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Synthesis, Structure, and Reactivity of a Bridging Difluorocarbene Complex, $[CpFeIr(Cl)(CO)_2(PMe_2Ph)_2(\mu\text{-}CO)(\mu\text{-}CF_2)][BF_4]\cdot CH_2Cl_2$

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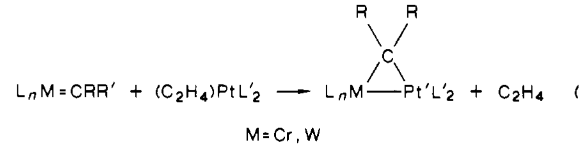
A heterobimetallic complex with a CF_2 bridge, $[CpFeIr(CO)_2(PMe_2Ph)_2(\mu\text{-}CO)(\mu\text{-}CF_2)][BF_4]$ (**1a**), was prepared by the oxidative addition of $[CpFe(CO)_2(CF_2)]^+$ to $Ir(Cl)(CO)(PMe_2Ph)_2$. The $[BPh_4]^-$ salt of the dimetal compound **1a** undergoes a Lewis acid displacement with BCl_3 to generate the BCl_3 adduct of $Ir(Cl)(CO)(PMe_2Ph)_2$ and $[CpFe(CO)_2(CF_2)][BPh_4]$. The crystal structure of **1a** reveals a nearly symmetric CF_2 bridge between Fe and Ir, whereas a CO ligand is in a semibridging position between these two metal atoms. Crystal data: monoclinic, space group $P2_1/n$, a = 9.308 (2) Å, b = 16.447 (3) Å, c = 20.997 (4) Å, β = 98.69 (2)°; Z = 4; 388 parameters were refined on 4901 reflections with $I > 3\sigma(I)$ to yield R = 0.036 and R_w = 0.049.

Introduction

Complexes with bridging CR_2, or carbene, moieties have been known since 1967, and many examples have been prepared.[1] However, bridging dihalocarbene complexes are extremely rare. Several bridging difluorocarbene complexes have been prepared,[2a] and only recently one of these has been structurally characterized by single-crystal X-ray diffraction.[2b] No stable dihalocarbene bridges are known for X = Cl, Br, or I, but a CCl_2-bridged dicobalt complex has been postulated as an intermediate in the formation of $Co_3(CO)_9CCl$ from CCl_4 and $Co_2(CO)_8$ in hexane.[3]

One approach to the synthesis of bridging carbene complexes, developed by Stone and co-workers, involves the reaction of terminal Fischer-type carbene complexes with electron-rich metal centers. This type of reaction exploits the electrophilic character of the carbene ligand (eq 1).[4] A similar strategy has been employed in the present research by using an iron difluorocarbene and an iridium(I) nucleophile to yield a cationic, mixed-metal, bridging difluorocarbene complex.



(1)

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of N_2 by using standard Schlenk techniques[5] or on a vacuum line equipped with Teflon-in-glass valves and O-ring joints. The Schlenkware was silylated and flame-dried prior to use to remove surface moisture. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl, dichloromethane was distilled from P_2O_5, and acetone was distilled from 4A molecular sieves. The following complexes were prepared by literature methods: $Ir(Cl)(CO)(PMe_2Ph)_2$[6] and $[CpFe(CO)_2(CF_2)][BF_4]$.[7] Purification of BCl_3 was accomplished by removing HCl in vacuo at −78 °C.

Table I. Summary of the Crystal Structure Data

formula	$C_{25}H_{27}BO_3F_6P_2ClFeIr\cdot CH_2Cl_2$
M_r	930.67
cryst size, mm	0.41 × 0.37 × 0.32
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	9.308 (2)
b, Å	16.447 (3)
c, Å	20.997 (4)
β, deg	98.69 (2)
V, Å^3	3178 (2)
Z	4
d(calcd), g cm^{-3}	1.92
μ(Mo Kα), cm^{-1}	53.2
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
scan type	$\theta/2\theta$
2θ range, deg	4-50
scan width	0.7 + 0.35 tan θ
no. of unique data	5801
no. of unique data with $I > 3\sigma(I)$	4901
no. of params	388
R	0.036
R_w	0.049

Infrared spectra were recorded on a Perkin-Elmer 283 or 399 spectrometer. NMR spectra were recorded on a JEOL FX-270 (^{31}P, 109.15 MHz; ^1H, 269.65 MHz; ^{13}C, 67.80 MHz) or a Varian XL-400 (^1H, 399.94 MHz; ^{19}F, 376.25 MHz) spectrometer.

Crystallization Data Collection and Structure Determination. Crystallographic data of **1a**·CH_2Cl_2 are summarized in Table I. Diffraction experiments were performed on an Enraf-Nonius CAD4 diffractometer at −120 °C using Mo Kα (λ = 0.71069 Å) radiation. Lattice parameters were determined by the least-squares technique applied to the setting angles of 24 reflections. The intensities of four standard reflections were measured every 3 h of X-ray exposure, showing no significant changes. The data were corrected for Lorentz and polarization effects. Numerical absorption corrections were applied with transmission factors ranging from 0.29 to 0.14.

