hydride ligand in the C–F activation of vinyl fluoride by substituting the hydride ligand by deuterium (1-D) proved to be challenging owing to the propensity of 1 to undergo H/D exchange with adventitious water. However, labeling was achieved by the deliberate addition of 15 equiv of  $D_2O$  to a solution of 1, forming a 4:1 mixture of 1-D and 1 within 24 h. This mixture of isotopologues reacts with vinyl fluoride to produce a protonated version of 2, in which the deuterium label is lost, indicating that the terminal hydride in the product originates from vinyl fluoride, and not from the original hydride or water. The substantial acceleration of the reaction upon the addition of water identifies that it plays a key role in the C–F activation process, but the role of the hydride ligand is not clear. The mechanism of C–F activation and the role of water



**Figure 1.** Perspective view of the complex cation of  $[Ir_2(H)(CO)_3(\mu-C=CH_2)(depm)_2][BAr^F_4]$  (2) 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 except for depm ethyl hydrogens, which are not shown. Relevant bond distances (Å) and angles (deg): Ir(1)–Ir(2) = 2.7960(4); Ir(1)–C(4) = 2.031(3); Ir(2)–C(4) = 2.126(3); C(4)–C(5) = 1.330(4); C(1)–Ir(1)–C(4) = 158.0(1); C(2)–Ir(2)–C(4) = 136.0(1); Ir(1)–C(4)–Ir(2) = 84.5(1); C(2)–Ir(2)–C(4) = 116.1(1); C(3)–Ir(2)–C(4) = 107.8(1); Ir(1)–C(4)–C(5) = 143.6(2); Ir(2)–C(4)–C(5) = 131.9(2).

in these processes will be addressed for this and other fluoroolefins later in the article.

The fluorovinylidene-bridged trihydride compound (3), the product of double C-H activation, displays two equal intensity multiplets at  $\delta$  -7.1 and 9.1 in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, again indicating the chemical inequivalence of each end of the diphosphines. A doublet at  $\delta$  6.61 in the <sup>1</sup>H NMR spectrum, representing the vinylidene proton, displays geminal fluorine coupling of 108.2 Hz. Three upfield signals are observed at  $\delta$ -12.54, -13.09, and -15.48 (all as multiplets), in which the first two correspond to the terminal hydrides, while the upfield signal corresponds to the bridging hydride. The  ${}^{13}C{}^{1}H$  NMR spectrum of a <sup>13</sup>CO-enriched sample displays only a single broad resonance at  $\delta$  171.1; however, integration relative to compound 2 indicates that this broad signal results from the coincidental overlap of two carbonyls. The lone vinylidene fluorine appears as a doublet at  $\delta$  -72.1 in the <sup>19</sup>F NMR spectrum, displaying the same geminal coupling as observed in the fluorovinylidene proton signal. The process of double C-H activation, promoted by CO loss, will not be discussed in this report since it has been addressed in a separate report dealing specifically with this topic.73

ii. Activation of 1,1-Difluoroethylene. The reaction of 1 with 1,1-difluoroethylene at -10 °C over 6 h gives three products in an approximate 1:2:1 ratio, and as noted above, water is again found to enhance the rate of reaction, in which all three products are formed within minutes when the reaction is repeated with the deliberate addition of ca. 15 equiv of water. One product,  $[Ir_2(CO)_3(\kappa^1:\eta^2-C\equiv CH)(depm)_2][BAr_4^F]$  (4), results from the apparent elimination of 2 equiv of HF from a 1,1-difluoroethylene adduct, while the remaining 2:1 mixture consists of two isomers of  $[Ir_2(C(F)=CH_2)(CO)_3(\mu CF_2CH_2)(depm)_2][BAr_4^F]$  (5a and 5b), differing only in the orientation of the fluorovinyl group, as shown in Scheme 2. Compounds 5a and 5b contain two fluorocarbyl units, and although we were unable to observe the stepwise incorporation of the two difluoroethylene molecules, we have successfully achieved this with trifluoroethylene, as will be discussed in what follows.

The acetylide-bridged product (4) is highly reminiscent of the propynyl-bridged analogue, observed in the activation of 1,1-difluoroethylene by a dppm-bridged methyl complex.<sup>69</sup> Complex 4 displays a broad singlet in the  ${}^{31}P{}^{1}H{}$  NMR spectrum, which changes little upon cooling to -80 °C, while the quintet at  $\delta$  181.6 ( ${}^{2}J_{CP}$  = 5.6 Hz) in the  ${}^{13}C{}^{1}H$  NMR spectrum of a <sup>13</sup>CO-enriched sample broadens slightly upon cooling. The static structure proposed should display two <sup>31</sup>P resonances, owing to the chemical inequivalence of both metals, and should also display three carbonyl resonances. We propose a fluxional process whereby the bridging acetylide group is undergoing a "windshield-wiper" process in which it migrates between the two metals as observed in other alkynylbridged compounds.<sup>69,74–78</sup> The acetylide proton appears at  $\delta$ 5.04, typical for such a group,  $^{75}$  and in the presence of  $\mathrm{D}_2\mathrm{O}$ undergoes H/D exchange to produce the deutero-acetylide analogue, indicative of the acidic nature of acetylides. Unfortunately, this rapid H/D exchange does not allow us to obtain information regarding the role of the hydride ligand in the formation of 4 by use of deuterium labeling of 1.

Compound **5a**, the major product formed, displays a broad multiplet at  $\delta$  –23.1 and a pseudotriplet at  $\delta$  –26.9 in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The breadth of the downfield signal results from additional <sup>19</sup>F coupling involving the  $\mu$ -CF<sub>2</sub>CH<sub>2</sub> group, as verified by <sup>31</sup>P{<sup>1</sup>H, <sup>19</sup>F} NMR experiments. In the <sup>1</sup>H NMR spectrum, the two fluorovinyl protons appear at  $\delta$  5.55 and 4.45, with cis (<sup>3</sup>J<sub>HF</sub> = 28.1 Hz) and trans coupling (<sup>3</sup>J<sub>HF</sub> = 62.1 Hz), respectively, to the single fluoro substituent, which appears in the <sup>19</sup>F NMR spectrum as a doublet of doublets at  $\delta$  –53.4 (<sup>31</sup>P coupling is not observed for this signal), as shown in Figure 2. Selective <sup>31</sup>P decoupling experiments show minor, unresolved coupling between the fluorovinyl protons and the upfield phosphorus signal, indicating that the fluorovinyl moiety is bound to the same metal as the "CH<sub>2</sub>" end of the







**Figure 2.** The <sup>19</sup>F{<sup>31</sup>P} NMR spectrum of a mixture of compounds **5a** and **5b**. The bridging olefin appears as a pair of overlapping triplets for **5a** and **5b**, with the latter slightly offset, resulting in the upfield shoulder feature at  $\delta$  –28.6. Integrations are shown underneath.

 $\mu$ -C<sub>2</sub>F<sub>2</sub>H<sub>2</sub> group. Similarly, the methylene protons of the bridging C<sub>2</sub>F<sub>2</sub>H<sub>2</sub> group appear as a multiplet in the <sup>1</sup>H NMR spectrum, which, upon selective decoupling of the upfield <sup>31</sup>P signal, collapses to a pseudotriplet at  $\delta$  1.58 due to coupling to the adjacent CF<sub>2</sub> fluorines (21.1 Hz). The single resonance for the bridging difluoroethylene unit at  $\delta$  –28.6 in the <sup>19</sup>F NMR is consistent with "top/bottom" mirror symmetry about the equatorial plane of the metals and displays coupling to the pair of olefin protons. Three carbonyl resonances appear in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at  $\delta$  177.1, 174.6, and 151.6 (the downfield signal as a multiplet, while the other signals are broad singlets), and selective <sup>31</sup>P decoupling experiments confirm that the upfield and downfield carbonyls are found on one metal, while also defining the orientation of the fluoroolefin as having the pair of fluorines adjacent to these carbonyls, as shown by the collapse of the signal at  $\delta$  177.1 to a triplet ( ${}^{3}J_{CF} = 17.7 \text{ Hz}$ ) upon <sup>31</sup>P decoupling, displaying residual coupling to the pair of fluorines.

