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Olefin Binding in a Binuclear Iridium Complex as a Function of Fluorine Substitution: Ethylene to Tetrafluoroethylene

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The reactions of the diiridium methyl complex $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**1**) with ethylene, fluoroethylene, *Z*-1,2-difluoroethylene, 1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene have been investigated. Reaction of **1** with ethylene at −78 °C yields $[Ir_2H(\eta^2\text{-}C_2H_4)(CO)_2(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2a**), resulting from C−H activation of the methyl group induced by ethylene coordination, whereas reaction at higher temperatures yields the simple ethylene adduct $[Ir_2(CH_3)(CO)(\eta^2\text{-}C_2H_4)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**2b**). Reactions of **1** with fluoroethylene and *Z*-1,2-difluoroethylene yield only the olefin adducts analogous to **2b**. At −78 °C reaction with 1,1-difluoroethylene yields the methylene-bridged hydride product $[Ir_2H(\eta^2\text{-}C_2F_2H_2)(CO)_2(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**5a**), which upon warming, yields first the olefin adduct $[Ir_2(CH_3)(CO)(\eta^2\text{-}C_2F_2H_2)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**5b**) followed by the olefin-bridged product $[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_2H_2)(dppm)_2][CF_3SO_3]$ (**5c**). Trifluoro- and tetrafluoroethylene yield only the olefin-bridged products $[Ir_2(CH_3)(CO)_2(\mu\text{-olefin})(dppm)_2][CF_3SO_3]$ (olefin = C_2F_3H (**6**), C_2F_4 (**7**)). The structure of the tetrafluoroethylene-bridged, tricarbonyl species $[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (**8**), determined by X-ray techniques, is reported.

Introduction

The formation of carbon−carbon bonds, promoted by metal complexes, is a fundamental process in a range of important catalytic reactions such as olefin polymerization, methanol carbonylation, olefin hydroformylation, and Fischer−Tropsch chemistry.[1] A key step in each of these processes involves the migration of an alkyl group or other hydrocarbyl fragment to either a bound olefin, a carbonyl ligand, or a methylene group, and examples of these processes have been documented for the prototype methyl complexes.[2−4] Related transformations involving methyl migration to alkyne[5] or other unsaturated hydrocarbyl ligands[6] have also been reported.

The chemistry demonstrated by us in which the methyl ligand in $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**1**) (dppm = $\mu\text{-}Ph_2PCH_2PPh_2$) was transformed into methylene and hydride fragments upon addition of ligands (L), to yield $[Ir_2H(L)(CO)_2(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$,[7] represents a rare example of cooperative C−H activation of a methyl ligand by adjacent metals.[8] This transformation suggested additional routes to carbon−carbon bond formation in binuclear methyl complexes, either via coupling of an unsaturated organic substrate and the resulting methylene group or by prior insertion of the substrate into the metal−hydride bond followed by coupling of the resulting hydrocarbyl unit with the methylene group. The former transformation has been observed with olefins,[9] allenes,[10] and alkynes,[11] and although the latter sequence of events has appar-

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ently not been demonstrated, the individual steps are well documented.[12,13]

In this paper we report our investigations into the chemistry of ethylene and selected fluoroolefins with compound **1** in attempts to gain further information about the reactivity of compound **1** with unsaturated substrates and the effects of sequential fluorine substitution in reactions of fluoroolefins. Apart from tetrafluoroethylene, the coordination chemistry of which is well documented,[14] little has been published on partially fluorinated ethylene.[14k−m,15−17]

Experimental Section

General Comments. All solvents were dried (using appropriate drying agents), distilled before use, and stored under argon. 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 used as solids were purified by recrystallization. Prepurified argon and nitrogen were purchased from Linde, carbon-13-enriched CO (99%) was supplied by Isotec Inc, ethylene was supplied by Praxair, fluoroethylene, *Z*-1,2-difluoroethylene, and 1,1-difluoroethylene were supplied by Lancaster, trifluoroethylene was supplied by PCR or prepared by a literature method,[18] and tetrafluoroethylene was prepared by a literature method.[19] All purchased gases were used as received. Other reagents were obtained from Aldrich and were also 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,[7] and $[Ir_2(CD_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**1-CD$_3$**) was prepared identically except using perdeuteriomethyl triflate.

Proton NMR spectra were recorded on Varian Unity 400, 500, or 600 spectrometers or on a Bruker AM400 spectrometer. Carbon-13 NMR spectra were recorded on Varian Unity 400 or Bruker AM300 spectrometers, on samples that were ^{13}CO- or $^{13}CH_3$-enriched. Phosphorus-31 and fluorine-19 spectra were recorded on Varian Unity 400 or Bruker AM400 spectrometers. Two-dimensional NMR experiments (COSY, ROESY, and TOCSY) were obtained on Varian Unity 400 or 500 spectrometers. All elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 1.

Preparation of Compounds. (a) $[Ir_2(CH_3)(\eta^2\text{-}C_2H_4)(CO)_2(dppm)_2][CF_3SO_3]$ (2b). This product was obtained by passing ethylene through a solution of **1** (20 mg, 0.015 mmol) in 0.7 mL of CD_2Cl_2 in an NMR tube for 2 min at ambient temperature, followed by allowing the solution to stand for 1 h. The NMR spectra were found to be identical with those of the previously characterized compound **2b**.[20] These data are given in Table 1 for completeness.

(b) $[Ir_2(H)(\eta^2\text{-}C_2H_4)(CO)_2(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (2a). In a typical experiment 3 mL (5 equiv) of ethylene was added slowly by means of a gastight syringe to a solution of 30 mg (0.02 mmol) of **1** in 0.7 mL of CD_2Cl_2 in an NMR tube cooled to −78 °C in a solid CO_2/acetone bath, resulting in a change of color of the solution from red to orange. Before addition of the ethylene, the syringe needle was cooled in the chilled solution of **1** to minimize warming of the solution upon addition of ethylene. One-dimensional NMR spectra (^{1}H, ^{31}P, ^{13}C) were recorded at −80 °C. Warming to above −60 °C resulted in irreversible conversion of **2a** to **2b**.

(c) $[Ir_2(CH_3)(\eta^2\text{-}C_2H_3F)(CO)_2(dppm)_2][CF_3SO_3]$ (3). The reaction of **1** (30 mg in 0.7 mL of CH_2Cl_2) with 6 mL of fluoroethylene (10 equiv) at −78 °C was carried out as described in part b, again resulting in an orange solution. Between −80 and −50 °C only one product (**3**) was observed by NMR. Above −50 °C compound **3** decomposed to **1** and free fluoroethylene.

(d) $[Ir_2(CH_3)(\eta^2\text{-}CHF{=}CHF)(CO)_2(dppm)_2][CF_3SO_3]$ (4). This reaction was carried out as described in part c except that ca. 10 equiv of *Z*-1,2-difluoroethylene was added to compound **1**, yielding an orange solution of compound **4** at temperatures below −40 °C. Above this temperature decomposition to **1** and *Z*-1,2-difluoroethylene occurred.

(e) Reaction of 1 with 1,1-Difluoroethylene. In an NMR experiment, as described in parts c and d, the reaction of **1** with ca. 5 equiv of 1,1-difluoroethylene at −78 °C gave unreacted **1**, $[Ir_2(H)(\eta^2\text{-}F_2CCH_2)(CO)_2(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**5a**), and $[Ir_2(CH_3)(\eta^2\text{-}F_2CCH_2)(CO)_2(dppm)_2][CF_3SO_3]$ (**5b**) in an approximate 2:1:2 ratio, together with minor amounts of unidentified species. Warming the orange solution resulted in a transformation of **5a** into **5b**, such that at −30 °C this conversion was complete and compounds **1** and **5b** were the two major products. Leaving this solution at −20 °C overnight resulted in an approximately 50% conversion to $[Ir_2(CH_3)(CO)_2(\mu\text{-}CF_2CH_2)(dppm)_2][CF_2SO_3]$ (**5c**). Above 0 °C decomposition to unidentified products resulted.

(f) $[Ir_2(CH_3)(CO)_2(\mu\text{-}CHFCF_2)(dppm)_2][CF_3SO_3]$ (6). The reaction between **1** and ca. 5 equiv of trifluoroethylene was carried out at −78 °C as described in part c, causing the solution to change from red to orange. At −80 °C **1** disappeared slowly, giving way to **6**; however, warming to −50 °C resulted in rapid conversion to only **6**. At 20 °C this species decomposed to unidentified products over a period of several hours.

