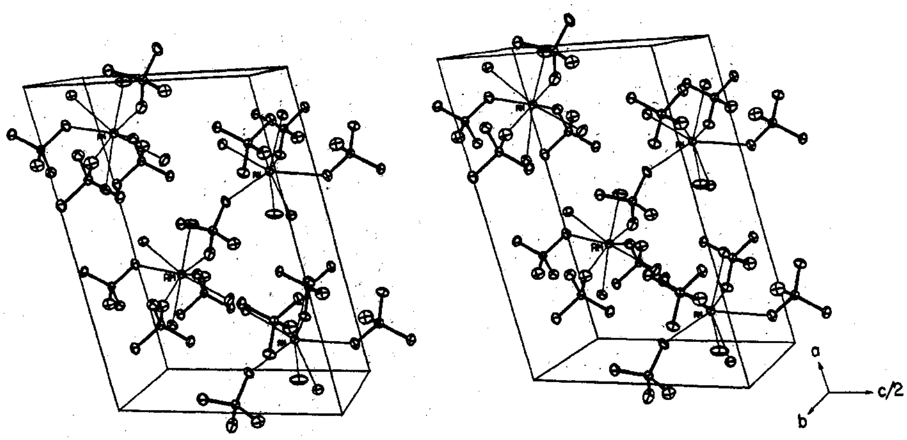

Figure 2.—A stereoscopic view of one-half of a unit cell content showing part of the cross-linking within layers. Atoms are identied by reference to Figure 1.

Figures 1b and 1c. There is very little distortion from regular tetrahedra, and the S–O bond lengths are in good agreement with other determinations, such as $Cu(NH_4)_2(SO_4)_2\cdot 6H_2O$.[26]

With four water molecules per americium to act as donors and these plus numerous sulfate oxygens present to act as acceptors there may be extensive hydrogen bonding in this structure. Since attempts to interpret difference Fourier maps to obtain hydrogen positions were unsuccessful, even when plausible sites were deduced geometrically, the possibilities for hydrogen bonds were analyzed by surveying the close O···O distances (less than 3.25 Å) and the reasonable O···O···O angles (105 ± 10°). The results are summarized in Table IV. In each of two cases, W(1) and W(3), a single, highly probable orientation for the water molecule emerged. In the other two cases, W(2) and W(4), a decision could not be made among three and four possibilities, respectively; but the existence of these short distances and suitable angles suggests that these water molecules are also involved in hydrogen bonding, possibly in a disordered arrangement including several of the directions.

(26) G. M. Brown and R. Chidambaram, *Acta Crystallogr., Sect. B*, **25**, 676 (1969), and references therein.

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The Crystal and Molecular Structure of Carbonylchlorobis(trimethylphosphine)-(1,2,3-triphenylpropenylium-1,3-diyl)iridium(1+) Tetrafluoroborate(1−)-Dichloromethane, $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$, an Oxidative Addition Derivative Formed by Carbon–Carbon Bond Cleavage

By R. M. TUGGLE and D. L. WEAVER*[1]

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The crystal and molecular structure of $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$ has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as discrete molecular units in the orthorhombic space group $P2_12_12_1$ with four formula units in a unit cell of dimensions a = 9.808 (1), b = 17.758 (2), and c = 19.971 (3) Å. The structure has been refined by full-matrix least-squares methods to a conventional R factor of 0.060 for the 3248 intensities above background. In reacting with $IrCl(CO)(P(CH_3)_3)_2$ the cyclopropenium ring is cleaved to give the monopositive bidentate propenylium-1,3-diyl group. This group, the trans phosphines, the chlorine, and the carbonyl are disposed about the six-coordinate iridium(III) ion in a distorted octahedral fashion. Iridium–phosphorus distances are 2.360 and 2.369 (5) Å; iridium–chlorine, 2.472 (5) Å; iridium–carbon (carbonyl), 1.94 (2) Å; and iridium–carbon (propenylium), 2.099 and 1.990 (15) Å. Carbon–carbon distances in the propenylium group are 1.36 and 1.41 (2) Å. A 1,3 $p\pi$–$p\pi$ interaction is suspected to occur in the propenylium group.

Investigations of transition metal triphenylcyclopropenyl derivatives[2,3] have shown some striking similarities between cyclopropenyl and nitrosyl metal complexes. This is perhaps not surprising when the electronic structures of $C_3(C_6H_5)_3^+$ and NO^+ are compared. Both cations are thought to have a highest occupied orbital of π symmetry and a lowest unoccupied π^* orbital which is energetically accessible. Although NO^+ is considered to be a good π-acceptor ligand,[4] further

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[2] R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 1504 (1971).

[3] R. M. Tuggle and D. L. Weaver, *ibid.*, **10**, 2599 (1971).

[4] See, for example, P. T. Manoharan and H. B. Gray, *ibid.*, **5**, 823 (1966).

studies are required to establish the π-accepting ability of the cyclopropenyl group.

One of the more interesting aspects of nitrosyl chemistry is the occurrence of compounds which contain either a formally coordinated NO^+ or NO^- group. Many of the NO^- derivatives[5] are formed in oxidative addition reactions[6] when a complex is oxidized by an NO^+ species with subsequent formation of a nonlinear M–NO group. For example treatment of $IrCl(CO)(P(C_6H_5)_3)_2$ with $NOBF_4$ produces a complex,[7] $[IrCl(NO)CO(P(C_6H_5)_3)_2]BF_4$, with an Ir–N–O angle of 124.1 (9)°. In view of the similarities that exist between nitrosyl and cyclopropenyl complexes it was of interest to react $C_3(C_6H_5)_3^+$ with the iridium(I) system. The present X-ray study has shown that the cyclopropenyl ring is cleaved and oxidatively adds to the d^8 complex to form $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2]^+$. This novel compound represents one of the few authenicated examples[8] of an oxidative addition reaction which involves carbon–carbon bond cleavage.

