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THE STRUCTURE OF HYDRIDOCARBONYL(FUMARONITRILE)BIS(TRIPHENYLPHOSPHINE)IRIDIUM, AN OLEFIN-METAL HYDRIDE COMPLEX

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SUMMARY

The structure of the complex hydridocarbonyl(fumaronitrile)bis(triphenylphosphine)iridium, IrH(CO)(*trans*-NC–CH=CH–CN)$[P(C_6H_5)_3]_2$, has been determined from a single crystal X-ray analysis. The complex crystallizes in a monoclinic cell of dimensions $a=21.289(14)$, $b=9.383(3)$, $c=21.650(10)$ Å, $\beta=123.87(2)°$. The observed density is 1.53 $g \cdot cm^{-3}$, whereas the density calculated for four formula units per unit cell is 1.524 $g \cdot cm^{-3}$. On the basis of a successful structure analysis, the space group is *C2/c*. The structure has been refined by least-squares methods to a conventional *R*-factor of 0.056 for the 2274 independent reflections whose intensities were above background, when measured by counter techniques. The molecules are monomeric; the configuration around the iridium atom is trigonal bipyramidal, with the olefin and phosphine ligands in the equatorial plane, which also contains a twofold axis of crystallographic symmetry. The fumaronitrile ligand is nonplanar, the dihedral angle between the two planes which contain a carbon atom of a cyanide group and both olefinic carbon atoms is 136(2)°. The Ir–P and Ir–C distances are respectively 2.317(3) and 2.110(9) Å, while the C=C distance is 1.431(20) Å. Assuming an Ir-H bonded distance of 1.6 Å, the nonbonded contact between the hydridic hydrogen atom and an olefin carbon atom is 2.6 Å. It is of interest that the hydridic hydrogen atom is *cis* to the olefin since complexes related to the present one are believed to play a role in the catalyzed hydrogenation reactions of olefins.

INTRODUCTION

The nature of the bonding in transition metal complexes containing alkenes and other unsaturated covalent molecules has recently become the subject of renewed interest[1-3]. At present, there seems to be no universally accepted theoretical model for such bonding[1,2]. It is our contention[4] that accurate structural information on a number of closely related transition metal complexes is necessary for a fuller understanding of both the mode of attachment of the alkene to the metal, and the electronic state of the bound alkene. Accordingly, we have undertaken an X-ray crystal structure analysis of hydridocarbonyl(FUMN)bis(triphenylphosphine)iridium (FUMN= fu-

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maronitrile = *trans*-1,2-dicyanoethene)[4], in order to compare it with the structure of the related complex bromocarbonyl(TCNE)bis(triphenylphosphine)iridium (TCNE = tetracyanoethylene), which has been previously studied in this laboratory[5]. We have chosen to study cyanoethylene complexes since they are more stable than the corresponding complexes containing ethylene itself. In addition, the detection of geometrical changes in the olefin on complexing to a transition metal is simplified when the olefin has substituents other than hydrogen.

This work was also prompted by our interest in the relationship between the structures of the iridium–alkene complexes and those of analogous five-coordinate complexes formed by oxidative addition of unsaturated covalent molecules, other than olefins, to *trans*-$MX(CO)[P(C_6H_5)_3]_2$ (M = Ir, Rh; X = halogen). The configuration found in the molecular oxygen complexes $IrX(O_2)(CO)[P(C_6H_5)_3]_2$ (X = Cl, I)[6,7] is that of a trigonal bipyramid, with the phosphine ligands *trans* to one another in apical positions, while the sulfur dioxide complexes $MCl(CO)(SO_2)[P(C_6H_5)_3]_2$ (M = Rh, Ir)[8,9], and the nitrosyl complexes $\{IrX(CO)(NO)[P(C_6H_5)_3]_2\}[BF_4]$ (X = Cl, I)[10], exhibit a square pyramidal configuration, with *trans* phosphines in the basal plane. However, a third configuration is found in the TCNE complex[5], which is trigonal bipyramidal, but with the phosphines *cis* to each other in the equatorial plane.

The FUMN complex may be prepared by direct reaction of the olefin with $IrH(CO)[P(C_6H_5)_3]_3$, which is a catalyst for the hydrogenation of simple alkenes. Transition metal complexes containing both hydrido and olefinic ligands are believed to be important as intermediates in hydrogenation reactions; so far as we know, this is the first stucture determination of such a complex.

EXPERIMENTAL

Crystal data

$C_{41}H_{33}IrN_2OP_2$, mol.wt. = 823.9, monoclinic, $a = 21.289(14)$*, $b = 9.383(3)$, $c = 21.650(10)$ Å, $\beta = 123.87(2)°$ [temp. = 22°, λ (Mo-$K\alpha_1$) = 0.7093 Å], $U = 3591$ Å^3, $d_c = 1.524$ g·cm^{-3} for $Z = 4$, $d_o = 1.53(1)$ g·cm^{-3} (by flotation in bromoethane/1,1,2,2-tetrachloroethane). Systematic absences *hkl*: $h+k \neq 2n$, *h0l*: $l \neq 2n$. Linear absorption coefficient for X-rays of wavelength 0.7107 Å, $\mu = 40.7$ cm^{-1}.

