Journal of Organometallic Chemistry, 72 (1974) 415–423
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CARBENE PRECURSORS AND METAL COMPLEXES

THE SYNTHESIS AND STRUCTURE OF DICHLORO(DIFLUOROMETHYL)CARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(III), $IrCl_2(CHF_2)(CO)(PPh_3)_2$

ARTHUR J. SCHULTZ, JAMES V. McARDLE, GYANESHWARI P. KHARE
Department of Chemistry, Brown University, Providence, Rhode Island 02912 (U.S.A.)
and RICHARD EISENBERG*
Department of Chemistry, University of Rochester, Rochester, New York 14627 (U.S.A.)
(Received July 25th, 1973)

Summary

The complex $IrCl_2(CHF_2)(CO)(PPh_3)_2$ is synthesized by the thermal decomposition of $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$ or by the extended reaction of Vaska's complex, $IrCl(CO)(PPh_3)_2$, with the carbene precursor $CF_2ClCOONa$. The crystal and molecular structure of $IrCl_2(CHF_2)(CO)(PPh_3)_2$ has been determined from three dimensional X-ray data by standard heavy atom methods. The complex crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions a 10.47(1), b 14.45(2), c 24.58(2) Å, β 97.68(5)° and V 3865 Å^3. The molecular structure of the complex consists of a slightly distorted octahedron with *trans* phosphine ligands. The difluoromethyl group is *trans* to a chlorine atom with an Ir—C(1) distance of 2.19(3) Å. The existence of the proton of the difluoromethyl group is suggested by the bond angles about C(1), and is confirmed by a deuterium labelling experiment. The thermal composition of $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$ to give $IrCl_2(CHF_2)(CO)(PPh_3)_2$ in quantitative yield is discussed as a means of generating CF_2. Extension to other O-coordinated α-halocarboxylates is proposed.

Introduction

The interest in metal—carbene chemistry has been based in large part on the goal of obtaining new and easier methods of generating carbenes. Certain transition metal complexes are known to catalyze the decomposition of diazo

---

[*] Address correspondence to this author; Alfred P. Sloan Foundation Fellow 1972—1974.

alkanes by way of postulated metal—carbene intermediates [1, 2]. Fischer and coworkers [3] have recently reported the addition of phenylmethoxycarbene to olefins with the carbene complexes M[C(OMe)Ph](CO)$_5$ (M = Cr, Mo, W). However, the use of stable transition metal complexes for this purpose has met with only limited success.

We recently reported [4] the preparation and structure of IrCl(CHF$_2$)(OCOCF$_2$Cl)(CO)(PPh$_3$)$_2$, (I), which is the initial product obtained from the reaction between Vaska's complex, IrCl(CO)(PPh$_3$)$_2$, and the difluorocarbene precursor CF$_2$ClCOONa. The metal-promoted decomposition of one equivalent of CF$_2$ClCOO$^-$ leads to the coordinated —CHF$_2$ group. In addition, complex (I) also contains an *O*-coordinated chlorodifluoroacetate ligand that has remained intact through this part of the reaction sequence. In this paper we present the structure of IrCl$_2$(CHF$_2$)(CO)(PPh$_3$)$_2$, (II), which is the thermal decomposition product of (I). The change in the sixth coordination position in the quantitative conversion of (I) to (II) suggests that the chlorodifluoroacetate decomposes by decarboxylation and generation of CF$_2$. Furthermore, the reaction of Vaska's complex with α-halocarboxylic acids and the decomposition of the resulting *O*-coordinated acetates raises the possibility that this may be a useful synthetic route for the production of carbenes.

A preliminary report of this work has been published [5].

Experimental

Preparation of IrCl$_2$(CHF$_2$)(CO)(PPh$_3$)$_2$

Method A. Dry CF$_2$ClCOONa (0.61 g), prepared from CF$_2$ClCOOH and NaOH), 0.78 g of IrCl(CO)(PPh$_3$)$_2$, and 30 ml of diglyme dried and distilled over LiAlH$_4$ are refluxing with stirring under nitrogen. After about 6 min, the yellow mixture rapidly changes color to white. The mixture is refluxed for an additional 10 min and is then filtered while hot to remove NaCl and excess CF$_2$ClCOONa. Cooling of the filtrate and addition of hexane yields the desired complex in about 80% yield.