The minor isomer 5b displays similar spectroscopic parameters to 5a, with two signals in the  ${}^{31}P{}^{1}H{}$  NMR spectrum at  $\delta$  -24.2 and -28.7; the former is again broad, owing to coupling to the adjacent "CF2" fragment of the bridging  $C_2F_2H_2$  unit, while the latter appears as a pseudotriplet. The <sup>1</sup>H NMR spectrum displays two vinyl protons, each as doublets at  $\delta$  5.01 and 3.77, cis ( ${}^{3}J_{\rm HF}$  = 29.8 Hz) and trans  $({}^{3}J_{HF} = 64.1 \text{ Hz})$  coupling, respectively, to the vinylic fluorine, together with minor unresolved coupling to the upfield <sup>31</sup>P signal, indicating that the fluorovinyl group is again adjacent to the "CH2" portion of the bridging 1,1-difluoroethylene unit, as for compound 5a. The methylene protons of the bridging  $C_2F_2H_2$  unit appear as a multiplet at  $\delta$  1.31, which, upon <sup>31</sup>P decoupling (either broadband or selective at  $\delta$ -28.7), collapses to a pseudotriplet ( ${}^{3}J_{HF} = 21.2 \text{ Hz}$ ) in which coupling to the adjacent fluorines remains. The <sup>19</sup>F NMR spectrum displays two signals (Figure 2), a doublet of doublets at  $\delta$  -14.6 due to the vinylic fluorine, with couplings matching those observed in with the vinylic proton resonances, while the "CF2" unit of the bridging olefin overlaps with the equivalent signal from 5a. Phosphorus decoupling simplifies the overlapping signals to triplets, with the resonance from 5b appearing as a slightly upfield-shifted shoulder on the signal for 5a; integration confirms that the CF<sub>2</sub> resonance for 5b is overlapping with the signal for 5a. Three carbonyl resonances

are observed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at similar shifts to those of **5a**. The similarities in all spectral parameters of **5a** and **5b**, *except* for the chemical shifts of the vinyl fluorines, which indicates significantly different environments for these substituents, suggest that their difference is a result of rotation of this fluorovinyl group around the Ir–C bond. Presumably, the crowded octahedral environment at Ir results in a significant barrier to rotation. Consistent with this interpretation, a spinsaturation transfer experiment at 0 °C, in which saturation of the vinyl proton signal at  $\delta$  5.01 of compound **5b** results in the disappearance of the corresponding signal at  $\delta$  5.55 for compound **5a**, demonstrates exchange between these isomers.

Increasing the temperature above 0 °C results in the conversion of both 5a and 5b to an initial vinylidene-bridged product, which slowly converts to a second vinylidene-bridged product after 12 h; both products are the result of C-F activation of the fluorovinyl moiety and accompanying loss of difluoroethylene. The only signals evident in the <sup>19</sup>F NMR spectrum after these transformations are those of the free olefin, BAr<sup>F</sup><sub>4</sub>, and solvated HF. This transformation is the result of adventitious water, as confirmed by the rate enhancement upon the deliberate addition of water. Both products appear to have the formulation  $[Ir(OH)(CO)_3(\mu C=CH_2$  (depm)<sub>2</sub>]<sup>+</sup> (6a and 6b; possibly also having coordinated H<sub>2</sub>O), as confirmed by three distinct carbonyl resonances in the <sup>13</sup>C NMR spectrum; however, our inability to identify the coordination modes of the presumed hydroxido ligands owing to our inability to identify the <sup>1</sup>H NMR resonances of this group (in the presence of H<sub>2</sub>O) and our inability to separate these species, does not allow their structural characterization. Identification of the vinylidene ligands is unambiguous in the <sup>1</sup>H NMR spectrum, with 6a displaying two doublets at  $\delta$  6.32 and 5.81 (<sup>2</sup>J<sub>HH</sub> = 3.8 Hz), whereas **6b** shows two resonances at  $\delta$  6.05 and 6.00 ( ${}^{2}J_{\rm HH}$  = 4.6 Hz).

iii. Activation of Trifluoroethylene. Compound 1 reacts with trifluoroethylene (ca. 5 equiv) over 2 h at -30 °C to give a 1:1 mixture of two isomers of  $[Ir_2(H)(CO)_3(\mu\text{-}CFHCF_2)-(depm)_2][BAr^F_4]$  (7a and 7b), both the result of trifluoroethylene coordination in the position bridging the two metal centers; these isomers differ only in the orientation of this bridging trifluoroethylene group (Scheme 3), as explained below.



The  ${}^{31}P{}^{1}H$  spectrum for 7a shows two broad multiplets at  $\delta$  -13.8 (2P) and -15.9 (2P), whereas 7b displays three broad signals at  $\delta$  -13.1 (1P), -14.6 (1P), and -15.9 (2P). Although, for each isomer, all four phosphorus nuclei are chemically inequivalent and are expected to produce four signals each, as a result of the top/bottom asymmetry and the inequivalence of both metals, the slight top/bottom asymmetry resulting from the orientation of the C2F3H ligand leads to coincidental overlaps in some resonances, as previously reported for the trifluoroethylene-bridged complex  $[Ir_2(CH_3)(CO)_2(\mu-C_2F_3H) (dppm)_2$ <sup>+.68</sup> However, the <sup>1</sup>H NMR spectrum confirms the loss of both "top/bottom" and "front/back" symmetry with the appearance of eight unique signals corresponding to the methylene protons for the depm backbone of both isomers. The bridging trifluoroethylene proton for 7a appears at  $\delta$  5.50, showing geminal fluorine coupling  $({}^{2}J_{HF} = 65.6 \text{ Hz})$ , whereas for 7b, this signal appears at  $\delta$  5.13 (<sup>2</sup>J<sub>HF</sub> = 64.5 Hz); however, the breadth of both signals masks other fluorine couplings. The terminal hydride resonances for 7a and 7b appear as pseudotriplets at  $\delta$  -8.77 and -8.42, respectively, displaying coupling to the adjacent <sup>31</sup>P nuclei. TROSEY NMR experiments<sup>79</sup> confirm the bridging orientation of trifluoroethylene, with the olefinic proton showing correlation to one methylene resonance of the depm backbone for each compound. The <sup>19</sup>F NMR spectrum of 7a and 7b displays six fluorine signals: three belonging to the bridging fluoroolefins of each isomer (7a:  $\delta$ -108.7, -118.7, and -195.9) (7b:  $\delta$  -93.5, -104.2, and -216.5). The distinct geminal F-F couplings for 7a and 7b  $(^{2}J_{FF} = 198.3, 155.3 \text{ Hz}, \text{ respectively})$  confirms rehybridization of the bridging group toward  $sp^3$ , with the large geminal coupling exceeding that of  $sp^2$ -hybridized fluoroolefins.<sup>80,81</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum displays three terminal carbonyl resonances for each compound (7a:  $\delta$  188.1, 183.7, and 182.2) (7b:  $\delta$  187.6, 185.8, and 182.3). In the case of 7a, the upfield and downfield carbonyl signals show mutual trans coupling  $(^{2}J_{CC} = 42.9 \text{ Hz})$ , while the remaining signal appears as a broad doublet ( ${}^{3}J_{CF}$  = 15.8 Hz), confirming its location opposite the "CFH" end of the olefin. For compound 7b, a mutual trans carbonyl coupling ( ${}^{2}J_{CC} = 41.8 \text{ Hz}$ ) is again evident, this time between two downfield resonances, while the remaining signal appears as a broad triplet ( ${}^{3}J_{CF} = 12.4$  Hz), indicating its location trans to the "CF2" end of the olefin. Further support for the proposed ligand arrangement in 7a and 7b is evident in the HMBC NMR spectrum, in which exclusive correlation between the hydride ligand and the two mutually trans carbonyls is observed for each compound. Interestingly, compounds 7a and 7b are the only ones in this study to assume the geometries in which one metal is square-planar and coordinatively unsaturated, while the other is octahedral and saturated. Most others have a pseudosymmetrical ligand arrangement having two terminal and one bridging ligand (omitting depm) at each metal.