A sample of $IrH(CO)(FUMN)[P(C_6H_5)_3]_2$ was kindly supplied by Professor W. H. Baddley. The crystals were colorless transparent needles with well formed faces. The systematic absences, determined from a preliminary photographic investigation, are consistent with the space groups *C*2/*c* and *Cc*. A morphological study indicates that the crystals belong to the point group 2/*m*; typically, all members of the forms $\{100\}$, $\{001\}$, $\{10\bar{1}\}$, and $\{11\bar{1}\}$ are exhibited. We were unable to detect any piezoelectric effect. Neither of these results is conclusive, but they both favor the centrosymmetric space group *C*2/*c*. The molecule is required to possess either C_2 or C_i symmetry if the space group is *C*2/*c*; no symmetry conditions are imposed on the molecule if the space group is *Cc*.

Intensity measurements were made with a Picker Four Circle Diffractometer, using procedures which have been described in detail elsewhere[11]. A needle-shaped

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* Throughout this paper limits of error are estimated standard deviations and are in units of the least significant digits of the quantity to which they refer.

crystal of dimensions $0.39 \times 0.13 \times 0.10$ mm was mounted on the instrument so that the symmetry axis made an angle of roughly 16° with the Φ axis. The half-widths of a number of narrow-source open-counter ω scans[12] ranged from 0.06 to 0.11°, indicating that the mosaicity of the crystal was satisfactorily small. The setting angles of 15 reflections were determined manually through a narrow vertical slit at a take-off angle of approximately 0.5°. From these observations the crystal orientation and preliminary values of the cell parameters wêre derived by a least-squares procedure[11]. The data were collected using molybdenum radiation, in conjunction with a 3 mil niobium β filter. The pulse height analyzer was set to accept a 90% window centered on the Mo-$K\alpha$ peak. Peak intensities were measured using the θ–2θ scan technique, the scan rate being 1° in 2θ per minute. A symmetrical scan of 1.5° in 2θ, centered on the α_1 peak, was used for reflections in the sphere with 2θ (Mo-$K\alpha_1$) $\leqslant 36°$, while, for the remainder, the scan started 0.65° below the α_1 peak and ended 0.85° above it. The local background was counted for 10 seconds at each extreme of the scan range. Copper foil attenuators were automatically inserted into the exit beam until the maximum counting rate was less than 7000 counts per second. A take-off angle of 1.7° was used throughout the experiment. The counter-crystal and source-crystal distances were respectively 31 and 21 cm. The dimensions of the counter aperture were 5×5 mm.

A total of 3024 independent reflections was measured in the range 2θ (Mo-$K\alpha_1$) $\leqslant 49°$. No further data were collected, as at higher scattering angles only a small proportion of the intensities were significantly above background. The intensities of four strong reflections were measured periodically during the run to monitor crystal and electronic stability. Only random fluctuations in the intensities of these standards were observed; the maximum fluctuation in a standard was 2% of its average intensity.

The observed peak counts were corrected for background to yield the net integrated intensity I. The standard deviation of I was estimated by

$$\sigma(I) = [C_{tot} + (t_p^2/4t_b^2)(B_1 + B_2) + (p \cdot I)^2]^{\frac{1}{2}}$$

where C_{tot} is the total peak count obtained in t_p seconds, and B_1 and B_2 are the background counts, each obtained in t_b seconds, and where $I = C_{tot} - (t_p/2t_b)(B_1 + B_2)$. The factor p was taken as 0.04. For 2274 reflections the condition $I \geqslant 3\sigma(I)$ was met, and only these reflections were used in the subsequent analysis. The intensities and their standard deviations were corrected for Lorentz-polarization and absorption effects. For the latter, the dimensions of the crystal were carefully measured by means of a micrometer eyepiece and the indices of the bounding faces were determined by optical goniometry. The calculated transmission factors* ranged from 0.65 to 0.73. When all intensity measurements had been made, 10 strong reflections in the range $36 \leqslant 2\theta$ (Mo-$K\alpha_1$) $\leqslant 42°$ were centered manually as before, and the crystal orientation and cell parameters again derived by a least-squares procedure. The cell parameters from this refinement were taken as the final values. No significant change was found to have occurred in the crystal orientation.

