Crystal and Molecular Structure of μ-(Acetyl-*O:C*)-μ-(benzoyl-*O:C*)-μ-(diphenylphosphido-*P*)-tricarbonyl[(η^5-cyclopentadienyl)iridium(III)]manganese Hemibenzene[1]

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Abstract: The structure of $(\eta^5\text{-}C_5H_5)Ir\text{-}\mu[C(C_6H_5)O]\text{-}\mu\text{-}[C(CH_3)O]\text{-}\mu\text{-}[P(C_6H_5)_2]\text{-}Mn(CO)_3\cdot\frac{1}{2}C_6H_6$ has been determined by a three-dimensional X-ray diffraction study. The yellow solid crystallizes in the space group $P2_1/c$ of the monoclinic system with $a = 21.089$ (4) Å, $b = 8.576$ (2) Å, $c = 16.530$ (2) Å, $\beta = 102.50$ (1)°, $V = 2918.6$ (11) Å^3, $Z = 4$, $\rho_{\text{measd}} = 1.72$ (2) g/cm^3, $\rho_{\text{calcd}} = 1.75$ g/cm^3. Diffraction data were collected to $2\theta = 46°$ using Mo Kα radiation and a Syntex P$\bar{1}$ automated diffractometer. The structure was refined by a full-matrix least-squares procedure to a conventional discrepancy factor of $R_1 = 0.035$ for 2906 unique nonzero reflections having $I \geq 3.0\sigma(I)$. The molecule contains a novel tricyclic construction in which the iridium atom is bonded to the manganese atom through three bridging groups: formal iridium acetyl and benzoyl groups, each coordinated through oxygen to manganese, and a bridging diphenylphosphido group. The long Ir–Mn distance of 3.543 (2) Å and the large Ir–P–Mn angle of 99.1 (1)° indicate the absence of metal-metal bonding in conformity with the EAN rule. The short Ir–C distances and long C–O distances of the formal acetyl and benzoyl bridges are discussed in terms of electron delocalization and strain in the tricyclic system.

The title compound was obtained in 80% yield from the reaction of $(\eta^5\text{-}C_5H_5)Ir(CO)[P(C_6H_5)_3]$ with $CH_3Mn(CO)_5$ as described in the previous paper.[2] Based on spectroscopic evidence of a novel structure, it was subsequently subjected to crystallographic analysis as described below.

Experimental Section

Collection and Reduction of X-Ray Data. The complex crystallizes as air- and X-ray-stable yellow elongated hexagonal platelets from a benzene-pentane mixture at 0°. Nearly all of these were relatively thin plates whose most prominent face was later identified as {100}. A crystal was cut and mounted along its *b* axis on a glass fiber. Preliminary oscillation and Weissenberg (*h*0*l* and *h*1*l*) photographs taken with Cu Kα radiation indicated a monoclinic space group with systematic absences, $l = 2n + 1$, for all *h*0*l* reflections. The crystal was remounted approximately along the *c* axis and centered on a Syntex P$\bar{1}$ autodiffractometer equipped with a scintillation counter and graphite-monochromatized Mo Kα radiation. From the observed systematic absences in 0*k*0 for $k = 2n + 1$, the space group was determined to be $P2_1/c$.[3] The crystal was measured to be 0.195 × 0.090 × 0.255 mm along the *a*, *b*, and *c* axes, respectively, in preparation for an absorption correction, for which μ(Mo Kα) = 53.7 cm^{-1}. The crystal faces were identified as {100}, {$\bar{1}00$}, {001}, {$00\bar{1}$}, {$0\bar{1}0$}, {$11\bar{1}$}, and {$\bar{1}11$}.

The 2θ, ω, ϕ, and χ settings of the Mo Kα peaks of 15 reflections ($2\theta = 2$–21°) were determined. These values were used in a least-squares refinement of cell parameters and orientation parameters using λ 0.71069 Å (Mo Kα). The resulting unit cell parameters (at 27.2 ± 0.5°) and their estimated standard deviations are $a = 21.089$ (4) Å, $b = 8.576$ (2) Å, $c = 16.530$ (2) Å, and $\beta = 102.50$ (1)°. The unit cell volume is $V = 2918.6$ (11) Å^3. The density, measured by flotation in a mixture of 1,2-dibromoethane and bromobenzene, is 1.72 (2) g/cm^3 (calculated density 1.75 g/cm^3 with $Z = 4$). Thus, there is one formula unit of $C_{29}H_{23}O_5PMnIr\cdot\frac{1}{2}C_6H_6$ in the asymmetric unit, and molecular symmetry is crystallographically required only for C_6H_6. Intensities were measured by the θ–2θ scan technique with a scan rate of 2°/min and a scan range from 1.0° below the Kα_1 peak to 1.0° above the Kα_2 peak with a background time to scan time ratio of 0.8:1. The takeoff angle was 4°. The pulse height analyzer was set at an 85% window for Mo Kα radiation and attenuation was used for counting rates in excess of 10^3 counts/sec. Crystal and instrument stability were monitored by a set of three standard reflections ($\bar{5}00$, $\overline{214}$, 018) measured after every 97 reflections; no significant variation in the intensities was found. One quadrant of 4601 intensities accessible with $2\theta \leq 46°$ was collected. Net intensities were calculated assuming a linear background profile between the scan limits of each reflection. The 2906 unique reflections for which $I \geq 3.0\sigma(I)$ were used in the solution and refinement of the structure.