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Table 1. Spectral Data[a,b] for Reactions of Compound 1 with Ethylene and Fluoroolefins

		NMR[a,b]			
product[c]	IR[d]	$\delta(^{31}P\{^1H\})$[e]	$\delta(^1H)$[f,g]	$\delta(^{13}C)$[f]	$\delta(^{19}F)$[h]
$[Ir_2(H)(\eta^2\text{-}C_2H_4)(CO)_2(\mu\text{-}CH_2)(dppm)_2]^+$ (**2a**)		−2.0 (m), −3.7 (m)	5.02 (b, 2H), 4.91 (b, 2H), 3.16 (b, 2H), 1.16 (b, 4H), −12.3 (b, 1H)	189.1 (b), 178.4 (t, $^2J_{PC}$ = 10 Hz)	
$[Ir_2(CH_3)(\eta^2\text{-}C_2H_4)(CO)_2(dppm)_2]^+$ (**2b**)[20]	1971 (vs), 1787 (s),[d] 1978 (s), 1790 (m)[i]	19.0 (m), 5.7 (m)	3.25 (m, 4H), 1.05 (t, 3H), 0.70 (t, 4H)	204.0 (t)	
$[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CHF{=}CH_2)(dppm)_2]^+$ (**3**)		18.8 (m), 6.1 (m)	3.50 (b, 2H), 3.10 (b, 1H), 3.00 (b, 1H), 2.2 (b, 1H), 1.13 (t, 3H, $^3J_{PC}$ = 8.5 Hz), 0.96 (b, 2H)	208.3 (b), 209.8 (b)	−172.1 (b)
$[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CHF{=}CHF)(dppm)_2]^+$ (**4**)		17.2 (m), 2.6 (m)	1.18 (t, 3H, $^3J_{PH}$ = 9.0 Hz)	207.4 (b)	−211.6 (b)
$[Ir_2(H)(\mu\text{-}CH_2)(CO)_2(\eta^2CF_2{=}CH_2)(dppm)_2]^+$ (**5a**)		−2.8 (m), −4.3 (m)	5.37 (b, 2H), 5.11 (b, 2H), 3.28 (b, 2H), 0.08 (b, 2H), −12.4 (b, 1H)	191.3 (b)	−80.4 (b)
$[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CH_2{=}CF_2)(dppm)_2]^+$ (**5b**)		16.1 (m), 6.4 (m)	3.80 (m, 2H), 3.02 (m, 2H), 1.15 (t, 3H, $^3J_{PH}$ = 8.8 Hz), 0.37 (m, 2H)	210.7 (b), 202.3 (b)	−83.7 (b)
$[Ir_2(CH_3)(CO)_2(\mu\text{-}CH_2{=}CF_2)(dppm)_2]^+$ (**5c**)		16.1 (m), 5.9 (m)	4.44 (m, 2H), 3.60 (m, 2H), 2.47 (m, 2H), 0.18 (t, 3H, $^3J_{PH}$ = 4.8 Hz)	196.6 (b), 185.6 (b)[j]	−45.8 (m)
$[Ir_2(CH_3)(CO)_2(\mu\text{-}CHF{=}CF_2)(dppm)_2]^+$ (**6**)		14.9 (m), 5.1 (m)	3.97 (m, 1H), 3.92 (m, 2H), 3.56 (m, 1H), 0.36 (t, 3H, $^3J_{PH}$ = 6.0 Hz)	196.9 (t, $^2J_{PC}$ = 8.6 Hz), 184.5 (b)[j]	−52.6 (d, $^2J_{FF}$ = 253 Hz), −81.6 (d, $^2J_{FF}$ = 253 Hz), −193.8 (b)
$[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_4))(dppm)_2]^+$ (**7**)	2020 (vs), 2001 (s)	16.8 (m), 5.2 (m)	3.89 (m, 4H), 0.41 (t, 3H, $^3J_{PH}$ = 5.0 Hz)	191.9 (m), 181.6 (m), −7.4 (bt)	−79.7 (m) −86.4 (m)
$[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2]^+$ (**8**)	2062 (sh), 2018 (br, vs)	−7.61 (m), −15.5 (m)	4.61 (m, 4H), 0.79 (t, 3H, $^3J_{PH}$ = 6.0 Hz)	178.8 (m), 177.8 (m), 156.5 (bs), −13.2 (bs)	−73.6 (t), −84.7 (b)
$[Ir_2(CH_3)(PMe_3)(CO)_2(\mu C_2F_4))(dppm)_2]^+$ (**9**)	2006 (vs), 1990 (s)	−18.2 (m), −19.0 (m), −68.8 (t, $^3J_{PF}$ = 55 Hz)	5.23 (m, 2H), 4.99 (m, 2H), 0.92 (bt, 3H, $^3J_{PH}$ = 6.5 Hz), 0.80 (d, 9H)	185.2 (m), 180.1 (t, $^2J_{PC}$=13 Hz), −18.9 (dm, $^3J_{PC}$ = 14 Hz)	−70.0 (dt, $^3J_{PF}$ = 55 Hz), −83.3 (m)

[a] NMR abbreviations: s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet, b = broad. [b] NMR data in CD_2Cl_2 unless otherwise stated. [c] The anion in all cases is trifluoromethane sulfonate. [d] All samples as solids unless otherwise noted. IR abbreviations (ν(CO) values given): s = strong, vs = very strong, sh = shoulder, br = broad. [e] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4. [f] ^1H and ^{13}C chemical shifts are referenced vs external TMS. [g] Chemical shifts for the phenyl hydrogens are not given in the ^1H data. [h] ^{19}F chemical shifts are referenced vs external $CFCl_3$. [i] Recorded in CH_2Cl_2. [j] Recorded in acetone-d_6.

(g) $[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (7). Compound **1** (40 mg, 0.029 mmol) was dissolved in 5 mL of CH_2Cl_2, and tetrafluoroethylene was passed over the solution for 1 min. The solution was then stirred under a static atmosphere of the gas for ca. 72 h, during which the color changed from red to dark red-brown. No species other than **1** and **7** was observed by NMR at intermediate times, over a range of temperatures from −80 °C to ambient. The solution of compound **7** was evaporated to ca. 2 mL in vacuo, and a brown powder was precipitated and washed with pentane (3 × 10 mL) and dried under vacuum. Yield: 93%. Anal. Calcd for $Ir_2SP_4F_7O_5C_{56}H_{47}$: C, 45.65; H, 3.22. Found: C, 45.38; H, 3.02.

(h) $[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (8). Compound **7** (30 mg, 0.020 mmol) was slurried in 5 mL of CH_2Cl_2. Carbon monoxide was passed over the solution, causing a color change from dark red-brown to bright yellow. An elemental analysis was not obtained since carbonyl loss, yielding **7**, occurs upon flushing the solution with N_2 or upon applying vacuum.

(i) $[Ir_2(CH_3)(PMe_3)(CO)_2(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (9). Compound **7** (30 mg, 0.020 mmol) was slurried in 5 mL of CH_2Cl_2, and 1 equiv of trimethylphosphine (2.1 μL, 0.020 mmol) was added, causing the solution to turn yellow. After 10 min the solvent was evaporated to ca. 2 mL in vacuo, and a pale yellow powder was precipitated. The solid was isolated, washed with pentane (3 × 10 mL), and dried under vacuum. Yield: 76%. Anal. Calcd for $Ir_2SP_5F_7O_5C_{59}H_{56}$: C, 45.73; H, 3.65. Found: C, 45.70; H, 3.42.

X-ray Data Collection. Pale yellow crystals of $[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]\cdot CH_2Cl_2$ (**8**), suitable for X-ray diffraction, were grown via slow diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of the compound under a CO atmosphere. A suitable crystal was mounted and flame-sealed in a glass capillary under solvent vapor to minimize decomposition or deterioration due to solvent loss. Data were collected at −60 °C on a Siemens P4/RA diffractometer using graphite-monochromated Cu Kα radiation,[21] and unit cell parameters were obtained from a least-squares refinement of 50 reflections in the range 56.7° < 2θ < 59.2°. The orthorhombic cell, the diffraction symmetry, and the systematic absences defined the space group as *Fdd*2. Three reflections were chosen as intensity standards and were remeasured every 120 min of X-ray exposure time; in no case was decay evident. Crystal parameters and details of data collection are summarized in Table 2. The crystal faces were indexed and measured, with absorption corrections being carried out using Gaussian integration.