Collection and Reduction of X-Ray Intensity Data

$[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$ was prepared as previously[9] described. Intense purple crystals were obtained from a CH_2Cl_2–CCl_4 mixture. Precession and equiinclination photographs established that the crystals belong to the orthorhombic system. The observed systematic absences $h00$ (h odd), $0k0$ (k odd), and $00l$ (l odd) are consistent with and uniquely determine the acentric space group $P2_12_12_1$ (D_2^4). Accurate unit cell parameters were obtained on a GE XRD-5 diffractometer using Cu Kα_1 radiation (λ 1.5405 Å), a takeoff angle of 2°, and a 0.05° slit. Least-squares treatment of 12 reflections ($65° < 2\theta \leq 110°$) gave unit cell dimensions of a = 9.808 (1), b = 17.758 (2), and c = 19.971 (3) Å. Four formula units of the monomethylene chloride solvate correspond to a calculated density of 1.616 g cm^{-3}. The density of a single crystal was found to be 1.62 (1) g cm^{-3} by flotation in a CCl_4–$CHBr_3$ mixture. The presence of a CH_2Cl_2 molecule of crystallization was borne out in the subsequent X-ray analysis.

Intensity data were collected at 20° on a crystal of dimensions 0.36 × 0.09 × 0.10 mm along a, b, and c, respectively. This crystal was mounted on a glass fiber and the a axis was coincident with the ϕ axis of a GE XRD-5 diffractometer. The crystal faces were indexed and measured for absorption correction purposes. Measurement of the kinematic intensity profile[10] by the ω-scan technique (takeoff angle = 4°) gave a peak width at half-maximum intensity of 0.38° for several reflections.

The θ–2θ scan method, with symmetric scan ranges of 3° ($0° < 2\theta \leq 100°$) and 4° ($100° < 2\theta \leq 140°$) and a scan rate of 2° min^{-1}, was employed to measure the intensities. At the lower and upper limits of each scan, 10-sec stationary-crystal, stationary-counter background counts were measured. Possible crystal deterioration and misalignment were monitored by measuring the intensities of three standard reflections at regular intervals throughout data collection. These standards were used to linearly scale all data to a common base. Initially the intensities showed only a random 1% fluctuation, but during the last third of data collection a slow decrease of 5.6% in intensity was noted which is presumably the result of crystal deterioration. Cu Kα radiation, obtained by passing the primary and diffracted beam through a 0.35-mil thickness of nickel foil, was used for intensity measurement. The pulse height analyzer was set to accept approximately a 90% window when centered on the Cu Kα peak. Nine reflections with intensities that exceeded the linear response range of the counter were remeasured by reducing the current on the X-ray tube.

A complete set (one octant) of 3731 independent reflections with $2\theta \leq 140°$ ($\sin \theta/\lambda \leq 0.61$) was collected. These intensities were reduced to values of F^2 by correction for Lorentz, polarization, and absorption effects. Standard deviations were calculated using the expression $\sigma(I) = [CT + 0.25(t_s/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$, where I is the net intensity, CT is the total integrated scan count obtained in time t_s, t_b is the time required for each background count B_1 and B_2, and p is a factor to account for random fluctuations encountered during data collection. For this structure determination p was chosen to be 0.03. Use of the criterion $I > 2.0\sigma(I)$ gave 3248 reflections which were classified as observed and used in the solution and refinement of the structure. Transmission coefficients ranged from 0.29 to 0.53 (μ_1 = 105 cm^{-1} for Cu Kα radiation) and were obtained using a modified version of Coppens' program.[11]

Solution and Refinement of the Structure

A three-dimensional unsharpened Patterson function[12] gave the position of the iridium atom. A set of structure factors phased on this atom gave $R_1 = 0.290$ and $R_2 = 0.407$. The conventional agreement factor is defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and the weighted agreement factor as $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$, where $|F_o|$ is the observed structure factor amplitude, $|F_c|$ is the calculated structure-factor amplitude, and the weights $w = 4F_o^2/\sigma^2(F_o^2)$. All full-matrix least-squares refinements were on F, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors for the neutral atoms were those of Cromer and Waber[13] for iridium, those of Stewart, *et al.*,[14] for hydrogen, and the usual tabulation[15] for all other elements. The effects of anomalous dispersion were allowed for in the Ir, P, and Cl scattering factors; values of $\Delta f'$ and $\Delta f''$ were taken from Cromer.[16]

Additional structure factor calculations and difference Fourier syntheses located the remaining 40 nonhydrogen atoms. Several cycles of least-squares refinement on all atoms in which the Ir, two P, and coordinated Cl atoms were assigned anisotropic thermal parameters led to values for R_1 of 0.062 and R_2 of 0.074. A difference Fourier map phased on this last set of structure factors showed 12 out of the 15 possible phenyl group hydrogen atoms as peaks ranging from 0.26 to 0.53 e/Å^3. Since inclusion of hydrogen atom parameters in the least-squares refinement would cause an unnecessarily large increase in computing time, the 15 hydrogen atoms of the phenyl groups were fixed at their idealized positions (d_{C-H} = 1.08 Å) and assigned isotropic temperature factors of 6.0 Å^2. Four additional cycles of least-squares refinement reduced the agreement factors to their final converged values of $R_1 = 0.0604$ and $R_2 = 0.0672$.