Method B. IrCl(CHF$_2$)(OCOCF$_2$Cl)(CO)(PPh$_3$)$_2$ is isolated by filtering the above reaction solution immediately after the color change. This intermediate product is then added to 30 ml of diglyme and refluxed for 10 min to give the desired complex in quantitative yields. IR(cm^{-1}): ν(CO), 2065; ν(—CHF$_2$), 2940 (C—H), 1090, 950. (Found*: C, 53.01; H, 3.86; F, 4.20; Cl, 7.88; P, 6.77. $C_{38}H_{31}Cl_2F_2IrOP_2$ calcd.: C, 52.66; H, 3.48; F, 4.39; Cl, 8.20; P, 7.16%.)

Preparation of IrCl$_2$(CDF$_2$)(CO)(PPh$_3$)$_2$.

The same as method A for the —CHF$_2$ complex, except 0.5 ml of D$_2$O is added to the diglyme which is then dried and degassed over a molecular sieve (Fischer-Type 4A) before adding to the reaction flask. The color change is not as dramatic and the reaction time is extended to about 30 min.

Addition of CF$_2$ClCOOH to IrCl(CO)(PPh$_3$)$_2$

CF$_2$ClCOOH is added dropwise to 0.78 g IrCl(CO)(PPh$_3$)$_2$ in benzene until

---

* Alfred Berhardt.

the reaction mixture turns from a yellow suspension to a clear solution. The solution is stripped to near dryness, cyclohexane is added, and a pure white solid collected and dried under vacuum. The product is identified as $IrHCl(OCOCF_2Cl)(CO)(PPh_3)_2$ from its infrared spectrum [ν(Ir—H) 2240; ν(CO) 2025; ν(acetate) 1670 cm^{-1}].

This initial product is then refluxed in benzene or diglyme to yield $IrHCl_2(CO)(PPh_3)_2$ [ν(Ir—H) 2240; ν(CO) 2025 cm^{-1})].

Addition of $CH_3CHBrCOOH$ to $IrCl(CO)(PPh_3)_2$

$CH_3CHBrCOOH$ is added dropwise to $IrCl(CO)(PPh_3)_2$ in benzene or methylene chloride to produce a cloudy white reaction mixture. The white solid is collected and dried and identified as $IrHBrCl(CO)(PPh_3)_2$ from an authentic sample [ν(Ir—H) 2240; ν(CO) 2025 cm^{-1}].

X-ray data collection and structure determination of $IrCl_2(CHF_2)(CO)(PPh_3)_2$

From precession and Weissenberg photographs, the space group of a clear colorless crystal was uniquely determined to be $P2_1/c$ (No. 14—C_{2h}^5) [6]. The diffractometer angular settings of 19 reflections were used to calculate refined cell dimensions of a 10.47(1), b 14.52(2), c 24.58(2) Å, β 97.68(5)° and V 3865 $Å^3$. The experimental density of 1.65(2) g/cm^3 determined by the flotation method agrees with the calculated density of 1.65 g/cm^3 for four molecules per unit cell.

Because of anisotropic decomposition, two crystals, both mounted along the b^* axis, were used for data collection on a Picker automated diffractometer in a manner described previously [4] with a scan range of 1.40°. The two crystals had dimensions of 0.53×0.23×0.06 mm and 0.44×0.15×0.04 mm, and average mosaic spreads of 0.17° and 0.13°, respectively. Of the 2812 reflections measured with calculated 2θ values between 5° and 40° (λ 0.7107 Å), 1945 were found to have $F_o^2 \geqslant 2\sigma(F_o^2)$. An absorption correction on the data yielded transmission coefficients ranging from 0.15 to 0.85 with a calculated linear absorption coefficient μ of 46.12 cm^{-1}.

The position of the iridium atom was determined from a three-dimensional Patterson function map. All of the other non-hydrogen atoms in the structure were located and refined in the usual manner. The Ir, P, and Cl atoms were treated for anomalous dispersion with anisotropic thermal parameters for all Ir, P, Cl and F atoms, and the phenyl rings were refined as rigid groups. However, an Ir—C(2) distance of 1.95 Å and a C(2)—O distance of 0.95 Å indicated that the carbonyl ligand atoms had refined to chemically unreasonable positions. The carbonyl was then treated as a group with Ir—C and C—O distances of 1.85 and 1.13 Å, respectively, and an Ir—C—O angle of 180°. This resulted in final R-factors of 0.059 and 0.071 for R and Rw, respectively.