The data were reduced and processed by utilization of the following equations.[4]

$$I = N - (t_s/2t_b)(B_1 + B_2)$$

$$\sigma(I) = [N + (t_s/2t_b)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$$

$$|F_o| = K[I/(\text{Lp})]^{1/2}$$

$$\sigma(F_o) = (K/2)[\sigma(I)/I(\text{Lp})]^{1/2}$$

where N is the total scan count, B_1 and B_2 are the individual background counts, t_s is the scan time (sec), and t_b is the time (sec) each background is counted. Lp, defined as

$$\text{Lp}^{-1} = \sin 2\theta/(\cos^2 2\theta + \cos^2 2\theta_m)^6$$

where $2\theta_m$ is the monochromator angle (12.16°), is the correction for Lorentz and polarization effects. In the present case, $t_b = 0.4t_s$. Absorption correction terms (in F) varied from 0.655 to 0.796; therefore an absorption correction was applied.

Structure Solution and Refinement. An inner sphere ($2\theta < 40°$) of 2103 reflections was used for the solution and early refinement of the structure. The positions of the iridium and manganese atoms were located from a three-dimensional Patterson synthesis. Three Fourier syntheses yielded the positions of all non-hydrogen atoms except those of the benzene of crystallization. Least-squares refinement with isotropic temperature factors followed by a difference Fourier located the carbon atoms of the benzene of crystallization. Refinement was carried out by use of full-matrix least-squares procedures using atomic scattering factors compiled by Hanson et al.[5a] for all non-hydrogen atoms while those used for the hydrogen atoms were derived from Stewart et al.[5b] Dispersion corrections ($\Delta f'$ and $\Delta f''$) were applied to the form factors for iridium, manganese, and phosphorus.[6] Least-squares refinement for all non-hydrogen atoms with isotropic temperature factors converged at $R_1 = 0.048$ and $R_2 = 0.056$ for 2906 reflections.[7] The conventional

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and the weighted residual factor

$$R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$$

where $w = 1/\sigma^2(F_o)$.

Table I. Atomic Positional Parameters

Atom	x	y	z
Ir	0,22015 (2)[a]	0.21166 (4)	0.28670 (2)
Mn	0.26844 (7)	0.49976 (16)	0.15869 (8)
P	0,3116 (1)	0.3521 (3)	0.2774 (1)
O1	0.1972 (4)	0.6866 (9)	0.0165 (5)
O2	0,3288 (5)	0.7936 (10)	0.2285 (5)
O3	0,3779 (3)	0.4564 (9)	0.0769 (5)
O4	0.2252 (3)	0.2949 (7)	0.1174 (3)
O5	0,1936 (3)	0.5237 (7)	0.2180 (4)
C1	0.2224 (5)	0.6098 (12)	0.0698 (6)
C2	0.3044 (5)	0.6782 (13)	0.2018 (6)
C3	0.3353 (5)	0.4733 (11)	0.1093 (6)
C4	0.2084 (4)	0.1930 (11)	0.1633 (6)
C5	0.1768 (4)	0.4164 (11)	0.2608 (6)
C6	0.1790 (5)	0.0444 (13)	0.1186 (7)
C7	0.1551 (6)	0.0527 (16)	0.3427 (8)
C8	0.2013 (8)	−0.0406 (13)	0.3178 (7)
C9	0.2630 (7)	−0.0015 (16)	0.3627 (9)
C10	0.2543 (7)	0.1217 (17)	0.4163 (7)
C11	0.1881 (8)	0.1495 (15)	0.4055 (7)
H7[b]	0.107	0.047	0.320
H8[b]	0.192	−0.123	0.274
H9[b]	0.306	−0.050	0.358
H10[b]	0.291	0.177	0.456
H11[b]	0.167	0.225	0.437
$H6_1$[c]	0.140	0.014	0,139
$H6_2$[c]	0.209	−0.030	0.130
$H6_3$[c]	0.167	0.062	0.057

[a] The numbers given in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digit. [b] These hydrogen positional parameters were not refined. [c] These methyl hydrogen positional parameters were obtained from the final difference Fourier and HPOSN; they were not refined.

A difference Fourier aided the location of the cyclopentadienyl, phenyl, and benzene hydrogens. The positions of the cyclopentadienyl hydrogens were checked with program HPOSN.[4] In all subsequent least-squares refinements the phenyl rings and the benzene of crystallization were treated as rigid groups of D_{6h} symmetry with C–C = 1.395 Å and C–H = 1.084 Å. Several cycles of refinement followed in which the iridium, manganese, and phosphorus atoms were permitted to vibrate anisotropically, and all other non-hydrogen atoms were assigned isotropic thermal parameters. With the hydrogen atoms fixed, this refinement converged to R_1 = 0.039 and R_2 = 0.044.