Structure solution and refinement

The structure was solved in the space group $C2/c$ using standard Patterson,

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* In addition to various local programs for the CDC 6400, local versions of Zalkin's FORDAP Fourier program, Hamilton's GONO absorption correction program, Busing and Levy's function and error program, and Johnson's ORTEP thermal ellipsoid plotting program were used.

least-squares and Fourier methods. From a Patterson synthesis of 1131 low-angle data it was possible to locate the iridium atom on the twofold axis, and also to determine the positions of the atoms P, C, O, and C(1) (see Fig. 1). These positions were consistent with a trigonal bipyramidal configuration of the molecule, with the phosphine and FUMN ligands in the equatorial plane. Since this plane also contains the twofold axis, a 50% occupancy of each apical site by carbonyl and hydride is required by symmetry. At this stage the agreement factors $R(\Sigma|\Delta|/\Sigma|F_o|, \Delta=|F_o|-|F_c|)$ and $R_w[(\Sigma w\cdot\Delta^2/\Sigma w\cdot F_o^2)^{\frac{1}{2}}]$ were 0.20 and 0.28 respectively. The locations of the remaining nonhydrogen atoms were determined from a subsequent electron density synthesis.

Refinement of the structure was continued by the method of full-matrix least-squares. The function minimized was $\Sigma w\cdot\Delta^2$, where $w=1/\sigma^2(F_o)=4F_o^2/\sigma^2(F_o^2)$. Throughout the refinement the phenyl rings were constrained to $6/mmm$ (D_{6h}) symmetry, and the C–C bond distance was fixed at 1.392 Å. In these and subsequent calculations, the atomic scattering factors used were taken from the usual compilation[13], with the exceptions of those of Ir and H*. The anomalous dispersion corrections of Cromer[16] for Ir and P were applied to the calculated structure factors[17]. In all cycles the scale factor and the group and nongroup positional parameters were refined, with the exceptions noted below.

Initially, the temperature factors of the nongroup atoms were restricted to isotropic values, and a single overall isotropic thermal parameter was adjusted for each group. This refinement led to agreement factors $R=0.102$ and $R_w=0.113$. The most significant features on a difference map calculated at this stage were attributable to anisotropic thermal motions of the heavier atoms; peaks which could be ascribed to some of the phenyl ring hydrogen atoms were also observed on this map. Fixed contributions for the ring hydrogen atoms were accordingly included in all subsequent structure factor calculations; the C–H distance was taken to be 1.0 Å, and the temperature factor of each hydrogen atom was set equal to that of the carbon atom to which it was bonded.

In a further round of calculations, anisotropic thermal parameters for all the nongroup atoms and individal isotropic thermal parameters for the phenyl ring carbon atoms were refined. The hydrogen atom H(1), bonded to C(1), was included in the structure factor calculations, after it had been observed on a difference map; it was positioned so as to give an idealized geometry about C(1) and its parameters were not refined. Inclusion of H(1) in the calculations caused no appreciable change in the C(1)–C(1)′ bond length. This refinement converged to $R=0.056$ and $R_w=0.062$. The disordered hydridic hydrogen was excluded from these calculations.

In the final cycle no parameter shifted by more than 0.6 of its estimated standard deviation. The standard deviation of an observation of unit weight was 1.67. However, the relative correctness of the weighting scheme, judged by the variation in mean $w\cdot\Delta^2$ with $\lambda^{-1}\cdot\sin\theta$ and $|F_o|$, was highly satisfactory. When the $\sigma(F_o)$ were scaled to make the standard deviation of an observation of unit weight equal to unity, $|\Delta|/\sigma(F_o)$ was less than 5 for all reflections and greater than 4 for only one. For the weak reflections not used in the refinement it was true that either $|\Delta|/\sigma(F_o)<3$ or $|F_c^2|/\sigma(F_o^2)<4$. Inspection of the structure factor agreement at low angle did not indicate that extinction corrections were required.

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* Ir scattering factor: see ref. 14; H scattering factor: see ref. 15.

The assumption that the space group is *C*2/*c* thus led to a model which was satisfactory, in terms both of structure factor agreement and molecular geometry. However, some features of the model seemed to merit further consideration. The thermal parameters of some of the ring carbon atoms, especially those of ring R3, were unexpectedly high. The height of the largest peak in a difference map, calculated at this stage, was 1.5 e/Å^3 or 34% of the mean height of a ring carbon atom in an electron density synthesis; this peak lay midway between atoms R3C4 and R3C5. There were also peaks of height 0.6–0.8 e/Å^3 associated with carbon atoms of the other two rings; these appeared to be due to our failure to correct for the anisotropic motions of these atoms.