For the acentric space group $P2_12_12_1$ there exist two possible enantiomeric configurations of the asymmetric unit—the structure just determined, A, and its enantiomer, B. In order to test the possibility that B is the correct structure, the signs of the coordinates for all the atoms were inverted and the resulting structure B was refined by least squares. This converged to give residual factors of $R_1 = 0.0669$ and $R_2 = 0.0781$ which are significantly higher than those obtained from the refinement of enantiomer A. Thus, it was concluded that A (*vide supra*) was the correct enantiomer.

In the final cycle of refinement the largest parameter shift was 0.23σ and the average shift was 0.03σ. The estimated standard deviation of an observation of unit weight was 2.57 electrons. This rather high value probably reflects the simplified model used for the BF_4^- and CH_2Cl_2 groups since both undergo large thermal motions. The final difference Fourier showed four peaks ranging from 0.91 to 2.16 e/Å^3 (0.3 to 0.65 times the value of a typical phenyl carbon atom) at approximately 1.0 Å from the iridium atom. This residual electron density was not located along any bond directions and no chemical significance is attached to it. Structure factors of the 483 unobserved reflections were calculated and three reflections had $|F_c|$ greater than twice the minimum observable value.

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(5) See C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971), and references therein.

(6) See K. R. Laing and W. R. Roper, *J. Chem. Soc. A*, 2149 (1970), and references therein.

(7) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(8) J. L. Burmeister and L. M. Edwards, *J. Chem. Soc. A*, 1663 (1971), and references therein.

(9) R. M. Tuggle and D. L. Weaver, *J. Amer. Chem. Soc.*, **92**, 5523 (1970).

(10) L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **15**, 983 (1962).

(11) P. Coppens, L. Leiserowitz, and D. Rabinovich, *ibid.*, **18**, 1035 (1965).

(12) Patterson and Fourier syntheses were calculated using a modified version of Zalkin's FORDAP program, and structure factor and least-squares refinement calculations were performed using Prewitt's SFLS-5.

(13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(16) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table I

Final Positional and Thermal Parameters[a]

Atom	x	y	z	B, Å^2
Ir	0.31507 (7)	0.47139 (4)	0.37596 (3)	3.09[b]
Cl(1)	0.2246 (4)	0.3875 (3)	0.4642 (2)	4.37[b]
P(1)	0.2637 (5)	0.3754 (3)	0.2982 (2)	4.09[b]
P(2)	0.3750 (5)	0.5590 (3)	0.4604 (2)	4.10[b]
O	0.0225 (14)	0.5288 (8)	0.3651 (6)	6.01 (28)
C(1)	0.1311 (18)	0.5107 (9)	0.3699 (9)	4.38 (34)
C(2)	0.3715 (26)	0.2918 (14)	0.2996 (11)	6.98 (56)
C(3)	0.0914 (24)	0.3335 (13)	0.3077 (11)	6.28 (52)
C(4)	0.2655 (22)	0.4072 (11)	0.2103 (10)	5.93 (46)
C(5)	0.2333 (26)	0.6142 (13)	0.4895 (11)	7.08 (57)
C(6)	0.4935 (28)	0.1255 (15)	0.0609 (12)	7.83 (61)
C(7)	0.0550 (26)	0.4815 (15)	0.0374 (11)	7.73 (57)
C(10)	0.4773 (16)	0.9444 (8)	0.1326 (7)	3.46 (29)
C(11)	0.3822 (19)	0.8998 (10)	0.0902 (9)	4.12 (35)
C(12)	0.4374 (19)	0.8468 (10)	0.0466 (9)	4.44 (36)
C(13)	0.3528 (21)	0.8063 (11)	0.0049 (9)	5.14 (42)
C(14)	0.2084 (28)	0.8227 (14)	0.0084 (11)	7.38 (57)
C(15)	0.1591 (21)	0.8773 (11)	0.0467 (10)	5.33 (42)
C(16)	0.2463 (19)	0.9141 (10)	0.0887 (9)	4.31 (35)
C(20)	0.4522 (16)	0.9922 (8)	0.1847 (7)	3.05 (27)
C(21)	0.3220 (18)	0.0072 (8)	0.2241 (7)	3.75 (29)
C(22)	0.2629 (21)	0.9493 (10)	0.2592 (9)	4.92 (39)
C(23)	0.1462 (22)	0.9659 (13)	0.2987 (10)	6.25 (46)
C(24)	0.0888 (24)	0.0359 (14)	0.2977 (10)	6.60 (50)
C(25)	0.1506 (21)	0.0941 (12)	0.2629 (10)	5.56 (44)
C(26)	0.2642 (20)	0.0790 (10)	0.2257 (9)	4.69 (37)
C(30)	0.4201 (15)	0.5266 (10)	0.3062 (6)	3.25 (25)
C(31)	0.3816 (17)	0.5802 (9)	0.2532 (8)	3.71 (31)
C(32)	0.2808 (22)	0.6335 (12)	0.2674 (10)	5.35 (45)
C(33)	0.2323 (24)	0.6824 (12)	0.2190 (11)	6.33 (50)
C(34)	0.2966 (30)	0.6782 (14)	0.1578 (13)	8.24 (62)
C(35)	0.3925 (23)	0.6294 (12)	0.1426 (10)	6.37 (50)
C(36)	0.4419 (20)	0.5801 (11)	0.1916 (9)	4.75 (37)
B	0.1636 (30)	0.2420 (14)	0.1562 (13)	17.40 (82)
F(1)	0.0190 (19)	0.3223 (11)	0.1163 (11)	12.39 (52)
F(2)	0.1636 (30)	0.2420 (14)	0.1562 (13)	17.40 (82)
F(3)	0.0472 (35)	0.2225 (17)	0.0682 (15)	20.4 (11)
F(4)	0.0494 (31)	0.7169 (16)	0.3393 (14)	18.23 (92)
C(8)	0.3213 (40)	0.8494 (19)	0.4428 (17)	11.93 (95)
Cl(2)	0.4409 (11)	0.8206 (6)	0.3782 (6)	14.08 (29)
Cl(3)	0.3525 (12)	0.9494 (7)	0.4535 (6)	15.38 (37)