In further refinement the five carbonyl carbon and oxygen atoms and the five cyclopentadienyl carbon atoms were also allowed to vibrate anisotropically. The hydrogen atoms on the rigid groups and the cyclopentadienyl ring were assigned an isotropic thermal parameter of 6.0 Å^2. The agreement factors R_1 and R_2 decreased to their final values of 0.035 and 0.040, respectively.

In the final least-squares cycle, the largest shift for a group positional parameter was 0.13σ, for a nongroup non-hydrogen positional parameter 0.11σ, and for a nongroup non-hydrogen thermal parameter 0.12σ. The error in a reflection of unit weight was 1.2368. The final difference summation showed residuals in the range from −0.48 to +0.99 e/Å^3, most of which were in the immediate vicinity of the Ir and Mn atoms. Three of the residual peaks, however, were located in tetrahedral positions about the methyl carbon of the bridging acetyl group. The program HPOSN confirmed the location of these three hydrogens.

Results of Structural Study

The final least-squares parameters with their standard deviations are given in Tables I, II, and III. The parameters of those atoms which were refined as rigid groups are listed in Table IV. The final values of the observed and calculated structure factors are shown in Table V.[8] Selected bond lengths and angles are given in Tables VI and VII, respectively. Tables VIII and IX list several least-squares planes and the deviations of atoms from them. Plane 1 is chosen to illustrate planarity of the bottom of the boat configuration in the tricyclic bridge; planes 2 and 3 demonstrate the degrees of distortion in the tricyclic bridge of each of the four atoms comprising the sides of the boat. Planes 4 and 5 contain the two three-coordinate carbon atoms in the bridges and the atoms bonded to each of them. Plane 6 describes the η^5-bonded cyclopentadienyl ring. The deviations from idealized octahedral symmetry about the manganese atom are shown with planes 7–9.

Discussion of Structure

Intermolecular Contacts and Crystal Packing. The overall structure and numbering key are depicted in Figure 1. A crystal packing diagram viewed down the b axis is shown in Figure 2. It can be seen that the benzene molecules of crystallization help fill the voids in the unit cell, but no close intermolecular contacts are present. The closest intermolecular contact is 2.36 Å, between methyl hydrogen $H6_1$ and Ph1(H4) (sum of van der Waals radii = 2.4 Å).[9] The closest intermolecular distance not involving hydrogen is 3.16 Å between O2 and Ph3(C3) (sum of van der Waals radii = 2.97 Å).[9] Therefore, the compound is clearly monomeric.

The tricyclic construction consists of a bridging diphenylphosphido group and formal iridium acetyl and benzoyl groups coordinated to manganese through oxygen; the salient features are shown in Figure 3. The characteristic ab-

Table II. Atomic Thermal Parameters ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	18.0 (1)	112.5 (6)	27.2 (2)	0.3 (3)	5.0 (1)	4.6 (3)
Mn	21,5 (4)	124.0 (23)	28.8 (6)	−3.7 (8)	5.0 (4)	2.9 (9)
P	18.6 (6)	124.1 (37)	26.2 (9)	−1.8 (13)	4.2 (7)	2.4 (16)
O1	43 (3)	185 (15)	46 (3)	13 (5)	0 (3)	28 (6)
O2	52 (3)	167 (14)	76 (5)	−33 (6)	6 (3)	−21 (7)
O3	23 (2)	284 (17)	52 (4)	−3 (5)	13 (2)	8 (6)
O4	23 (2)	135 (10)	26 (2)	−11 (4)	3 (2)	−7 (5)
O5	21 (2)	122 (10)	34 (3)	2 (3)	6 (2)	6 (4)
C1	31 (3)	147 (18)	37 (5)	6 (6)	10 (3)	4 (8)
C2	29 (3)	187 (23)	41 (5)	1 (7)	7 (3)	9 (8)
C3	25 (3)	141 (17)	29 (4)	−7 (6)	2 (3)	−5 (7)
C4	20 (3)	118 (16)	38 (4)	−3 (5)	8 (3)	−1 (7)
C5	19 (3)	126 (15)	32 (4)	−9 (5)	3 (3)	−22 (7)
C7	34 (4)	233 (25)	55 (6)	−23 (9)	9 (4)	48 (11)
C8	55 (5)	127 (19)	47 (6)	−21 (8)	14 (5)	12 (8)
C9	38 (4)	196 (24)	77 (8)	32 (8)	24 (5)	70 (12)
C10	39 (5)	228 (26)	48 (6)	−16 (9)	−3 (4)	49 (11)
C11	58 (6)	195 (22)	41 (6)	5 (9)	28 (5)	23 (9)
C6	5.4 (2)[b]					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All hydrogen atoms were assigned fixed isotropic thermal parameters of 6.0 Å^2. [b] Isotropic temperature parameter B of the form $\exp[-B \sin^2 \theta/\lambda^2]$.