All calculations were performed on a VAX 11/730 computer using the TEXSAN program package.[8] The structure was solved by Patterson and Fourier techniques. Refinement was performed by full-matrix least-squares calculations initially with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were found from difference Fourier maps and were included in the calculations but not refined. The goodness of fit was 1.72, and the highest peak (2.37 e/Å^3) in the final difference synthesis was located near the Ir atom. Atomic scattering factors were those tabulated by Cromer and

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Table II. Fractional Coordinates of Non-Hydrogen Atoms for $[CpFeIr(Cl)(CO)_2(PMe_2Ph)_2(\mu\text{-}CO)(\mu\text{-}CF_2)][BF_4]\cdot CH_2Cl_2$ (**1a**$\cdot CH_2Cl_2$)

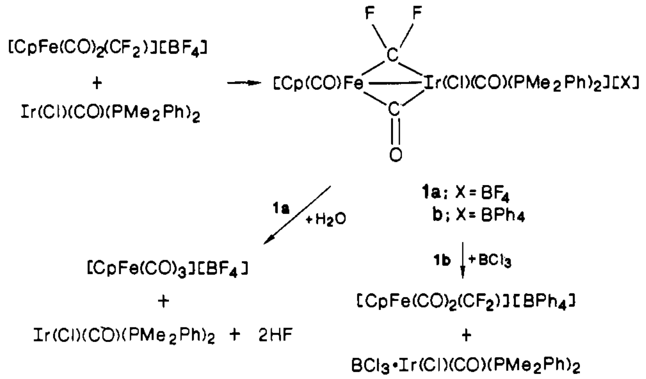
atom	*x*	*y*	*z*
Ir	0.22164 (2)	0.20197 (1)	0.017948 (8)
Fe	0.37569 (8)	0.13720 (4)	0.12636 (3)
Cl1	0.2170 (1)	0.07469 (7)	−0.03667 (6)
Cl2	0.9069 (2)	0.0926 (1)	0.24023 (9)
Cl3	1.0740 (2)	−0.0572 (1)	0.2431 (1)
P1	−0.0414 (1)	0.20749 (7)	0.00266 (7)
P2	0.2571 (1)	0.25675 (8)	−0.08110 (6)
F1	0.5251 (3)	0.1417 (2)	0.0166 (1)
F2	0.5188 (3)	0.2592 (2)	0.0599 (2)
F3	0.0540 (5)	0.3544 (3)	0.1813 (2)
F4	0.0858 (8)	0.2919 (4)	0.2755 (3)
F5	−0.019 (1)	0.4128 (3)	0.2664 (3)
F6	−0.133 (1)	0.3103 (6)	0.2275 (4)
O2	0.0846 (4)	0.0698 (2)	0.1046 (2)
O3	0.2420 (4)	0.3662 (2)	0.0788 (2)
O4	0.4645 (5)	−0.0224 (2)	0.0849 (2)
C1	0.4411 (6)	0.1882 (3)	0.0499 (3)
C2	0.1886 (6)	0.1078 (3)	0.1013 (2)
C3	0.2291 (6)	0.3039 (3)	0.0570 (3)
C4	0.4302 (6)	0.0410 (3)	0.0991 (2)
C5	0.3162 (9)	0.1958 (5)	0.2074 (3)
C6	0.431 (1)	0.2388 (4)	0.1862 (3)
C7	0.5492 (7)	0.1846 (4)	0.1899 (3)
C8	0.5083 (7)	0.1105 (4)	0.2132 (3)
C9	0.3675 (7)	0.1163 (4)	0.2247 (3)
C10	−0.1318 (6)	0.1204 (3)	−0.0379 (3)
C11	−0.1187 (7)	0.2155 (4)	0.0765 (3)
C12	0.1260 (7)	0.2240 (3)	−0.1486 (3)
C13	0.4279 (6)	0.2260 (4)	−0.1041 (3)
C14	−0.1228 (6)	0.2958 (3)	−0.0411 (3)
C15	−0.2061 (6)	0.2901 (3)	−0.1013 (3)
C16	−0.2688 (6)	0.3586 (3)	−0.1328 (3)
C17	−0.2463 (6)	0.4339 (3)	−0.1035 (3)
C18	−0.1646 (6)	0.4404 (3)	−0.0431 (3)
C19	−0.1033 (6)	0.3725 (3)	−0.0122 (3)
C20	0.2610 (6)	0.3670 (3)	−0.0882 (2)
C21	0.1376 (6)	0.4091 (3)	−0.1176 (3)
C22	0.1450 (7)	0.4912 (4)	−0.1280 (3)
C23	0.2742 (7)	0.5333 (3)	−0.1090 (3)
C24	0.3928 (7)	0.4927 (4)	−0.0787 (3)
C25	0.3885 (6)	0.4094 (3)	−0.0681 (3)
C26	0.9019 (8)	−0.0125 (5)	0.2209 (4)
B	0.007 (1)	0.3451 (4)	0.2400 (4)

Waber[9] with anomalous dispersion correction taken from ref 10. Final coordinates for all non-hydrogen atoms of the compound are reported in Table II.