Warming the mixture of the trifluoroethylene-bridged isomers (7a and 7b) to -20 °C results in the conversion of 7a to a 1:1 mixture of  $[Ir_2(H)(CO)_3(\mu\text{-C}=CF_2)(\text{depm})_2]$ - $[BAr^F_4]$  (8) and  $[Ir_2(H)(CO)_3(\mu\text{-CHCF}_3)(\text{depm})_2][BAr^F_4]$  (9) after 5 h, while leaving 7b intact at this temperature. Warming slightly to -15 °C results in the disappearance of 7b after 5 h and a corresponding increase in the concentrations of 8 and 9, which remain in a 1:1 ratio, as shown in Scheme 4.



Compound 8, the difluorovinylidene analogue to 2, results from geminal C-H/C-F activation of the bridging trifluoroethylene ligand, while the 2,2,2-trifluoroethylidene-bridged compound 9 is a result of a [1,2]-fluoride shift within the bridging trifluoroethylene units of 7a and 7b. Performing this reaction in the presence of added water greatly enhances the rate of conversion to both products (1 h vs 5 h), again suggesting that water is playing a pivotal role in the activation processes. The possible effect of added fluoride ion in the transformation to 9 was not investigated.

Compound 8 displays NMR parameters nearly identical to those of 2, with the exception of two mutually coupled doublets in the <sup>19</sup>F NMR spectrum at  $\delta$  –68.4 and –77.2 (<sup>2</sup>J<sub>FF</sub> = 98.6 Hz). The terminal hydride appears at  $\delta$  –12.46 in the <sup>1</sup>H NMR spectrum as a triplet of doublets, the doublet resulting from long-range coupling to a fluorine of the bridging difluor-ovinylidene unit (<sup>4</sup>J<sub>HF</sub> = 7.7 Hz).

An X-ray structure determination of 8 confirms the formulation noted above, revealing a bridged difluorovinylidene group adjacent to the hydride ligand, as shown in Figure 3. The iridium/iridium separation (Ir(1)-Ir(2) = 2.7914(5) Å) is consistent with a metal/metal interaction, and much like compound 2, the vinylidene unit is bound more strongly to the hydride-containing iridium (Ir(1)-C(4) = 2.08(1) Å), Ir(2)-C(4) = 2.03(1) Å), presumably a consequence of less crowding at this metal. All other crystallographic parameters are as expected and are in close agreement to those of compound 2.

Deuterium labeling of the terminal hydride of 7a and 7b (by starting with 1-D), in conjunction with the differing reaction rates of 7a and 7b, enables us to obtain some mechanistic



Figure 3. Perspective view of the complex cation of  $[Ir_2(H)(CO)_3(\mu-C=CF_2)(depm)_2][BAr^F_4]$  (8) showing the atom labeling scheme. Thermal parameters are as described in Figure 1. Relevant bond distances (Å) and angles (deg): Ir(1)–Ir(2) = 2.7914(5); Ir(1)–C(4) = 2.08(1); Ir(2)–C(4) = 2.03(1); C(4)–C(5) = 1.28(2); C(1)–Ir(1)–C(2) = 114.9(5); C(1)–Ir(1)–C(4) = 108.4(5); C(2)–Ir(1)–C(4) = 136.7(5); C(3)–Ir(2)–C(4) = 158.7(7); Ir(1)–C(4)–Ir(2) = 85.5(5), F(1)–C(5)–F(2) = 106(1).

information regarding their conversion to compound 8. Compound 9 forms from a [1,2]-fluoride shift with the deuterium incorporation found exclusively at the terminal hydride position, with no deuterium incorporation into the trifluoroethylidene unit. As shown in Scheme 5, reaction of

#### Scheme 5



either 7a or its deutero analogue (7a-D) with  $D_2O$  yields 8, in which the terminal hydride position is completely protonated, indicating that trifluoroethylene is the source of this hydride ligand. However, compound 7b or 7b-D reacts with  $D_2O$  to produce 8-D, in which the hydride is completely deuterated, and, therefore, originating from  $D_2O$ . The significance of this study will be addressed later.

The 2,2,2-trifluoroethylidene-bridged species (9) displays four signals in the  ${}^{31}P{}^{1}H{}$  spectrum, indicative of four inequivalent phosphorus environments, with pairs of signals displaying a large mutual coupling of 351.9 and 302.9 Hz, consistent with a mutually trans arrangement of the

diphosphines at both metals. The proton of the bridging 2,2,2-trifluoroethylidene group appears as a broad multiplet at  $\delta$  4.94 in the <sup>1</sup>H NMR spectrum, resulting from coupling to four phosphorus and three fluorine nuclei, and broad-band <sup>31</sup>P decoupling results in collapse of this signal to a quartet ( ${}^{3}J_{\rm HF} = 17.0$  Hz), while the hydride signal appears at  $\delta -10.52$  as a broad multiplet. Three terminal carbonyl signals were found in the  ${}^{13}C{}^{1}H{}$  NMR, all appearing as multiplets, whereas the  ${}^{19}F$  NMR spectrum displays a doublet at  $\delta -46.6$  ( ${}^{3}J_{\rm FH} = 17.0$  Hz), a shift typical for a bridging trifluoroethylidene group.

Interestingly, in the presence of excess trifluoroethylene, compound 9 converts to  $[Ir_2(C(F)=CFH)(CO)_3(\mu-CHCF_3)-(depm)_2][BAr^F_4]$  (10) overnight at ambient temperatures, the result of C-F bond activation of a second equivalent of trifluoroethylene, as outlined in Scheme 6. Again, the deliberate

Scheme 6



addition of water results in an order-of-magnitude rate increase. The NMR spectral parameters for 10 are similar to those of 9, apart from the additional resonances of the cis-difluorovinyl group and the disappearance of the hydride resonance. The difluorovinyl proton appears as a doublet of doublets at  $\delta$  5.75 in the <sup>1</sup>H NMR spectrum with geminal (81.6 Hz) and trans (24.1 Hz) fluorine coupling, while the two additional fluorine resonances at  $\delta$  -84.4 and -138.1 each appear as doublets in the <sup>19</sup>F NMR spectrum, with the former showing trans proton coupling and the latter displaying geminal proton coupling. Surprisingly, no cis coupling is observed between the two fluorine resonances; however, the chemical shifts of the two <sup>19</sup>F signals, in conjunction with the coupling values observed with the vinylic proton, lead us to assign the cis arrangement. The stepwise transformations of 1 through 9, followed by the conversion of 9 to 10, are reminiscent of the reaction of 1 with 1,1-difluoroethylene, in which 2 equiv of fluoroolefin was again incorporated, except that incorporation of the second equivalent of trifluoroethylene did not occur until after isomerization of the first equivalent to a bridging trifluoroethylidene group (9). Although, for 1,1-difluoroethylene, we were unable to observe intermediates involving the first equivalent of  $C_2F_2H_2$ , the reaction of 1 with trifluoroethylene demonstrates the stepwise C-F activation of two fluoroolefins units. It is curious that the structurally similar difluorovinylidene-bridged species does not also incorporate a second C<sub>2</sub>F<sub>3</sub>H unit.

iv. Activation of Tetrafluoroethylene. Compound 1 reacts with tetrafluoroethylene at 0 °C over 1 h to produce the tetrafluoroethylene-bridged complex,  $[Ir_2(H)(CO)_3(\mu-CF_2CF_2)(depm)_2][BAr_4]$  (11), in ~60% yield based upon <sup>31</sup>P{<sup>1</sup>H} NMR integrations (Scheme 7) together with unidentified decomposition products. Compound 11 has resulted from  $C_2F_4$  coordination in the bridging site, accompanied by movement of the hydride ligand from a bridging to a terminal position. As such, compound 11 very much resembles the trifluoroethylidene-bridged species (9),



while having a surprisingly different structure from those of the trifluoroethylene adducts 7a and 7b. This product gives rise to two broad resonances in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, the breadth of which is a consequence of <sup>19</sup>F coupling from the adjacent "CF<sub>2</sub>" units of the bridging tetrafluoroethylene ligand. The terminal hydride appears in the <sup>1</sup>H NMR spectrum at  $\delta$  –12.63 as a triplet of triplets, displaying coupling to the adjacent pair of <sup>31</sup>P nuclei and to two fluorines from one end of the bridging tetrafluoroethylene moiety (<sup>2</sup>J<sub>HP</sub> = 17.3 Hz, <sup>3</sup>J<sub>HF</sub> = 17.3 Hz). The <sup>19</sup>F NMR spectrum displays a triplet at  $\delta$  –74.4 and a doublet of triplets at  $\delta$  –80.7, with each displaying coupling to the terminal hydride (<sup>3</sup>J<sub>FH</sub> = 17.3 Hz) for the second signal. Surprisingly, no F–F coupling was observed in either signal.