Table III. Group Parameters

Group	x^a	y	z	ϕ	θ	ρ
Ph1	0.1183 (3)	0.4589 (7)	0.2958 (4)	−0.535 (4)	−2.614 (4)	2.682 (5)
Ph2	0,3438 (3)	0.4763 (7)	0.3673 (3)	−1.419 (5)	2.744 (4)	2.180 (5)
Ph3	0.3791 (3)	0.2145 (7)	0.2794 (4)	--0.654 (33)	−1.673 (4)	0.090 (33)
Hemibenzene	−0.0010 (6)	0.0010 (17)	0.4983 (9)	−0.018 (17)	2.467 (16)	−2.509 (20)

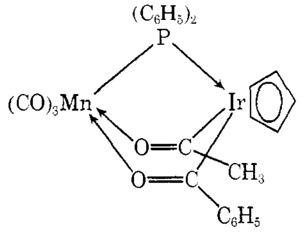
[a] The definitions of these parameters are given by C. Scheringer, *Acta Crystallogr.*, 16, 546 (1963).

Table IV. Derived Positional and Isotropic Thermal Parameters for Group Atoms

Group	Atom	x	y	z	B, Å^2
Ph1	C1	0.1183	0,4589	0.2958	3.5 (2)
	C2	0.0602	0.3757	0.2747	5.1 (2)
	C3	0.0073	0.4188	0.3078	5.8 (3)
	C4	0.0124	0.5450	0.3621	6.2 (3)
	C5	0.0705	0.6282	0.3832	6.4 (3)
	C6	0.1234	0.5851	0.3501	4.9 (2)
	H2	0.0562	0.2775	0.2326	6.0[a]
	H3	−0.0379	0.3541	0.2914	6.0[a]
	H4	−0.0287	0.5785	0.3878	6.0[a]
	H5	0.0745	0.7263	0.4254	6.0[a]
	H6	0.1686	0.6498	0.3665	6.0[a]
Ph2	C1	0.3438	0.4763	0.3673	3.8 (2)
	C2	0.3096	0.5066	0.4290	4.5 (2)
	C3	0.3357	0.6064	0.4943	6.1 (3)
	C4	0.3960	0.6760	0.4981	6.8 (3)
	C5	0.4303	0.6458	0.4364	7.0 (3)
	C6	0.4042	0.5460	0.3710	5.4 (2)
	H2	0.2627	0.4525	0.4261	6.0[a]
	H3	0.3090	0.6299	0.5422	6.0[a]
	H4	0.4163	0.7536	0.5488	6.0[a]
	H5	0.4772	0.6999	0.4393	6.0[a]
	H6	0.4308	0.5225	0.3231	6.0[a]
Ph3	C1	0.3791	0.2145	0.2794	3.9 (2)
	C2	0.3873	0.1480	0.2053	4.1 (2)
	C3	0.4361	0.0379	0.2061	5.6 (2)
	C4	0.4767	−0.0057	0.2810	5.7 (2)
	C5	0.4685	0.0608	0.3550	6.1 (3)
	C6	0.4197	0.1709	0.3542	4.9 (2)
	H2	0.3557	0.1818	0.1471	6.0[a]
	H3	0.4425	−0.0138	0.1485	6.0[a]
	H4	0.5147	−0.0913	0.2816	6.0[a]
	H5	0.5001	0.0269	0.4132	6.0[a]
	H6	0.4133	0.2226	0.4118	6.0[a]
Hemibenzene	C1	0.0595	0.0587	0.5383	7.3 (3)
	C2	0.0364	−0.0802	0.5651	6.9 (3)
	C3	−0.0242	−0.1379	0.5251	6.8 (3)
	H1	0.1066	0.1035	0.5693	6.0[a]
	H2	0.0654	−0.1432	0.6169	6.0[a]
	H3	−0.0422	−0.2458	0.5459	6.0[a]

[a] Assigned isotropic hydrogen thermal parameters.

sorption (1508 cm^{-1}) associated with the acyl groups coordinated to metal through oxygen and comparison with other compounds in which these are observed are presented in the paper immediately preceding.[2] A valence bond representation may be written which conforms to the noble-gas formalism[10] (EAN rule), without the need for a metal-metal bond.



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Accordingly, the Mn-Ir separation is observed to be 3.543 (2) Å, rather long compared to the sum of covalent radii (2.44 Å).[9]

Table VI. Selected Interatomic Distances (Å)

Ir–Mn	3.543 (2)	C4–O4	1.257 (10)
Ir–P	2.307 (2)	C5–O5	1.258 (10)
Ir–C4	2.008 (9)	C4–C6	1.535 (14)
Ir–C5	1.983 (10)	C5–Ph1(C1)	1.516
Ir–O4	2.912 (6)	C7–C8	1.390 (17)
Ir–O5	2.913 (6)	C8–C9	1.391 (17)
Ir–C7	2.268 (10)	C9–C10	1.416 (18)
Ir–C8	2.278 (10)	C10–C11	1.390 (17)
Ir–C9	2.290 (11)	C11–C7	1.392 (16)
Ir–C10	2.244 (11)	C7–H7	1.004 (12)
Ir–C11	2.274 (10)	C8–H8	1.001 (12)
Mn–P	2.348 (3)	C9–H9	1.017 (12)
Mn–O4	2.028 (6)	C10–H10	1.017 (12)
Mn–O5	2.040 (6)	C11–H11	0.994 (12)
Mn–C4	2.927 (9)	P–Ph2(Cl)	1.835
Mn–C5	2.917 (9)	P–Ph3(C1)	1.843
Mn–C1	1.837 (11)	C1–O1	1.135 (11)
Mn–C2	1.786 (12)	C2–O2	1.158 (12)
Mn–C3	1.790 (11)	C3–O3	1.150 (11)
Mn–O1	2.969 (8)		
Mn–O2	2.944 (8)		
Mn–O3	2.940 (8)		