Structure Solution and Refinement. The positions of the iridium and phosphorus atoms were found using the direct-methods program SHELXS-86;[22] the remaining atoms were found using a succession of least-squares and difference Fourier maps. Refinement proceeded using the program

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(21) Programs for diffractometer operation and data collection were those of the XSCANS systems supplied by Siemens.

(22) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

Table 2. Crystallographic Data for Compound 8

A. Crystal Data	
	$[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2]$-$[CF_3SO_3]$ (**8**)
formula	$C_{58}H_{49}Cl_2F_7Ir_2O_6P_4S$
fw	1586.21
cryst dimens, mm	0.46 × 0.10 × 0.10
color	yellow
cryst syst	orthorhombic
space group	*Fdd*2 (No. 43)
unit cell params[a]	
a, Å	37.872(2)
b, Å	53.711(3)
c, Å	11.7901(6)
V, Å3	23983(2)
Z	16
d_{calcd}, g cm^{-3}	1.757
μ, mm^{-1}	11.230
B. Data Collection and Refinement Conditions	
diffractometer	Siemens P4/RA[b]
radiation (λ, Å)	graphite-monochromated Cu Kα (1.54178)
T, °C	−60
scan type	$\theta-2\theta$
2θ (max), deg	113.5
total data collected	8494 ($-40 \leq h \leq 40$, $-58 \leq k \leq 58$, $-12 \leq l \leq 12$)[c]
no. of unique reflns	8025
no. of observations (NO)	7082 ($F_o^2 \geq 2\sigma(F_o^2)$)
no. of variables (NV)	683
range of transm factors	0.3997−0.0788
Flack absolute structure param[d]	0.00 (2)
residual density, e Å^{-3}	2.182 and −1.284
$R_1(F_o^2 \geq 2\sigma(F_o^2))$[e]	0.0577
$wR_2(F_o^2 \geq -3\sigma(F_o^2))$[e]	0.1583
goodness-of-fit (*S*)[f]	1.062

[a] Obtained from least-squares refinement of 50 reflections with 56.7° < 2θ < 59.2°. [b] Programs for diffractometer operation and data collection were those of the XSCANS system supplied by Siemens. [c] Data were collected in Friedel-opposite octants with indices of the form $+h+k+l$ and $-h-k-l$. [d] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881. The Flack parameter will refine to a value near 0 if the structure is in the correct configuration and will refine to a value near 1 for the inverted configuration. [e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$. [f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\delta^2(F_o^2) + (a_0P)^2 + a^1P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$; $a_0 = 0.1016$, $a_1 = 455.6115$).

SHELXL-93.[23] Hydrogen atom positions were calculated by assuming idealized sp^2 or sp^3 geometries about their attached carbon atoms (as appropriate) and were given thermal parameters 120% of the equivalent isotropic displacement parameters of their attached carbons. Further details of structure refinement (other than described below) and final residual indices may be found in Table 2.

Location of all atoms in the complex cation proceeded smoothly; however the triflate anion was not well behaved, so the bond lengths were constrained to enforce an idealized geometry as follows: $d(S-C(91)) = 1.80$ Å; $d(S-O(91)) = d(S-O(92)) = d(S-O(93)) = 1.45$ Å; $d(F(91)-C(91)) = d(F(92)-C(91)) = d(F(93)-C(91)) = 1.35$ Å; $d(F(91)-F(92)) = d(F(91)-F(93)) = d(F(92)-F(93)) = 2.20$ Å; $d(O(91)-O(92)) = d(O(91)-O(93)) = d(O(92)-O(93)) = 2.37$ Å; $d(F(91)-O(92)) = d(F(91)-O(93)) = d(F(92)-O(91)) = d(F(92)-O(93)) = d(F(93)-O(91)) = d(F(93)-O(92)) = 3.04$ Å.

Results and Compound Characterization

Scheme 1

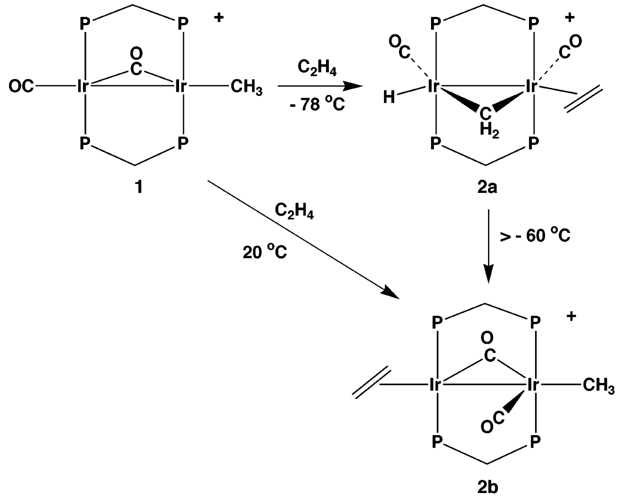
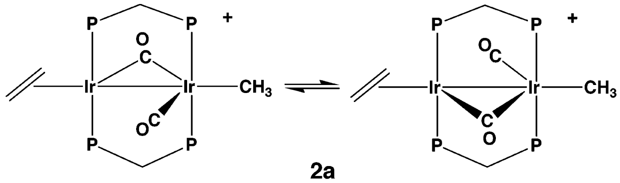


Chart 1



1. Reactions with Ethylene. At ambient temperature the reaction of **1** with ethylene has been reported to yield $[Ir_2(CH_3)(\eta^2\text{-}C_2H_4)(\mu\text{-}CO)_2(dppm)_2][CF_3SO_3]$ (**2b**), in which the methyl ligand is bound to one metal while the ethylene ligand is bound to the other.[20] The geometry shown in Scheme 1, which is slightly different than originally proposed, was established by IR spectroscopy and by a series of ^1H and ^{13}C NMR experiments in which selective ^{31}P decoupling established that the methyl and carbonyl ligands all coupled to the pair of ^{31}P nuclei on one metal, thereby establishing that these ligands were all bound to this metal, while the ethylene ligand was bound to the adjacent metal. In the $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of **2b** only one carbonyl resonance was observed at δ 204.0, indicating that both carbonyls are chemically equivalent on the NMR time scale. The low-field chemical shift for these carbonyls (compare, compound **2a**) suggests that they are engaged in a semibridging interaction with the adjacent metal, and this is supported by selective ^{31}P decoupling experiments which show a resolvable coupling (giving a triplet) to one pair of ^{31}P nuclei and unresolved coupling to the other pair that results in peak broadening. However, the IR spectrum of **2b** suggests a somewhat different interpretation. The solution IR spectrum displays one stretch for a terminal carbonyl at 1978 cm^{-1} and another due to a bridging carbonyl at 1790 cm^{-1}. Taken together with the NMR results this suggests the fluxional process shown in Chart 1, in which exchange between a terminal and a bridging carbonyl is occurring. We would expect this exchange to be facile since it involves only very slight movement of the two exchanging carbonyls. Even at −80 °C this exchange is rapid on the NMR time scale, resulting in the observation of only one carbonyl resonance. However, the much faster IR time scale[24] allows

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(23) Sheldrick, G. M. *SHELXL-93*, Program for crystal structure determination; University of Göttingen: Germany, 1993.

(24) Drago, R. S. *Physical Methods in Chemistry*, W.B. Saunders Co.: Philadelphia, PA, 1977; Chapter 4.

both carbonyl binding modes to be identified. The greater coupling of the carbonyl ligands to the ^{31}P nuclei adjacent to the methyl group, in the ^{13}C NMR spectrum, is consistent with the process shown in Chart 1, which gives rise to an average structure in which the carbonyls are more strongly bound to the iridium center bearing the methyl ligand.