The final parameters of the structure exhibit larger estimated standard deviations, and the final difference Fourier map exhibits larger peaks (equivalent in height to some of the carbon atoms in the structure) than we might ordinarily consider satisfactory. This is due in part to the fact that the maximum 2θ value for the reflections measured was 40° and to the slight anisotropic decomposition. However, since none of the final difference Fourier peaks was in a chemically reasonable position, and since the primary purpose of this structure

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $IrCl_2(CHF_2)(CO)(PPh_3)_2$

Atom	x^a	y	z	B^b
Ir	0.1965(1)[c]	0.0565(1)	0.1448(1)	d
Cl(1)	0.0081(7)	0.1362(5)	0.1625(3)	d
Cl(2)	0.3153(9)	0.0952(6)	0.2358(4)	d
P(1)	0.2729(8)	0.1992(5)	0.1079(3)	d
P(2)	0.1217(7)	−0.0813(5)	0.1860(3)	d
F(1)	0.109(2)	−0.079(2)	0.060(1)	d
F(2)	0.171(2)	0.044(1)	0.025(1)	d
C(1)	0.104(3)	0.008(2)	0.064(1)	3.7(7)

ANISOTROPIC THERMAL PARAMETERS[e]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	89(2)	27(1)	12(0)	−2(1)	3(0)	0(1)
Cl(1)	95(10)	47(6)	18(2)	−2(5)	2(3)	3(3)
Cl(2)	171(13)	68(7)	30(3)	−6(7)	−1(4)	−7(4)
P(1)	115(11)	26(5)	11(2)	−1(6)	0(3)	2(3)
P(2)	95(10)	31(6)	12(2)	−8(5)	5(3)	3(3)
F(1)	245(31)	91(19)	24(5)	4(17)	6(9)	−9(8)
F(2)	262(31)	86(16)	26(5)	−42(19)	8(10)	−24(9)

GROUP PARAMETERS

Group	x_c^f	y_c	z_c	ϕ	θ	ρ	$B(A^2)$
CO[g]	0.1965	0.0565	0.1448	−0.377(8)	2.688	−0.365(7)	0.0
P1R(1)	0.5399(13)	0.1525(9)	0.0630(7)	−1.55(3)	−2.05(1)	−1.32(3)	2.0(3)
P1R(2)	0.3333(12)	0.3729(9)	0.1884(5)	1.86(1)	−2.51(1)	0.76(1)	3.3(3)
P1R(3)	0.0897(13)	0.3098(10)	0.0143(6)	2.24(1)	−2.93(1)	−0.65(1)	2.1(3)
P2R(1)	0.3253(12)	−0.2411(10)	0.1752(6)	−0.98(2)	−2.38(1)	−0.27(2)	1.0(3)
P2R(2)	0.0894(11)	−0.0668(10)	0.3160(6)	0.42(1)	3.03(1)	1.69(1)	4.6(3)
P2R(3)	−0.1594(12)	−0.1639(10)	0.1431(5)	0.31(1)	2.68(1)	−2.96(1)	2.1(3)

[a] x, y, z are in fractional coordinates. [b] Isotropic thermal parameter in A^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 × 10^4. [f] x_c, y_c, z_c are the fractional coordinates of the rigid-group. The angles ϕ, θ, ρ have been previously defined. See ref. 10. [g] The group parameters x_c, y_c, z_c, θ and β of the carbonyl were not refined. See text for further discussion.

was to establish the coordination geometry of (II) relative to (I), it did not seem worthwhile to remeasure and extend the set of intensity data. The parameters obtained from this refinement are thus taken as the final parameters for the structure and are presented in Table 1. The derived positional and thermal parameters for the carbon and oxygen atoms of the carbonyl group and the carbon and hydrogen atoms of the phenyl rings are tabulated in Table 2. Table 3 presents the root-mean-square amplitudes of thermal motion for the atoms refined anisotropically. A tabulation of the final values of $|F_o|$ and $|F_c|$ for the 1645 reflections with $F_o^2 \geqslant 2\sigma(F_o^2)$ used in the final refinement is available*.