Monitoring the reaction for longer periods (>5 h) shows the formation of two other products, namely,  $[Ir_2(C(F)=CF_2)-(CO)_3(depm)_2][BAr^F_4]$  (12) (ca. 20%), the result of C–F activation of the bridging tetrafluoroethylene unit with concomitant loss of the hydride ligand, and  $[Ir_2(C_2F_3)-(CO)_x(\mu-C_2F_4)(depm)_2][BAr^F_4]$  (13) (<5%) containing an intact tetrafluoroethylene and a trifluorovinyl group. The incomplete characterization of this minor species has not allowed us to determine its origin. The rate of this transformation is again enhanced upon the addition of 5 equiv of water, increasing the yield of 12 to ca. 40% after 2 h, but with no appreciable change in the quantity of 13 produced. Attempts to favor the formation of 13 by increasing the temperature to 40 °C or increasing the pressure of tetrafluoroethylene had no result.

Compound **12** displays two resonances in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, indicating the inequivalence of the two metals. In the <sup>1</sup>H NMR spectrum, only depm resonances appear, with the bridging methylene protons of the depm backbone appearing as a single resonance, indicative of front/back symmetry about the Ir<sub>2</sub>P<sub>4</sub> plane. The <sup>19</sup>F NMR spectrum displays three signals for the trifluorovinyl moiety at  $\delta$  –93.8, –123.9, and –136.1, each appearing as a doublet of doublets (<sup>3</sup>*J*<sub>FFtrans</sub> = 111.6 Hz, <sup>2</sup>*J*<sub>FF</sub> = 93.0 Hz, and <sup>3</sup>*J*<sub>FFcis</sub> = 39.7 Hz). The 2:1 ratio of carbonyl resonances in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum and the apparent "front/back" symmetry lead us to suggest the structure shown in Scheme 7, with a terminal trifluorovinyl group on the metal containing two carbonyls, while the other metal has the remaining carbonyl.

As noted above, compound 13 is never obtained in an appreciable yield, even after extended periods (2 days) or upon heating (40 °C) and has only been identified by <sup>19</sup>F NMR spectra owing to our inability to locate its <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} resonances. Nevertheless, the five signals in a 2:2:1:1:1 ratio in the <sup>19</sup>F NMR identifies that two fluorocarbyl groups are present; two signals appear for each set of olefinic CF<sub>2</sub> units ( $\delta$  -76.3 and -80.4), with three signals at  $\delta$  -94.3, -121.3, and

-132.4, showing mutual coupling ( ${}^{3}J_{FFtrans} = 110.8$  Hz,  ${}^{2}J_{FF} = 92.9$  Hz,  ${}^{3}J_{FFcis} = 33.4$  Hz), identifying the trifluorovinyl group.

# C. DISCUSSION

We initiated our current investigation into the C-F bond activation in fluoroolefins, promoted by a pair of adjacent metals, using depm (bis(diethylphosphino)methane) as an ancillary bridging ligand, on the assumption that this smaller and more basic diphosphine would result in enhanced reactivity over our previously studied dppm-bridged complexes. This has certainly proven to be the case in a number of ways. First, a comparison of  $[Ir_2(CO)_3(\mu-H)(depm)_2]^+$  (1) and its dppm analogue has shown that, while the latter is unreactive to all fluoroolefins studied in this report, the depm compound (1)reacts readily with all of them. Second, although we had observed water-promoted C-F activation in some of the previous dppm chemistry,<sup>68,69</sup> this involvement was not nearly as extensive as it has proven to be in the current depm system, as will be discussed. Furthermore, in much of the chemistry reported herein, the smaller size of depm (and possibly its greater basicity) has allowed the incorporation of two fluoroolefin-derived fragments, whereas with dppm, only a single fluorocarbyl unit was incorporated. The facile incorporation of two fluoroolefins was most prevalent with 1,1difluoroethylene, occurring readily, even at low temperature.

i. Trifluoroethylene Activation. Of the four fluoroolefins investigated (vinyl fluoride, 1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene) we initiate our discussion with trifluoroethylene, since this fluoroolefin is the best behaved, in the sense that the stepwise transformations could be easily followed in which the reactions first yielded an olefin adduct, followed by its C–F activation, and (for one C–F activation product) the incorporation of a second fluoroolefin, accompanied by its C–F activation.

As shown earlier in Scheme 3, reaction of 1 with trifluoroethylene yields two isomeric adducts in which the fluoroolefin unit bridges the pair of metals, differing only in its orientation with respect to the chemically inequivalent metal centers. Both isomers react further to yield the same two final products (8 and 9; see Scheme 4), although the isomer having the "CHF" end of the olefin adjacent to the  $Ir^{(I)}$  center (7a) reacts at slightly lower temperature than the isomer having this end of the olefin adjacent to the  $Ir^{(III)}$  center (7b). It appears that the slower conversion of 7b to subsequent products cannot be rationalized on the basis of its prior isomerization to 7a, since spin-saturation transfer experiments failed to detect isomerization between these isomers at -20 °C. Furthermore, the conversion of 7a to 8 and 9 at -20 °C is sufficiently slow (1 h) that the isomerization of 7b to 7a should be visible upon warming, which is not observed. Finally, the different H/Dlabeling studies for the two isomers indicate that 7a cannot be a common intermediate.

Both products in the conversion of 7a and 7b are the result of fluoride-ion loss; in one case, fluoride-ion recoordination at the  $\beta$ -carbon of the resulting 2,2-difluorovinyl group occurs (formally a 1,2-fluoride shift) to give a 2,2,2-trifluoroethylidenebridged product (9), while in the second case, the fluoride ion is eliminated as HF, accompanied by subsequent C-H activation, yielding the difluorovinylidene-bridged product (8). Formation of 9 is not surprising, having been previously observed in the dppm system,<sup>68</sup> and being favored by the increase in C–F bond strengths that occurs upon increasing the fluorine substitution at carbon.<sup>27,82,83</sup> The acceleration of this 1,2-fluoride shift in the presence of water leads us to suggest that fluoride-ion transfer is water-assisted. Given that this 1,2shift involves loss of fluoride ion from the "CHF" end of the olefin and recoordination at the "CF2" end, the somewhat more facile transfer involving 7a can be rationalized by greater  $\pi$ back-donation from the Ir^{(I)} center into the adjacent C–F  $\sigma^*$ orbital in this isomer. In isomer 7b, the "CHF" end is bound to the Ir<sup>(III)</sup> center from which  $\pi$ -back-donation and the resulting labilization of the fluoride ion should be less (see Scheme 3 for the structures of 7a and 7b).

In the transformation of isomers 7a and 7b to 8, formally by HF loss, water again plays a role, as seen by acceleration upon  $H_2O$  addition. Labeling studies have proved useful in allowing us to propose a mechanism for the C–F and C–H activation steps in converting the trifluoroethylene ligand in 7a to the difluorovinylidene ligand in 8. In the reactions of 7a and the deuteride analogue (7a-D), carried out in the presence of  $D_2O$ , compound 8 is observed exclusively as the hydride, with no deuterium incorporation. This hydride can only come from the trifluoroethylene ligand. We propose that HF loss occurs first through protonation by water, yielding the 2,2-difluorovinyl group, as shown in Scheme 8. Presumably,  $H_2O$  coordination at





the vacant site on the unsaturated metal adjacent to the "CHF" end of the olefin increases its acidity, allowing protonation of the nearby fluorine substituent, much as observed in a previous study on trifluoroethylene.<sup>68</sup> Water-assisted fluoride-ion abstraction involving the  $\alpha$ -fluorines of fluoroalkyl groups has been well documented by Hughes and co-workers.<sup>29,54,84,85</sup> Subsequent deprotonation of the acidic Ir–H in the dicationic intermediate can then give rise to oxidative addition of the

fluorovinyl C–H bond to give the observed cis arrangement of difluorovinylidene and hydride ligands.

