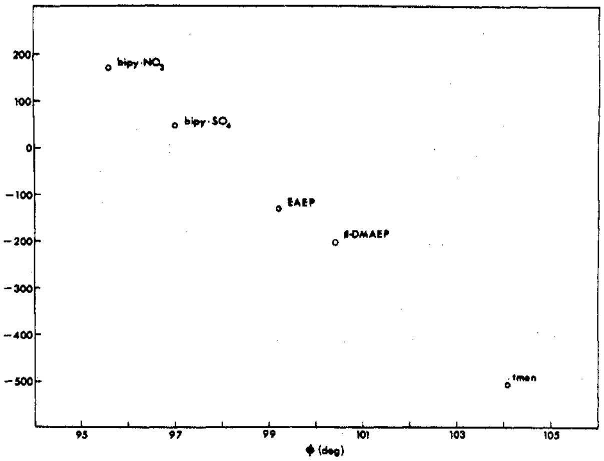

**Figure 5.** Plot of the Cu–O–Cu bridging angle, $\phi$, *vs.* the singlet–triplet splitting, $2J$, for the five completely characterized dihydroxo-bridged copper(II) complexes.

inverse relationship between the copper-copper separation and the magnitude of the exchange energy indicates that direct exchange is not present in these systems but that superexchange *via* the bridging ligands is the mechanism responsible for the spin-spin interaction.

A comparison of the structures of the $\alpha$ and $\beta$ forms of the DMAEP complex reveals some information which is germane to the question of the mechanism of the exchange interaction. The copper-copper separation in the $\alpha$ form is 2.94 Å, the mean Cu-O in-plane length is 1.94 Å, and the Cu-O-Cu bridge angle is 98.4°. Perhaps the most important difference in the two forms is that the long out-of-plane Cu-O bond in the $\alpha$ form is part of a bidentate perchlorato bridge.[14]

Preliminary magnetic susceptibility data[16] indicate that the exchange interaction in the $\alpha$ form results in a singlet ground state with $|2J|$ less than 10 cm$^{-1}$. Although the bridge angle correlation would predict a smaller singlet-triplet splitting for $\alpha$-DMAEP than for $\beta$-DMAEP, the predicted value of $2J$ (see Figure 5) should be closer to $-60$ cm$^{-1}$. Thus, as would be expected for a superexchange mechanism, the perchlorato bridge significantly affects the exchange interaction and appears to make a positive contribution to it. This is not necessarily to say that the perchlorate bridge transmits spin-spin interactions by superexchange, but that the presence of four bridges in the $\alpha$ form complicates the discussion of the spin-spin coupling mechanism and removes the $\alpha$ form from the class of compounds which obeys the near linear $2J$ *vs.* $\phi$ relationship.

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**Registry No.** $\beta$-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$, 50600-14-1.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1013.

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# Carbene Precursors and Metal Complexes. Synthesis and Structure Determination of Chloro(difluoromethyl)(*O*-chlorodifluoroacetato)carbonylbis(triphenylphosphine)iridium(III)-Benzene, IrCl(CHF$_2$)(OCOCF$_2$Cl)(CO)(PPh$_3$)$_2$·C$_6$H$_6$

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The complex IrCl(CHF$_2$)(OCOCF$_2$Cl)(CO)(PPh$_3$)$_2$ has been isolated as the initial product from the reaction between IrCl(CO)(PPh$_3$)$_2$ and the difluorocarbene percursor NaCF$_2$ClCOO. Its crystal and molecular structure have been determined from three-dimensional X-ray data collected by the $\theta$-$2\theta$ scan technique and refined by least-squares methods to a discrepancy factor of 0.048 based on 3759 reflections with $F_o^2 > 5.0\sigma(F_o^2)$. The complex crystallizes in space group $P\bar{1}$ of the triclinic system with cell dimensions of $a = 18.31$ (2) Å, $b = 12.15$ (1) Å, $c = 10.92$ (1) Å, $\alpha = 106.98$ (5)°, $\beta = 94.75$ (5)°, $\gamma = 108.98$ (5)°, and $V = 2154$ Å$^3$. The experimental and calculated densities of 1.60 (2) and 1.60 g/cm$^3$ agree for $Z = 2$ with one molecule of benzene per molecule of complex. An essentially octahedral coordination geometry about the iridium is found with the difluoromethyl group and the O-coordinated chlorodifluoroacetate in trans positions. Evidence for the existence of the hydrogen atom in the proposed difluoromethyl group is discussed. The Ir–C bond length of 2.09 (2) Å indicates that the –CHF$_2$ group is coordinated solely as a $\sigma$ donor. The chlorodifluoroacetate ion coordinates in monodentate fashion with an Ir–O distance of 2.12 (1) Å. Despite the monodentate coordination of the carboxylate group, the two C–O distances do not differ significantly, averaging 1.25 (2) Å. All other structural parameters are as expected for an Ir(III) octahedral complex.

## Introduction

There are presently many reported examples of metal-carbene complexes, most of which have been synthesized by the conversion of coordinated carbonyl or isocyanide ligands to coordinated carbenes.[2] In addition, other carbene complexes have been synthesized by procedures ranging from sub-

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(2) For reviews of this area see E. O. Fischer, *Pure Appl. Chem.*, 30, 1161 (1972); F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 16, 487 (1972).