---

* The table of structure factors has been deposited as NAPS Document No. 02393, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 2

DERIVED POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR GROUP ATOMS[a, b]

Group Atom	x	y	z	B(A^2)
CO—C	0.341	−0.006	0.129	4.2(7)
CO—O	0.429	−0.044	0.119	6.2(5)
P1R1C(1)	0.424(2)	0.174(4)	0.082(1)	1.0(6)
P1R1C(2)	0.535(2)	0.164(2)	0.119(1)	3.2(8)
P1R1C(3)	0.651(2)	0.143(3)	0.100(1)	3.6(8)
P1R1C(4)	0.656(2)	0.131(4)	0.044(1)	4.1(9)
P1R1C(5)	0.545(2)	0.141(2)	0.007(1)	6.6(11)
P1R1C(6)	0.428(2)	0.163(3)	0.026(1)	3.8(9)
P1R1H(2)	0.532(3)	0.172(2)	0.157(1)	4.0
P1R1H(3)	0.728(2)	0.136(5)	0.125(1)	4.0
P1R1H(4)	0.735(3)	0.116(6)	0.032(1)	4.0
P1R1H(5)	0.548(3)	0.133(3)	−0.031(1)	4.0
P1R1H(6)	0.352(2)	0.170(5)	0.000(1)	4.0
P1R2C(1)	0.309(2)	0.295(1)	0.156(1)	−0.1(7)
P1R2C(2)	0.232(2)	0.314(1)	0.196(1)	0.5(7)
P1R2C(3)	0.256(2)	0.393(1)	0.299(1)	0.8(7)
P1R2C(4)	0.358(2)	0.451(1)	0.221(1)	2.1(7)
P1R2C(5)	0.435(2)	0.431(1)	0.181(1)	2.9(9)
P1R2C(6)	0.411(2)	0.353(1)	0.148(1)	1.9(8)
P1R2H(2)	0.163(2)	0.274(2)	0.201(1)	2.7
P1R2H(3)	0.204(2)	0.407(2)	0.256(1)	2.7
P1R2H(4)	0.374(4)	0.505(2)	0.243(1)	2.7
P1R2H(5)	0.504(2)	0.472(2)	0.176(1)	2.7
P1R2H(6)	0.463(2)	0.339(2)	0.120(1)	2.7
P1R3C(1)	0.169(2)	0.257(1)	0.052(1)	2.4(8)
P1R3C(2)	0.040(2)	0.233(1)	0.038(1)	1.7(7)
P1R3C(3)	−0.039(1)	0.286(2)	0.000(1)	3.9(9)
P1R3C(4)	0.011(2)	0.363(2)	−0.024(1)	4.3(9)
P1R3C(5)	0.139(2)	0.387(1)	−0.010(1)	3.9(9)
P1R3C(6)	0.219(1)	0.334(2)	0.028(1)	3.8(8)
P1R3H(2)	0.006(3)	0.180(2)	0.055(1)	4.0
P1R3H(3)	−0.127(2)	0.270(2)	−0.009(1)	4.0
P1R3H(4)	−0.044(3)	0.399(2)	−0.049(1)	4.0
P1R3H(5)	0.173(3)	0.439(2)	−0.026(1)	4.0
P1R3H(6)	0.307(2)	0.350(2)	0.038(1)	4.0
P2R1C(1)	0.233(2)	−0.174(2)	0.181(1)	3.3(7)
P2R1C(2)	0.348(2)	−0.174(1)	0.216(1)	3.2(7)
P2R1C(3)	0.441(1)	−0.241(2)	0.210(1)	3.9(8)
P2R1C(4)	0.418(2)	−0.308(2)	0.170(1)	5.3(9)
P2R1C(5)	0.302(2)	−0.308(1)	0.135(1)	4.6(9)
P2R1C(6)	0.210(2)	−0.241(2)	0.140(1)	3.9(7)
P2R1H(2)	0.364(3)	−0.128(2)	0.244(1)	5.0
P2R1H(3)	0.520(2)	−0.241(3)	0.234(1)	5.0
P2R1H(4)	0.481(3)	−0.354(3)	0.166(1)	5.0
P2R1H(5)	0.287(3)	−0.354(2)	0.107(1)	5.0
P2R1H(6)	0.131(2)	−0.241(3)	0.116(1)	5.0
P2R2C(1)	0.109(2)	−0.072(2)	0.261(1)	−0.6(7)
P2R2C(2)	0.052(2)	0.007(1)	0.281(1)	1.2(9)
P2R2C(3)	0.032(2)	0.011(1)	0.336(1)	1.4(9)
P2R2C(4)	0.070(2)	−0.062(2)	0.371(1)	1.9(8)
P2R2C(5)	0.127(2)	−0.140(1)	0.351(1)	1.0(8)
P2R2C(6)	0.147(2)	−0.145(1)	0.297(1)	0.6(8)
P2R2H(2)	0.027(2)	0.056(2)	0.256(1)	1.5
P2R2H(3)	−0.007(2)	0.064(2)	0.349(1)	1.5
P2R2H(4)	0.056(3)	−0.059(2)	0.408(1)	1.5
P2R2H(5)	0.152(2)	−0.190(2)	0.376(1)	1.5
P2R2H(6)	0.186(2)	−0.198(1)	0.283(1)	1.5