Preparation of $[CpFeIr(Cl)(CO)_2(\mu\text{-}CO)(PMe_2Ph)_2(CF_2)][BF_4]$ (1a). Freshly prepared, solid $[CpFe(CO)_2(CF_2)][BF_4]$ (0.215 g, 0.687 mmol) and $Ir(Cl)(CO)(PMe_2Ph)_2$ (0.263 g, 0.494 mmol) were combined in a silylated, flame-dried Schlenk flask. Approximately 5 mL of CH_2Cl_2 was added to the solids via vacuum transfer from P_2O_5. The slurry was stirred for 20 min at room temperature. The deep orange solution was then filtered through a fritted-glass disk to remove the white solid (excess $[CpFe(CO)_2(CF_2)][BF_4]$, which is insoluble in CH_2Cl_2). The product was crystallized as deep orange crystals by slow diffusion of Et_2O into CH_2Cl_2. Drying in vacuo for 1 h or more removed the CH_2Cl_2 of solvation, as determined by ^1H NMR in acetone-d_6; yield 0.277 g, 66%. Anal. Calcd for $C_{25}H_{27}O_3FeIrClF_6P_2B$: C, 35.50; H, 3.22; Fe, 6.60; Ir, 22.73; F, 13.48; Cl, 4.19. Found: C, 36.18; H, 3.15; Fe, 6.68; Ir, 22.20; F, 13.09; Cl, 4.04. IR (cm^{-1}): ν_{CO} (Nujol mull) 2045 (vs), 1999 (s), 1897 (m); ν_{IrCl} (CsI pellet) 312.

Metathesis of 1a to $[CpFeIr(Cl)(CO)_2(\mu\text{-}CO)(PMe_2Ph)(CF_2)][BPh_4]$ (1b). A solution of **1a** (0.110 g, 0.130 mmol) and $K[BPh_4]$ (0.048 g, 0.134 mmol) in 15 mL of acetone was stirred for 10 min at room temperature. The orange solution was then filtered through a fritted-glass disk to remove insoluble KBF_4 as well as some product, **1b**, which is only slightly soluble in acetone. The remaining solid product was extracted by repeatedly cooling the top flask of the filtration apparatus with liquid N_2, condensing acetone from the solution in the bottom flask. The acetone was then warmed and allowed to pass through the frit, carrying dissolved **1b** to the bottom flask. Upon addition of 10 mL of diethyl ether to the acetone solution and cooling to −20 °C, the orange, microcrystalline product was filtered and dried in vacuo; yield 0.081 g, 58%.

Scheme I



Reaction of 1b with BCl_3. Solid **1b** (0.066 g, 0.61 mmol) was loaded into one side of a silylated, flame-dried H-cell, and 3 mL of CH_2Cl_2 (distilled directly on a high-vacuum line from P_2O_5) was added to form a slurry. Boron trichloride (0.67 mmol) was added to the slurry via vacuum transfer. Stirring for 10 min produced a light yellow solution and a white precipitate. The solution was filtered through the fritted-glass disk in the H-cell, and the contents of the cell were dried in vacuo. The white precipitate was identified by its mull IR spectrum in Nujol as $[CpFe(CO)_2(CF_2)][BPh_4]$,[7] yield 5 mg, 15%. The residue from the yellow solution was extracted three times with 2-mL portions of benzene, and the extracts were filtered, giving a yellow solution. The benzene-insoluble portion was determined to be $[CpFe(CO)_3][BPh_4]$[11] by its IR spectrum in CH_2Cl_2. The benzene solution was reduced in volume to approximately 2 mL and layered with 5 mL of pentane. The resulting pale yellow solid was filtered and dried in vacuo, yielding 9 mg (23% yield) of $BCl_3\cdot Ir(Cl)(CO)(PMe_2Ph)_2$. In a separate experiment this complex was identified by comparison of its ^{31}P NMR and IR spectra with an authentic sample prepared by the addition of 1 equiv of BCl_3 to $IrCl(CO)(PMe_2Ph)_2$. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2040. ^{31}P NMR: δ −24.6 (s).

Reactions of MCX_3 with $Ir(Cl)(CO)(PMe_2Ph)_2$. The complexes $Mn(CO)_5CX_3$ (X = Cl, Br)[12] and $CpFe(CO)_2CCl_3$[12] were allowed to react with 1 equiv of $Ir(Cl)(CO)(PMe_2Ph)_2$ in dichloromethane. The trichloromethyl compounds were allowed to react overnight, and the tribromomethyl complex was allowed to react for 1 h. The reactions were monitored by IR spectroscopy, and the final IR spectra were consistent with the presence of $Mn(CO)_5X$ or $CpFe(CO)_2Cl$ and $IrX_3(CO)(PMe_2Ph)_2$. The identity of the products was confirmed by mass spectrometry. The isotopic envelopes of the parent peaks of $IrX_3(CO)(PMe_2Ph)_2$ were analyzed by the program MASPAN,[13] and they all fit with $R < 10\%$.