stitution at the carbene carbon[3] to intramolecular cyclization reactions[4] and proposed three fragment oxidative additions.[5] In our laboratory, we have been investigating the possibility that a carbene generated from a known carbene precursor could be stabilized *via* coordination to a transition metal ion thus yielding a stable carbene complex. Stabilization of the carbene ligand would result from $d\pi \rightarrow p\pi$ bonding. In 1966 a reaction of this type between Vaska's complex, $IrCl(CO)(PPh_3)_2$, and diazomethane was reported by Mango and Dvoretzky,[6] and an intermediate methylene complex was proposed. However, this complex was never completely characterized and its $\nu_{CO}$ of 1942 $cm^{-1}$ is more indicative of a resultant chloromethyl complex than of a stabilized carbene system. In our studies we have focused on trihaloacetate ions and in particular chlorodifluoroacetate as our carbene precursors. To date, we have found that the difluorocarbene precursor $NaCF_2ClCOO$ reacts with Vaska's complex in two different ways.[7] Initially, the reaction yields $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$, which can then quantitatively decompose to $IrCl_2(CHF_2)(CO)(PPh_3)_2$. Although these complexes are not the hoped for difluorocarbene systems, they do possess two interesting structural features which may have important chemical implications. The first of these is the occurrence of the difluoromethyl group in the two complexes for which a novel mechanism involving a metallo carbanion is proposed. The second is the decomposition of the coordinated acetate in going from the title complex to $IrCl_2(CHF_2)(CO)(PPh_3)_2$, apparently analogous to the generation of $CF_2$ from the free chlorodifluoroacetate ion.[8]

In this paper we report the synthesis and structure determination of the first of these complexes, $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$. A preliminary communication of these results has been published.[7]

## Experimental Section

**Preparation of $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$.** A 0.61-g sample of dry $NaCF_2ClCOO$ (prepared from $CF_2ClCOOH$ and NaOH), 0.78 g of $IrCl(CO)(PPh_3)_2$, and 30 ml of diglyme (dried and distilled over $LiAlH_4$) are refluxed with stirring under nitrogen. After 6 min, the yellow mixture rapidly changes color to white. The reaction flask is immediately removed from the heat and filtered to remove NaCl and excess $NaCF_2ClCOO$. Cooling of the filtrate and addition of hexane yields the desired complex in about 80% yield. The compound can be further purified by recrystallization using a benzene-hexane mixture.

Ir ($cm^{-1}$): $\nu_{CO}$ 2065; $\nu_{-CHF_2}$ 2940 (C–H), 1090, 950; $\nu_{acetate}$ 1670 (C–O), 1370 (C–O), 1140 (C–F), 850, 820.

*Anal.* Calcd for $C_{40}H_{31}Cl_2F_4IrO_3P_2 \cdot C_6H_6$: C, 53.2; H, 3.5; F, 7.3; Cl, 6.8. Found: C, 53.1; H, 3.7; F, 5.9; Cl, 6.9.

**Collection and Reduction of the X-Ray Data.** Single-crystal precession and Weissenberg photographs of $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2 \cdot C_6H_6$ showed no systematic extinctions or other indications of symmetry. Therefore, a primitive *reduced* cell for the triclinic space group $P\bar{1}$ (No. 2-$C_i^1$)[9] was chosen with cell dimensions, refined[10] from centering 17 reflections on a diffractometer, of $a$ = 18.31 (2) Å, $b$ = 12.15 (1) Å, $c$ = 10.92 (1) Å, $\alpha$ = 106.98 (5)°, $\beta$ = 94.75 (5)°, $\gamma$ = 108.98 (5)°, and $V$ = 2154 Å$^3$. The assumption of the centrosymmetric space group $P\bar{1}$ is justified by the satisfactory agreement ultimately obtained. A calculated density of 1.60 g/cm$^3$ for two formula weights of $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2 \cdot C_6H_6$ agrees with an experimental density of 1.60 (2) g/cm$^3$ obtained by the flotation method.

A clear colorless crystal mounted on a glass fiber along the $a^*$ axis was used for data collection on a Picker automated diffractometer. The crystal, of dimensions 0.44 × 0.22 × 0.14 mm, was found to have an average mosaic spread of 0.24° as determined from open-counter, narrow-source $\omega$ scans of several strong reflections.[11]

The intensity data were collected by the $\theta$–$2\theta$ scan technique using Zr-filtered Mo K$\alpha$ radiation at a 1.5° takeoff angle. An unsymmetrical scan range in $2\theta$ was used from $-0.6$ to $+0.7°$ of the Mo K$\alpha$ value of the peak with allowance made for K$\alpha_1$-K$\alpha_2$ separation. Data were collected for reflections with $2\theta$ values between 5 and 50° at a scan rate of 1°/min and with background counts of 10 sec at each end of the scan. As participants in a single-crystal radiation damage survey conducted by Abrahams,[12] we monitored nine standard reflections plus their Friedel-related pairs at least 10 times over the entire data collection period. No standard deviated by more than 4% from its mean value, and although a general decline of most of the standards was observed, no attempt was made to correct for this.

The intensities of 8062 independent reflections were measured and corrected for the usual Lorentz and polarization effects to yield a set of $|F_o|^2$ values where $F_o$ is the observed structure factor amplitude. This led to 5815 reflections having $F_o^2 \geqslant 2\sigma(F_o^2)$. The sigmas were estimated according to the formula

$$\sigma(F_o^2) = (Lp)^{-1}\{C + 0.825 + 0.25(t_c/t_b)^2(B_1 + B_2 + 1.65) + q^2(C^2 + (B_1 + B_2)^2)\}^{1/2}$$

where $Lp$ is the Lorentz–polarization factor, $C$ is the *estimated* total count obtained in time $t_c$, $B_1$ and $B_2$ are the *estimated* background counts each obtained in time $t_b$, and $q$ is the uncertainty parameter with a value of 0.03 for this structure. Because the Picker instrument truncates the least significant figure from the scaler without proper roundoff, the estimated total count $C$ is the recorded total count $C' + 0.45$, and the estimated background count $B_i$ is the recorded background count $B_i + 0.45$ where $i = 1, 2$. The constants 0.825 and 1.65 appear in the equation for $\sigma(F_o^2)$ as estimates of the errors associated with the 0.45 term which is added to each raw count in calculating $F_o^2$ as a means of eliminating the systematic error resulting from the truncation. It should be noted that the 0.45 term is not a constant, but only a best estimate of the truncated number. Four reflections required attenuation when the diffracted beams exceeded 9000 counts/sec during the scan. The attenuators were brass foil of thickness sufficient to give an attenuation factor of 3.0. At a later stage in the solution of the structure, an absorption correction was performed on the reflections included in the refinements. The linear absorption coefficient $\mu$ of the crystal is 36.78 $cm^{-1}$ and the calculated transmission coefficients ranged from 0.331 to 0.603.[10]