Anisotropic Temperature Factors[c] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	65.0 (6)	31.0 (2)	17.9 (1)	0.5 (4)	−2.7 (3)	1.4 (2)
Cl(1)	84.3 (48)	46.4 (19)	25.2 (11)	−4.3 (23)	5.7 (18)	9.5 (12)
P(1)	91.9 (55)	36.8 (18)	25.7 (12)	−7.7 (26)	−9.0 (21)	−2.7 (12)
P(2)	111.4 (54)	37.3 (16)	20.8 (10)	4.7 (26)	−7.2 (21)	−3.4 (11)

[a] Numbers in parentheses are esd's in the last figure quoted. [b] Equivalent isotropic B's. [c] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

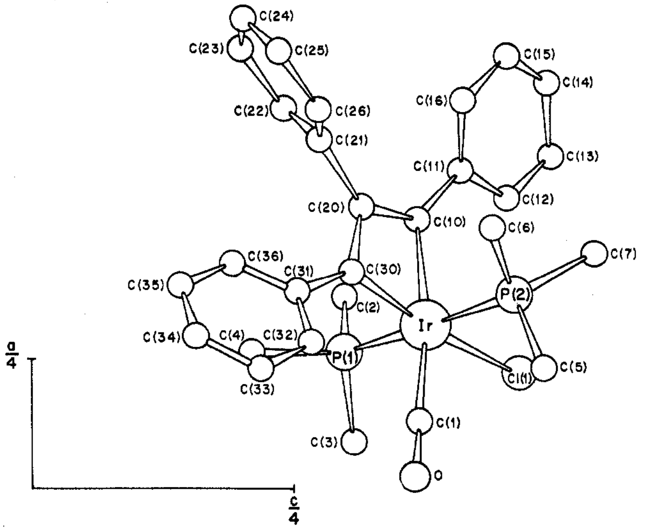

Figure 1.—Projection of the $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2]^+$ ion on the crystallographic *ac* plane.

Description of the Structure

$[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$ crystallizes in discrete ionic units as a 1:1 aggregate with dichloromethane (see Figure 1). Figure 2 gives a stereoscopic view of the contents of a unit cell in this structure. The closest cation–anion contacts are between the fluorine atoms of BF_4^- and phenyl group hydrogen atoms. However, all distances are within 0.1 Å of the normal van der Waals contacts. No unusual contacts are noted for the dichloromethane molecules in the structure which is consistent with the high atomic thermal parameters found for this solvent molecule.

Solution of the structure has revealed a singularly remarkable fact: the three-membered ring of the triphenylcyclopropenium cation has been opened and oxidation addition of this group to *trans*-$[IrCl(CO)(P(CH_3)_3)_2]$ has occurred to form a four-membered iridocycle. In view of the aromaticity attributed to the cyclopropenyl cation, this is a cogent demonstration of the tendency for coordinatively unsaturated complexes of the type $IrCl(CO)(PR_3)_2$ to undergo oxidative addition.

A view of the complex ion projected on the crystallographic *ac* plane is given in Figure 1. Selected intramolecular distances and angles are given in Table III. A distorted octahedral geometry is found around the six-coordinate Ir(III) atom. The major distortion in the coordination sphere is a C(10)–Ir–C(30) angle of 63.5 (3)° which is due to the steric requirements of the

Table II

Root-Mean-Square Amplitudes of Vibration (Å) and Their Direction Cosines[a] (in Parentheses)

Atom	Minimum	Intermediate	Maximum
Ir	0.174 (0.894, −0.077, 0.442)	0.192 (−0.449, −0.163, 0.879)	0.224 (−0.004, 0.984, 0.180)
Cl(1)	0.186 (0.725, 0.332, −0.603)	0.219 (0.688, −0.327, 0.647)	0.288 (−0.017, 0.885, 0.466)
P(1)	0.189 (0.777, 0.341, 0.529)	0.241 (−0.577, 0.050, 0.816)	0.249 (−0.252, 0.939, −0.236)
P(2)	0.195 (0.350, 0.194, 0.916)	0.229 (0.776, −0.608, −0.168)	0.256 (0.525, 0.770, −0.364)

[a] Direction cosines are referred to the crystal axes *a*, *b*, and *c*.

The positional and thermal parameters obtained in the final structure factor calculation for enantiomer A (*vide supra*) are given in Table I.[17] Analysis of the anisotropic temperature factors of the heavier atoms (Ir, Cl, and P) shows that the thermal motion of these atoms is nearly isotropic (Table II). The largest rms vibration amplitudes are those expected, *e.g.*, that associated with Cl(1) is approximately normal to the Cl(1)–Ir bond vector.