Results and Discussion

Synthesis of $[CpFeIr(Cl)(CO)_2(\mu\text{-}CO)(PMe_2Ph)_2(\mu\text{-}CF_2)][BF_4]$ (1a). The iron difluorocarbene complex $[CpFe(CO)_2(CF_2)][BF_4]$ reacts quickly and quantitatively to yield the bridging difluorocarbene mixed-metal compound **1a** (Scheme I). The iridium center formally undergoes oxidative addition from 16-electron Ir(1) to 18-electron Ir(III) (assigning the positive charge to Ir). The product is quite moisture sensitive, undergoing hydrolysis of the μ-CF_2 ligand and dissociation into mononuclear fragments (Scheme I). Complex **1a** is also thermally sensitive. When a sample in $ClCD_2CD_2Cl$ is heated in an NMR tube to 56 °C, rapid decomposition occurs to give a complex mixture of products, including $Ir(Cl)(CO)(PMe_2Ph)_2$. The reaction analogous with the top equation in Scheme I was attempted with the rhodium derivatives $Rh(Cl)(CO)(PR_3)_2$ (R_3 = Me_3, Me_2Ph) and with $Ir(Cl)(CO)(PPh_3)_2$. No reaction was observed in either case, presumably because of the lower basicity of the metal atom in these complexes.

Reactions of MCX_3 with $Ir(Cl)(CO)(PMe_2Ph)_2$. The reactions of the trihalomethyl compounds $Mn(CO)_5CX_3$ (X = Cl, Br) and

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Table III. NMR Spectral Data for **1a**[a]

$^{1}H^{b}$	
7.49–7.03 (m, 10 H, Ph)	1.90 (d, 3 H, Me) [$^{2}J_{P-H}$ = 13.0]
5.3, (s, Cp)	1.73 (d, 3 H, Me) [$^{2}J_{P-H}$ = 16.5]
1.91 (d, 3 H, Me) [$^{2}J_{P-H}$ = 10.1]	1.71 (d, 3 H, Me) [$^{2}J_{P-H}$ = 15.3]
$^{19}F^{c}$	
+46.2 (ddd, 1 F, CF*F'*) [$^{2}J_{F-F'}$ = 58, $^{3}J_{P-F'}$ = 28, $^{3}J_{P'-F'}$ = 15]	
+32.4 (ddd, 1 F, C*F*F') [$^{2}{}_{F-F'}$ = 58, $^{3}J_{P-F}$ = 28, $^{3}J_{P'-F}$ = 8]	
−152.9 (s, 4 F, $[BF_4]^-$)	
$^{31}P\{^{1}H\}^{d}$	
−17.4 (ddd, 1 P, *P'Me*$_2$Ph) [$^{2}J_{P'-P}$ = 20, $^{3}J_{P'-F'}$ = 15, $^{3}J_{P'-F}$ = 8]	
−41.5 (ddd, 1 P, *P*Me$_2$Ph) [$^{2}J_{P'-P}$ = 20, $^{3}J_{P-F'}$ = 28, $^{3}J_{P-F}$ = 28]	
$^{13}C^{b}$	
216.1 (d, μ-*C*O) [$^{2}J_{C-P}$ = 33]	91.7 (d, Cp) [J_{C-H} = 183]
205.2 (d, Fe*C*O) [$^{3}J_{C-F}$ = 18]	15.3 (d, Me)[e] [$^{a}J_{C-P}$ = 33]
202.1 (ddd, *C*F$_2$) [$^{1}J_{C-F}$ = 392, 366, $^{2}J_{C-P}$ = 93]	14.2 (d, Me)[e] [J_{C-P} = 40]
157.2 (s, Ir*C*O)	12.1 (d, Me)[e] [J_{C-P} = 44]
133.2–127.9 (m, Ph)	8.3 (d, Me)[e] [J_{C-P} = 33]

[a] In CD_2Cl_2; chemical shifts in ppm, coupling constants in Hz. [b] Relative to external TMS. [c] Relative to external $CFCl_3$. [d] Relative to external H_3PO_4. [e] ^{1}H decoupled.