(continued)

TABLE 2 (continued)

Group Atom	x	y	z	B(A^2)
P2R3C(1)	−0.037(1)	−0.128(2)	0.159(1)	2.0(7)
P2R3C(2)	−0.130(2)	−0.075(1)	0.127(1)	2.6(7)
P2R3C(3)	−0.252(1)	−0.111(1)	0.112(1)	2.5(8)
P2R3C(4)	−0.282(1)	−0.200(2)	0.127(1)	3.0(8)
P2R3C(5)	−0.189(2)	−0.253(1)	0.159(1)	2.8(8)
P2R3C(6)	−0.067(2)	−0.217(1)	0.175(1)	2.1(7)
P2R3H(2)	−0.109(3)	−0.014(1)	0.117(1)	4.0
P2R3H(3)	−0.316(2)	−0.074(2)	0.090(1)	4.0
P2R3H(4)	−0.366(2)	−0.224(2)	0.116(1)	4.0
P2R3H(5)	−0.210(3)	−0.314(1)	0.169(1)	4.0
P2R3H(6)	−0.003(2)	−0.253(2)	0.196(1)	4.0

[a] Because the carbonyl group origin was not refined, the standard derivations in the coordinates of the carbonyl atoms were not determined. [b] See Table 1 for overall group temperature factor. Individual hydrogen atom temperature factors were not refined. They were assigned to give a sum of 6.0 when added to the group temperature factor.

Discussion

The molecular structure of $IrCl_2(CHF_2)(CO)(PPh_3)_2$, (II), consists of a six-coordinate iridium(III) ion with an octahedral geometry. As shown in the stereoscopic view of the molecule in Fig. 1, the phosphine ligands are *trans* and the chlorine ligands are *cis* to each other. Figure 2 is a perspective drawing of the molecule with the phenyl rings omitted for clarity. Principal intramolecular distances and angles are given in Table 4.

The $-CHF_2$ group is coordinated to the iridium *trans* to a chloride with an Ir—C bond length of 2.19(3) Å. In $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$, (I), the difluoromethyl group is *trans* to the acetate and the Ir—C distance is 2.09(2) Å. As in (I), the presence of the hydrogen on the $-CHF_2$ group is proposed on the basis of the geometry about C(1), and, most convincingly, on the substitution of the hydrogen atom with deuterium (vide infra). The bond angles about C(1) are 112(2)°, 109(2)° and 107(3)°, clearly indicating a tetrahedral geometry. Iridium—chlorine bond lengths of 2.375(8) Å for the chlorine *trans* to the carbonyl and 2.475(10) Å for the chlorine *trans* to the difluoromethyl group is further evidence that the $-CHF_2$ group bonds predominantly as a σ donor. The

TABLE 3

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (A)

Atom	Min	Intermed	Max
Ir	0.170(2)	0.189(2)	0.222(2)
Cl(1)	0.21(1)	0.22(1)	0.25(1)
Cl(2)	0.25(1)	0.30(1)	0.33(1)
P(1)	0.16(2)	0.19(2)	0.26(1)
P(2)	0.16(2)	0.20(1)	0.23(1)
F(1)	0.25(3)	0.32(3)	0.37(2)
F(2)	0.20(4)	0.34(3)	0.40(2)