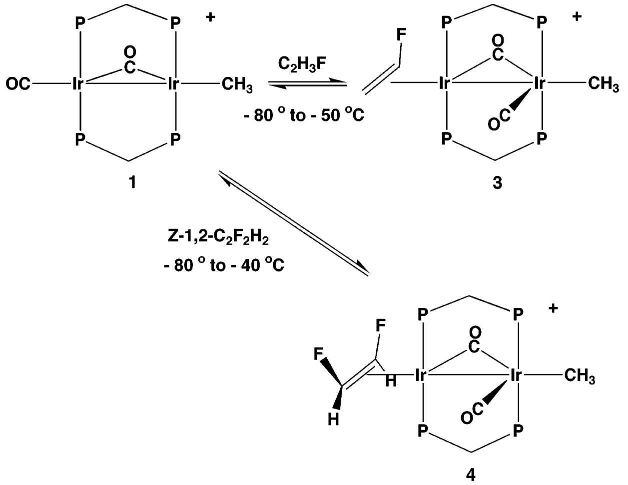
When the reaction of **1** with ethylene is carried out at −78 °C, an additional product, $[Ir_2H(CO)_2(\eta^2\text{-}C_2H_4)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2a**), is observed. This species can be obtained as the major product, together with **2b** (approximate 4:1 ratio, respectively), upon slow addition of a prechilled sample of ethylene. However, warming the sample to −60 °C or above results in irreversible conversion of **2a** to **2b**. Compound **2a** shows the normal $^{31}P\{^1H\}$ NMR spectrum typical of an AA′BB′ spin system, consistent with two chemically inequivalent phosphorus environments. In the ^{13}C NMR spectrum, two resonances for terminal carbonyls are observed at δ 189.1 and 178.4; the former is a broad singlet and the latter is a triplet. The ^1H NMR spectrum displays a broad hydride resonance at δ −12.3, an approximate quintet at δ 5.02, corresponding to a methylene group, and a very broad resonance at δ 1.16 for the four ethylene protons. The structure proposed for **2a** is analogous to that established for the PMe_3 adduct $[Ir_2H(CO)_2(PMe_3)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$,[7] in which ligand attack (C_2H_4 or PMe_3) at one metal results in C−H activation of the methyl ligand by the adjacent metal.

Reaction of the perdeuteriomethyl analogue of **1**, $[Ir_2(CD_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$, with ethylene at −78 °C followed by slow warming of the solution to 25 °C yielded $[Ir_2(CD_3)(C_2H_4)(\mu\text{-}CO)_2(dppm)_2][CF_3SO_3]$, in which no detectable incorporation of deuterium into the ethylene ligand was seen.

2. Reactions with Fluoroolefins. (a) Fluoroethylene. Addition of a 3-fold excess of fluoroethylene to a CD_2Cl_2 solution of $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**1**) in an NMR tube at −78 °C gives ca. 90% conversion to $[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CH_2{=}CHF)(dppm)_2][CF_3SO_3]$ (**3**). As the sample is warmed in the NMR spectrometer from −80 °C, the amount of adduct decreases until above −50 °C none of the product is observed, having reverted to starting material (**1**). Complex **3** appears in the $^{31}P\{^1H\}$ NMR spectrum as two equal intensity multiplets at δ 18.8 and 6.1, with the higher field multiplet having a more complex appearance, suggesting that it is due to the partial overlap of the resonances of two inequivalent phosphorus nuclei, while the lower field multiplet is due to two almost equivalent phosphorus nuclei. Overall, the pattern is characteristic of an ABCD spin system, in which two nuclei have accidentally equivalent chemical shifts.

Exchange between free and coordinated fluoroethylene was demonstrated by a 500 MHz ^1H-TOCSY experiment at −60 °C which showed exchange between the protons giving rise to the two signals at δ 4.78 and 4.52, due to the "$=CH_2$" end of the free fluoroethylene molecule, and the equivalent protons of the coordinated ligand, which resonate at δ 0.96. By comparison, the protons of the ethylene ligand in $[Ir_2(CH_3)(CO)_2(\eta^2\text{-}C_2H_4)(dppm)_2][CF_3SO_3]$ (**2b**) appear as a triplet at δ 0.70 at room temperature.[20] A very broad resonance at ca. δ 2.2 is assigned to the vinylic proton, geminal to fluorine, in complex **3**. The dppm methylene protons are also broad and appear at δ 3.50 (2H), 3.10 (1H), and 3.00 (1H), while the iridium-bound methyl group appears as a triplet at δ 1.13 ($^3J_{PH}$ = 8.5 Hz), with equal coupling to two adjacent phosphorus nuclei. This resonance is shifted downfield from the δ 0.58 seen for unreacted **1**. Coordination of fluoroethylene, shown in Scheme 2, does not induce activation of the iridium-bound methyl group at the temperatures studied; this methyl group remains intact over the temperature range from −80 to −50 °C, above which the complex is not stable. The facile exchange of free and coordinated fluoroethylene is consistent with it remaining intact upon coordination, but the possibility of reversible C−H or C−F activation cannot be unambiguously ruled out. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of **3** shows two broad carbonyl resonances at δ 209.8 and 208.3, comparable to the chemical shift of the time-averaged carbonyls in $[Ir_2(CH_3)(CO)_2(\eta^2\text{-}C_2H_4)(dppm)_2][CF_3SO_3]$ (**2b**), at δ 204.0.[20] These resonances are intermediate between the values usually observed in related complexes for terminal and bridging carbonyls[25] and are more in line with what we have observed for the semibridging geometry.[26] Although we were unable to acquire the IR spectrum of **3** (or other low-temperature intermediates) at the required temperature, we assume a ground-state structure like that of **2b** in which exchange between terminal and bridging carbonyls gives average signals resembling an intermediate semibridging geometry. In this case two signals result because of the inequivalence of both sides of the Ir_2P_4 plane. The ^{19}F NMR spectrum shows an upfield shift for the coordinated ligand, from δ −116.4 in the free olefin to δ −172.1 in complex **3**.

Scheme 2



(b) *Z*-1,2-Difluoroethylene. *Z*-1,2-Difluoroethylene binds reversibly to **1**, forming the adduct $[Ir_2(CH_3)(CO)_2(\eta^2\text{-}Z\text{-}CHF{=}CHF)(dppm)_2][CF_3SO_3]$ (**4**), visible in the NMR spectra between −80 and −40 °C. At the lower

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[25] See for example: (a) Torkelson, J. R.; Oke, O.; Muritu, J.; McDonald, R.; Cowie, M. *Organometallics* **2000**, *19*, 854. (b) Ristic-Petrovic, D.; Torkelson, J. R.; Hilts, R. W.; McDonald, R.; Cowie, M. *Organometallics* **2000**, *19*, 4432. (c) Dell'Anna, M. M.; Trepanier, S. J.; McDonald, R.; Cowie, M. *Organometallics* **2001**, *20*, 88.

[26] See for example: (a) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463. (b) Antonelli, D. M.; Cowie, M. *Organometallics* **1991**, *10*, 2550. (c) Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 1297.

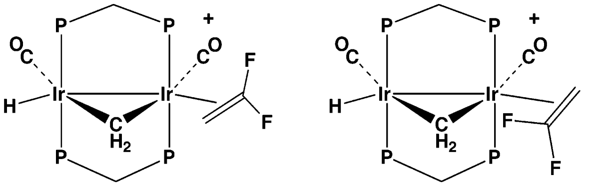
temperature there is only about 60% conversion when 5 equiv of olefin are employed, by −40 °C conversion to the adduct is reduced to about 20%, and above this temperature only starting material remains.

The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a pair of complex multiplets at δ 17.2 and 2.6, each of which is due to two overlapping signals, consistent with an ABCD spin system resulting from four chemically inequivalent phosphorus nuclei. The ^1H NMR spectrum shows the methyl resonance as a triplet at δ 1.18 ($^3J_{PH}$ = 9.0 Hz), indicating that it is terminally bound to one metal. Unfortunately, it is not possible to assign the remaining resonances because of the poor quality of the spectra resulting from the presence of a large excess of the free olefin, impurities in the olefin, and broad signals. The ^{13}C NMR spectrum shows a single broad peak at δ 207.4, consistent with the proposed structure shown in Scheme 2 and a fluxional process as described earlier for compounds **2b** and **3**. The ^{19}F NMR spectrum shows a single broad peak at δ −211.6 due to the two equivalent fluorine nuclei in the η^2 complex. An olefin-bridged complex is ruled out on the basis that two inequivalent fluorines would have been expected owing to the inequivalence of the metals (one having a methyl ligand attached), and similarly, two terminal ^{13}CO resonances at higher field than those observed would have been expected. The NMR spectral parameters of the η^2 adducts **3** and **4** resemble those of the ethylene adduct $[Ir_2(CH_3)(CO)_2(\eta^2\text{-}C_2H_4)(dppm)_2][CF_3SO_3]$ (**2b**).[20]

(c) 1,1-Difluoroethylene. When an excess (>5 equiv) of 1,1-difluoroethylene is added to a solution of **1** at −78 °C, the ^{31}P NMR spectrum acquired at this temperature typically shows three compounds, **1**, **5a**, and **5b**, in a ratio of ca. 2:1:2, together with small amounts of several uncharacterized species.