The structural features of the bridging diphenylphosphido group also reflect the absence of a metal-metal bond. The phosphorus atom in this group forms an angle of 99.1 (1)° with the two metal atoms. This is in the range 92-102° observed by Dahl et al.[11] for ligand-bridged transition metal dimer complexes containing no metal-metal interactions. In ligand-bridged metal complexes containing such interactions, the angle formed by the bridging atom with the two metal atoms is observed to be in the range of 68-74°.[11,12] Mason and Mingos[13] have demonstrated a correlation between the metal-metal separation and the M-P-M bond angles in a variety of transition metal complexes based on molecular orbital symmetry arguments. The metal-metal distance observed by us at 3.54 Å appears at the far end of their graph in which uncertainty in the bond angle is at its highest. From their correlation, we would expect an angle above 105° while we observe this angle to be 99° no doubt due to the presence of the formal bridging acetyl and benzoyl groups, suggesting the existence of some strain in the triply bridging system. This is also indicated by the fact that the P-Ir distance (2.307 (2) Å) is considerably shorter than the P-Mn distance (2.348 (3) Å), opposite to what is expected from the sum of the respective covalent radii (P-Ir, 2.36 Å; P-Mn, 2.27 Å).[9] As shown in Table VII the angles between bridging groups on iridium are P-Ir-C4, 84.0 (3)°, P-Ir-C5, 82.9 (3)°, and C4-Ir-C5, 84.4 (4)°. An idealized pseudo-octahedral geometry about iridium, composed of the cyclopentadienyl ring and three bonded groups opposite, may be estimated from complexes containing similar groupings such as $(\eta^5\text{-}C_5H_5)Mn(CO)_3$[14] and $(\eta^5\text{-}C_5H_5)Mn(CO)_2[P(C_6H_5)_3]$.[15] In these the angles between groups around the manganese atom opposite the cyclopentadienyl rings are, for $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, C-Mn-C, 91, 91, and 94°, and, for $(\eta^5\text{-}C_5H_5Mn(CO)_2[P(C_6H_5)_3]$, P-Mn-C, 90.5 and 92.6°, and C-Mn-C, 92.4°. These values are much higher than the interligand angles in the present complex. Another parameter to describe the geometry of ligands in this type of situation is the angle formed by the

Table VII. Observed Bond and Other Selected Angles

Atoms	Angle (deg)	Atoms	Angle (deg)
Mn–Ir–P	40.87 (6)	Ir–C4–O4	124.7 (6)
Mn–Ir–C4	55.7 (3)	Ir–C5–O5	126.6 (7)
Mn–Ir–C5	55.4 (3)	Ir–C4–C6	120.2 (7)
P–Ir–C4	84.0 (3)	Ir–C5–Ph1(C1)	120.4
P–Ir–C5	82.9 (3)	O4–C4–C6	115.1 (8)
C4–Ir–C5	84.4 (4)	O5–C5–Ph1(C1)	113.1
B[a]–Ir–P	127.2	Ir–P–Mn	99.1 (1)
B–Ir–C4	130.4	Ir–P–Ph2(C1)	114.7
B–Ir–C5	131.0	Ir–P–Ph3(C1)	108.6
C7–Ir–C8	35.6 (4)	Mn–P–Ph2(C1)	111.8
C8–Ir–C9	35.4 (4)	Mn–P–Ph3(C1)	121.2
C9–Ir–C10	36.4 (5)	Ph2(C1)–P–Ph3(C1)	102.0
C10–Ir–C11	35.8 (4)	C5–Ph1(C1)–Ph1(C4)	178.3
C11–Ir–C7	35.7 (4)	P–Ph2(C1)–Ph2(C4)	176.7
Ir–Mn–P	40.02 (6)	P–Ph3(C1)–Ph3(C4)	177.2
Ir–Mn–O4	55.3 (2)	Ir–C7–C11	72.4 (6)
Ir–Mn–O5	55.3 (2)	Ir–C7–C8	72.6 (6)
P–Mn–O4	83.0 (2)	Ir–C8–C7	71.8 (6)
P–Mn–O5	81.6 (2)	Ir–C8–C9	72,7 (6)
C1–Mn–C2	89.1 (5)	Ir–C9–C8	71.8 (6)
C1–Mn–C3	91.9 (4)	Ir–C9–C10	70.1 (6)
C1–Mn–O4	93.1 (4)	Ir–C10–C9	73.5 (7)
C1–Mn–O5	90.1 (3)	Ir–C10–C11	73.2 (6)
C1–Mn–P	171.1 (3)	Ir–C11–C10	70.9 (7)
C2–Mn–C3	89.0 (5)	Ir–C11–C7	71.9 (6)
C2–Mn–O4	175.8 (4)	C11–C7–C8	107.1 (11)
C2–Mn–O5	91.6 (4)	C7–C8–C9	109.8 (11)
C2–Mn–P	94.2 (3)	C8–C9–C10	106.4 (11)
C3–Mn–O4	94.5 (3)	C9–C10–C11	108.0 (12)
C3–Mn–O5	177.9 (3)	C10–C11–C7	108.7 (12)
C3–Mn–P	96.4 (3)		
O4–Mn–O5	84.9 (2)		
Mn–C1–O1	174.8 (9)		
Mn–C2–O2	178.3 (10)		
Mn–C3–O3	179.5 (8)		
Mn–O4–C4	124.3 (5)		
Mn–O5–C5	122.6 (6)		