Accordingly, we decided to refine the structure on the assumption that it was ordered, and that the space group was *Cc*. *Cc* is a polar space group, and the two molecular enantiomorphs possible, corresponding to placing a carbonyl at one or other of the two apical positions, are therefore not equivalent. For each choice of hand, the scale factor and the positional and thermal parameters of the atoms of the carbonyl ligand were adjusted by least-squares, while the rest of the parameters were fixed at the values obtained from the refinement in *C*2/*c*. For one choice, both agreement factors increased slightly, compared with the centrosymmetric model, while, for the other, they decreased slightly ($R=0.055$ and $R_w=0.061$). Refinement of the latter model was therefore continued, the scale factor and the positional and thermal parameters of both the nongroup and group atoms being adjusted; small arbitrary shifts were given to all the atoms to destroy the twofold symmetry. During these calculations the temperature factors of five of the nongroup carbon and nitrogen atoms became non-positive definite, even when attempts were made to refine them from their isotropic values. After four cycles of calculations R was 0.052 and R_w was 0.058. Assuming that the data contain only random errors, this improvement is significant at less than the 0.5% probability level[18]. However, chemically equivalent bond lengths after this refinement showed unacceptably large discrepancies. Thus, the P–C distances ranged over 0.16 Å, compared with a spread of 0.03 Å in the centrosymmetric model, and the two C(1)–C(2) distances differed by 0.33 Å. The Ir–P and C(1)–C(1)′ distances, however, did not alter appreciably during this refinement. Refinement in *Cc* thus leads to model which is physically less likely than the centrosymmetric model. Such a situation is to be expected for mathematical reasons if the structure is very close to centrosymmetric, since the normal matrix will then be nearly singular. An identical space group ambiguity occurs in the case of potassium hydrogen malonate[19], and there it appears that a final decision on the space group will have to be made on purely chemical grounds. That the FUMN structure is, at least, very close to being centrosymmetric is evidenced by our ability to observe some of the hydrogen atoms on difference maps. We therefore consider the results of the refinement in *C*2/*c* to be the best we can obtain. The final parameters from this refinement are listed in Tables 1 and 2, and the structure factors derived from these parameters are presented in Table 3. Views of the inner coordination sphere around the iridium atom and of the entire molecule are given in Figs. 1 and 2. For the sake of clarity the disorder of the apical ligands is not shown in these figures, nor are any of the hydrogen atoms.

(*Continued* p. 183)

TABLE 1

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $IrH(CO)(FUMN)[P(C_6H_5)_3]_2$

Atom	x	y	z	β_{11}[a] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0	0.19199(7)	0.25	403(3)	813(10)	282(3)	0	198(2)	0
P	0.01905(16)	0.32625(29)	0.34888(15)	368(11)	891(37)	308(9)	−43(16)	194(8)	−24(15)
C(1)	0.00688(63)	−0.01950(100)	0.28635(57)	457(47)	726(121)	357(39)	59(63)	235(39)	62(55)
C(2)	−0.05183(82)	−0.06929(125)	0.29310(67)	696(67)	1057(153)	449(49)	−200(86)	398(51)	−57(72)
N	−0.09949(80)	−0.10851(129)	0.29853(70)	942(76)	1632(181)	665(58)	−307(97)	598(60)	−153(83)
C	0.1108(12)	0.1922(26)	0.2988(12)	279(75)	1366(302)	399(78)	−198(155)	157(65)	−291(154)
O	0.1760(11)	0.1951(23)	0.3271(11)	458(79)	2684(376)	600(83)	42(159)	257(68)	−439(161)
H(1)	0.0571	−0.0546	0.3284	5.4					

Group[b]	x_c	y_c	z_c	δ	ε	η
R_1	0.11857(29)	0.61450(59)	0.39792(29)	−0.5856(61)	2.5773(45)	−1.5269(62)
R_2	−0.13508(37)	0.41286(78)	0.33316(32)	2.8866(60)	−3.1419(64)	−2.6762(57)
R_3	0.11730(44)	0.14866(74)	0.50111(41)	1.4778(105)	−2.3919(69)	−1.0921(98)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\beta_{12}\cdot h\cdot k+2\beta_{13}\cdot h\cdot l+2\beta_{23}\cdot k\cdot l)]$. The β_{ij}'s have been multiplied by 10^5.

[b] x_c, y_c, and z_c are the fractional coordinates of the ring centroids. The angles δ, ε, η (in radians) are rotations about the axes of an internal coordinate system for each ring. These rotations bring about alignment of the ring axial system (apart from translation) with an orthogonal axial system, a*, b, c, defined by the crystal (See *e.g.* ref. 20).

TABLE 2

PARAMETERS OF GROUP CARBON ATOMS

Atom	x	y	z	B(Å^2)
R_1C_1[a]	0.0765(5)	0.4892(8)	0.3775(4)	4.4(2)
R_1C_2	0.0969(4)	0.5589(9)	0.4430(4)	6.1(3)
R_1C_3	0.1390(6)	0.6842(10)	0.4634(4)	7.1(3)
R_1C_4	0.1606(6)	0.7398(8)	0.4183(5)	6.7(3)
R_1C_5	0.1402(4)	0.6701(8)	0.3529(4)	6.1(3)
R_1C_6	0.0982(5)	0.5449(9)	0.3325(4)	5.0(2)
R_2C_1	−0.0670(4)	0.3794(10)	0.3416(5)	5.0(2)
R_2C_2	−0.0838(5)	0.5205(8)	0.3468(5)	6.0(3)
R_2C_3	−0.1519(6)	0.5539(9)	0.3384(6)	8.1(4)
R_2C_4	−0.2032(4)	0.4463(13)	0.3247(6)	9.1(4)
R_2C_5	−0.1863(5)	0.3053(11)	0.3195(6)	10.7(5)
R_2C_6	−0.1182(6)	0.2718(8)	0.3280(6)	8.0(4)
R_3C_1	0.0733(7)	0.2250(16)	0.4352(6)	5.6(3)
R_3C_2	0.1450(6)	0.1781(10)	0.4575(6)	8.2(4)
R_3C_3	0.1890(5)	0.1017(17)	0.5234(7)	10.4(5)
R_3C_4	0.1614(8)	0.0723(18)	0.5670(6)	10.5(5)
R_3C_5	0.0896(8)	0.1192(12)	0.5448(6)	12.2(6)
R_3C_6	0.0456(6)	0.1956(17)	0.4789(7)	9.2(4)

[a] The atoms in each ring are numbered so that *e.g.* R_1C_1 is the carbon atom of ring R_1 bonded to phosphorus; R_1C_4 is *para* to R_1C_1.