The adduct, $[Ir_2(H)(CO)_2(\eta^2\text{-}CF_2{=}CH_2)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**5a**), in which the iridium-bound methyl of the starting complex **1** has undergone intramolecular C−H activation to form a hydride and a methylene ligand bridging the two metals, is characterized in the $^{31}P\{^1H\}$ NMR spectrum by equal intensity resonances at δ −2.8 and −4.3, which are broad with some multiplet structure visible. These chemical shifts are very similar to those of the ethylene adduct (**2a**), proposed to have a similar structure. The proton NMR spectrum of **5a** displays a broad hydride signal at δ −12.40 and a broad resonance at δ 5.37 due to the bridging methylene group. In addition, the dppm methylene protons appear as broad peaks at δ 5.11 and 3.28 with some partially resolved coupling to the ^{31}P nuclei, while the methylene group of the coordinated 1,1-difluoroethylene appears as a broad resonance at δ 0.08, displaying the upfield shift expected of the protons of a coordinated olefin.[27] Only a tentative assignment of the ^{13}C NMR spectrum could be made because of the difficulty encountered in producing sufficient quantities of **5a** in solution and the presence of other products. Only a single very broad carbonyl resonance at δ 191.3 could be attributed to **5a**, whereas a pair of resonances would normally be expected, unless the carbonyl carbons were accidentally isochronous. In the ^{19}F NMR spectrum a single broad peak is observed at δ −80.4, shifted only slightly downfield from the free olefin at δ −82.2.

Chart 2



Although two isomers of **5a** might be expected, as diagrammed in Chart 2, only one species is observed in the NMR spectra. Whether this corresponds to only one of the isomers shown or whether the one observed species results from facile exchange between both isomers is not known, although no evidence of fluxionality was observed over the temperature range investigated.

Warming a solution of **5a** from −80 to −30 °C causes the transformation of **5a** into the second product, $[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CF_2{=}CH_2)(dppm)_2][CF_3SO_3]$ (**5b**), and by −30 °C only **5b** and a small quantity of **1** remain. Compound **5b** displays equal intensity multiplets at δ 16.1 and 6.4 in the $^{31}P\{^1H\}$ NMR spectrum, consistent with an AA′BB′ spin system. Because this species predominates in solution at −30 °C, its NMR characterization was carried out at this temperature. Its dppm methylene resonances, at δ 3.80 and 3.02 in the ^1H NMR spectrum, are sharper than those of **3**, and the methylene signal of the coordinated difluoroethylene ligand shows resolved coupling (this signal is a broad envelope for the fluoroethylene complex, **3**). This methylene signal in **5b** is a virtual quintet at δ 0.37, collapsing to a triplet ($^3J_{HF}$ = 9.2 Hz) upon broadband ^{31}P decoupling, indicating that this group is coupled approximately equally to two phosphorus nuclei, and also to two fluorines of the difluoromethylene group. The iridium-bound methyl group appears as a triplet at δ 1.15, with a coupling of 8.8 Hz to two equivalent phosphorus nuclei. In the ^{19}F NMR spectrum, the difluoromethylene resonance appears as a broad peak at δ −83.7. Decoupling experiments (^{31}P or ^1H decoupling) did not succeed in resolving this resonance into a multiplet. The ^{13}C NMR spectrum of a ^{13}CO-enriched sample reveals two inequivalent carbonyls at δ 210.7 and 202.3. Again, we assume a structure as shown in Scheme 3 accompanied by carbonyl exchange as proposed for **2b**, **3**, and **4**.

Warming a solution of **5b** above −20 °C results in its disappearance with concomitant appearance of **1**, until by 10 °C only starting material is observed. After 24 h at ambient temperature, a mixture of **1** and the olefin gives decomposition products. However, maintaining a solution of **5b** at ca. −20 °C overnight results in approximately 50% conversion to a third species, $[Ir_2(CH_3)(CO)_2(\mu\text{-}CF_2{=}CH_2)(dppm)_2][CF_3SO_3]$ (**5c**). This third isomer appears in the ^{31}P NMR spectrum as multiplets at δ 16.1 and 5.9; the lower field multiplet is coincident with the lower field multiplet of compound **5b**. As **5c** forms, the integral ratio of the δ 16.1 multiplet to the sum of the δ 5.9 and 6.4 resonances remains constant, indicating that this low-field resonance is due to both compounds. In the ^1H NMR spectrum the dppm methylenes for **5c** appear at δ 4.44 and 3.60, the olefin protons appear as a multiplet at δ 2.47, and the intact

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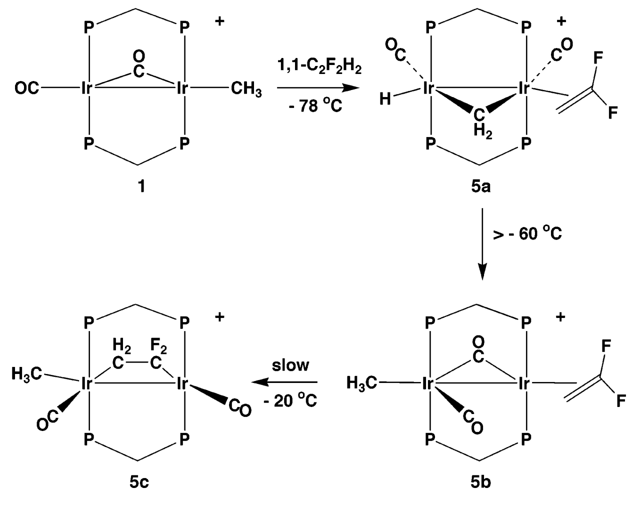
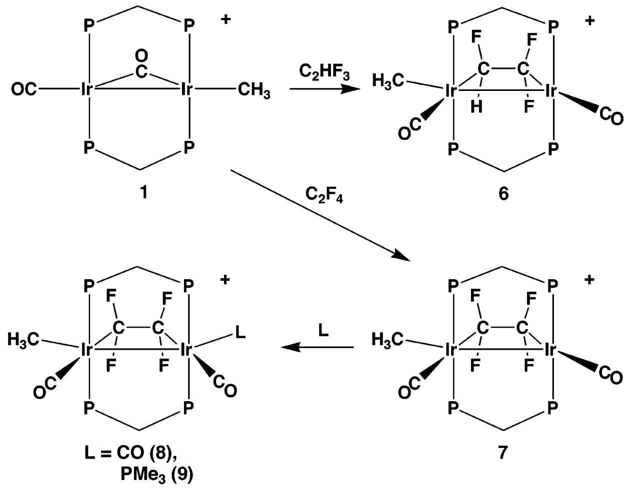
[27] Elsenbroich, Ch.; Salzer, A. *Organometallics: A Concise Introduction*; VCH Publishers: New York, 1989; p 298.

Scheme 3



Scheme 4



iridium-bound methyl group appears as a triplet at δ 0.18, with a 4.8 Hz coupling to two equivalent phosphorus nuclei. The olefinic methylene resonance collapses to a triplet ($^3J_{HF}$ = 20 Hz) upon broadband ^{31}P irradiation, and this coupling is also found in the resonance for the difluoromethylene group in the $^{19}F\{^{31}P\}$ spectrum, which appears as a triplet at δ −45.8. The olefinic methylene ^1H resonance appears at lower field than that in the η^2-coordinated complexes **5a** and **5b**, where it appears at δ 0.08 and 0.37, respectively, and is consistent with the proposed dimetallacyclobutane formulation. The ^{13}C NMR spectrum of a ^{13}CO-enriched sample shows two inequivalent terminal carbonyls at δ 196.6 and 185.6.

The olefinic fluorine signal of the 1,1-difluoroethylene ligand is shifted downfield in the ^{19}F NMR spectrum by 36.4 ppm from the free olefin, comparable to the coordination shift displayed in the formation of the tetrafluoroethylene-bridged complex $[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (**7**), where an average downfield shift of ca. 52 ppm is observed (vide infra). Unfortunately, we were unable to confirm the orientation of the bridging difluoroethylene group in **5c**, but it is shown in Scheme 3 in the orientation having the larger fluorine atoms closer to the less crowded metal.