[a] B = centroid of the η^5-cyclopentadienyl ring.

Table VIII. Least-Squares Planes

Plane no.	Direction cosines ($\times 10^4$) with respect to *a*	*b*	*c**	Atoms involved
1	8277	−0265	5605	C4, O4, C5, O5
2	8935	−4327	1203	Ir, C4, O4, Mn
3	4578	3892	7993	Ir, C5, O5, Mn
4	9032	−4097	1278	Ir, C4, O4, C6
5	4323	3883	8138	Ir, C5, O5, Ph1(C1)
6	−2353	−6787	6956	C7 through C11
7	−8849	1929	4240	Mn, P, O4, C1, C2
8	3340	8342	4387	Mn, P, O5, C1, C3
9	3556	−4802	8018	Mn, O4, O5, C2, C3

first atom of the ligands around the metal with the axis going through the metal and the centroid (B) of the η^5-cyclopentadienyl ring. Such angles in the present complex are P-Ir-B, 127.2°, C4-Ir-B, 130.4°, and C5-Ir-B, 131.0°. Those in the comparison compounds, calculated by us from the atom positional parameters listed for these are, for (η^5-C_5H_5)Mn(CO)$_3$, C-Mn-B, 123.3, 123.9, and 124.0°, and, for (η^5-C_5H_5)Mn(CO)$_2$[P(C_6H_5)$_3$], P-Mn-B, 126.0°, and C-Mn-B, 122.7 and 123.0°. Thus, both of these sets of parameters indicate considerable strain in the coordination geometry around iridium which could lead to an apparent foreshortening of the separations between iridium and its bonded atoms, in this case one phosphorus and two carbons.

A rigid body analysis was attempted for the group of seven atoms (Ir, P, Mn, O4, C4, O5, C5) comprising the central basket conformation of the structure. No fit in terms of the rigid body tensors of translation, libration, and screw motion was accomplished.

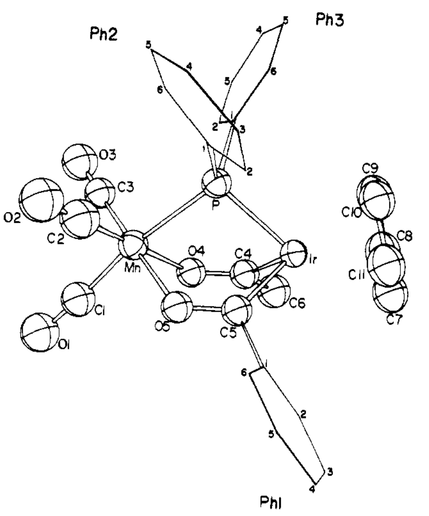


Figure 1. Molecular structure of (η^5-C_5H_5)Ir-μ-[C(C_6H_5)O]-μ-[C(CH_3)O]-μ-[P(C_6H_5)$_2$]-Mn(CO)$_3$ illustrating the numbering used. Thermal ellipsoids enclose 50% of the electron density; hydrogen atoms are omitted for clarity.