Table IV. Selected Bond Lengths for $[CpFeIr(Cl)(CO)_2(PMe_2Ph)_2(\mu\text{-}CO)(\mu\text{-}CF_2)][BF_4]\cdot CH_2Cl_2$ (**1a**·CH_2Cl_2)[a]

Ir–Fe	2.7178 (9)	F2–C1	1.373 (6)
Ir–Cl1	2.384 (1)	O2–C2	1.163 (7)
Ir–P1	2.423 (2)	O3–C3	1.122 (6)
Ir–P2	2.335 (1)	O4–C4	1.143 (6)
Ir–C1	2.064 (5)	C5–C6	1.41 (1)
Ir–C2	2.392 (5)	C5–C9	1.42 (1)
Ir–C3	1.863 (5)	C6–C7	1.41 (1)
Fe–C1	1.986 (5)	C7–C8	1.39 (1)
Fe–C2	1.807 (6)	C8–C9	1.37 (1)
Fe–C4	1.782 (6)	C14–C15	1.384 (8)
Fe–C5	2.102 (6)	C14–C19	1.400 (7)
Fe–C6	2.107 (6)	C15–C16	1.390 (7)
Fe–C7	2.084 (6)	C16–C17	1.385 (8)
Fe–C8	2.088 (6)	C17–C18	1.380 (8)
Fe–C9	2.106 (6)	C18–C19	1.373 (8)
P1–C10	1.807 (6)	C20–C21	1.402 (7)
P1–C11	1.810 (6)	C20–C25	1.387 (8)
P1–C14	1.820 (5)	C21–C22	1.372 (8)
P2–C12	1.807 (6)	C22–C23	1.393 (9)
P2–C13	1.802 (5)	C23–C24	1.363 (9)
P2–C20	1.821 (5)	C24–C25	1.389 (8)
F1–C1	1.361 (6)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

$CpFe(CO)_2CCl_3$ with $Ir(Cl)(CO)(PMe_2Ph)_2$ were undertaken in the hope that they would oxidatively add to the Ir(I) complex, producing a bridging CX_2 ligand. However, this does not occur. Instead, the oxidative addition of two halogen atoms takes place, producing the Ir(III) trihalide (eq 2). In the case of X = Br,

$$L_nMCX_3 + Ir(Cl)(CO)(PMe_2Ph)_2 \rightarrow IrClX_2(CO)(PMe_2Ph)_2 + L_nMX \quad (2)$$

$$X = Cl \text{ or } Br$$

exchange of Br for Cl also occurs. The fate of the carbon originally present as a trihalomethyl group is uncertain.

It is conceivable that a CX_2-bridged species may form as an intermediate in this reaction, but it is unstable and decomposes with C–X bond cleavage to form the Ir(III) trihalide. Carbon–fluorine bond dissociation energies are larger than C–Cl or C–Br bond dissociation energies, which may explain why **1a** and other CF_2-bridged complexes are stable but no CCl_2- or CBr_2-bridged species have been prepared.[2]

Spectroscopy. The infrared spectrum of the carbonyl region of **1a** contains two peaks in the terminal region (2045, 1999 cm^{-1}) and one at lower frequency (1897 cm^{-1}), which could be assigned to a bridging or semibridging CO ligand. The Ir–Cl stretching frequency is also observed at 312 cm^{-1}. A large amount of experimental data supports the fact that Ir–Cl stretching frequencies depend mainly on the nature of the trans ligand and are insensitive to the cis ligand.[14] The observed frequency (312 cm^{-1}) falls in the region typical of Cl ligands trans to CO. The C–F stretching modes were obscured by bands due to the PMe_2Ph ligands.

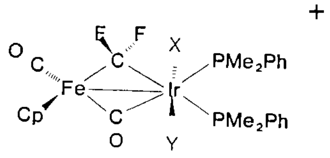
The NMR spectral data for **1a** are summarized in Table III. The ^{19}F NMR spectrum of **1a** displays two resonances for the inequivalent fluorine atoms on the CF_2 bridge, each split into a pattern of eight lines by coupling to the other F and two inequivalent P nuclei. Therefore, the cation of **1a** contains no mirror planes, rendering F atoms of the CF_2 group and the P atoms of the PMe_2Ph ligands inequivalent. Correspondingly, the ^{31}P NMR spectrum shows two resonances for the inequivalent phosphorus nuclei, each split by the other three inequivalent $I = {}^{1}/_{2}$ nuclei.

The low value of $^{2}J_{P-P}$ (20 Hz) indicates that the PMe_2Ph ligands are mutually cis. The ^{1}H NMR spectrum confirms this configuration; each of the four inequivalent methyl groups is split into a doublet, not a pseudotriplet as would be expected for trans-PMe_2Ph ligands.[15]

The bridging carbon atom of the CF_2 ligand appears at 202.1 ppm in the ^{13}C NMR spectrum, a typical position for bridging carbene ligands.[2,4] This resonance consists of eight lines of equal intensity, due to splitting by the two attached fluorines and the phosphorus in the trans position. The coupling to the cis phosphorus is presumably too small to observe.

The ^{13}C NMR resonances due to the CO ligands can be definitively assigned on the basis of chemical shifts and coupling patterns. The farthest downfield peak (d, 216.1 ppm, $^{2}J_{C-P}$ = 33 Hz) is attributed to the bridging carbonyl ligand, coupled to the trans-phosphorus nucleus. The ^{13}C NMR shifts of CO ligands attached to third-row transition metals tend to be upfield of those on first-row metals, so the singlet at 157.2 ppm must arise from the terminal CO on Ir.[16] Since $^{2}J_{C-P}$ is too small to observe, this CO ligand must be cis to the two PMe_2Ph ligands on Ir. The remaining resonance at 205.2 ppm is assigned to the terminal CO on Fe. It exhibits three-bond coupling, J = 18 Hz, to either F2 or P2. A reviewer pointed out that the former is more likely.