The mechanism for C-F and C-H activation in the isomer 7b is not so easily rationalized since the same deuteriumlabeling experiments with this isomer give the deuteride (8-D) exclusively. We assume that, since the rates of reactions of 7a and 7b, although not identical, are very similar, the mechanisms differ only slightly, giving an isomer of 8 in which the hydride ligand migrates to its final location in 8 by a water-assisted deprotonation/reprotonation sequence, as has been observed in related dppm chemistry.<sup>69</sup> Proton transfer in the presence of  $D_2O$  would give predominately the deuteride (8-D). Activation of the C-F bond of the "CHF" end of the olefin is favored over those at the "CF2" end owing to the greater C-F bond strengths involving the more substituted carbon.<sup>27,82,83</sup> Certainly, the isomerization of 7b to the 2,2,2-trifluoroethylidene-bridged complex (8), noted above, already demonstrates the lability of this isolated fluorine.

Although the difluorovinylidene-bridged product (8) is unreactive toward additional trifluoroethylene, the related 2,2,2-trifluoroethylidene-bridged product (9) reacts with this olefin, resulting in HF loss and replacement of the hydride ligand by a *cis*-difluorovinyl group in the product (10; see Scheme 9). Acceleration of this reaction by added water again



suggests water-assisted fluoride-ion loss, which would give a dicationic vinyl/hydride species, which, upon deprotonation, yields **10**. In Scheme 9, we show the trifluoroethylene group as  $\eta^2$ -bound to one metal since it seems improbable that it could attain a bridging geometry in a structure already having the trifluoroethylidene group bridging on one face of the complex. However, we cannot rule out the possibility of reversible CO loss in this transformation. The exclusive formation of the *cis*-difluorovinyl group is consistent with the stability gained in this cis geometry through hyperconjugation,<sup>83,86</sup> although it is surprising that fluoride-ion loss has not occurred from the "CHF" end of the olefin.

**ii. 1,1-Difluoroethylene Activation.** Although, as noted earlier, no intermediates are observed in the reaction of 1 with 1,1-difluoroethylene, the formation of two of the products (isomers **5a** and **5b**; see Scheme 2) is reminiscent of compound **10**, in which 2 equiv of the fluoroolefin has been incorporated. It is tempting, therefore, to rationalize the formation of **5a** and

5b as occurring in a sequence paralleling that shown for 10 in Scheme 9, whereby fluorovinyl-group formation occurred as the last step. However, we feel that this is unlikely, because we have previously shown that fluoroolefins are more susceptible to fluoride-ion loss when bridging than when terminally bound. Consistent with this idea, activation of the bridging trifluoroethylene ligand in 7 first occurs to give the trifluoroethylidenebridged product (9), which subsequently reacts with the second equivalent of the olefin at a slower rate. Although we have no data to support our proposal beyond the acceleration of the reaction by water, we propose water-promoted fluoride-ion loss from a 1,1-difluoroethylene-bridged intermediate, followed by deprotonation of the hydrido ligand to yield a 1-fluorovinyl complex, which subsequently coordinates the additional difluoroethylene ligand. Consistent with the idea that the second difluoroethylene ligand in 5a and 5b coordinates after conversion of the first to the fluorovinyl group, warming a mixture of these isomers to above 0 °C results in loss of the fluoroolefin, confirming that it is weakly bound. Fluoroolefin loss is accompanied by removal of the remaining fluorine substituent on the fluorovinyl group, yielding the two incompletely characterized vinylidene products (6a, 6b) as described earlier. This is the only example in this study in which sequential activation of a pair of geminal C-F bonds occurs; for the more highly substituted fluoroolefins ( $C_2F_3H$  and  $C_2F_4$ ), their stronger C-F bonds presumably inhibit loss of a second fluoride.<sup>27,82,83</sup> In any case, for the trifluoroethylene adducts (7a and 7b), the geminal C-F/C-H activation is more favorable. We have previously observed geminal C–F activation in tri- and tetrafluoroethylene;<sup>68,69</sup> however, fluoride-ion removal in these cases required the very strong fluorophile,  $Me_3Si^+$  (as the triflate salt).

Possibly the most fascinating transformation in the chemistry reported herein is the complete loss of both equivalents of HF from the presumed 1,1-difluoroethylene adduct of 1 to yield the acetylide-bridged product  $[Ir_2(CO)_3(\mu-C\equiv CH)(depm)_2]^+$ (4). As noted earlier, this reactivity parallels that of the dppm-bridged species,  $[Ir_2(CH_3)(CO)_2(\mu-C_2F_2H_2)(dppm)_2]^+$ , which, in the presence of CO, slowly yielded the propynylbridged product  $[Ir(CO)_3(\mu-C \equiv CCH_3)(dppm)_2]^+$ , again by loss of both equivalents of HF.<sup>69</sup> In this previous case, the source of the propynyl methyl group was clearly the methyl ligand in the precursor. However, in the present case, neither the source of the acetylide hydrogen nor the role of the hydrido ligand in the precursor could be ascertained, owing to facile H/ D scrambling. How the loss of both equivalents of HF occurs remains a mystery. We considered the possibility that loss of a second fluoride ion could be catalyzed by HF generated in the first abstraction, as has already been shown by Caulton and coworkers;<sup>22</sup> however, the addition of triethylamine, in attempts to trap the HF produced, has no effect on the product distribution shown in Scheme 2.

iii. Tetrafluoroethylene Activation. The sequence, proposed above, for the reaction of 1 with 1,1-difluoroethylene finds support in the reactivity of compound 1 with tetrafluoroethylene, in which the tetrafluoroethylene-bridged complex (11) is initially formed, followed by the subsequent C-F activation of the bridging unit to produce a trifluorovinyl complex 12 (refer to Scheme 7). Although there is evidence for a bridging-tetrafluoroethylene/trifluorovinyl complex (13) that is analogous to the 1,1-difluoroethylene adducts 5a and 5b, its origin is uncertain, owing to its low abundance and consequent incomplete characterization.

As with all previous olefin adducts in this study, fluoride-ion removal from the tetrafluoroethylene-bridged **11** is accelerated by the addition of water. The failure of a related  $C_2F_4$ -bridged complex of dppm, namely,  $[Ir_2(CH_3)(CO)_2(\mu-C_2F_4)-(dppm)_2]^+$ , to react with water is certainly a further reflection of the influence of the more basic depm ligand on the reactivity. However, the absence of a vacant site on the saturated metals in **11**, which does not allow coordination of water, combined with the accompanying loss of the hydrido ligand, suggests a possible role of this ligand in the overall dehydrofluorination of **11**, in which water could be simultaneously involved in hydrogen bonding with a fluorine substituent and the hydrido ligand, as shown in Chart 1, leading to loss of HF. Therefore, although



the hydrido ligand is not directly involved in fluoride-ion abstraction from the fluoroolefin, this proposed hydrogenbonding interaction should increase water's acidity, promoting HF loss.

iv. Vinyl Fluoride Activation. Finally, the fluoroolefin activation, about which we have the least information, involves vinyl fluoride, for which no olefin adduct is observed. On the basis of our previous work and the observations discussed above, we suggest that this olefin also binds in the bridging site between the metals. As for the trifluoroethylene adduct 7a, deuterium-labeling studies indicate that the hydrido ligand in the C-H/C-F activation product originates from the fluoroolefin, so we suggest a stepwise series of transformations consisting of HF loss upon protonation by water and H<sup>+</sup> loss from the resulting dicationic hydrido intermediate, followed by C-H bond activation of the resulting vinyl group by the adjacent metal, much as outlined in Scheme 8.

In summary, the depm complex  $[Ir_2(CO)_3(\mu-H)(depm)_2]^+$ has proven to be much more active toward C-F bond activation than either its dppm analogue or the related species  $[Ir_2(CH_3)(CO)_2(dppm)_2]^+$ . In all of the chemistry described herein, water plays a pivotal role, being involved in protonation of the coordinated fluoroolefin, resulting in subsequent HF loss and, in one case, in the water-assisted 1,2-fluoride migration in trifluoroethylene, yielding a bridging 2,2,2-trifluoroethylidene group. In the two fluoroolefins investigated having a geminal arrangement of H and F substituents (vinyl fluoride and trifluoroethylene), activation of *both* of these bonds occurred in a stepwise manner in which, as described above, water-assisted fluoride-ion loss (as HF) is followed by oxidative addition of the  $\alpha$ -C–H bond of the resulting vinyl or 2,2-difluorovinyl group at the adjacent metal. The hydride ligand in the precursor complex (1) appears to play no direct role in the activation processes and, instead, appears to be lost as H<sup>+</sup> during the subsequent transformations, replacing the proton lost by water in protonation of a fluorine substituent.