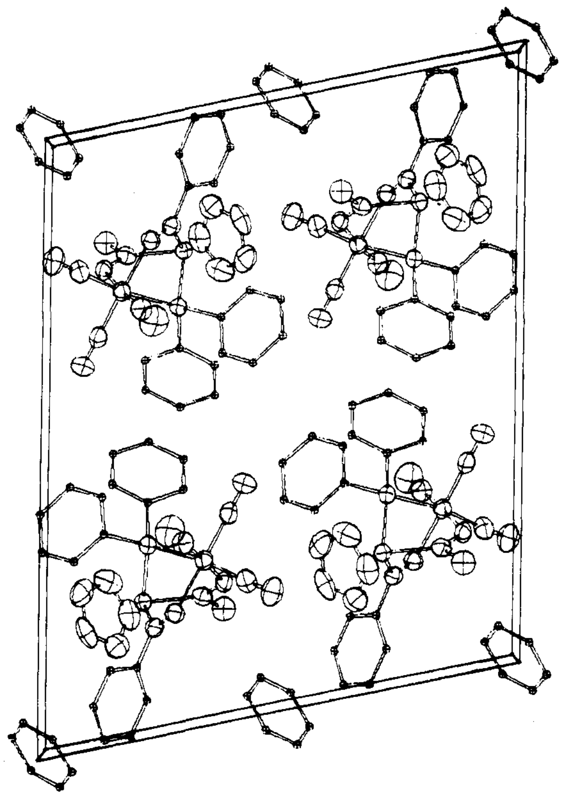


Figure 2. The 010 projection of the unit cell for (η^5-C_5H_5)Ir-μ-[C(C_6H_5)O]-μ-[C(CH_3)O]-μ-[P(C_6H_5)$_2$]-Mn(CO)$_3$·½C_6H_6 (ORTEP drawing). The *a* axis is horizontal and the *c* axis is vertical. Thermal ellipsoids enclose 50% of the electron density for all atoms except those confined to rigid groups (see text). Hydrogen atoms are omitted for clarity.

The bridging acetyl and benzoyl moieties together with the two metal atoms define a six-membered ring in a boat configuration. The four-atom system at the bottom of the boat composed of C4, C5, O4, and O5 is essentially coplanar, the largest perpendicular deviation from the least-squares plane being only 0.005 Å. The Ir-C4-O4-Mn and Ir-C5-O5-Mn groups are both planar, the greatest deviations from their least-squares planes being 0.002 and 0.020 Å, respectively. A similar bisacyl bridging system has been observed in only one previous case, i.e., in the dimeric iron

Table IX. Deviations of Atoms from Least-Squares Planes (Å × 10^3)[a]

	Plane no.[b]								
	1	2	3	4	5	6	7	8	9
Ir		-1^c	7^c	3^c	3^c	-1936			
Mn		1^c	-7^c				-80^c	26^c	-28^c
P	2465						58^c	-28^c	2289
O4	-5^c	-2^c		4^c			-25^c	-1987	9^c
O5	5^c		19^c		4^c		1949	19^c	4^c
C1							72^c	-34^c	-1864
C2							-24^c	1809	10^c
C3							-1866	17^c	5^c
C4	5^c	2^c		-11^c					
C5	-5^c		-20^c		-11^c				
C6				3^c					
C7						-12^c			
C8						2^c			
C9						9^c			
C10						-17^c			
C11						18^c			
Ph1(C1)					3^c				

[a] A negative deviation from a plane indicates that the atom with the coordinates given in Table I lies between that plane and the origin. [b] Least-squares planes as defined in Table VIII. [c] Indicates atoms used to define the respective least-squares planes.

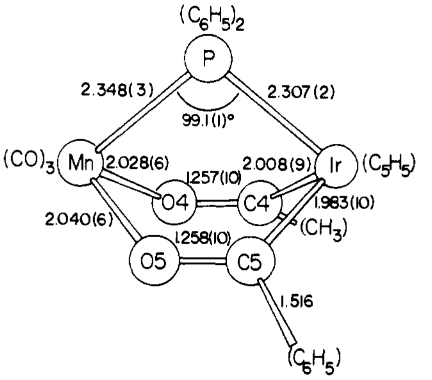
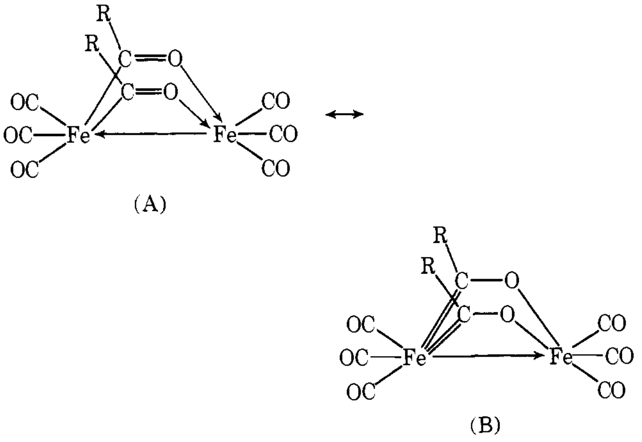


Figure 3. The salient features of the central basket construction.

carbonyl complex containing two bridging benzoyl groups and a strong metal-metal interaction, **2**, reported by Lindley and Mills.[16] The M-C-O bridge bond angles in this complex reflect the presence of the metal-metal bond: Fe-C-O, 114.6 (5)°; Fe-Fe = 2.568 (2) Å. In **1** the Ir-C4-O4 and Ir-C5-O5 angles are 124.7 (6) and 126.6 (7)°, respectively.