**Solutions and Refinement of the Structure.** The position of the iridium atom was determined from a Patterson map. Refinement of the iridium positional and isotropic thermal parameters led to discrepancy factors of 0.332 and 0.401 for $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, respectively. A succession of difference Fourier maps and least-squares refinement revealed the positions of all the nonhydrogen atoms in the structure except the benzene molecule. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with the weights $w$ taken as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors for the nonhydrogen atoms were taken from Cromer and Waber[13a] while the hydrogen scattering factors were taken from Stewart, *et al.*[13b] The iridium, chlorine, and phosphorus atoms were treated for anomalous dispersion using the values of $\Delta f'$ and $\Delta f''$ tabulated by Cromer.[14] Throughout all refinements, the phenyl rings were treated as rigid groups ($d$(C–C) = 1.392 Å, $d$(C–H) = 0.95 Å) in the manner described previously.[15]

Refinement of the complex with anisotropic temperature factors

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(10) The programs used in this study were our PICKLST refinement and setting program and local versions of the Busing-Levy ORFLS least-squares program, the Ibers-Doedens group refinement least-squares program, the Zalken FORDAP Fourier program, the Busing-Martin-Levy ORFFE function and error program, and C. K. Johnson's ORTEP plotting program. All computing was performed on Brown University's IBM 360/67 computer.

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**Table I.** Final Positional and Thermal Parameters for $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$

| Atom | $x^a$ | $y$ | $z$ | $B^b$ |
|---|---|---|---|---|
| Ir | −0.21106 (4)[c] | 0.00007 (6) | 0.14495 (7) | *d* |
| Cl(1) | −0.0994 (2) | −0.0613 (3) | 0.1462 (4) | *d* |
| Cl(2) | −0.2353 (5) | 0.1036 (8) | −0.2997 (7) | *d* |
| P(1) | −0.1242 (2) | 0.1989 (4) | 0.2971 (4) | *d* |
| P(2) | −0.2864 (2) | −0.1902 (4) | −0.0294 (5) | *d* |
| F(1) | −0.2543 (7) | 0.0052 (11) | 0.3929 (11) | *d* |
| F(2) | −0.3153 (6) | −0.1721 (10) | 0.2473 (11) | *d* |
| F(3) | −0.1493 (9) | 0.2972 (11) | −0.1224 (15) | *d* |
| F(4) | −0.1045 (9) | 0.1551 (15) | −0.1724 (14) | *d* |
| O(1) | −0.3545 (8) | 0.0640 (12) | 0.1739 (14) | 6.9 (3) |
| O(2) | −0.1740 (6) | 0.0702 (9) | −0.0055 (10) | 3.7 (2) |
| O(3) | −0.2617 (8) | 0.1635 (11) | −0.0122 (13) | 6.6 (3) |
| C(1) | −0.2453 (10) | −0.0780 (16) | 0.2875 (19) | 4.8 (4) |
| C(2) | −0.2998 (12) | 0.0401 (17) | 0.1549 (20) | 5.7 (4) |
| C(3) | −0.2072 (10) | 0.1293 (16) | −0.0486 (18) | 4.8 (4) |
| C(4) | −0.1715 (12) | 0.1735 (19) | −0.1564 (21) | 6.2 (6) |

| Atom[e] | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ir | 25 (0) | 70 (1) | 70 (1) | 18 (0) | 7 (0) | 32 (1) |
| Cl(1) | 32 (2) | 76 (4) | 102 (5) | 23 (2) | 4 (2) | 34 (4) |
| Cl(2) | 119 (5) | 319 (13) | 125 (9) | 18 (7) | −14 (5) | 96 (9) |
| P(1) | 28 (2) | 71 (4) | 68 (5) | 17 (2) | 3 (2) | 24 (4) |
| P(2) | 25 (2) | 73 (4) | 91 (6) | 16 (2) | 48 (3) | 32 (4) |
| F(1) | 62 (6) | 214 (16) | 131 (15) | 44 (8) | 37 (8) | 89 (13) |
| F(2) | 51 (5) | 170 (14) | 146 (16) | −13 (7) | 9 (7) | 76 (12) |
| F(3) | 136 (11) | 125 (15) | 281 (26) | 33 (10) | 89 (14) | 97 (16) |
| F(4) | 96 (8) | 367 (26) | 250 (24) | 116 (13) | 101 (12) | 218 (22) |

Group Parameters

| Group | $x_c{}^f$ | $y_c$ | $z_c$ | $\phi$ | $\theta$ | $\rho$ | $B^b$ |
|---|---|---|---|---|---|---|---|
| P1R(1) | 0.0008 (4) | 0.2145 (6) | 0.5331 (7) | 2.425 (6) | −2.919 (6) | −0.733 (6) | 2.9 (2) |
| P1R(2) | −0.0068 (4) | 0.3593 (6) | 0.1570 (7) | −2.833 (7) | 2.665 (6) | 0.666 (7) | 2.7 (2) |
| P1R(3) | −0.2139 (4) | 0.3709 (6) | 0.4456 (8) | −2.212 (12) | −2.198 (6) | −1.306 (12) | 2.7 (2) |
| P2R(1) | −0.2766 (4) | −0.4500 (7) | −0.0309 (9) | 1.539 (13) | 2.109 (8) | 0.102 (13) | 2.8 (2) |
| P2R(2) | −0.4690 (5) | −0.2284 (7) | −0.0538 (7) | −0.189 (7) | 2.744 (7) | −0.162 (8) | 2.8 (2) |
| P2R(3) | −0.2361 (5) | −0.1962 (6) | −0.3059 (8) | −1.725 (7) | −2.875 (6) | 1.405 (7) | 3.0 (2) |