# **D. EXPERIMENTAL SECTION**

**i.** 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., vinyl fluoride and 1,1-difluoroethylene were supplied by Aldrich, and trifluoroethylene and tetrafluoroethylene were 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). Compound **1** was prepared as described.<sup>73</sup> Trimethylamine-*N*-oxide dihydrate was dried by azeotropic distillation as described in literature.<sup>87</sup> All other reagents were obtained from Aldrich and were used as received (unless otherwise stated).

Proton NMR spectra were recorded on Varian Unity 400 or 500 spectrometers, or on a Bruker AM400 spectrometer. 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 <sup>1</sup>H–<sup>13</sup>C HMQC) were obtained on Varian Unity 400 or 500 spectrometers. All ethyl resonances corresponding to depm appeared as expected in the <sup>1</sup>H NMR spectrum ( $\delta$  1.00–2.50) with the appropriate integrations. In cases when these resonances interfered with relevant ligand resonances that were important for compound characterization, depm-D<sub>20</sub> was used.<sup>88,89</sup>

a. Preparation of Compounds. Reaction of Compound 1 with Vinylfluoride. Method i: To an NMR tube charged with compound 1 (54 mg, 0.031 mmol) was added 0.8 mL of CD<sub>2</sub>Cl<sub>2</sub>, resulting in a clear, orange solution. Vinylfluoride gas was then added via a gastight syringe (5 mL, 0.219 mmol) to the headspace, and the tube was mixed vigorously. After 30 min, NMR spectroscopy showed complete conversion to a mixture of  $[Ir_2(H)(CO)_3(\mu$ -C=CH<sub>2</sub>)(depm)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] (2) and  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-C=CHF)(depm)_2][BAr_4^F]$  (3) in a 20:1 ratio. The solution was transferred to a Schlenk tube, and the solvent was removed under vacuum. The mixture was redissolved in 2 mL of diethyl ether, and 25 mL of pentane was added to induce precipitation of a yellow solid. (94% yield of compound 2). Method ii: A round-bottom flask containing compound 1 (78 mg, 0.045 mmol) dissolved in 10 mL of  $CH_2Cl_2$  was cooled to -80 °C via a dry ice/acetone bath. In a separate round-bottom flask, trimethylamine-N-oxide (4 mg, 0.053 mmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> and cooled to -80 °C. The TMNO solution was transferred, via a cannula, to the solution of 1, followed by the addition of vinyl fluoride via a gastight syringe (10 mL, 0.438 mmol). The solution was slowly warmed to ambient temperature and left to stir for 1 h. The solvent was then removed, leaving a yellow/orange residue. NMR of the residue revealed exclusive formation of compound 3. Attempts to recrystallize the mixture were unsuccessful due to the high solubility of the product (83% yield of compound 3)

Compound 2: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  6.33 (s, 1H,  $\mu$ -C=CH<sub>2</sub>), 6.29 (s, 1H,  $\mu$ -C=CH<sub>2</sub>), 2.71 (m, 2H, depm), 2.09 (m, 2H, depm), -11.95 (t, 1H, <sup>2</sup>J<sub>HP</sub> = 16.2 Hz, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  179.3 (t, 1C, <sup>2</sup>J<sub>CP</sub> = 7.6 Hz), 179.0 (t, 1C, <sup>2</sup>J<sub>CP</sub> = 9.2 Hz), 164.8 (t, 1C, <sup>2</sup>J<sub>CP</sub> = 11.5 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  -8.1 (t, 2P, <sup>2</sup>J<sub>PP</sub> = 34.3 Hz), -16.9 (t, 2P, <sup>2</sup>J<sub>PP</sub> = 34.3 Hz). Elemental analysis calcd (%) for Ir<sub>2</sub>P<sub>4</sub>F<sub>24</sub>O<sub>3</sub>C<sub>55</sub>H<sub>59</sub> (1743.2): C, 37.90; H, 3.41. Found: C, 38.06; H, 3.68.

Compound 3: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  6.61 (d, 1H, <sup>2</sup>J<sub>HF</sub> = 108.2 Hz,  $\mu$ -C=CHF), 2.77 (m, 2H, depm), 1.67 (m, 2H, depm), -12.54 (m, 1H, Ir-H), -13.09 (m, 1H, Ir-H), -15.48 (m, 1H, Ir-H-Ir). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  171.1 (bm, 2C). <sup>19</sup>F NMR (469 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  -72.1 (d, 1F, <sup>2</sup>J<sub>HF</sub> = 108.2 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  -7.1 (m, 2P), -9.1 (m, 2P).

b. Reaction of Compound 1 with 1,1-Difluoroethylene. An NMR tube charged with compound 1 (84 mg, 0.049 mmol) was dissolved in 0.8 mL of CD<sub>2</sub>Cl<sub>2</sub> and cooled to -80 °C via a dry ice/acetone bath. 1,1-Difluoroethylene (5 mL, 0.219 mmol) was added via a gastight syringe, and the reaction was monitored by variable-temperature, multinuclear NMR spectroscopy. Leaving the mixture at -10 °C for 5 h resulted in the mixture of  $[Ir_2(CO)_3(\mu-\kappa^1:\eta^2-C\equiv CH)(depm)_2]$ -[BAr<sup>F</sup><sub>4</sub>] (4), and two isomers of  $[Ir_2(\kappa^1-C(F)=CH_2)(CO)_3(\mu-C_2F_2H_2)(depm)_2]$ [BAr<sup>F</sup><sub>4</sub>] (5a and 5b) in a 1:2:1 ratio, respectively. Warming both 5a and 5b to 27 °C resulted in the conversion to  $[Ir_2(OH)(CO)_3(\mu-C=CH_2)(depm)_2]$ [BAr<sup>F</sup><sub>4</sub>] (6a), and leaving the mixture at this temperature for 12 h converts 6a to a second vinylidene-bridged product (6b). Attempts to isolate any product prior to the formation of 6b were unsuccessful due to the high solubility in polar and nonpolar solvents. (76% yield of compound 6b).

*Compound* 4: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 5.04 (s, 1H,−C≡CH), 1.99 (m, 2H, depm), 1.72 (m, 2H, depm). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 181.6 (quin, 3C, <sup>2</sup>J<sub>CP</sub> = 5.6 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ −6.1 (s, 4P). HRMS *m*/ *z* calcd for [<sup>193</sup>Ir]<sub>2</sub>P<sub>4</sub>O<sub>3</sub>C<sub>23</sub>H<sub>45</sub> [M\*]<sup>+</sup>: 879.1586. Found: 879.1572.

Compound **5a**: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ 5.55 (d, 1H, <sup>3</sup>J<sub>HFcis</sub> = 28.1 Hz, C(F)=CHH), 4.45 (d, 1H, <sup>3</sup>J<sub>HFtrans</sub> = 62.1 Hz, C(F)=CHH), 3.38 (m, 2H, depm), 2.49 (m, 2H, depm), 1.58 (m, 2H, <sup>3</sup>J<sub>HF</sub> = 21.1 Hz,  $\mu$ -C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>), -10 °C): δ 177.1 (m, 1C, <sup>3</sup>J<sub>CF</sub> = 17.7 Hz), 174.6 (bs, 1C), 151.6 (bs, 1C). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ -28.6 (m, 2F), -53.4 (dd, 1F, <sup>3</sup>J<sub>HFtrans</sub> = 62.1 Hz, <sup>3</sup>J<sub>HFcis</sub> = 28.1 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ -23.1 (bm, 2P), -26.9 (t, 2P, <sup>2</sup>J<sub>PP</sub> = 38.5 Hz).