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(17) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number INORG-72-2237. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III
SELECTED INTRAMOLECULAR DISTANCES AND ANGLES[a]

Distances, Å

Ir–C(10)	2.099 (15)	C(21)–C(22)	1.37 (2)
Ir–C(30)	1.990 (15)	C(22)–C(23)	1.42 (3)
Ir–C(1)	1.939 (18)	C(23)–C(24)	1.36 (3)
Ir–Cl(1)	2.472 (5)	C(24)–C(25)	1.38 (3)
Ir–P(1)	2.360 (5)	C(25)–C(26)	1.37 (3)
Ir–P(2)	2.369 (5)	C(26)–C(21)	1.40 (2)
C(1)–O	1.12 (2)	C(31)–C(32)	1.40 (3)
C(10)–C(20)	1.36 (2)	C(32)–C(33)	1.38 (3)
C(20)–C(30)	1.41 (2)	C(33)–C(34)	1.38 (3)
C(10)–C(11)	1.49 (2)	C(34)–C(35)	1.31 (4)
C(20)–C(21)	1.52 (2)	C(35)–C(36)	1.40 (3)
C(30)–C(31)	1.47 (2)	C(36)–C(31)	1.37 (2)
P(1)–C(2)	1.82 (3)	B–F(1)	1.30 (4)
P(1)–C(3)	1.86 (2)	B–F(2)	1.44 (5)
P(1)–C(4)	1.84 (2)	B–F(3)	1.18 (5)
P(2)–C(5)	1.80 (3)	B–F(4)	1.28 (5)
P(2)–C(6)	1.80 (3)	C(8)–Cl(2)	1.82 (4)
P(2)–C(7)	1.87 (2)	C(8)–Cl(3)	1.81 (4)
C(11)–C(12)	1.39 (3)	C(10)···C(30)	2.15 (2)
C(12)–C(13)	1.38 (3)	Ir···C(20)	2.610 (15)
C(13)–C(14)	1.45 (3)	Cl(1)···H(12)	2.45
C(14)–C(15)	1.33 (3)	C(1)···H(32)	2.67
C(15)–C(16)	1.36 (3)	Ir···H(12)	3.18
C(16)–C(11)	1.36 (3)	Ir···H(32)	3.24

Angles, Deg

P(1)–Ir–P(2)	174.8 (2)	Ir–P(1)–C(2)	117.0 (8)
P(1)–Ir–Cl(1)	87.6 (2)	Ir–P(1)–C(3)	114.6 (8)
P(1)–Ir–C(1)	91.2 (5)	Ir–P(1)–C(4)	113.8 (7)
P(1)–Ir–C(10)	89.4 (4)	Ir–P(2)–C(5)	113.3 (7)
P(1)–Ir–C(30)	90.3 (5)	Ir–P(2)–C(6)	116.1 (9)
P(2)–Ir–Cl(1)	88.7 (1)	Ir–P(2)–C(7)	115.9 (8)
P(2)–Ir–C(1)	92.2 (5)	C(2)–P(1)–C(3)	101.5 (10)
P(2)–Ir–C(10)	88.1 (4)	C(2)–P(1)–C(4)	105.0 (10)
P(2)–Ir–C(30)	92.6 (5)	C(3)–P(1)–C(4)	103.2 (10)
Cl(1)–Ir–C(1)	85.9 (5)	C(5)–P(2)–C(6)	105.8 (12)
Cl(1)–Ir–C(10)	105.6 (4)	C(5)–P(2)–C(7)	105.8 (11)
Cl(1)–Ir–C(30)	168.9 (5)	C(6)–P(2)–C(7)	98.2 (11)
C(1)–Ir–C(10)	168.6 (7)	C(10)–C(20)–C(30)	102.0 (13)
C(1)–Ir–C(30)	105.1 (7)	C(10)–C(11)–C(12)	118 (2)
C(10)–Ir–C(3)	63.5 (3)	C(11)–C(12)–C(13)	120 (2)
Ir–C(1)–O	175 (2)	C(12)–C(13)–C(14)	117 (2)
Ir–C(10)–C(20)	95.5 (10)	C(13)–C(14)–C(15)	122 (2)
Ir–C(30)–C(20)	99.0 (10)	C(14)–C(15)–C(16)	118 (2)
Ir–C(10)–C(11)	123.1 (11)	C(15)–C(16)–C(11)	123 (2)
Ir–C(30)–C(31)	133.5 (11)	C(16)–C(11)–C(12)	120 (2)
C(16)–C(11)–C(10)	122 (2)	C(31)–C(32)–C(33)	122 (2)
C(11)–C(10)–C(20)	131 (1)	C(32)–C(33)–C(34)	115 (2)
C(10)–C(20)–C(21)	131 (1)	C(33)–C(34)–C(35)	125 (2)
C(20)–C(21)–C(22)	119 (1)	C(34)–C(35)–C(36)	120 (2)
C(21)–C(22)–C(23)	117 (2)	C(35)–C(36)–C(31)	119 (2)
C(22)–C(23)–C(24)	121 (2)	C(36)–C(31)–C(32)	119 (2)
C(23)–C(24)–C(25)	120 (2)	C(36)–C(31)–C(30)	122 (2)
C(24)–C(25)–C(26)	119 (2)	F(1)–B–F(2)	104 (3)
C(25)–C(26)–C(21)	121 (2)	F(1)–B–F(3)	110 (3)
C(26)–C(21)–C(22)	120 (2)	F(1)–B–F(4)	115 (3)
C(26)–C(21)–C(20)	121 (2)	F(2)–B–F(3)	108 (3)
C(21)–C(20)–C(30)	127 (1)	F(2)–B–F(4)	104 (3)
C(20)–C(30)–C(31)	127 (1)	F(3)–B–F(4)	115 (4)
C(30)–C(31)–C(32)	118 (1)	Cl(2)–C(8)–Cl(3)	104 (2)

Angles of Tilt of Phenyl Groups, Deg		Angles of Twist of Phenyl Groups, Deg	
[C(11)···C(16)][b,c]	8.5	[C(11)··C(16)][b,d]	18.1
[C(21)···C(26)]	−2.2	[C(21)···C(26)]	60.6
[C(31)···C(36)]	−3.9	[C(31)···C(36)]	33.5

[a] Numbers in parentheses are the esd's in the last figure quoted. [b] [C(11)···C(16)] denotes the phenyl group containing carbon atoms C(11) through C(16). [c] This tilt angle is defined by the arcsin (d_1/d_2), where d_1 is the distance of atom C(11) from the weighted least-squares plane through atoms Ir, C(10), C(20), and C(30) (see Table IV) and d_2 is the C(10)–C(11) bond length. The other tilt angles are similarly defined. A positive angle indicates that the phenyl ring is tilted toward the atom P(1). [d] This twist angle is the complement of the dihedral angle between the [C(11)···C(16)] plane and the least-squares plane containing atoms Ir, C(10), C(20), and C(30) in the absence of tilting motion.

propenylium chelate ring. A well-defined plane is formed by the iridium atom and the three carbon atoms of the propenylium group. (Some pertinent weighted least-squares planes are given in Table IV.)