[a] $x, y, z$ are in fractional coordinates. [b] Isotropic thermal parameters in Å$^2$. [c] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figure. [d] Atoms refined anisotropically. [e] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The anisotropic thermal parameters given are $\times 10^4$. [f] $x_c, y_c, z_c$ are the fractional coordinates of the rigid-group centers. The angles $\phi, \theta, \rho$ have been previously defined: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 771 (1965).

for all iridium, phosphorus, chlorine, and fluorine atoms led to $R_1 = 0.055$ and $R_2 = 0.097$ for 3860 reflections above $5\sigma(F_o{}^2)$ and 181 variable positional and thermal parameters and two scale factors. From the density determination and the elemental analyses, it was apparent that a molecule of benzene was present in the structure as a solvent of crystallization. A difference Fourier map at this point revealed two concentrations of electron density about the centers of symmetry ($^1/_2$, $^1/_2$, $^1/_2$) and ($^1/_2$, 0, $^1/_2$). Various attempts to refine the benzene molecules showed them to be disordered. Both individual atom and rigid-group models were employed but no model for the disordered benzenes refined satisfactorily. After numerous attempts it was finally decided to abandon any further efforts along these lines since the amount of computer time required and the influence of the solvent molecules on the rest of the structure did not seem to justify the cost. The residual peaks on the final difference Fourier map due to the disordered benzene molecules range from 50 to 20% of the lowest density carbon atom in the rest of the structure.

After the elimination of a number of redundant reflections (the $h\bar{k}0$'s) and a number of incorrectly measured reflections, several additional cycles of least-squares refinement were performed. The parameters obtained from the final refinement with $R_1 = 0.048$ and $R_2 = 0.073$ are taken as the final parameters of the structure. In Table I, all positional, thermal, and group parameters for the structure are presented. Table II presents a tabulation of the positional parameters of the phenyl ring carbon and hydrogen atoms along with their isotropic temperature factors. In Table III the root-mean-square amplitudes of vibrations for the anisotropically refined atoms are given. A tabulation of the 3759 observed and calculated structure factor amplitudes used in the final refinements of the structure is available upon request.[16]

## Description of the Structure

The crystal structure described by the parameters of Table I, the symmetry of the space group, and the unit cell constants consists of the packing of discrete octahedral complexes and benzene solvent molecules which are disordered about the ($^1/_2$, $^1/_2$, $^1/_2$) and ($^1/_2$, 0, $^1/_2$) centers of symmetry. The closest intermolecular contacts are F(3)· · ·P1RH(4), C(1)· · ·P2R2H(5), F(3)· · ·P2R1H(4), and F(4)· · ·P1R1H(5) at values of 2.457, 2.577, 2.678, and 2.707 Å, respectively. Since all intermolecular contacts are normal, they are not tabulated.

Within the complex the coordination geometry about the iridium atom is octahedral with triphenylphosphine ligands in trans positions. The other trans ligand pairs in the coordination sphere are chlorine and carbonyl, and difluoromethyl and monodentate O-coordinated chlorodifluoroacetate. A stereoscopic view of the complex is presented in Figure 1 and all important intramolecular distances and angles are summarized in Table IV. Selected least-squares planes with deviations of the atoms from their respective planes are given in Table V. Figure 2 presents a view of the inner coordination geometry of the complex with the phenyl rings omitted for clarity.

One of the most unexpected features of the structure is the occurrence of the difluoromethyl ligand, -$CHF_2$. Although the hydrogen atom of the -$CHF_2$ group was not located with certainty in the X-ray study, its presence is strongly supported

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(16) See paragraph at end of paper regarding supplementary material.