Two possible structures, I and II, are consistent with the spectroscopic data. In each configuration, Ir is coordinated by cis-phosphine ligands and a Cl ligand trans to CO. The difference lies in the disposition of the Cl and CO ligands on Ir relative to that of the Cp and CO ligands on Fe. A single-crystal X-ray structure determination was undertaken to distinguish between these two configurations and also to gain information about the bonding of this unusual complex.



I X = CO, Y = Cl

II X = Cl, Y = CO

Reaction with BCl$_3$. Perfluoroalkyl transition-metal complexes are known to undergo halide exchange with boron trihalides.[12,17] In light of this fact, **1b** was treated with BCl_3, in the hope of producing a CCl_2-bridged dimer by halide exchange. The $[BPh_4]^-$ salt **1b** was employed in the reaction with BCl_3 to prevent scrambling of the halides between BCl_3 and $[BF_4]^-$ in **1a**. The

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Table V. Selected Bond Angles for $[CpFeIr(Cl)(CO)_2(PMe_2Ph)_2(\mu\text{-}CO)(\mu\text{-}CF_2)][BF_4]\cdot CH_2Cl_2$ (**1a**$\cdot CH_2Cl_2$)[a]

Fe–Ir–Cl1	91.59 (4)	P1–Ir–C2	83.2 (1)
Fe–Ir–P1	121.36 (4)	P2–Ir–C1	93.8 (2)
Fe–Ir–P2	140.30 (4)	P2–Ir–C2	162.3 (1)
Fe–Ir–C1	46.6 (1)	C1–Ir–C2	85.5 (2)
Fe–Ir–C2	40.8 (1)	Ir–Fe–C2	59.9 (2)
Fe–Ir–C3	90.2 (2)	C4–Fe–C2	88.7 (2)
Cl1–Ir–P1	91.42 (4)	F1–C1–F2	103.0 (4)
Cl1–Ir–P2	84.56 (4)	Ir–C2–Fe	79.3 (2)
Cl1–Ir–C1	90.3 (1)	Ir–C1–Fe	84.3 (2)
Cl1–Ir–C2	77.8 (1)	Ir–C2–O2	126.3 (4)
P1–Ir–P2	98.26 (5)	Fe–C2–O2	154.2 (5)
P1–Ir–C1	167.9 (2)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

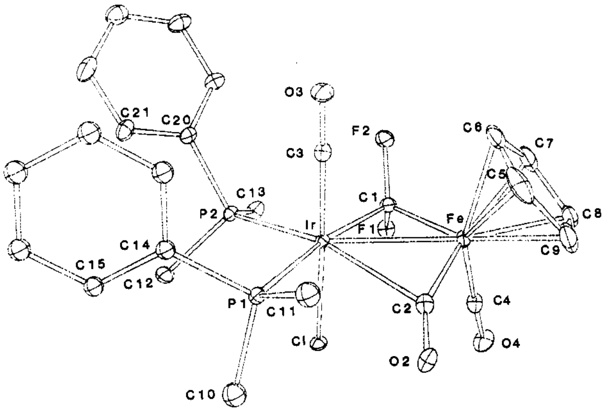

Figure 1. ORTEP diagram of the cation of **1a** showing the numbering scheme.

anticipated reaction did not occur. Instead, BCl_3 split the iron–iridium compound into mononuclear fragments, $[CpFe(CO)_2(CF_2)][BPh_4]$, and the Lewis acid adduct $BCl_3\cdot Ir(Cl)(CO)(PMe_2Ph)_2$ (Scheme I). Reactions between boron trihalides and $M(X)(CO)(PR_3)_2$ complexes are well-known, but the structures of the adducts are uncertain.[18] This reaction suggests that **1** can be described as a donor–acceptor complex. Boron trichloride must behave as a stronger acceptor than $[Cp(CO)_2Fe(CF_2)]^+$, since it displaces the iron fragment.

Structure of 1a·CH_2Cl_2. Bond distances and angles for **1a**·CH_2Cl_2 are listed in Tables IV and V. An ORTEP diagram appears in Figure 1. The structure consists of discrete anions, cations, and dichloromethane molecules of solvation, with no close contacts between these species.