TABLE 4

PRINCIPAL INTRAMOLECULAR DISTANCES AND ANGLES FOR $IrCl_2(CHF_2)(CO)(PPh_3)_2$

Distances (Å)		Angles (deg.)	
Ir—Cl(1)	2.375(8)	Ir—C(1)—F(1)	112(2)
Ir—Cl(2)	2.475(10)	Ir—C(1)—F(2)	109(2)
Ir—P(1)	2.429(8)	F(1)—C(1)—F(2)	107(3)
Ir—P(2)	2.412(8)	Cl(1)—Ir—Cl(2)	93.1(3)
Ir—C(1)	2.19(3)	Cl(1)—Ir—P(1)	88.8(3)
Ir—C(2)[a]	1.85	Cl(1)—Ir—P(2)	89.9(3)
C(1)—F(1)	1.27(3)	Cl(1)—Ir—C(1)	92.5(8)
C(1)—F(2)	1.38(3)	Cl(1)—Ir—C(2)[a]	178.4
C(2)—O[a]	1.13	Cl(2)—Ir—P(1)	89.7(3)
P(1)—P1R1C(1)	1.82(2)	Cl(2)—Ir—P(2)	87.6(3)
P(1)—P1R2C(1)	1.82(2)	Cl(2)—Ir—C(1)	173.6(9)
P(1)—P1R3C(1)	1.83(2)	Cl(2)—Ir—C(2)[a]	88.5
P(2)—P2R1C(1)	1.79(2)	P(1)—Ir—P(2)	177.0(3)
P(2)—P2R2C(1)	1.88(2)	P(1)—Ir—C(1)	93.5(9)
P(2)—P2R3C(1)	1.83(2)	P(1)—Ir—C(2)[a]	91.0
		P(2)—Ir—C(1)	89.4(9)
		P(2)—Ir—C(2)[a]	90.4
		C(1)—Ir—C(2)[a]	85.9
		Ir—C(2)—O[a]	180

[a] Standard derivations in distances and angles involving the carbonyl atoms were not determined. See the text and Table 2, footnote a, for further explanation.

difference in the C—F distances of 1.27(3) and 1.38(3) Å is only possibly significant. In (I), the four C—F distances range from 1.33(2) to 1.35(2) Å.

The change in the coordination site *trans* to the difluoromethyl group from chlorodifluoroacetate in (I) to a chloride in (II) provides the major interest in this structure. The decomposition of (I) to (II) occurs in quantitative yields in refluxing diglyme without any additional reagents. In an analogous reaction, $IrHCl(OCOCF_2Cl)(CO)(PPh_3)_2$ decomposes to $IrHCl_2(CO)(PPh_3)_2$ in refluxing benzene. While the addition of $CH_3CHBrCOOH$ to Vaska's complex does not yield a stable metal—carboxylate complex, the isolation of $IrHBrCl(CO)(PPh_3)_2$ from this reaction indicates that the α-bromopropionate anion may decompose via an unstable metal—carboxylate complex. The importance of these reactions

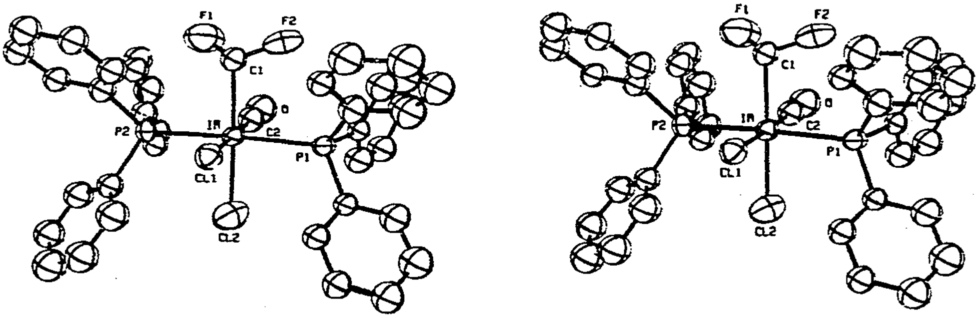


Fig. 1. A stereoscopic view of the complex $IrCl_2(CHF_2)(CO)(PPh_3)_2$.