(d) Trifluoroethylene. Trifluoroethylene reacts with **1** at −78 °C, forming $[Ir_2(CH_3)(CO)_2(\mu\text{-}CHF{=}CF_2)(dppm)_2][CF_3SO_3]$ (**6**), as shown in Scheme 4. The ^{19}F NMR spectrum shows three broad signals, at δ −52.6, −81.6, and −193.8, all of which are shifted to low field from the free ligand, the corresponding resonances of which appear at δ −100.0, −125.9, and −205.0, respectively. The two lower field resonances show mutual coupling of 253 Hz, which is consistent with an sp^3-hybridized "CF_2" group.[28] Coupling to the high-field fluorine at δ −193.8 is not discernible. The broadness of the peaks in the ^{19}F NMR spectrum is not due to unresolved coupling to phosphorus, as revealed by the failure of the resonances to sharpen upon broadband ^{31}P decoupling.

All three fluorine nuclei of trifluoroethylene have moved to lower field upon complexation, with the geminal fluorines having moved the farthest. The average coordination shift is 45.9 ppm for this pair of geminal nuclei, consistent with rehybridization toward sp^3 for the carbon bearing two fluorines due to substantial back-donation from the metals. This shift is similar to that observed for the analogous tetrafluoroethylene complex described below. As noted, the coordination shift of the remaining fluorine, while not as pronounced, is also downfield.

The $^{31}P\{^1H\}$ NMR spectrum reveals the presence of a pair of complex multiplets at δ 14.9 and 5.1, in which each multiplet is actually comprised of two closely spaced resonances, consistent with four inequivalent phosphorus nuclei. The ^1H NMR spectrum shows the dppm protons as multiplets at δ 3.97 (1H), 3.92 (2H), and 3.56 (1H), while the iridium-bound methyl appears as a triplet at δ 0.36 ($^3J_{PH}$ = 6.0 Hz), indicating a terminally bound methyl group, the protons of which couple approximately equally to an adjacent pair of phosphorus nuclei. We were unable to locate the single vinylic proton of the coordinated trifluoroethylene moiety. The ^{13}C NMR spectrum of a ^{13}CO-enriched sample of **6** shows two inequivalent terminal carbonyl resonances at δ 196.9 and 184.5, which are very similar to the terminal carbonyls of the 1,1-difluoroethylene-bridged compound **5c** (δ 196.6 and 185.6).

The product **6** persists in CD_2Cl_2 solution upon warming to room temperature, but decomposes after several hours to a mixture of unidentified products.

(e) Tetrafluoroethylene. Unlike the other fluoroolefins, which react rapidly with **1**, even at −80 °C, the reaction of **1** with tetrafluoroethylene occurs very slowly over a several day period at ambient temperature. No evidence for any species containing a terminally bound η^2-tetrafluoroethylene unit was observed at any temperature between −80 °C and ambient. The $^{31}P\{^1H\}$ NMR spectrum of the product $[Ir_2(CH_3)(CO)_2(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (**7**) shows two resonances at δ 5.2 and 16.8, having patterns typical of an AA′BB′ spin system. A $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO- and $^{13}CH_3$-enriched sample of **7** shows the terminal carbonyls at δ 191.9 and 181.6 as multiplets and the methyl group at δ −7.4 as a broad triplet. Selective ^{31}P decoupling indicates that the methyl and the high-field carbonyl are coupled to the same pair of phosphorus nuclei, so are probably on the same metal, while the other carbonyl couples to the phosphorus nuclei on the other metal. The methyl

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[28] Dungan, C. H.; VanWazer, J. R. *Compilation of Reported ^{19}F NMR Chemical Shifts*; Wiley-Interscience: New York, 1970.

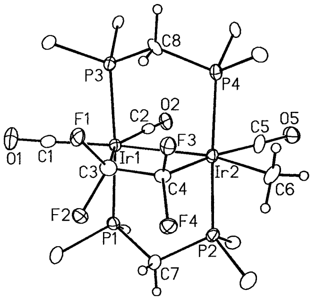

Figure 1. Perspective view of the complex cation of $[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (**8**) showing the atom-labeling scheme. Only the ipso carbons of the phenyl rings are shown. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, except for hydrogen atoms, which are drawn arbitrarily small.

resonance in the ^1H NMR spectrum appears at δ 0.41 and displays 139 Hz coupling in the $^{13}CH_3$-enriched sample. As expected, two fluorine resonances for the different ends of the bridging tetrafluoroethylene ligand appear at δ −86.4 and −79.7, and each is coupled to different pairs of ^{31}P nuclei, as shown by selective decoupling experiments, confirming the bridging arrangement of this olefin.

Reaction of **7** with CO yields the labile tricarbonyl complex $[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (**8**). Spectroscopic data for this species, given in Table 1, are consistent with the structure diagrammed in Scheme 4, in which CO addition to the unsaturated metal in **7** has occurred. In the ^{13}C NMR spectrum the three carbonyl resonances appear as multiplets at δ 178.8, 177.8, and 156.5. Selective ^{31}P decoupling suggests that the low-field carbonyl (δ 178.8) and the methyl group are bound to one metal, with the other two carbonyls on the other. The two low-field carbonyl resonances are proposed to correspond to the adjacent pair that are cis to the metal−metal bond, while the high-field signal corresponds to the carbonyl lying opposite the metal−metal bond. The low-field chemical shift of terminal carbonyls that are adjacent to another metal, compared to terminal carbonyls that are remote from another metal, has been noted.[29] Reaction of a ^{13}CO-enriched sample of **7** with ^{12}CO gives a ^{13}C NMR spectrum in which the two low-field carbonyl resonances dominate. A very weak resonance (ca. 10% of the intensity of each of the others) appears at δ 156.5. This indicates that CO attack occurs at the unsaturated metal, predominantly at the site opposite the Ir−Ir bond; the small amount of ^{13}CO at the high-field site suggests that some ^{12}CO attack at the site adjacent to the Ir−Ir bond might occur. Leaving the sample solution overnight causes no change in the intensities of the ^{13}CO resonances, indicating that if exchange of the carbonyls is occurring, it is very slow.

The structure proposed for **8** has been confirmed by an X-ray determination, and a view of the complex cation is shown in Figure 1, with important bond lengths and angles given in Table 3. The coordination geometry at each metal is distorted octahedral, in which the constraints induced by the bridging olefin give rise to distortions from idealized geometries. These distortions are clear from the Ir−Ir−C(olefin) angles of 71.2(5)° and 71.0(5)°. However, the origins of other subtle distortions that give rise to differences in geometry at each metal are not as obvious. For example, carbonyl C(5)O(5) is almost opposite the one olefinic carbon C(4) (170.1(7)°) and bent away from Ir(1) with an Ir(1)−Ir(2)−C(5) angle of 118.6(5)°, whereas the equivalent carbonyl on Ir(1) (C(2)O(2)) is bent toward Ir(2), yielding an Ir(2)−Ir(1)−C(2) angle of 82.7(5)° and, as seen from Figure 1, is not opposite the olefinic carbon C(3). The tilting of C(2)O(2) toward Ir(2) gives rise to angles at Ir(1) between the carbonyls and the olefin of greater than 97°, whereas the opposite tilt of C(5)O(5) compresses the equatorial angles at Ir(2) to less than 85°. The metal−metal separation, of 2.8967(9) Å, is at the long end of typical single bonds in such complexes,[7,25a,30,31] but is shorter than the nonbonded intraligand P−P separations (3.011(6) and 3.019(6) Å), showing mutual attraction of the metals.