The Ir–Fe distance, 2.7178 (9) Å, is slightly larger than the sum of the covalent radii for these elements.[19] Only two structures of organometallic complexes containing Ir–Fe bonds are available in the literature for comparison. The trinuclear cluster $(\eta^5\text{-}C_5Me_5)IrFe_2(\mu\text{-}CO)_2(CO)_7$ contains two shorter Ir–Fe distances of 2.616 (7) and 2.698 (7) Å, which are bridged by two CO ligands and unbridged, respectively.[20] The distance of 2.960 (1) Å found in the dimer $FeIr(CO)_5(PPh_3)_2(\mu\text{-}PPh_2)$ implies only a weak metal–metal interaction.[21]

As predicted by spectroscopy, the Ir–Fe bond is bridged by both a CF_2 and a CO ligand. The CF_2 ligand bridges symmetrically between the two metals, while the CO is semibridging, with a short C2–Fe and long C2–Ir bond (1.807 (6) and 2.392 (5) Å, respectively). The reason for this weak Ir–C2 interaction may be the steric bulk of the ligands around Ir, which prevents the close approach of C2. The F1–C1–F2 angle of 103.0 (4)° is very close to the analogous F–C–F angle of 102.7 (2)° seen in $Mn_2(CO)_8(\mu\text{-}CF_2)_2$.[2b] These angles are considerably smaller than the F–C–F angles of about 108° usually seen at sp^3-hybridized carbon atoms in organic systems.[22] However, it is not unusual for the R–C–R angle in bridging carbene ligands to vary greatly from the normal sp^3 value.[1]

The geometry around Ir is approximately octahedral. Five vertices of a fairly regular octahedron are described by C1, C4, P1, P2, and Cl. The sixth vertex is assigned to C2, which lies out of the P1–P2–C1–Ir plane, as indicated by the large deviations of the C3–Ir–C2 and C1–Ir–C2 angles from 90° (105.1 (2) and 77.8 (1)°, respectively). The terminal CO ligands are on opposite sides of the Fe–Ir vector, in agreement with the proposed structure II. The PMe_2Ph ligands are mutually cis, as predicted by spectroscopy. The Ir–P2 bond (2.335 (1) Å) is considerably shorter than the Ir–P1 bond (2.423 (2) Å). The Ir–P1 bond, which is trans to the bridging CF_2 group, is the longest Ir–PMe_2Ph bond yet seen.[23] This large trans influence indicates that the bridging CF_2 ligand forms a very strong covalent bond to Ir.[24] Bridging CH_2 moieties are known to be stronger π-acceptors and σ-donors than are bridging CO ligands,[25] and replacement of H by the highly electronegative F would be expected to enhance its strength as an acceptor.

The M–CF_2 bond lengths in terminal CF_2 complexes are shorter than M–CO bond lengths in the same complex, which supports this picture of CF_2 as a stronger π-acceptor than CO.[26] This property may explain why the CO ligand opts for a semibridging interaction with Ir, presumably to relative steric crowding, when CF_2 is actually the bulkier ligand.

Extended Hückel calculations have been reported by Hoffman and co-workers on bridged and unbridged binuclear complexes with octahedral coordination at each metal atom.[25] For d^7–d^7 complexes, the bridging mode $(M_2L_8(\mu\text{-}L')_2)$ is favored by strong acceptor ligands in the bridging position. A comparison of $Mn_2(CO)_{10}$ (unbridged) and $Mn_2(CO)_8(\mu\text{-}CF_2)_2$[2b] (bridged) provides an example of this effect. The cation of **1a** is also formally a d^7–d^7 complex, if the CF_2 ligand is counted as a neutral two-electron donor. Thus, replacement of the CF_2 bridge with CO would be expected to disrupt the bridging in this complex. This replacement is accomplished by exposure of **1a** to water, as in Scheme I above, which results in not only loss of the bridging interaction but scission of the dimetal compound. Thus, the ability

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of CF_2 to act as a strong acceptor is essential for the integrity of the iron–iridium compound **1a**.

Conclusions

An iridium(I) complex, $IrCl(CO)(PMe_2Ph)_2$, has been shown to undergo oxidative addition by a cationic difluorocarbene complex, $[CpFe(CO)_2(CF_2)]^+$. The product is an unusual CF_2-bridged compound with an Fe–Ir bond. The iron difluorocarbene cation can be displaced by using BCl_3, which generates the BCl_3 adduct of $Ir(Cl)(CO)(PMe_2Ph)_2$.

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Registry No. **1a**, 112173-03-2; **1a**·CH_2Cl_2, 112318-74-8; **1b**, 112318-73-7; $[CpFe(CO)_2(CF_2)][BF_4]$, 88211-34-1; $Ir(Cl)(CO)(PMe_2Ph)_2$, 21209-82-5; $[CpFe(CO)_2(CF_2)][BPh_4]$, 112173-04-3; $[CpFe(CO)_3][BPh_4]$, 31781-41-6; $Mn(CO)_5CCl_3$, 86392-59-8; $Mn(CO)_5CBr_3$, 86392-60-1; $CpFe(CO)_2CCl_3$, 86392-66-7; $K[BPh_4]$, 3244-41-5; BCl_3, 10294-34-5; Fe, 7439-89-6; Ir, 7439-88-5; BCl_3·$Ir(Cl)(CO)(PMe_2Ph)_2$, 112481-46-6.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and additional bond lengths and angles, a ^{19}F NMR spectrum of CF_2 resonances of **1a**, and a ^{31}P NMR spectrum of **1a** (4 pages); a table of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Protonation and Bonding in Heterometallic Butterfly Carbide Clusters