TABLE IV
WEIGHTED[a] LEAST-SQUARES PLANES IN THE FORM
$Ax + By + Cz + D = 0$[b]

Plane	Atoms	*A*	*B*	*C*	*D*
1	Ir, C(10), C(20), C(30)	0.2284	0.7128	0.6631	−11.6519
2	Ir, C(1), Cl(1), C(10), C(20), C(30)	0.2324	0.6857	0.6897	−11.6316
3	C(11)···C(16)[c]	−0.1342	0.6923	0.7090	−9.9219
4	C(21)···C(26)	0.5704	−0.2299	0.7885	−6.0697
5	C(31)···C(36)	0.6838	0.6670	0.2959	−10.9469

Distances of Atoms from Mean Planes (Å)

Plane	Atom	Dist	Atom	Dist	Atom	Dist	Atom	Dist
1	Ir	0.000	C(10)	0.010	C(20)	−0.019	C(30)	0.011
	Cl(1)	−0.096	C(11)	0.220	C(21)	−0.051	C(31)	−0.099
	C(1)	0.006						

Dihedral Angles (Deg)

Planes	Angle	Planes	Angle
1,2	1.1	1,4	60.7
1,3	21.1	1,5	34.1

[a] Atoms are weighted by the reciprocals of their variances. [b] *x*, *y*, and *z* are coordinates (Å) in an orthogonal system relative to the crystal axes *a*, *b*, and *c*, respectively. [c] C(11)···C(16) refers to the plane containing phenyl group carbon atoms C(11) through C(16).

The average Ir(III)–P distance of 2.365 (3) Å in this complex is that expected for two iridium–phosphorus bonds trans to each other. Comparable bond lengths (average = 2.363 (6) Å) were found[18] for the two trans metal–phosphine bonds in *mer*-$Ir(P(CH_3)_2(C_6H_5))_3Cl_3$.

Consideration of complex metal–halogen distances shows that they are lengthened when the halogen atom is trans to a σ-bonded carbon atom and the present complex is consistent with this trend. The Ir(III)–Cl bond distance of 2.472 (5) Å where the chlorine atom is trans to a carbon atom of the propenylium group is similar to that found in $[IrCl_2(CH_3)(CO)_2]_2$, 2.52 Å,[19] and the benzylacetophenone complex, $IrCl_2(C_{15}H_{13}O)((CH_3)_2SO)_2$, 2.496 (9) Å,[20] where the chlorine atom is trans to a methyl and methylene group, respectively. Analogous arguments apply to the Ir–C(O) distance of 1.94 (2) Å since it is longer than that found in $IrI_2(COOCH_3)(CO)(C_{10}N_2H_8)$, 1.80 (2) Å[21] (CO group trans to an N atom of the bipyridine ligand), and $[IrCl_2(CH_3)(CO)_2]_2$, 1.74 and 1.76 Å[19] (CO trans to terminal and bridging chlorine atoms, respectively). Presumably the Ir–C(O) bond in the present study is lengthened because of the substantial structural trans influence of the carbon atom of the propenylium fragment.

Iridium–propenylium carbon bond distances were determined to be 2.099 (15) and 1.990 (15) Å. These may be contrasted with the Ir(III)–C distances of 2.16 (2) Å[20] in $IrCl_2(C_6H_5CHCH_2COC_6H_5)((CH_3)_2SO)_2$, 2.10 (2) Å[19] for Ir–C(CH_3) in $[IrCl_2(CH_3)(CO)_2]_2$, and 2.05 (2) Å[19] for Ir–C($COOCH_3$) in $IrI_2(COOCH_3)(CO)(C_{10}N_2H_8)$. If the metal ion is assumed to have

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(18) L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Commun.*, 30 (1970).

(19) N. A. Bailey, C. J. Jones, B. L. Shaw, and E. Singleton, *ibid.*, 1051 (1967).

(20) M. McPartlin and R. Mason, *J. Chem. Soc. A*, 2206 (1970).

(21) V. G. Albano, P. L. Bellon, and M. Sansoni, *Inorg. Chem.*, **8**, 298 (1969).

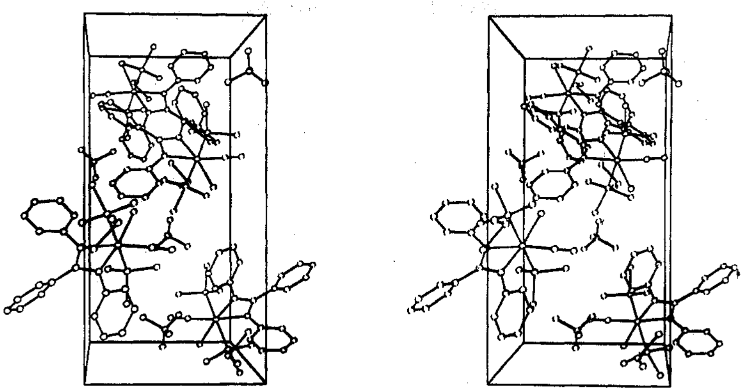

Figure 2.—Stereoscopic projection along the crystallographic *b* axis of the crystal packing of $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$.