Table 3. Selected Interatomic Distances and Angles for Compound 8

(a) Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Ir(1)	Ir(2)	2.8967(9)	Ir(2)	P(4)	2.346(5)
Ir(1)	C(1)	1.95(2)	F(1)	C(3)	1.40(2)
Ir(1)	C(2)	1.93(2)	F(2)	C(3)	1.46(2)
Ir(1)	C(3)	2.10(2)	F(3)	C(4)	1.40(2)
Ir(2)	C(4)	2.10(2)	F(4)	C(4)	1.37(2)
Ir(2)	C(5)	1.84(2)	O(1)	C(1)	1.11(2)
Ir(2)	C(6)	2.16(2)	O(2)	C(2)	1.10(2)
Ir(1)	P(1)	2.376(5)	O(5)	C(5)	1.19(2)
Ir(1)	P(3)	2.393(4)	C(3)	C(4)	1.54(3)
Ir(2)	P(2)	2.344(5)			

(b) Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ir(2)	Ir(1)	C(1)	168.5(5)	Ir(1)	C(2)	O(2)	178(2)
Ir(2)	Ir(1)	C(2)	82.7(5)	Ir(1)	C(3)	F(1)	116(1)
Ir(2)	Ir(1)	C(3)	71.0(5)	Ir(1)	C(3)	F(2)	111(1)
P(1)	Ir(1)	P(3)	174.2(2)	Ir(1)	C(3)	C(4)	109(1)
C(1)	Ir(1)	C(2)	108.8(7)	F(1)	C(3)	F(2)	100(1)
C(1)	Ir(1)	C(3)	97.5(7)	F(1)	C(3)	C(4)	112(1)
C(2)	Ir(1)	C(3)	153.7(7)	F(2)	C(3)	C(4)	108(1)
Ir(1)	Ir(2)	C(4)	71.2(5)	Ir(2)	C(4)	F(3)	114(1)
Ir(1)	Ir(2)	C(5)	118.6(5)	Ir(2)	C(4)	F(4)	115(1)
Ir(1)	Ir(2)	C(6)	154.9(6)	Ir(2)	C(4)	C(3)	109(1)
P(2)	Ir(2)	P(4)	177.1(2)	F(3)	C(4)	F(4)	102(1)
C(4)	Ir(2)	C(5)	170.1(7)	F(3)	C(4)	C(3)	107(1)
C(4)	Ir(2)	C(6)	83.7(7)	F(4)	C(4)	C(3)	111(1)
C(5)	Ir(2)	C(6)	86.5(8)	Ir(2)	C(5)	O(5)	172(2)
Ir(1)	C(1)	O(1)	179(2)				

Binding of the tetrafluoroethylene molecule in the bridging site has clearly resulted in a rehybridization of the olefinic carbons such that this unit is best described as a dimetallacyclobutane moiety. As a result, all angles around the olefinic carbons are now close to the tetrahedral value and the C(3)−C(4) bond (1.54(3) Å) is that expected for a single bond.[32] The Ir−C bonds to the bridging olefin (2.10(2), 2.10(2) Å) are slightly shorter than that involving the methyl ligand (2.16(2) Å) as might be expected for stronger bonds involving fluoroalkyl groups.[33] Despite the slight asymmetry at

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each metal, the tetrafluoroethylene is symmetrically bridging, with identical bond lengths and angles within the "Ir_2C_2" framework.

Reaction of **7** with 1 equiv of PMe_3 yields the PMe_3 adduct $[Ir_2(CH_3)(PMe_3)(CO)_2(\mu\text{-}C_2F_4)(dppm)_2][CF_3SO_3]$ (**9**). The $^{31}P\{^1H\}$ NMR spectrum of this product shows the dppm resonances at δ −18.2 and −19.0 and the PMe_3 resonance at δ −68.8. This latter signal is a triplet, showing 55 Hz coupling to one end of the tetrafluoroethylene ligand. No coupling between the PMe_3 group and the dppm ^{31}P nuclei is resolved. In the ^{13}C NMR spectrum of a ^{13}CO- and $^{13}CH_3$-enriched sample of **9** the terminal carbonyls appear at δ 185.2 and 180.1 and the methyl group appears at δ −18.9 and displays 14 Hz coupling to the PMe_3 phosphorus nucleus. The ^1H NMR spectrum shows the expected resonances for the phosphines and displays the methyl ligand signal at δ 0.92. Two resonances appear in the ^{19}F NMR spectrum, at δ −70.0 and −83.3, with the former displaying the above-noted 55 Hz coupling to PMe_3.

On the basis of the reaction of **7** with CO, in which the added carbonyl occupies the axial site opposite the metal−metal bond, we had anticipated that PMe_3 would react likewise. This proposal is supported by the observed 14 Hz coupling in the ^{13}C NMR spectrum between the $^{13}CH_3$ and the PMe_3 groups. Such coupling through the metal−metal bond has been observed when the ligands occupied the axial sites.[25c,34] However, the very large coupling (55 Hz) between the PMe_3 group and the fluorines on one end of the tetrafluoroethylene ligand strongly suggests that these groups are mutually trans at one metal; this would mean that PMe_3 attack occurred at the unsaturated metal in the site between the metals. By comparison, three-bond P−F coupling when a phosphine ligand is cis to a CF_3 ligand is normally in the range 4−25 Hz,[35] whereas trans coupling in the range 40−50 Hz has been reported.[35c] The location of the PMe_3 group (i.e., trans to or cis to the Ir−Ir bond) at this stage remains uncertain, and we have not succeeded in growing suitable crystals of the complex to unambiguously determine this.

Discussion

In comparing the binding of ethylene and a series of fluoroethylenes to the binuclear complex $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**1**), we observe two olefin binding modes—terminal and bridging—depending upon the degree and nature of the fluorine substitution. For olefins containing three or four fluorines (i.e., tri- or tetrafluoroethylene) only the bridging mode is observed, whereas with zero or one fluorine substituents (ethylene or fluoroethylene) only the terminal, η^2-binding mode is observed. For difluoro substitution, two cases are observed; for *Z*-1,2-difluoroethylene only the terminal mode is observed, whereas for 1,1-difluoroethylene the terminal mode is observed at low temperatures with slow rearrangement to bridging at higher temperatures. We find that only fluoroolefins, having two fluorines on at least one of the olefin carbons, display the bridging coordination mode. On the basis that lower fluorine substitution gives rise to terminal coordination whereas greater substitution favors the bridging mode, it is tempting to conclude that the bridging site is more accessible since it is able to coordinate the bulkier (more substituted) olefins. However, this is inconsistent with the kinetic product in the case of 1,1-difluoroethylene being an η^2-adduct. Furthermore, the electronic effects of substituting hydrogens by the much more electronegative fluorines must also be considered. In the bridging mode, the olefin can be viewed as a dimetallaalkane in which the organic fragment is now saturated, with rehybridization of the olefin carbons to sp^3, as was clearly demonstrated in the structure of the tetrafluoroethylene complex **8**. According to Bent's rule,[36] the electronegative fluorine substituents should favor rehybridization of the olefinic carbons, rendering them *less* electronegative (less s character in the sp^3 compared to sp^2 hybrids). On the basis of this argument, the observation that greater fluorine substitution favors the bridging mode is not surprising. In the case of the difluorinated cases (*Z*-1,2- and 1,1-difluoroethylene) it appears that only the latter olefin, having two fluorines on the same carbon, yields a bridged adduct. From this we assume that more is gained from rehybridization of a CF_2 and a CH_2 carbon than is gained from rehybridization of two CHF carbons. The tendency of *gem*-difluoroolefins to form saturated compounds is well documented.[37] Of course, steric repulsions must also be considered since it may also be that the relative repulsions between the terminal and bridging sites differ between these two olefins.

That no terminal η^2-adduct is observed with either trifluoro- or tetrafluoroethylene, even at low temperature, suggests that this bonding mode is sterically unfavorable. This is especially true for the tetrafluoroethylene adduct **7**, which is formed only slowly, but for which no terminal adduct is observed. Certainly there seems to be no obvious electronic rationale for the absence of η^2-tetrafluoroethylene adducts since there is plenty of documentation in which binding of tetrafluoroethylene to a single low-valent, late transition metal has been shown to be favorable.[14]

We have found that the ^{19}F chemical shift in these fluoroolefin complexes can be diagnostic for the olefin coordination mode. Thus, in the η^2-complexes **3**, **4**, and **5b** the coordination shift of the fluorine nuclei in the ^{19}F NMR spectrum, compared to the free olefin, is toward higher field, whereas in the bridged complexes **5c** and **6**−**9** the shift is to lower field. The changes in chemical shift ($\Delta\delta$) upon complexation are summarized in Table 4. Although for the olefins $HFC{=}CH_2$, *Z*-$CFH{=}CFH$, $HFC{=}CF_2$, and C_2F_4 and for