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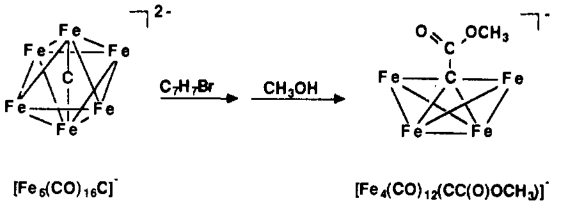
The protonation of the heterometallic butterfly carbide clusters $[CrFe_3(CO)_{13}C]^{2-}$, $[WFe_3(CO)_{13}C]^{2-}$, $[MnFe_3(CO)_{13}C]^-$, and $[RhFe_3(CO)_{12}C]^-$ was studied by multinuclear NMR spectroscopy, and the protonation products were characterized. With 1 equiv of acid all of the clusters protonate at the carbide ligand to produce an agostic C–H–Fe linkage with a wingtip iron atom. This contrasts with the behavior of the isoelectronic homometallic cluster $[Fe_4(CO)_{12}C]^{2-}$, for which the first proton adds across the Fe–Fe hinge of the cluster. Fenske–Hall molecular orbital calculations were carried out for $[RhFe_3(CO)_{12}C]^-$ and $[MnFe_3(CO)_{13}C]^-$, and the electronic structures of these heterometallic clusters were compared with that of $[Fe_4(CO)_{12}C]^{2-}$. The introduction of a heterometal perturbs the metal framework bonding orbitals, and the relative energies of the resulting orbitals depend on the nature of the heterometal. In both heterometallic clusters the nature of the HOMO correlates with the site of proton attack.

Introduction

Reactivity of a cluster-bound carbide ligand was first reported by Bradley and co-workers, who discovered that the oxidative degradation of a hexametallic iron carbide cluster leads to a tetranuclear cluster with a functionalized carbide ligand:[1]

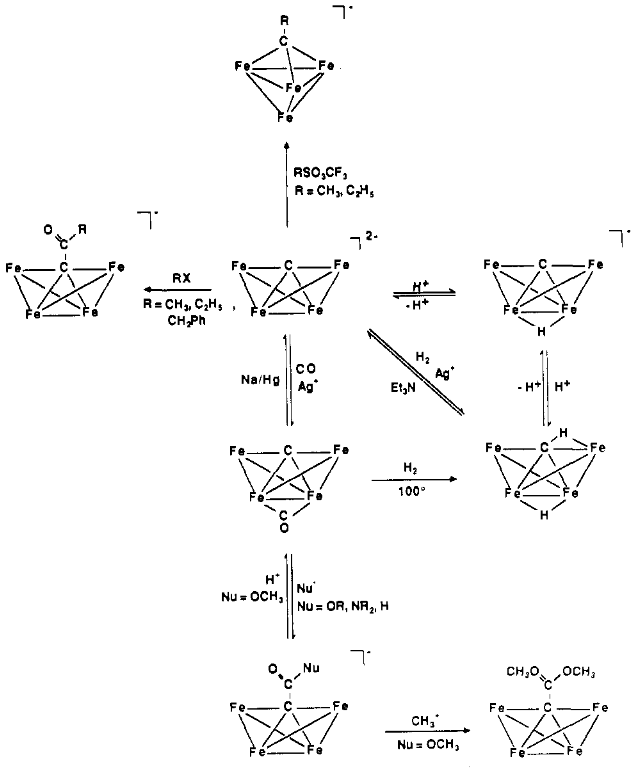


(1)

This work was quickly followed by the isolation and characterization of a family of four-iron carbide clusters: $[Fe_4(CO)_{12}C]^{2-}$, $[HFe_4(CO)_{12}C]^-$, and $Fe_4(CO)_{13}C$.[2-4] All of these compounds display reactivity at the carbide ligand, and several reactions involving C–H or C–C bond formation have been reported (Scheme I).[1-6]

Earlier we reported the syntheses of the mixed-metal butterfly carbide clusters $[CrFe_3(CO)_{13}C]^{2-}$, $[WFe_3(CO)_{13}C]^{2-}$, $[MnFe_3(CO)_{13}C]^-$, and $[RhFe_3(CO)_{12}C]^-$.[7,8] These clusters are all "isoelectronic" with the four-iron carbide cluster $[Fe_4(CO)_{12}C]^{2-}$, but they are characterized by the presence of a heterometal occupying one of the hinge positions in the metal butterfly framework. In this paper we describe a study aimed at determining how both the reactivity and the electronic structure of these clusters are affected by the introduction of a heterometal into the metal butterfly framework. It is quite common for bimetallic catalysts to exhibit activity that is greater than the sum of the activities of the individual metals;[9] so it is of interest to explore how the presence of a heterometal in a molecular cluster affects the reactivity. It is equally important, however, to study how the introduction of a heterometal alters the electronic structure of a

Scheme I



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