Fig. 1.

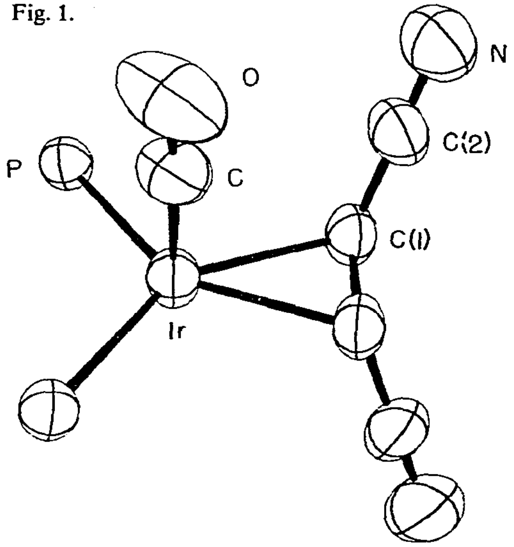


Fig. 2.

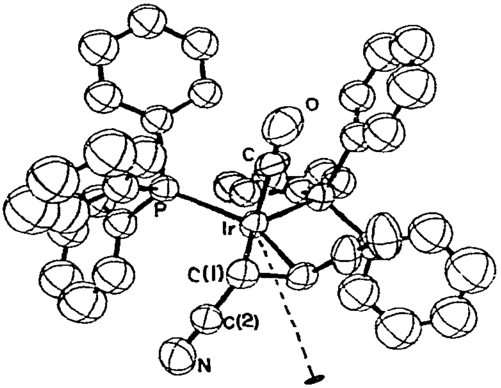


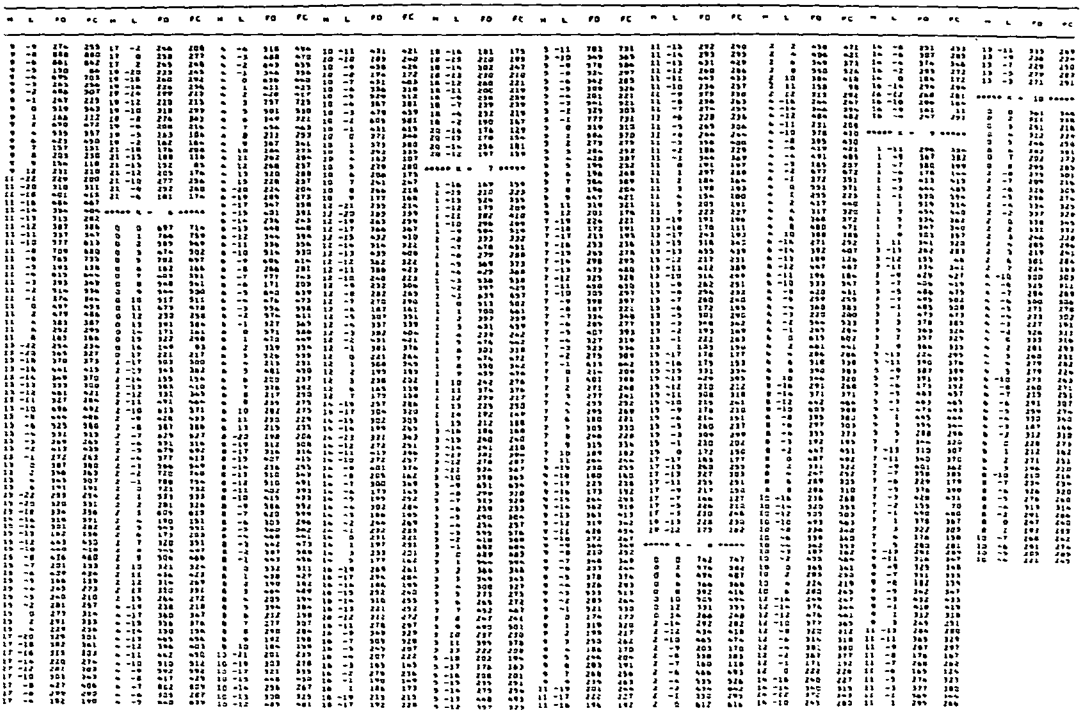
Fig. 1. A perspective view of the coordination sphere around the iridium atom in IrH(CO)(FUMN)-$[P(C_6H_5)_3]_2$. (FUMN=*trans*-1,2-dicyanoethene). Here, and in Fig. 2, the 50% probability ellipsoids for thermal motion are displayed. Hydrogen atoms are not shown .