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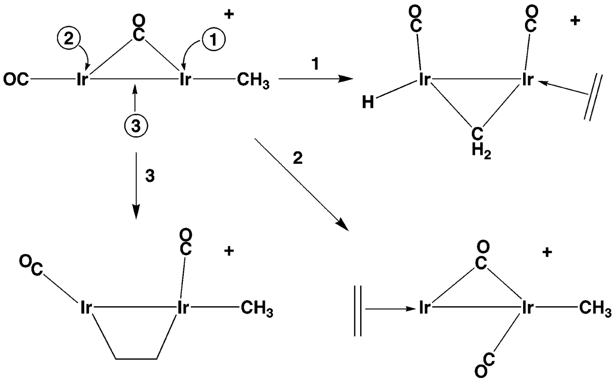
Table 4. Chemical Shift Change upon Coordination for Fluorinated Ethylenes

compound[a]	change in chemical shift upon complex formation (ppm), $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$
$[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CHF{=}CH_2)(dppm)_2]^+$ (**3**)	−56
$[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CHF{=}CHF)(dppm)_2]^+$ (**4**)	−47
$[Ir_2(H)(\mu\text{-}CH_2)(CO)_2(\eta^2\text{-}CH_2{=}CF_2)(dppm)_2]^+$ (**5a**)	2
$[Ir_2(CH_3)(CO)_2(\eta^2\text{-}CH_2{=}CF_2)(dppm)_2]^+$ (**5b**)	−2
$[Ir_2(CH_3)(CO)_2(\mu\text{-}CH_2{=}CF_2)(dppm)_2]^+$ (**5c**)	36
$[Ir_2(CH_3)(CO)_2(\mu\text{-}CHF{=}CF_2)(dppm)_2]^+$ (**6**)	47, 44, 11
$[Ir_2(CH_3)(CO)_2(\mu\text{-}CF_2{=}CF_2)(dppm)_2]^+$ (**7**)	55, 49
$[Ir_2(CH_3)(CO)_3(\mu\text{-}C_2F_4)(dppm)_2]^+$ (**8**)	61, 50
$[Ir_2(CH_3)(PMe_3)(CO)_2(\mu\text{-}C_2F_4)(dppm)_2]^+$ (**9**)	65, 52

[a] In all cases the anion is $CF_3SO_3^-$.

Scheme 5



the bridging $CF_2{=}CH_2$ group these shifts are unambiguous, the η^2-$CF_2{=}CH_2$ complexes **5a** and **5b** undergo shifts of only ±2 ppm from the free olefin. Even here, however, the chemical shift differences between terminal and bridging (i.e., **5a** and **5b** vs **5c**) are substantial (34 and 38 ppm, respectively).

As described earlier, the products in the reactions of **1** with ethylene and selected fluoroolefins can be grouped into three structural types. With 1,1-difluoroethylene all three products are observed at different temperatures, while for the other olefins only one or two of these structure types are observed. These three product types are shown in Scheme 5 (dppm groups above and below the plane of the drawing are omitted and no substituents are shown on the olefin) and can be viewed as resulting from substrate attack at the three different sites on compound **1**. Attack at site 1 forces the methyl ligand toward the adjacent metal, where it undergoes C−H bond cleavage and formation of the methylene-bridged hydride species as observed in **2a** (olefin = ethylene) and **5a** (olefin = 1,1-difluoroethylene). Substrate attack at site 2, between the carbonyls, yields the species in which the methyl and olefin groups lie opposite the metal−metal bond, flanked by the carbonyls. This species type was observed for ethylene (**2b**), fluoroethylene (**3**), *Z*-1,2-difluoroethylene (**4**), and 1,1-difluoroethylene (**5b**). Finally, attack at site 3, between the metals, yields the olefin-bridged products as observed for 1,1-difluoroethylene (**5c**), trifluoroethylene (**6**), and tetrafluoroethylene (**7**). We assume that olefin attack in this last case occurs at one metal, followed by movement of the olefin into the bridging site with concomitant movement of the bridging carbonyl on the opposite face of the complex to a terminal position. Extended Hückel calculations on related dppm-bridged complexes have suggested that direct attack at the metal−metal bond is symmetry forbidden and that an unsymmetrical intermediate is involved.[38]

Attack at sites 1 and 2 is clearly reversible since warming either product type results in regeneration of the free olefin and compound **1**. Furthermore, exchange between free and coordinated fluoroethylene in the olefin adduct **3** was established by ^1H TOCSY NMR experiments. In contrast, attack at site 3 leading to the bridged adducts is apparently irreversible. Although the bridged adducts **5c** and **6** are not stable at ambient temperature, their decomposition leads not to compound **1** and free olefin but to mixtures of unidentified products. We have preliminary evidence suggesting that this results from C−F bond activation via HF loss, which is a subject of ongoing studies.[39] Labilization of a C−F bond in a tetrafluoroethylene-bridged, diiron complex has previously been observed.[14e]

It appears that the methylene hydride species are the least stable products and are not observed at all for the weakly coordinating fluoroethylene and *Z*-1,2-difluoroethylene. Although not observed for these olefins at temperatures down to −80 °C, we assume that this structural type would be observed at lower temperatures. At temperatures above −80 °C the methylene hydride species transform into the more stable olefin adducts $[Ir_2(CH_3)(olefin)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$, which are observed for all olefins in this study except trifluoroethylene and tetrafluoroethylene.

As demonstrated for 1,1-difluoroethylene, the most stable adduct for olefins containing geminal fluorines is the olefin-bridged species. For trifluoro- and tetrafluoroethylene this structural type was the only one observed. Even at temperatures down to −80 °C no η^2-olefin adduct was observed with these olefins. We assume that steric factors inhibit attack at sites 1 and 2 for these highly substituted ethylenes. As noted earlier, the rehybridization of the olefin carbons that accompanies the bridged-olefin bonding mode appears to require at least one CF_2 group within the olefin. Consequently only 1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene achieve the bridging configuration.

The transformations from one isomeric olefin adduct to another at increasing temperature presumably involve olefin loss from one site and recoordination at the next most favorable site. Within the series of olefins investigated only 1,1-difluoroethylene displays the complete set of three isomeric structures, presumably hav-

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ing the appropriate combination of steric factors to allow favorable access to all three sites and electronic factors to allow observation of the least stable adduct (type 1) at low temperature while also favoring the bridging mode at higher temperature.

The olefin−metal bond in an η^2-olefin complex is commonly described in terms of the Dewar−Chatt−Duncanson (DCD) model,[40] in which the two synergic components of the bonding involve σ-donation from the filled olefin π orbital to the metal and π back-donation from the metal into the ligand π^* orbital. On the basis of this model we would anticipate that for a low-valent, late transition metal complex increased substitution by electronegative fluorines on the olefin should strengthen the metal−olefin bond through enhanced π back-donation from the electron-rich metal. This is clearly not the case in the series of olefins studied. Although ethylene forms a stable η^2-adduct at ambient temperature, the mono- and difluoroolefins yield labile adducts only at low temperatures. This decrease in metal−olefin bond strength upon increasing fluorine substitution has previously been observed[14k] and has been ascribed to a combination of steric repulsions involving the fluorine substituents and the greater energy required to deform the coordinated olefinic carbons toward the sp^3 limit, as occurs with increasing fluorine substitution.[41] Only at tetrafluoroethylene does the olefin binding energy match that of ethylene, with both giving isolable complexes at ambient temperature, although in this study these olefins display different binding modes. It is difficult to establish how trifluoroethylene compares since its decomposition at ambient temperature seems not to be a function of olefin binding affinity, but appears to result from other factors (vide supra).

Conclusions

This study has reconfirmed that increasing the fluorine substitution in fluoroolefin ligands does not necessarily lead to increased binding affinity to an electron-rich metal,[14k] as anticipated from the Dewar−Chatt−Duncanson model.[40] We find that the binding affinities of fluoroethylene, *Z*-1,2-difluoroethylene, and 1,1-difluoroethylene, when bound in an η^2-mode to one metal, are less than that of ethylene. This study also demonstrates the greater diversity observed for a binuclear system compared to a similar mononuclear one in which the η^2-olefin binding mode is the only one anticipated. Although such an adduct could display a number of geometric isomers, we would not expect significant chemical differences to arise as a consequence. By contrast, the binuclear species **1** displays three structural types with different olefins. In the product in which C−H activation of the methyl group has occurred one might anticipate coupling of the olefin and the bridging methylene group, although in this study no evidence of such reactivity was observed. Similarly, in the olefin-bridged products migratory insertion of the olefin and the methyl ligand could occur, although again this was not observed; even ligand addition (CO, PMe$_3$) to the tetrafluoroethylene adduct **7** does not induce a migratory−insertion reaction. Nevertheless, the facile decomposition of the olefin-bridged adducts of 1,1-difluoroethylene and trifluoroethylene has suggested that these fluoroolefins could be susceptible to fluoride ion loss in this coordination mode, a reactivity that has precedent in a diiron tetrafluoroethylene-bridged complex.[14e] Studies are underway in pursuit of the idea that binding of fluoroolefins in a bridging arrangement could lead to unusual reactivity of these groups.

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Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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