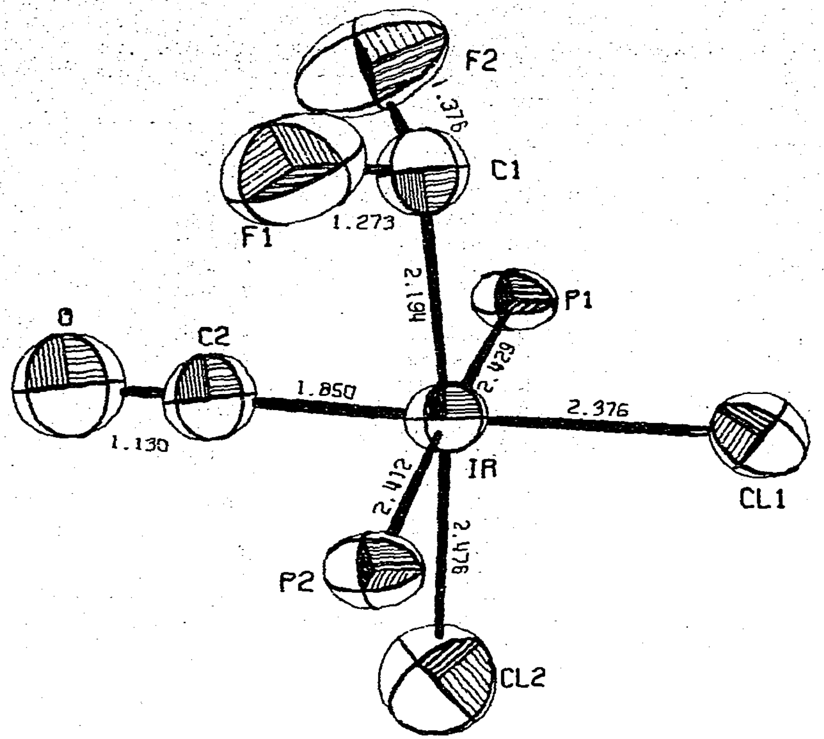
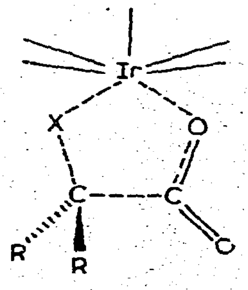


Fig. 2. A perspective drawing of $IrCl_2(CHF_2)(CO)(PPh_3)_2$ with the phenyl rings omitted for clarity.

is that they may provide a general route for the production of a variety of carbenes. Based on the relative ease of decomposing the coordinated carboxylates as compared to the free carboxylates [7], it appears that an intramolecular transition state, such as (A) may be involved. This would account for the failure to isolate the $CH_3CHBrCOO^-$ complex due to the weaker C—Br bond relative to C—Cl. Furthermore, it is known [8] that the acetates CF_2XCOO^- (X = Cl, Br, I) decompose in a concerted manner, as is suggested by an intramolecular transition state such as (A) prior to decarboxylation and difluorocarbene generation. However, attempts to trap the CF_2 species generated by the conversion of (I) to (II) using olefins have been unsuccessful to date.



(A)

The source of the proton on the —CHF_2 group is apparently attributable to traces of water in the reaction mixture when the solvent is not scrupulously dried. This has been demonstrated by the isolation of $IrCl_2(CDF_2)(CO)(PPh_3)_2$, ν(C—D) 2200 cm^{-1}, when D_2O is introduced to the initial reaction system. Since a metallocarbanion is proposed in the formation of (I) [4, 5], it is possible that proton abstraction from the diglyme solvent occurs when the system has been carefully dried. Proton abstractions from diglyme in the presence of strong bases have been noted previously [9].

Acknowledgements

We wish to thank the National Science Foundation (GP-35667X) and the Petroleum Research Fund for support of this work.

References

1 C. Rüchardt and G.N. Schrauzer, Chem. Ber., 93 (1960) 1840.
2 F.D. Mango and I. Dvoretzky, J. Amer. Chem. Soc., 88 (1966) 1654.
3 E.O. Fischer and K.H. Dotz, Chem. Ber., 105 (1972) 3966.
4 A.J. Schultz, G.P. Khare, C.D. Meyer and R. Eisenberg, Inorg. Chem., in press.
5 A.J. Schultz, G.P. Khare, J.V. McArdle and R. Eisenberg, J. Amer. Chem. Soc., 95 (1973) 3434.
6 International Tables of X-Ray Crystallography, Vol. 1, Kynoch Press, Birmingham, England, 1952. p. 99.
7 J.M. Birchall, G.W. Cross, and R.M. Haszeldine, Proc. Chem. Soc., (1960) 81.
8 J. Hine, Divalent Carbon, Ronald Press, New York, 1964, p. 47.
9 (a) W.H. Snyder, J. Parascandola and M. Wolfinger, J. Org. Chem., 31 (1966) 2037;
(b) F.E. Herkes and D.J. Burton, J. Org. Chem., 32 (1967) 1311.
10 R. Eisenberg and J.A. Ibers, Inorg. Chem., 4 (1965) 771.