**Table II.** Derived Positional and Isotropic Thermal Parameters for Group Atoms

| Group atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| P1R1C(1) | −0.0531 (5) | 0.2038 (10) | 0.4285 (9) | 0.9 (3)[a] |
| P1R1C(2) | 0.0193 (6) | 0.3016 (8) | 0.4701 (10) | 1.4 (3) |
| P1R1C(3) | 0.0732 (5) | 0.3123 (8) | 0.5746 (10) | 1.9 (4) |
| P1R1C(4) | 0.0547 (6) | 0.2253 (11) | 0.6376 (9) | 2.1 (4) |
| P1R1C(5) | −0.0177 (6) | 0.1275 (9) | 0.5961 (11) | 2.4 (4) |
| P1R1C(6) | −0.0716 (5) | 0.1167 (8) | 0.4915 (11) | 2.4 (4) |
| P1R1H(2) | 0.0317 (8) | 0.3607 (11) | 0.4268 (14) | 3.1 |
| P1R1H(3) | 0.1227 (6) | 0.3789 (11) | 0.6033 (15) | 3.1 |
| P1R1H(4) | 0.0915 (8) | 0.2327 (16) | 0.7090 (12) | 3.1 |
| P1R1H(5) | −0.0300 (9) | 0.0683 (12) | 0.6393 (15) | 3.1 |
| P1R1H(6) | −0.1211 (6) | 0.0501 (11) | 0.4628 (15) | 3.1 |
| P1R2C(1) | −0.0612 (6) | 0.2889 (8) | 0.2125 (10) | 0.4 (3) |
| P1R2C(2) | −0.0532 (5) | 0.4109 (9) | 0.2315 (10) | 1.5 (3) |
| P1R2C(3) | 0.0012 (7) | 0.4813 (7) | 0.1760 (12) | 2.7 (4) |
| P1R2C(4) | 0.0475 (7) | 0.4297 (9) | 0.1015 (12) | 2.6 (4) |
| P1R2C(5) | 0.0395 (5) | 0.3077 (9) | 0.0826 (10) | 2.0 (4) |
| P1R2C(6) | −0.0148 (7) | 0.2373 (7) | 0.1381 (11) | 1.4 (3) |
| P1R2H(2) | −0.0849 (7) | 0.4458 (12) | 0.2823 (14) | 3.3 |
| P1R2H(3) | 0.0069 (11) | 0.5646 (8) | 0.1887 (17) | 3.3 |
| P1R2H(4) | 0.0846 (10) | 0.4777 (12) | 0.0637 (17) | 3.3 |
| P1R2H(5) | 0.0713 (7) | 0.2728 (13) | 0.0317 (14) | 3.3 |
| P1R2H(6) | −0.0205 (10) | 0.1540 (8) | 0.1254 (16) | 3.3 |
| P1R3C(1) | −0.1753 (10) | 0.2957 (17) | 0.3827 (10) | 0.7 (3) |
| P1R3C(2) | −0.2280 (6) | 0.3244 (9) | 0.3099 (8) | 2.0 (4) |
| P1R3C(3) | −0.2665 (8) | 0.3996 (15) | 0.3728 (11) | 2.6 (4) |
| P1R3C(4) | −0.2524 (11) | 0.4461 (17) | 0.5085 (11) | 2.9 (4) |
| P1R3C(5) | −0.1998 (7) | 0.4175 (10) | 0.5814 (8) | 3.6 (5) |
| P1R3C(6) | −0.1612 (8) | 0.3423 (15) | 0.5185 (10) | 2.5 (4) |
| P1R3H(2) | −0.2374 (9) | 0.2924 (12) | 0.2172 (8) | 3.3 |
| P1R3H(3) | −0.3025 (13) | 0.4194 (24) | 0.3234 (15) | 3.3 |
| P1R3H(4) | −0.2787 (17) | 0.4975 (27) | 0.5514 (15) | 3.3 |
| P1R3H(5) | −0.1903 (10) | 0.4495 (13) | 0.6740 (8) | 3.3 |
| P1R3H(6) | −0.1253 (13) | 0.3225 (24) | 0.5678 (14) | 3.3 |
| P2R1C(1) | −0.2812 (15) | −0.3365 (11) | −0.0254 (10) | 0.9 (3) |
| P2R1C(2) | −0.2425 (9) | −0.3479 (9) | 0.0827 (9) | 3.6 (5) |
| P2R1C(3) | −0.2379 (10) | −0.4614 (13) | 0.0773 (11) | 4.1 (5) |
| P2R1C(4) | −0.2720 (15) | −0.5634 (11) | −0.0364 (12) | 3.6 (5) |
| P2R1C(5) | −0.3107 (10) | −0.5520 (8) | −0.1445 (10) | 4.1 (5) |
| P2R1C(6) | −0.3153 (9) | −0.4386 (12) | −0.1391 (10) | 3.3 (5) |
| P2R1H(2) | −0.2193 (15) | −0.2781 (11) | 0.1601 (11) | 3.2 |
| P2R1H(3) | −0.2116 (15) | −0.4696 (20) | 0.1508 (13) | 3.2 |
| P2R1H(4) | −0.2689 (24) | −0.6408 (16) | −0.0401 (16) | 3.2 |
| P2R1H(5) | −0.3339 (15) | −0.6219 (10) | −0.2219 (12) | 3.2 |
| P2R1H(6) | −0.3416 (15) | −0.4304 (19) | −0.2126 (11) | 3.2 |
| P2R2C(1) | −0.3905 (5) | −0.2166 (12) | −0.0480 (12) | 0.8 (3) |
| P2R2C(2) | −0.4420 (7) | −0.3076 (10) | −0.0102 (12) | 2.3 (4) |
| P2R2C(3) | −0.5206 (6) | −0.3194 (11) | −0.0160 (13) | 4.8 (5) |
| P2R2C(4) | −0.5476 (5) | −0.2402 (14) | −0.0596 (13) | 4.6 (5) |
| P2R2C(5) | −0.4960 (7) | −0.1491 (11) | −0.0974 (13) | 3.6 (5) |
| P2R2C(6) | −0.4175 (6) | −0.1373 (9) | −0.0916 (11) | 2.5 (4) |
| P2R2H(2) | −0.4234 (10) | −0.3615 (14) | 0.0194 (18) | 3.2 |
| P2R2H(3) | −0.5559 (8) | −0.3814 (15) | 0.0096 (18) | 3.2 |
| P2R2H(4) | −0.6012 (6) | −0.2482 (20) | −0.0636 (20) | 3.2 |
| P2R2H(5) | −0.5147 (10) | −0.0952 (16) | −0.1270 (18) | 3.2 |
| P2R2H(6) | −0.3821 (8) | −0.0753 (13) | −0.1173 (16) | 3.2 |
| P2R3C(1) | −0.2592 (6) | −0.1903 (10) | −0.1867 (9) | 0.7 (3) |
| P2R3C(2) | −0.3153 (5) | −0.2254 (11) | −0.2987 (12) | 2.7 (4) |
| P2R3C(3) | −0.2922 (7) | −0.2313 (10) | −0.4180 (10) | 4.1 (5) |
| P2R3C(4) | −0.2129 (7) | −0.2020 (11) | −0.4252 (9) | 3.2 (5) |
| P2R3C(5) | −0.1569 (5) | −0.1669 (11) | −0.3132 (12) | 2.4 (4) |
| P2R3C(6) | −0.1800 (6) | −0.1611 (8) | −0.1939 (9) | 1.1 (3) |
| P2R3H(2) | −0.3693 (5) | −0.2453 (17) | −0.2934 (17) | 3.0 |
| P2R3H(3) | −0.3302 (9) | −0.2552 (14) | −0.4947 (12) | 3.0 |
| P2R3H(4) | −0.1972 (10) | −0.2061 (16) | −0.5066 (11) | 3.0 |
| P2R3J(5) | −0.1029 (6) | −0.1471 (16) | −0.3185 (17) | 3.0 |
| P2R3H(6) | −0.1419 (7) | −0.1371 (13) | −0.1172 (11) | 3.0 |

[a] See Table I for overall group temperature factors. Individual hydrogen atom temperature factors were not refined and were assigned values to give a sum of 6.0 when added to the group temperature factor.