2

Two different canonical bonding descriptions were suggested for the bridging acyl groups in **2**.[16] One (A) involves a bridging benzoyl group and the other (B) a phenylferroxycarbene. Similar possibilities exist in **1**; the C6-C4-O4 and Ph1(C1)-C5-O5 angles of 115.1 (8) and 113.1° are comparable to those found in carbene complexes.[17] The C4-O4 bond length is 1.257 (10) Å, and the C5-O5 bond distance is 1.258 (10) Å. These values are identical with those reported in the iron dimer. Since a double-bonded CO, as reported in the structure of acetophenone,[18] has a bond distance of 1.216 Å, and single C-O bonds are of the order of 1.43 Å,[19] it would appear that the C-O bond order lies between 1 and 2. The Ir-C4 and Ir-C5 distances are 2.008 (9) and 1.983 (10) Å, respectively. However, single iridium-carbon bond distances are in the range of 2.05-2.16 Å.[19] This could arise from delocalization in both the Ir-C and C-O bonds, comparable to that suggested for the analogous bonds in the bridged iron dimer mentioned above. There is, however, also the possibility that some of this foreshortening could arise from strain in the triply bridging system discussed above.

Coordination around the manganese atom is best defined as a distorted octahedral arrangement. The three terminal carbonyl groups are situated nearly at right angles to each other; the C-Mn-C angles for the three carbonyl groups range from 89.0 (5) to 91.9 (4)° with an average value of 90.0°. However, the angles between the carbon atoms of the terminal carbonyl groups and the phosphorus atom, i.e., C1-Mn-P (171.1 (3)°), C2-Mn-P (94.2 (3)°), and C3-Mn-P (96.4 (3)°), deviate the most from idealized octahedral geometry due to the fact that the diphenylphosphido group is bridging the two metals. The two-atom bridging formal acetyl and benzoyl groups, however, are given a greater degree of freedom. The deviations of atoms from several least-squares planes through the manganese atom and its surrounding ligands are given in Table IX. The data indicate the greatest deviations in the least-squares planes from idealized octahedral coordination around the manganese atom are in those two containing the phosphorus atom. The Mn-O4 and Mn-O5 bond distances are 2.028 (6) and 2.040 (6) Å, respectively, which compare favorably with the Mn-O distances of 2.05-2.07 Å in complexes containing manganese-coordinated acyl groups.[20]

For the η^5-cyclopentadienyl ring, the Ir-C(C_5H_5) distances vary from 2.244 (11) to 2.290 (11) Å with an average value of 2.271 Å. Within the C_5H_5 ring, the average C-C bond distance is 1.396 Å. This value compares favorably with that, 1.42 Å, reported for (η^5-cyclopentadienyl)(η^4-duroquinone)iridium(II).[21] The cyclopentadienyl C-C-C bond angles are listed in Table VII. As shown in Tables VIII and IX, the C_5H_5 ring is planar, the largest deviation of a carbon atom from a least-squares plane through the five carbon atoms being only 0.018 Å. The perpendicular distance to this least-squares plane from the iridium atom is 1.936 Å.

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Supplementary Material Available. A listing of structure factor amplitudes (Table V) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2686.

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Resonance Raman and Electronic Spectra of Various Salts of the $Mo_2Cl_8{}^{4-}$ Ion[1]

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Abstract: Rigorous resonance Raman spectra of the complexes $(enH_2)_2Mo_2Cl_8{\cdot}2H_2O$, $K_4Mo_2Cl_8$, $Cs_4Mo_2Cl_8$, $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$, and $Rb_4Mo_2Cl_8$, all of which contain the discrete $Mo_2Cl_8{}^{4-}$ ion, have been observed by irradiating each complex with 514.5-nm Ar^+ excitation. This laser line approximately coincides with an electronic band maximum of the anion centered at ca. 19,000 cm^{-1}. Two overtone progressions in the metal-metal stretching frequency, ν_1(MoMo) a_{1g}, have been observed under these conditions to reach $11\nu_1$ for the first and $\nu_4 + 4\nu_1$ for the second, where ν_4 is probably the ν_2(MoCl) a_{1g} fundamental. The spectroscopic constants ω_1, x_{11}, and (less accurately) x_{14}, have been determined for the anion in each crystalline lattice. The relative intensities of the overtones to the fundamental are shown to depend on the exciting wavelength and also to decrease and the half-bandwidths to increase with increase in vibrational quantum number. Diffuse reflectance studies on the complexes have revealed a further weak electronic transition centered at ca. 6250 cm^{-1} which displays vibrational structure at room temperature. The electronic spectrum of the $Mo_2Cl_8{}^{4-}$ ion is discussed in the light of these new experimental results.

Rigorous resonance Raman (RR) spectra have recently been reported not only for the halogen gases[2] but also for a large number of tetraatomic and bigger inorganic molecules and ions.[3-11] In all cases, these spectra were observed when the exciting frequency fell within the contour of an allowed transition of the scattering species. The compound $K_4Mo_2Cl_8$ has also been found to display a RR spectrum when irradiated with 514.5-nm Ar^+ excitation, a wavelength which virtually coincides with the maximum of a strong electronic transition of the anion at 19,000 cm^{-1}. The original spectrum of Angell et al.,[12] as corrected and improved upon by Clark and Franks,[13] was characterized by the appearance of five harmonics of the ν_1 (MoMo) stretching fundamental, which occurs at 346 cm^{-1}. This