Compound **5b**: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ 5.01 (d, 1H, <sup>3</sup>J<sub>HFcis</sub> = 29.8 Hz, C(F)=CHH), 3.77 (d, 1H, <sup>3</sup>J<sub>HFtrans</sub> = 64.1 Hz, C(F)=CHH), 3.36 (m, 2H, depm), 2.48 (m, 2H, depm), 1.31 (m, 2H, <sup>3</sup>J<sub>HF</sub> = 21.2 Hz,  $\mu$ -C<sub>2</sub>F<sub>2</sub>H<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ 177.6 (m, 1C, <sup>3</sup>J<sub>CF</sub> = 16.3 Hz), 174.6 (bs, 1C), 151.5 (bs, 1C). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ -14.6 (dd, 1F, <sup>3</sup>J<sub>HFtrans</sub> = 64.1 Hz, <sup>3</sup>J<sub>HFcis</sub> = 29.8 Hz), -28.6 (m, 2F). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ -24.2 (bm, 2P), -28.7 (t, 2P, <sup>2</sup>J<sub>PP</sub> = 38.5 Hz).

Compound **6a**: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  6.32 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 3.8 Hz, -C=CHH), 5.81 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 3.8 Hz, -C= CHH), 2.89 (m, 2H, depm), 1.95 (m, 2H, depm). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  180.0 (t, 1C, <sup>3</sup>J<sub>CP</sub> = 10.2 Hz), 172.1 (b, 1C), 157.7 (b, 1C). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$ -19.3 (bs, 4P).

Compound **6b**: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 6.05 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 4.6 Hz, -C=CHH), 6.00 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 4.6 Hz, -C=CHH), 2.91 (m, 2H, depm), 2.54 (m, 2H, depm). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 174.0 (m, 1C), 170.9 (m, 1C), 164.1 (m, 1C). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ -14.7 (t, 2P, <sup>2</sup>J<sub>PP</sub> = 35.5 Hz), -21.8 (t, 2P, <sup>2</sup>J<sub>PP</sub> = 35.5 Hz). *c. Reaction of Compound* **1** *with Trifluoroethylene.* In an NMR

tube containing compound 1 (64 mg, 0.037 mmol) dissolved in 0.8 mL of  $CD_2Cl_2$ , cooled to -80 °C in a dry ice/acetone bath, was added trifluoroethylene (5 mL, 0.219 mmol) via a gastight syringe. The mixture was monitored by variable-temperature, multinuclear NMR spectroscopy. Keeping the mixture at -30 °C for 2 h resulted in the formation of  $[Ir_2(H)(CO)_3(\mu$ -CFHCF<sub>2</sub>)(depm)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] (7a) and  $[Ir_{2}(H)(CO)_{3}(\mu$ -CF<sub>2</sub>CHF)(depm)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] (7b) in a 1:1 ratio. Warming to -20 °C shows the conversion of 7a to a 1:1 mixture of  $[Ir_{2}(H)(CO)_{3}(\mu-C=CF_{2})(depm)_{2}][BAr_{4}^{F}]$  (8) and  $[Ir_{2}(H)(CO)_{3}(\mu-C)]$  $CHCF_3)(depm)_2[BAr_4]$  (9), while warming to -15 °C leads to the conversion of 7b to compounds 8 and 9, again in a 1:1 ratio. Leaving the mixture of 8 and 9 overnight under an atmosphere of trifluoroethylene at ambient temperature leads to the conversion of 9 to  $[Ir_2(\kappa^1-C(F)=CFH)(CO)_3(\mu-CHCF_3)(depm)_2][BAr_4^F]$  (10), with compound 8 remaining in solution. The mixture was transferred to a Schlenk tube and the solvent was removed under vacuum, giving a vellow resin. The resin was redissolved in 2 mL of diethyl ether, and 25 mL of pentane was added to induce precipitation of a yellow solid. The

solid was further washed with  $2 \times 10$  mL of pentane and dried to produce a fine, yellow solid (73% yield of compound 8).

Compound **7a**: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ 5.50 (bd, 1H, <sup>2</sup>J<sub>HFgem</sub> = 65.6 Hz, μ-CF<sub>2</sub>CFH), 4.07 (m, 1H, depm), 3.72 (m, 1H, depm), 2.03 (m, 1H, depm), 1.71 (m, 1H, depm), -8.77 (t, 1H, <sup>2</sup>J<sub>HP</sub> = 12.9 Hz, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ 188.1 (dm, 1C, <sup>2</sup>J<sub>CC</sub> = 42.9 Hz), 183.7 (bd, 1C, <sup>3</sup>J<sub>CF</sub> = 15.8 Hz), 182.2 (dm, 1C, <sup>2</sup>J<sub>CC</sub> = 42.9 Hz). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ -108.7 (dd, 1F, <sup>2</sup>J<sub>FFgem</sub> = 198.3 Hz, <sup>3</sup>J<sub>FFtrans</sub> = 46.9 Hz), -118.7 (d, 1F, <sup>2</sup>J<sub>FFgem</sub> = 198.3 Hz), -195.9 (dd, 1F, <sup>2</sup>J<sub>FHgem</sub> = 65.6 Hz, <sup>3</sup>J<sub>FFtrans</sub> = 46.9 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ -13.8 (bm, 2P), -15.9 (bm, 2P).

*Compound 7b*: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ 5.13 (bd, 1H, <sup>2</sup>J<sub>HFgem</sub> = 64.5 Hz, μ-CHFCF<sub>2</sub>), 4.20 (m, 1H, depm), 3.68 (m, 1H, depm), 1.95 (m, 1H, depm), 1.86 (m, 1H, depm), -8.42 (t, 1H, <sup>2</sup>J<sub>HP</sub> = 12.7 Hz, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ 187.6 (dm, 1C, <sup>2</sup>J<sub>CC</sub> = 41.8 Hz), 185.8 (dm, 1C, <sup>2</sup>J<sub>CC</sub> = 41.8 Hz), 182.3 (bt, 1C, <sup>3</sup>J<sub>CF</sub> = 12.4 Hz). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ -93.5 (dd, 1F, <sup>2</sup>J<sub>FFgem</sub> = 155.3 Hz, <sup>3</sup>J<sub>FFtrans</sub> = 49.7 Hz), -104.3 (d, 1F, <sup>2</sup>J<sub>FFgem</sub> = 155.3 Hz), -216.5 (dd, 1F, <sup>2</sup>J<sub>FHgem</sub> = 64.5 Hz, <sup>3</sup>J<sub>FFtrans</sub> = 49.7 Hz). <sup>31</sup>P{<sup>1</sup>H</sup> NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C): δ -13.1 (bm, 1P), -14.6 (bm, 1P), -15.9 (bm, 2P).

Compound 8: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 2.67 (m, 2H, depm), 1.95 (m, 2H, depm), -12.46 (td, 1H, <sup>2</sup> $J_{HP} = 15.7$  Hz, <sup>4</sup> $J_{HF} = 7.7$  Hz, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 177.2 (bm, 1C), 169.4 (bm, 1C), 159.7 (bm, 1C). <sup>19</sup>F NMR (469 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ -68.4 (d, 1F, <sup>2</sup> $J_{FF} = 98.6$  Hz), -77.2 (d, 1F, <sup>2</sup> $J_{FF} = 98.6$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ -6.7 (t, 2P, <sup>2</sup> $J_{PP} = 28.5$  Hz), -16.2 (t, 2P, <sup>2</sup> $J_{PP} = 28.5$  Hz). HRMS *m/z* calcd for [<sup>193</sup>Ir]<sub>2</sub>P<sub>4</sub>O<sub>3</sub>C<sub>23</sub>H<sub>45</sub>F<sub>2</sub> [M\*]<sup>+</sup>: 917.1540. Found: 917.1543.

Compound 9: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 4.94 (m, 1H, <sup>3</sup>J<sub>HF</sub> = 17.0 Hz,  $-C(H)CF_3$ ), 2.53 (m, 1H, depm), 2.51 (m, 1H, depm), 1.95 (m, 1H, depm), 1.91 (m, 1H, depm), -10.52 (bm, 1H, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 177.3 (m, 1C), 176.8 (m, 1C), 159.3 (m, 1C). <sup>19</sup>F NMR (469 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  -46.4 (d, 3F, <sup>3</sup>J<sub>FH</sub> = 17.0 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  -11.0 (dm, 1P, <sup>2</sup>J<sub>PP</sub> = 351.9 Hz), -17.9 (dm, 1P, <sup>2</sup>J<sub>PP</sub> = 351.9 Hz), -18.0 (dm, 1P, <sup>2</sup>J<sub>PP</sub> = 302.9 Hz), -31.2 (dm, 1P, <sup>2</sup>J<sub>PP</sub> = 302.9 Hz).