**Table III.** Root-Mean-Square Amplitudes of Vibration (Å)

| Atom | Min | Intermed | Max |
|---|---|---|---|
| Ir | 0.171 (1) | 0.196 (3) | 0.208 (2) |
| Cl(1) | 0.183 (6) | 0.220 (6) | 0.245 (6) |
| Cl(2) | 0.230 (9) | 0.389 (9) | 0.513 (10) |
| P(1) | 0.178 (7) | 0.204 (7) | 0.213 (7) |
| P(2) | 0.185 (7) | 0.204 (7) | 0.227 (7) |
| F(1) | 0.225 (16) | 0.304 (13) | 0.358 (14) |
| F(2) | 0.218 (15) | 0.269 (15) | 0.401 (14) |
| F(3) | 0.240 (17) | 0.348 (17) | 0.488 (19) |
| F(4) | 0.232 (18) | 0.323 (15) | 0.494 (18) |

**Table IV.** Principal Intramolecular Distances and Angles for $IrCl(CF_2H)(OCOCF_2Cl)(CO)(PPh_3)_2$

| | | | |
|---|---|---|---|
| | Distances, Å | | |
| Ir–Cl(1) | 2.393 (4) | C(2)–O(1) | 1.15 (2) |
| Ir–P(1) | 2.418 (5) | C(3)–O(2) | 1.24 (2) |
| Ir–P(2) | 2.407 (5) | C(3)–O(3) | 1.25 (2) |
| Ir–O(2) | 2.12 (1) | C(3)–C(4) | 1.54 (3) |
| Ir–C(1) | 2.09 (2) | P(1)–P1R1C(1) | 1.83 (1) |
| Ir–C(2) | 1.84 (2) | P(1)–P1R2C(1) | 1.82 (1) |
| C(1)–F(1) | 1.35 (2) | P(1)–P1R3C(1) | 1.83 (2) |
| C(1)–F(2) | 1.34 (2) | P(2)–P2R1C(1) | 1.82 (2) |
| C(4)–F(3) | 1.35 (2) | P(2)–P2R2C(1) | 1.81 (1) |
| C(4)–F(4) | 1.33 (2) | P(2)–P2R3C(1) | 1.83 (1) |
| C(4)–Cl(2) | 1.68 (2) | | |
| | Angles, Deg | | |
| Ir–C(1)–F(1) | 111 (1) | O(2)–Ir–C(1) | 176.4 (6) |
| Ir–C(1)–F(2) | 113 (1) | O(2)–Ir–C(2) | 98.0 (7) |
| F(1)–C(1)–F(2) | 105 (1) | C(1)–Ir–C(2) | 84.8 (8) |
| Cl(1)–Ir–P(1) | 86.8 (1) | Ir–C(2)–O(1) | 173 (2) |
| Cl(1)–Ir–P(2) | 90.0 (1) | Ir–O(2)–C(3) | 122 (1) |
| Cl(1)–Ir–O(2) | 87.3 (3) | O(2)–C(3)–O(3) | 129 (2) |
| Cl(1)–Ir–C(1) | 89.9 (5) | O(2)–C(3)–C(4) | 114 (2) |
| Cl(1)–Ir–C(2) | 174.8 (6) | O(3)–C(3)–C(4) | 116 (2) |
| P(1)–Ir–P(2) | 171.6 (2) | C(3)–C(4)–Cl(2) | 111 (1) |
| P(1)–Ir–O(2) | 86.6 (3) | C(3)–C(4)–F(3) | 110 (2) |
| P(1)–Ir–C(1) | 95.4 (5) | C(3)–C(4)–F(4) | 113 (2) |
| P(1)–Ir–C(2) | 94.0 (6) | Cl(2)–C(4)–F(3) | 110 (2) |
| P(2)–Ir–O(2) | 85.5 (3) | Cl(2)–C(4)–F(4) | 109 (2) |
| P(2)–Ir–C(1) | 92.3 (5) | F(3)–C(4)–F(4) | 103 (2) |
| P(2)–Ir–C(2) | 89.9 (6) | | |

**Table V.** Weighted Least-Squares Planes (in Monoclinic Coordinates) and the Distances of Atoms from Their Respective Planes

| Atom | Distance, Å | Atom | Distance, Å |
|---|---|---|---|
| Plane through Ir, O(2), O(3), C(3), and C(4)<br>$6.26x + 6.07y + 4.30z = -0.70$ | | | |
| Ir | 0.000 (1) | C(3) | −0.02 (2) |
| O(2) | 0.01 (1) | C(4) | 0.01 (2) |
| O(3) | 0.00 (1) | | |
| Plane through Ir, Cl(1), P(1), P(2), and C(2)<br>$-3.78x - 6.78y + 10.00z = 2.24$ | | | |
| Ir | 0.009 (1) | P(2) | −0.161 (5) |
| Cl(1) | 0.014 (4) | C(2) | 0.17 (2) |
| P(1) | −0.146 (4) | | |
| Plane through Ir, P(1), P(2), O(2), and C(1)<br>$17.18x - 7.68y + 0.61z = -3.53$ | | | |
| Ir | −0.004 (1) | O(2) | 0.00 (1) |
| P(1) | 0.056 (4) | C(1) | 0.10 (2) |
| P(2) | 0.056 (4) | | |
| Plane through Ir, Cl(1), O(2), C(1), and C(2)<br>$3.84x + 7.09y + 4.38z = -0.18$ | | | |
| Ir | 0.000 (1) | C(1) | −0.06 (2) |
| Cl(1) | 0.000 (4) | C(2) | −0.01 (2) |
| O(2) | −0.02 (1) | | |