Table V

Comparison of Structural Data for Some Cyclopropenyl and Cyclobutenyl Species[a]

	$[C_3(C_6H_5)_3]^+$ [b]	$(\pi\text{-}C_5H_5)Ni\text{-}(\pi\text{-}C_3(C_6H_5)_3)$ [c]	$[\pi\text{-}C_3(C_6H_5)_3\text{-}NiCl(py)_2]\cdot py$ [d]	$[Ir(C_3(C_6H_5)_3)\text{-}Cl(CO)(P(CH_3)_3)_2]^+$ [e]	$[C_4(C_6H_5)_4Cl]^+$ [f]
C–C (av for C_3 group)	1.373 (5)	1.429 (7)	1.421 (7)	1.385 (14)	1.40 (6)[g]
C–C (range in C_3 group)	1.370–1.376	1.421–1.439	1.414–1.429	1.364–1.405	1.38–1.43[g]
C–C (exocyclic)	1.417 (8)	1.467 (8)	1.459 (12)	1.49 (2)	1.39 (6)[h]
	1.458 (8)	1.451 (8)	1.461 (12)	1.52 (2)	1.49 (6)
	1.434 (8)	1.439 (8)	1.456 (11)	1.47 (2)	1.41 (6)
Tilt angles	0.0	20.3	19.4	8.5	0
	1.1	18.5	16.7	−2.2	0
	0.8	20.6	20.2	−3.9	0
Twist angles	7.6	19.9	8.4	18.1	0
	21.2	20.1	13.4	60.6	57
	12.1	23.5	−18.9	33.5	0

[a] The distances are given in Å and angles in deg. The esd's are given in parentheses. [b] Reference 25. [c] Reference 2. [d] Reference 3. [e] This work. [f] Reference 24. [g] For this species the "C_3 group" refers to the three carbon atoms of the allylic fragment in the cyclobutenyl ring. [h] Only the three exocyclic distances involving the allylic portion of the cyclobutenyl ring are given.

an isotropic covalent radius (see, however, ref 22 for cautionary remarks regarding this assumption), a value of 1.31 Å results for the iridium(III) covalent radius in this compound when the average Ir–P distance of 2.365 (3) Å is considered in conjunction with the accepted radius of 1.06 Å for phosphorus. Thus, an Ir–C(sp^2) distance of 2.05 Å would be expected for the Ir–C(propenylium group) if there was no significant π interaction in this portion of the molecule. Since the Ir–C distances determined are within about 3σ of this value, no appreciable metal–ligand $d\pi$–$p\pi$ overlap is envisioned in the iridium–propenylium chelate ring. Thus, the positive charge is localized primarily on the propenylium fragment. The significantly different ($\Delta/\sigma = 7.3$) Ir–C(propenylium) bond lengths are probably due in part to the dissimilar trans influence of the CO and Cl moieties.[23a] Recent calculations[23b] have related the structural trans effect to $S^2/\Delta E$ where S is the overlap integral between the orbitals forming the bond and ΔE the energy separation between the orbitals being mixed. The overlap integrals calculated for Ir(III)–Cl(sp), $S = 0.43$, and Ir(III)–C(sp), $S = 0.54$, indicate that the carbonyl group is the more strongly trans influencing ligand which is consistent with the observations in this complex. It should be noted, however, that the π-accepting ability of carbon monoxide would be expected to reduce its structural trans influence. Inspection of intramolecular nonbonded contacts suggests an additional reason for the unequal Ir–C(propenylium) bond distances. A substantial contact of 2.45 Å exists between the ortho hydrogen, H(12), on one phenyl group and chlorine atom Cl(1), whereas the corresponding contact, H(32), with C(1) of the CO group is 2.67 Å.

The 1,2,3-triphenylpropenylium-1,3-diyliridium fragment in this complex shows some remarkable structural similarities to the 4-chloro-1,2,3,4-tetraphenylcyclobutenium cation, $[C_4(C_6H_5)_4Cl]^+$, in which the 4-carbon atom can be considered equivalent to the iridium atom. Substantial multiple bonding between the three carbon atoms in the ring is indicated by the average value of 1.385 (14) Å determined for the propenylium carbon–carbon distances. This may be compared (see Table V) with the following values: 1.40 (6) Å in the allylic fragment[24] of $C_4(C_6H_5)_4Cl^+$, 1.373 (5) Å in $[C_3(C_6H_5)_3]ClO_4$,[25] 1.429 (5) Å in $\pi\text{-}(C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$,[2] and 1.421 (7) Å in $(\pi\text{-}C_3(C_6H_5)_3)NiCl(C_5H_5N)_2\cdot C_5H_5N$,[3] where the latter two compounds still have an intact three-membered aromatic ring system.

The exocyclic carbon–carbon distances, 1.49 (2), 1.52 (2), and 1.47 (2) Å, are comparable to the value of 1.48 Å accepted for a C(sp^2)–C(sp^2) single bond length which suggests that conjugation with the phenyl rings is substantially decreased when compared to other complexes containing the triphenylcyclopropenium

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(22) R. Mason and L. Randaccio, *J. Chem. Soc.*, 1150 (1971).