 $\begin{array}{l} \mbox{Compound 10: $^{1}$H NMR (498 MHz, CD_2Cl_2, 27 $^{\circ}$C): $\delta$ 5.75 (dd, 1H, $^{2}J_{HF} = 81.6 Hz, $^{3}J_{HF} = 24.1 Hz, $-C(F)==CFH$), 4.89 (m, 1H, $^{3}J_{HF} = 17.4 Hz, $-C(H)CF_3$), 3.23 (m, 1H, depm), 3.11 (m, 1H, depm), 2.95 (m, 1H, depm), 2.14 (m, 1H, depm). $^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 27 $^{\circ}$C): $\delta$ 174.7 (m, 1C), 165.3 (m, 1C), 157.1 (m, 1C). $^{19}$F NMR (469 MHz, CD_2Cl_2, 27 $^{\circ}$C): $\delta$ $-47.1 (d, 3F, $^{3}J_{FH} = 17.4 Hz}), $-84.6 (d, 1F, $^{3}J_{FH} = 24.1 Hz}), $-138.1 (dm, 1F, $^{2}J_{FH} = 81.6 Hz}). $^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 27 $^{\circ}$C): $\delta$ $-18.8 (dm, 1P, $^{2}J_{FP} = 356.2 Hz}), $-22.5 (dm, 1P, $^{2}J_{FP} = 285.7 Hz}), $-28.7 (dm, 1P, $^{2}J_{FP} = 356.2 Hz}), $-32.3 (dm, 1P, $^{2}J_{FP} = 285.7 Hz}). HRMS $m/z$ calcd for $[^{193}Ir]_2P_4O_3C_25H_46F_5$ [M*]^+: 999.1571. Found: 999.1571. $\end{tabular}$ 

*d. Reaction of Compound* **1** *with Tetrafluoroethylene.* In an NMR tube containing compound **1** (91 mg, 0.053 mmol) dissolved in 0.8 mL of CD<sub>2</sub>Cl<sub>2</sub> was added tetrafluoroethylene (5 mL, 0.219 mmol) via a gastight syringe. The solution was mixed and left at 0 °C for 1 h. The reaction was verified by multinuclear NMR spectroscopy, confirming the formation of  $[Ir_2(H)(CO)_3(\mu$ -CF<sub>2</sub>CF<sub>2</sub>)(depm)<sub>2</sub>]-[BAr<sup>F</sup><sub>4</sub>] (**11**) (63% yield). Leaving the mixture at ambient temperature for 5 h results in the formation of minor amounts of  $[Ir_2(CF)=CF_2)(CO)_3(\mu$ -CF<sub>2</sub>CF<sub>2</sub>)(depm)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] (**12**) (22% yield) and  $[Ir_2(CF)=CF_2)(CO)_3(\mu$ -CF<sub>2</sub>CF<sub>2</sub>)(depm)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] (**13**) (<5% yield), as observed in the <sup>19</sup>F NMR spectrum. Leaving the mixture for longer periods of time (2 days) or heating to 40 °C results in the decomposition to numerous unidentified products.

Compound 11: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 3.28 (m, 2H, depm), 2.86 (m, 2H, depm), -12.63 (tt, 1H, <sup>2</sup>J<sub>HP</sub> = 17.3 Hz, <sup>3</sup>J<sub>HF</sub> = 17.3 Hz, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C): δ 174.4 (bm, 1C), 164.6 (bm, 1C), 153.9 (bm, 1C). <sup>19</sup>F NMR (469 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  -74.4 (t, 2F, <sup>3</sup>J<sub>FP</sub> = 17.0 Hz), -80.7 (dt, 2F, <sup>2</sup>J<sub>FH</sub> =

17.3 Hz,  ${}^{3}J_{\text{FP}} = 13.4$  Hz).  ${}^{31}P{}^{1}H$  NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$ -15.0 (bt, 2P,  ${}^{2}J_{\text{FP}} = 48.1$  Hz), -21.9 (bt, 2P,  ${}^{2}J_{\text{FP}} = 48.1$  Hz). Compound 12:  ${}^{1}H$  NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  2.96 (m,

Compound 12: <sup>1</sup>H NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  2.96 (m, 4H, depm). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  185.6 (t, 2C, <sup>2</sup>J<sub>CP</sub> = 13.3 Hz), 185.2 (bt, 1C, <sup>2</sup>J<sub>CP</sub> = 10.4 Hz). <sup>19</sup>F NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  –93.8 (dd, 1F, <sup>2</sup>J<sub>FF</sub> = 93.0 Hz, <sup>3</sup>J<sub>FFcis</sub> = 39.7 Hz), -123.9 (dd, 1F, <sup>3</sup>J<sub>FFtrans</sub> = 111.6 Hz, <sup>2</sup>J<sub>FF</sub> = 93.0 Hz), -136.1 (dd, <sup>3</sup>J<sub>FFtrans</sub> = 111.6 Hz, <sup>3</sup>J<sub>FFcis</sub> = 39.7 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  –17.4 (t, 2P, <sup>2</sup>J<sub>PP</sub> = 24.9 Hz), -20.5 (bt, 2P, <sup>2</sup>J<sub>PP</sub> = 24.9 Hz).

Compound 13: <sup>19</sup>F NMR (498 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C):  $\delta$  -76.3 (bs, 2F), -80.4 (bs, 2F), -94.3 (dd, 1F, <sup>2</sup>J<sub>FF</sub> = 92.9 Hz, <sup>3</sup>J<sub>FFcis</sub> = 33.4 Hz), -121.3 (dd, 1F, <sup>3</sup>J<sub>FFtrans</sub> = 110.8 Hz, <sup>2</sup>J<sub>FF</sub> = 92.9 Hz), -132.4 (dd, <sup>3</sup>J<sub>FFtrans</sub> = 110.8 Hz, <sup>3</sup>J<sub>FFcis</sub> = 33.4 Hz).

a. X-ray Structure Determinations. General. Crystals were grown via slow diffusion of n-pentane into a diethyl ether solution of the compound. Data were collected using a Bruker APEX II CCD detector/D8 diffractometer<sup>90</sup> with the crystals cooled to -100 °C; all data were collected using Mo K $\alpha$ radiation ( $\lambda = 0.71073$  Å). The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using Patterson search/ structure expansion (DIRDIF-2008<sup>91</sup> for 2) or direct methods (SHELXS- $97^{92}$  for 8). Refinements were completed using the program SHELXL-97.92 Nonhydridic hydrogen atoms were assigned positions based on the sp<sup>2</sup> or sp<sup>3</sup> hybridization geometries of their attached carbon atoms and were given isotropic displacement parameters 20% greater than those of their parent atoms. See the Supporting Information for a listing of crystallographic experimental data.

*i.* Special Refinement Conditions. **2.** The Ir(1)-H(1) distance was constrained to be 1.55(1) Å during refinement. F–C distances within two disordered trifluoromethyl groups (of the  $[B\{C_6H_3-3.5-(CF_3)_2\}_4]^-$  ion) were constrained to be equal (within 0.03 Å) to a common value during refinement: d(F(71A)-C(77)) = d(F(72A)-C(77)) = d(F(73A)-C(77))= d(F(71B)-C(77)) = d(F(72B)-C(77)) = d(F(73B)-C(77)) = d(F(74A)-C(78)) = d(F(75A)-C(78)) = d(F(76A)-C(78)) = d(F(74B)-C(78)) = d(F(75B)-C(78)) = d(F(76B)-C(78)).

*ii.* **8.** The Ir(2)–H(1) distance was fixed at 1.79 Å during refinement. The C–F and F…F distances within the disordered CF<sub>3</sub> groups (centered by carbon atoms C(58A), C(58B), and C(87)) of the anion were restrained to be 1.35(1) and 2.20(1) Å, respectively. Additionally, the C(43A)–C(44A) distance was restrained to be 1.50(1) Å.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Tables of crystallographic experimental details for 2 and 8; ORTEP diagrams for the complex cation of 8, showing the disorder in the depm groups; and atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for 2 and 8 in a CIF file. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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