Fig. 2. A perspective view of the molecule IrH(CO)(FUMN)$[P(C_6H_5)_3]_2$. Hydrogen atoms are not shown.

TABLE 3

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 10) FOR $IrH(CO)(FUMN)[P(C_6H_5)_3]_2$

H	L	FO	FC	H	L	FO	FC
***** K =		0	*****	18	-22	343	344
0	0		8110	18	-20	276	264
				18	-18	284	284
0	2	1830	1849	18	-16	309	343
0	4	837	737	18	-14	430	387
0	6	232	164	18	-12	443	331
0	8	361	322	18	-10	322	290
0	10	1430	1403	18	-8	243	292
0	12	644	864	18	-6	388	388
0	14	340	423	18	-4	300	481
0	16	315	291	18	-2	345	387
0	18	374	331	18	0	184	184
0	20	334	342	18	2	190	172
2	-22	330	309	20	-22	334	274
2	-20	399	438	20	-20	237	233
2	-18	423	422	20	-18	224	233
2	-16	417	373	20	-16	263	263
2	-14	402	341	20	-14	379	403
2	-12	783	832	20	-12	324	314
2	-10	1243	1347	20	-10	196	219
2	-8	1141	1263	20	-8	203	237
2	-6	876	943	20	-6	292	284
2	-4	239	183	20	-4	291	336
2	-2	2183	1930	20	-2	192	221
2	0	2773	2433	20	0	176	137
2	2	1719	1609	22	-22	197	203
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]



DISCUSSION

The crystal structure consists of discrete molecules of IrH(CO)(FUMN)[P$(C_6H_5)_3]_2$. Calculation of all intermolecular contacts less than 3.8 Å revealed none appreciably smaller than the sum of the Van der Waals radii of the atoms involved. Thus, the shortest carbon–carbon and carbon–hydrogen contacts between atoms in different molecules are 3.47 and 2.75 Å respectively. The thermal motions of the non-group atoms show no unusual features (see Fig. 1 and Table 4). The root-mean-square amplitudes of vibration are similar to those found in the TCNE complex for comparable atoms. The temperature factors of some of the ring carbon atoms, however, are unexpectedly high.

The molecular configuration is trigonal bipyramidal, with the phosphines and olefin in the equatorial plane*. This configuration is not necessarily determined by that of the parent complex, IrH(CO)[P$(C_6H_5)_3]_3$, which, from the known structure of the analogous rhodium complex[20], is almost certainly trigonal bipyramidal, with apical H and CO. In all the five-coordinate complexes of IrX(CO)-[P$(C_6H_5)_3]_2$ which have been studied by diffraction methods, the phosphines remain *trans*, as in the parent compound, with the exception of the olefin complexes, IrBr-(CO)(TCNE)[P$(C_6H_5)_3]_2$ (ref. 5) and IrI(CO)(C_2F_4)[P$(C_6H_5)_3]_2$ (ref. 21), in which a configuration similar to that of the FUMN complex described here is found. It seems more likely to us that the occurrence of only one of the seven geometric isomers possible for these trigonal bipyramidal iridium–olefin complexes is a consequence of

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* Throughout this paper olefins are counted as single ligands in describing metal coordination polyhedra.

TABLE 4

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	1	2	3
Ir	0.190(1)	0.208(1)	0.254(1)
P	0.198(4)	0.221(3)	0.243(4)
C(1)	0.177(15)	0.237(13)	0.271(14)
C(2)	0.200(17)	0.236(16)	0.338(16)
N	0.245(16)	0.269(15)	0.399(16)
C	0.178(36)	0.240(29)	0.300(31)
O	0.255(25)	0.272(23)	0.402(27)

TABLE 5

SELECTED INTRAMOLECULAR DISTANCES (Å)

Atoms	Distance	Atoms	Distance	Atoms	Distance
Ir-P	2.317(3)	P-C(1)	3.469(10)	C(2)-C	4.19(3)
Ir-C(1)	2.110(9)	P-C(1)'	4.195(10)	C(2)-C'	2.96(2)
Ir-C	1.975(21)	P-C	2.99(2)	C(2)-O	5.12(3)
C(1)-C(1)'[a]	1.431(20)	P-C'	3.10(2)	C(2)-O'	3.50(2)
C(1)-C(2)	1.416(16)	P-O	3.83(2)	N-C	5.29(3)
C(2)-N	1.145(15)	P-O'	3.96(2)	N-C'	3.45(2)
C-O	1.165(24)	C(1)-C	2.87(3)	N-O	6.23(2)
P-R_1C_1	1.84(1)	C(1)-C'	2.91(2)	N-O'	3.64(2)
P-R_2C_1	1.82(1)	C(1)-O	3.78(2)	P-P'	3.888(6)
P-R_3C_1	1.82(1)	C(1)-O'	3.82(2)		

[a] Here and elsewhere those atoms in the molecule which are related to the atoms listed in Tables 1 and 2 by the molecular twofold axis of symmetry are denoted by a prime.