by the stereochemistry at C(1) and the neutral charge and diamagnetism of the complex. The bond angles at C(1) are Ir-C(1)-F(1) = 111 (1)°, Ir-C(1)-F(2) = 113 (1)°, and F(1)-C(1)-F(2) = 105 (1)°. These values clearly indicate a tetrahedral geometry at C(1) as opposed to the trigonal hybridization of carbene carbon atoms found in the structures of known carbene metal complexes.[2,17] As would be expected,

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[17] R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 653 (1972), and references therein.

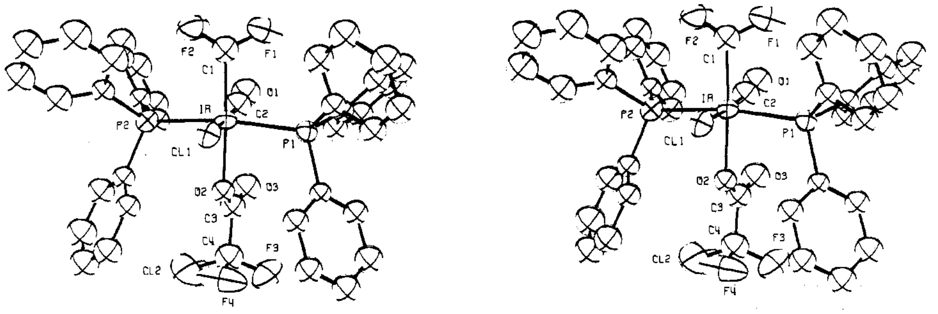

**Figure 1.** A stereoscopic view of the complex $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$.

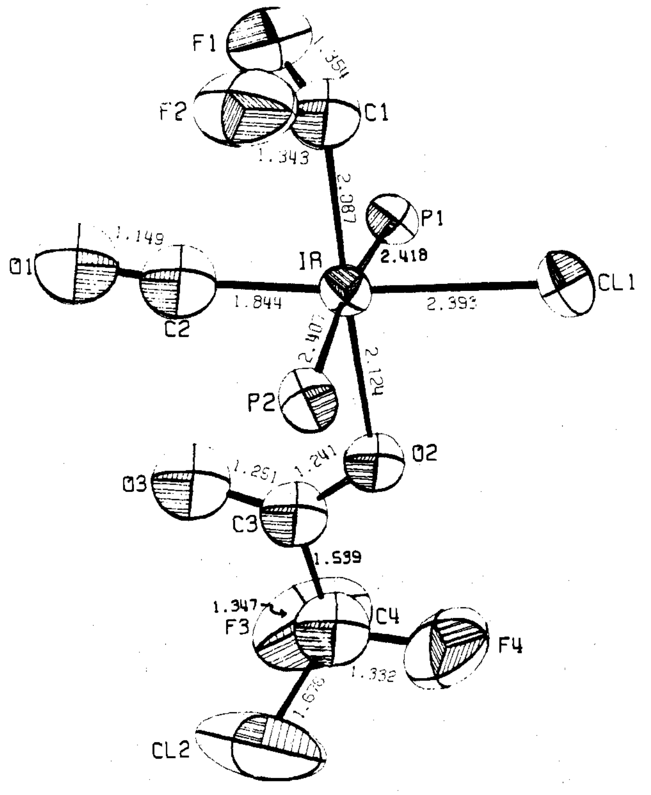

**Figure 2.** The inner coordination geometry of $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$ with the phosphine substituents omitted for clarity.

the Ir-C(1) bond length of 2.09 (2) Å suggests that the difluoromethyl group is coordinating to the Ir(III) ion exclusively as a $\sigma$ donor. This contrasts with the synergic bonding interaction between the metal and the carbonyl ligand which gives an Ir-C(2) bond length of 1.84 (2) Å. The $Ir-CHF_2$ bond length is slightly and possibly significantly shorter than the corresponding value of 2.19 (3) Å in $IrCl_2(CHF_2)(CO)(PPh_3)_2$[7] but is similar to $Ir(III)-CH_3$ distances reported in other structures such as 2.05 (4) Å in $IrI(CH_3)(NO)(PPh_3)_2$[18] and 2.10 (2) Å for $[IrCl_2(CH_3)(CO)_2]$.[19,20] Other evidence for the presence of the hydrogen atom bonded to C(1) is based on deuterium substitution as has been described in the preliminary report of this work.[7] While $\nu_{C-H}$ in the difluoromethyl group of both the title complex and its decomposition product, $IrCl_2(CHF_2)(CO)(PPh_3)_2$, are *ca.* 2940 $cm^{-1}$, the deuterium analog of the decomposition product exhibits $\nu_{C-D}$ at 2200 $cm^{-1}$. This evidence is taken as confirmation of the formulation of the ligand as $-CHF_2$.