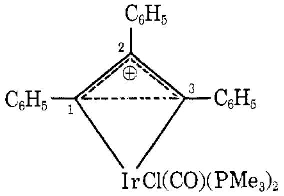
(23) (a) It is interesting to note that a recent determination of the ordered structure of $IrO_2(CO)Cl(P(C_6H_5)_2(C_2H_5))_2$ shows that the Ir–O distance trans to Cl is 2.036 (9) Å and the distance trans to CO is 2.084 (9) Å. See M. S. Weininger, I. R. Taylor, and E. L. Amma, *Chem. Commun.*, 1172 (1971); (b) R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, **47**, 20 (1969).

(24) (a) R. F. Bryan, *J. Amer. Chem. Soc.*, **86**, 733 (1964); (b) personal communication from R. F. Bryan to L. F. Dahl: L. F. Dahl and W. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965).

(25) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

ligand. This decreased phenyl conjugation is reflected in the increased rotation of the phenyl groups about their respective axes (see Table V). The distinctive arrangement of the phenyl groups relative to the plane of the iridocycle ring, namely the 2-phenyl group nearly perpendicular and the 1- and 3-phenyl groups more nearly coplanar, was also found[24] in $[C_4(C_6H_5)_4Cl]^+$. This result is in accord with predictions of valence-bond theory since no simple resonance structures can be envisioned which would localize the positive charge on the 2-carbon atom of the propenylium group (and subsequently allow it to be delocalized on the 2-phenyl group) as can be drawn for 1- and 3-carbon atoms. Resonance structures which do localize the positive charge on the 2-carbon atom are diradical in character and consequently of higher energy. Moreover, extended Hückel calculations[26] for the *trans*-1-phenylallyl and 2-phenylallyl cations indicate a very small charge delocalization into the phenyl ring for the latter case but a substantial effect in the former. In the 2-phenylallyl cation the low-lying nonbonding orbital which would stabilize the 2-phenyl group has a node at the central carbon atom of the allyl chain. Since a 2-phenyl group does not contribute significantly to the charge delocalization from an allyl or propenylium group, its rotational orientation is expected to be dictated primarily by steric factors rather than by conjugative effects. This is consistent with the present structural observations.

Comparison of the transannular distances in the iridocyclic ring, Ir···C(20), 2.610 (15) Å, and C(10)···C(30), 2.15 (2) Å, with the single bond distances expected from covalent radii, 2.06 and 1.54 Å, respectively, indicates that there are no σ-bonding interactions across this ring. It is believed, however, that there is an interaction between the pπ orbitals of the carbon atoms, C(10) and C(30), in the propenylium group, *viz.*



Katz and Gold[27] presented ultraviolet spectral evidence supporting a significant 1,3 π interaction in the cyclobutenyl cation, $C_4(CH_3)_4Cl^+$. These authors suggested a value of 0.33β for β_{13}, where β is the normal carbon–carbon 1,2 π-resonance integral and β_{13} is the cross-ring 1,3 resonance integral, to account for the electronic spectrum of $C_4(CH_3)_4Cl^+$. More recently, ^{13}C nmr evidence was presented[28] in support of a 1,3 interaction in this cation. In the same study, other noncyclic allylic cations showed no deshielding evidence for an interaction of this type since the steric constraints favoring overlap of the p orbitals on C_1 and C_3 in $C_4(CH_3)_4Cl^+$ are not present for the noncyclic cations. In order to further substantiate a C(10)···C(30) interaction in the present iridium complex, carbon pπ–pπ overlap integrals using orbitals of the type STO-6G[29] were obtained for various 1,3 distances. Actual values calculated are as follows: $C_3(C_6H_5)_3^+$, $d = 1.373$ Å, $S = 0.223$; $C_4(C_6H_5)_4Cl^+$, $d = 2.06$ Å, $S = 0.056$; $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2]^+$, $d = 2.15$ Å, $S = 0.046$; and $C_3H_5^+$ (idealized), $d = 2.42$ Å, $S = 0.025$, where d is the carbon–carbon distance and S is the value of the carbon–carbon pπ–pπ overlap integral. These values give support for making the structural comparison between the iridocyclic ring and cyclobutenyl cations.

Distances, P–C(av) = 1.832 Å, and angles, C–P–C(av) = 103.3 (4)°, within the trimethylphosphine groups do not differ significantly from those observed for other trimethylphosphine complexes.[30] High thermal motion makes the tetrafluoroborate anion and dichloromethane of crystallization particularly ill-defined. The B–F average distance of 1.30 (2) Å is shorter than the accepted value (1.42 Å) and obviously suffers from rotational oscillation effects.

Discussion

Our structural analysis shows that addition of $C_3(C_6H_5)_3^+$ to $IrCl(CO)(P(CH_3)_3)_2$ leads to incorporation of the propenylium group with formation of an Ir(III) heterocycle. Recently it has been suggested that certain metal-ion catalyzed rearrangements of strained cyclic hydrocarbons, which are thermally forbidden according to the rules of orbital symmetry conservation, proceed in a nonconcerted fashion. In these instances the intermediates are thought to be formed by oxidative addition of the metal ion across a carbon–carbon bond. In particular, evidence has been given for the occurrence of Rh(III) intermediates in Rh(I)-catalyzed conversion[31] of cubane to *syn*-tricyclooctadiene and the similarly catalyzed transformation[32] of quadricyclene to norbornadiene. There is a striking resemblence between the postulated Rh(III) intermediates in these valence isomerizations and the present iridium(III) cyclopropenyl derivative. It should be emphasized that the driving force in these reactions is twofold: (1) the propensity of the four-coordinate d^8 systems to undergo oxidative addition reactions and (2) relief of the steric strain involved in the σ bonds of the three- or four-membered rings.

Acknowledgments.—This work was generously supported by the National Science Foundation (Grant No. GP 30258). R. M. T. acknowledges with gratitude the receipt of an NDEA Fellowship, 1966–1969.

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(30) See, for example, G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).

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(32) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).