TABLE 6

SELECTED INTRAMOLECULAR ANGLES (°)

Atoms	Angle	Atoms	Angle	Atoms	Angle
P-Ir-P'	114.1(1)	C(1)-Ir-C'	90.8(7)	Ir-C(1)-C(1)'	70.2(3)
P-Ir-C(1)	103.1(3)	Ir-P-R_1C_1	120.4(4)	Ir-C(1)-C(2)	117.8(8)
P-Ir-C(1)'	142.8(3)	Ir-P-R_2C_1	114.8(3)	Ir-C-O	178.7(24)
P-Ir-C	87.9(6)	Ir-P-R_3C_1	110.4(5)	Cl(1)'-Pt-Cl(2)	117.5(12)
P-Ir-C'	92.1(7)	R_1C_1-P-R_2C_1	104.5(5)	C(1)-C(2)-N	179.5(14)
C(1)-Ir-C(1)'	39.7(5)	R_1C_1-P-R_3C_1	99.5(5)		
C(1)-Ir-C	89.3(8)	R_2C_1-P-R_3C_1	105.3(7)		

steric factors, either in the complexes themselves, or in the transition state through which they are formed. The angles subtended at the iridium atom by the bulky phosphine and olefin ligands are greatest when these substituents are equatorial, and an inspection of molecular models also suggests that this configuration is sterically favorable. None of the nonbonded distances between the phosphine and olefin ligands in the FUMN complex is less than the sum of the appropriate Van der Waals radii.

In the closely related molecular oxygen complexes, $IrX(O_2)(CO)[P(C_6H_5)_3]_2$ (X = Cl, I), an arrangement with apical phosphines *trans* to one another still leaves sufficient room for the smaller oxygen molecule in the trigonal plane[6,7]. If electronic effects were the overriding factor in determining the configurations of these systems then one would be falsely led to expect that the oxygen and olefin complexes would be the same. In $Fe(CO)_4A$, A = acrylonitrile[22] or fumaric acid[23], the only other five-coordinate d^8 complexes containing a transition metal bonded to an acyclic olefin for which structural evidence is available, the olefin again lies in the equatorial plane of a trigonal bipyramid; here also the observed configuration appears to be the more sterically favorable one.

In the FUMN complex the plane containing the iridium and phosphorus atoms makes an angle of 0.2(9)° with the plane containing the iridium atom and the olefinic carbon atoms. In the TCNE complex this angle is also not significantly different from zero. In Zeise's salt, $K[PtCl_3(C_2H_4)]H_2O$, on the other hand, the C=C vector is normal to the plane containing the platinum and chlorine atoms[24]. There is some evidence[25] that free rotation of the olefin about the $M-\overset{C}{\underset{C}{\parallel}}$ vector is possible in solution, and the observed conformations of these systems may simply be the result of nonbonded interactions between the ligands. Electronic effects may also be active here, however, since in such trigonal d^{10} systems as $Ni(C_2H_4)[P(C_6H_5)_3]_2$ (ref. 26) and $Pt(TCNE)[P(C_6H_5)_3]_2$ (ref. 27) the olefinic C–C bond also lies nearly in the equatorial plane, a result not expected from naive stereochemical arguments.

In all accurate diffraction studies of compounds containing simple olefins bound to transition metals, with the exception of Zeise's salt, the length of the C–C bond is found to be greater than in the free olefin[4]. In Zeise's salt the C–C bond length found in a neutron diffraction analysis is 1.354(15) Å[24]. However, in the iridium FUMN complex the C–C bond length is 1.431(20) Å, whereas in the iridium TCNE complex it is 1.506(15) Å*.

This lengthening of the C–C bond in the TCNE complex is accompanied by a change in the Ir–P distance from 2.317(3) Å to 2.400(3) Å. We believe that these differences are due to the greater electron withdrawing power of TCNE relative to FUMN, rather than to the substitution of apical bromine for apical hydrogen. In the closely related compounds $IrX(CO)(A)[P(C_6H_5)_3]_2$, X = Cl or I, A = olefin, Vaska has shown that both the stability constants and the carbonyl stretching frequencies increase steadily with the number of cyanide substituents on the olefin, whereas these properties are less sensitive to change of X from chlorine to iodine while the olefinic ligand remains the same[2]. Structural work on the analogous molecular oxygen complexes also shows that the Ir–P distances are unaltered when iodine replaces chlorine *cis* to phosphorus[6,7]. In terms of the Chatt–Dewar bonding scheme these results may be rationalized by supposing that the degree of back-donation from metal to olefin in d^8 systems is determined mainly by the electron withdrawing power of the olefin; the lengthening of the Ir–P distances in the TCNE complex relative to the

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* The TCNE molecule is planar and the length of the C–C double bond is 1.34 Å, close to that found in ethylene itself[28,29]. Although no structural data are available for the FUMN molecule there seems no reason to suppose that it is non-planar, or that the olefinic bond length differs much from 1.34 Å.