The chlorodifluoroacetate ion is coordinated in a monodentate fashion with an Ir-O bonding distance of 2.12 (1) Å and an Ir· · ·O nonbonding distance of 3.27 (1) Å. Despite the unsymmetrical coordination, the two C-O bond lengths in the carboxylate group are nearly identical (C(3)-O(2), 1.24 (2) Å, and C(3)-O(3), 1.25 (2) Å), which together with the planar geometry of the C(4)C(3)O(2)O(3) unit, indicates a delocalized structure for the $-CO_2$ moiety. One might have expected a difference in the C-O bond lengths as a result of the increased negative charge localized on the donor atom O(2), and the consequent inequivalence of the two carboxylate resonance structures. This has been observed for $Cu(OCOCH_2Cl)_2(\alpha\text{-pic})_2$,[21] where the C-O bond lengths of 1.22 (1) and 1.29 (1) Å are significantly different. However, this is not the case in the present structure. The average C-F distance of 1.34 (2) Å for both the acetate and the difluoromethyl group compares well with 1.346 (5) and 1.350 (3) Å for ammonium trifluoroacetate[22] and chlorodifluoromethane,[23] respectively, but is longer than the distance of 1.29 (1) Å found in $Mo_2(O_2CCF_3)_4(py)_2$.[24] The C-Cl distance of 1.68 (2) Å is significantly shorter than the corresponding values of 1.788 (9) and 1.747 (2) Å in $Cu(OCOCH_2Cl)_2(\alpha\text{-pic})_2$[21] and $CHF_2Cl$,[23] respectively.

The coordination of the carbonyl, chlorine, and triphenylphosphine ligands is similar to that found in other iridium(III) octahedral structures. The bond angles between cis ligands at the iridium atom range from 84.8 (8) to 95.4 (5)° and the trans angles range from 171.6 (2) to 176.4 (6)°.

## Discussion

The complex $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$ was an unexpected product from the reaction of $CF_2ClCOO^-$ with $IrCl(CO)(PPh_3)_2$. The formation of this complex requires 2 mol of the acetate/mol of Vaska's complex, and the different chemical and structural environments of the $CF_2$ moieties indicate that two different decomposition paths for the acetate ion are promoted by the metal complex. The first of these leads to the formation of the difluoromethyl group which is one of the most intriguing features of the present study. The source of the proton of the $-CHF_2$ group is of special concern because the solvent for the reaction was diglyme which had been dried over $LiAlH_4$. In our communication,[7] we proposed that a metallo carbanion, I, was formed

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(19) N. A. Bailey, C. J. Jones, B. L. Shaw, and E. Singleton, *Chem. Commun.*, 544 (1967).

(20) There appears to be no shortening of the Ir-C bond with increasing fluorine substitution on the carbon atom as has been observed in metal-alkyl complexes of the first transition series elements. See Table VIII of M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 161 (1970).

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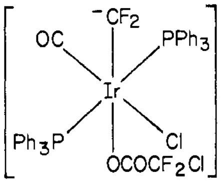


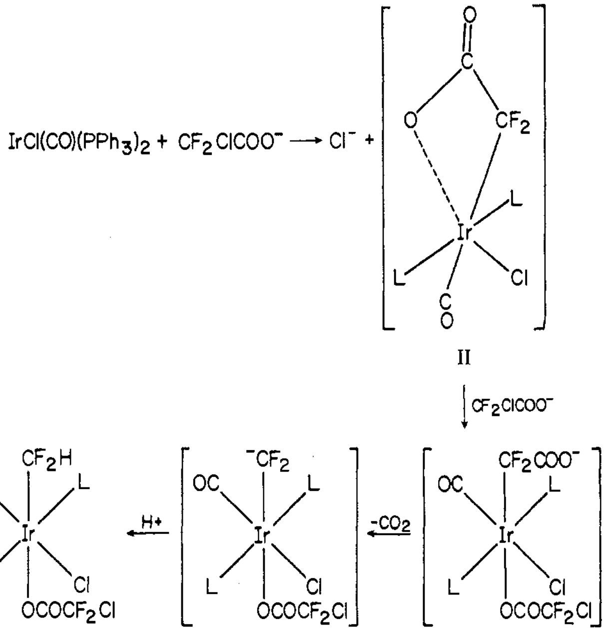
I

as a reactive intermediate and that traces of water in the diglyme served as the proton source. This proposal was tested by repeating the reaction using solvent to which $D_2O$ had been added prior to drying with molecular sieves (Fisher Type 4A). This reaction led to the observation of D-substitution of the difluoromethyl group in $IrCl_2(CDF_2)(CO)(PPh_3)_2$ which is the thermal decomposition product of the title complex. However, the reaction with the molecular sieve dried diglyme did not proceed as smoothly or rapidly as the original reaction and we now believe that diglyme itself serves as the proton source in this reaction. We note that proton abstraction from diglyme has been reported previously[25,26] when strong bases such as $(CH_3)_3CO^-$ and carbanions are present.

In addition, we believe that the steps leading to I should be modified from the previously published scheme. Specifically the formation of I may proceed through an "iridobetaine" intermediate, II, in analogy with the reaction of $CF_2ClCOO^-$ and $PPh_3$ to yield difluoromethylenetriphenylphosphorane.[26] This new proposal eliminates the substitution suggested for the first step in our previous scheme[7] which appears to be incorrect because the corresponding reaction between $IrCl(CO)(PPh_3)_2$ and $CF_3COO^-$ does not yield $Ir(OCOCF_3)(CO)(PPh_3)_2$.

We have been able to disprove an alternative mechanism involving $CF_2$ insertion into a metal-hydride bond by examining the reaction of $IrDCl_2(CO)(PPh_3)_2$ with chlorodifluoroacetate. The deuterated difluoromethyl group is not obtained from this reaction, and only the formation of $-CHF_2$ complexes is observed.

The second decomposition path involves the conversion of $IrCl(CHF_2)(OCOCF_2Cl)(PPh_3)_2$ to $IrCl_2(CHF_2)(CO)(PPh_3)_2$ with the possible generation of difluorocarbene. This reaction and its implications will be dealt with more fully in a subsequent paper.[27]



II

I

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**Registry No.** $NaCF_2ClCOO$, 1895-39-2; $IrCl(CO)(PPh_3)_2$, 15318-31-7; $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2 \cdot C_6H_6$, 50600-51-6.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1019.

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