FUMN complex is consistent with such a view. That this is also true for d^{10} metal–olefin complexes cannot yet be decided, since published structural studies are extremely few. The greater electron donating ability of d^{10} transition metals may make the electron withdrawing power of the olefin less important in such systems. Undoubtedly equally satisfactory rationalizations of the bonding may be given in terms other than those of the Chatt–Dewar model.

In addition to changes in the C–C bond length, the FUMN ligand distorts considerably from planarity on attachment to iridium. Thus the dihedral angle between the two planes defined by a cyanide carbon atom and the carbon atoms directly bonded to the iridium atom is 136(2)°. Another way of looking at this distortion, which has advantages when comparisons are being made between different compounds, is to consider the dihedral angle between the plane defined by the metal and olefinic carbon atoms and the plane defined by the olefinic carbon atoms and an atom directly bonded to one of them, such as the carbon of a cyanide group. This angle is 112(1)° in the FUMN complex; values ranging from 109 to 115° are found in the TCNE compound, whereas in Zeise's salt the distortions are smaller, the range being from 99 to 104°. Despite this distortion the angles C–C–CN remain close to 120° in both of the iridium complexes. Mason[1] has pointed out some electronic factors which could cause such distortion.

The metal–olefinic carbon distances in the FUMN and TCNE complexes of iridium, and in Zeise's salt, all lie in the range 2.11–2.15 Å. Evidently these distances are not sensitive to the degree of metal–olefin back-bonding.

Our failure to detect the position of the hydridic hydrogen atom in the difference maps is evidence that its scattering is dominated by the scattering from the half carbonyl group and hence that the hydrogen atom lies very nearly along the extension of the O–C–Ir axis. If one assumes this and also takes the Ir–H distance to be equal to 1.6 Å, the Mn–H distance in $HMn(CO)_5$ (ref. 30), then there is a C(1)···H nonbonded distance of 2.6 Å. The fact that the hydridic hydrogen atom and the olefin are *cis* to one another is of particular significance in view of the intermediate role which complexes closely related to the present one are believed to play in catalyzed hydrogenation reactions of olefins.

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REFERENCES

1 R. Mason, *Nature*, 217 (1968) 543.
2 L. Vaska, *Accounts Chem. Res.*, 1 (1968) 335
3 R. Jones, *Chem. Rev.*, 68 (1968) 785.
4 Lj. Manojlović–Muir, K. W. Muir and J. A. Ibers, *Disc. Faraday Soc.*, 47 (1969), in press.
5 J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, (1968) 235.
6 S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 87 (1965) 2581.
7 J. A. McGinnety, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6 (1967) 2243.

8 S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 5 (1966) 405.
9 K. W. Muir and J. A. Ibers, to be published.
10 D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 7 (1968) 2345; *Inorg. Chem.*, 8 (1969) 1282.
11 P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6 (1967) 197.
12 T. C. Furnas, *Single Crystal Orienter Instruction Manual*, General Electric Co., Milwaukee, Wisconsin, 1957.
13 J. A. Ibers, *International Tables for X-ray Crystallography*, Vol. 3, Kynoch Press, Birmingham, 1962.
14 D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18 (1965) 104.
15 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 42 (1965) 3175.
16 D. T. Cromer, *Acta Crystallogr.*, 18 (1965) 17.
17 W. C. Hamilton and J. A. Ibers, *Acta Crystallogr.*, 17 (1964) 781.
18 W. C. Hamilton, *Statistics in Physical Science*, Ronald Press, New York, 1964.
19 R. Parthsavathy, *Science*, 161 (1968) 179; G. Ferguson, J. G. Sime, R. B. Young and J. C. Speakman, *Chem. Commun.*, (1968) 162.
20 S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18 (1965) 511.
21 N. E. Kime, Doctoral Dissertation, Northwestern University, 1968.
22 A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, 15 (1962) 1117.
23 C. Pedone and A. Sirigu, *Acta Crystallogr.*, 23 (1967) 759; *Inorg. Chem.*, 7 (1968) 2614.
24 R. Spratley, K. Klanderman and W. C. Hamilton, Private Communication.
25 R. Cramer, *J. Amer. Chem. Soc.*, 86 (1964) 217.
26 C. D. Cook, C. H. Koo, S. C. Nyburg and M. T. Shiomi, *Chem. Commun.*, (1967) 426; W. Dreissig and H. Dietrich, *Acta Crystallogr. Sect. B.*, 24 (1968) 108.
27 C. Panattoni, G. Bombieri, U. Belluco and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 798.
28 *Chem. Soc. Spec. Publ.*, No. 18, Chemical Society, London, 1965.
29 D. A. Beko and K. N. Trueblood, Private Communication.
30 S. J. La Placa, W. C. Hamilton, J. A. Ibers and A. Davison, *Inorg. Chem.*, in press.