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X-Ray Crystallographic Studies on Fluxional Pentacoordinate Transition Metal Complexes. I. (Cycloocta-1,5-diene)bis(dimethylphenylphosphino)methyliridium(I)

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The fluxional pentacoordinate iridium(I) complex (cycloocta-1,5-diene)bis(dimethylphenylphosphino)methyliridium(I), $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$, crystallizes in the centrosymmetric orthorhombic space group *Pbca* (D_{2h}^{15}, No. 61) with $a = 8.111 \pm 0.007$, $b = 17.10 \pm 0.02$, $c = 34.53 \pm 0.05$ Å, $\rho_{obsd} = 1.63 \pm 0.01$, and $\rho_{calcd} = 1.641$ g cm^{-3} for $M = 591.72$ and $Z = 8$. X-Ray diffraction data to $\sin\theta = 0.80$ (Cu Kα radiation) were collected on a Supper-Pace diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 6.8\%$ for the 1724 symmetry-independent nonzero reflections. The central iridium(I) atom is in essentially trigonal-bipyramidal coordination, with two dimethylphenylphosphine ligands in equatorial positions [Ir–P(1) = 2.316 (5) and Ir–P(2) = 2.329 (5) Å] and the methyl ligand in an axial position, the Ir–CH_3 distance being 2.202 (22) Å. The bidentate cycloocta-1,5-diene ligand spans the remaining axial and equatorial positions. The equatorial P(1)–Ir–P(2) angle is 101.5 (2)°.

Introduction

For some time it has been known that certain pentacoordinate phosphorus(V) derivatives undergo rapid intramolecular rearrangements (*i.e.*, exhibit "fluxional" behavior) in the liquid phase or in solution,[1,2] and a mechanism (termed "pseudorotation" or "the Berry mechanism") has been proposed[3] and confirmed for these rearrangements.[4–6] Reported instances of stereochemical nonrigidity in pentacoordinate transition metal derivates are, however, rare,[7] and only recently have any mechanistic interpretations appeared.[7–10] The problem here is more complex than for main-group elements since the ground-state coordination geometry of a transition metal may be square pyramidal, trigonal bipyramidal, or even some distortion therefrom.

The first study attempting to distinguish between the various permutationally possible fluxional processes for pentacoordinate transition metal species was reported by Shapley and Osborn,[7] who, on the basis of the temperature-dependent ^{1}H nmr spectra of (C_8H_{12})-$[(C_6H_5)_{3-n}(CH_3)_nP]_2Ir(R)$ complexes (where C_8H_{12} = cycloocta-1,5-diene; $0 \leq n \leq 2$; R = H or Me), assigned trigonal-bipyramidal ground-state structures and proposed Berry "pseudorotation" as a possible mechanism operative in the intramolecular rearrangements of these species.

We have undertaken a series of X-ray diffraction studies on these complexes in order (1) to determine unambiguously their solid-state (and probable ground-state) structures, and (2) to discover possible relationships between the ease of intramolecular rearrangement and the various parameters (bond angles, bond distances, etc.) of the molecular geometry. Preliminary details of this structure have appeared elsewhere.[11]

Experimental Section

Unit Cell and Space Group.—A sample of $C_8H_{12}[(C_6H_5)(CH_3)_2$-$P]_2Ir(CH_3)$ was supplied by Professor J. A. Osborn and Dr. J. R. Shapley of Harvard University. The complex is air-stable for (at least) several months in the crystalline state and does not decompose upon exposure to X-irradiation. Optical examination and the reciprocal lattice symmetry indicated that the crystals belonged to the orthorhombic system. A careful survey of $h(0–1)l$ and $(0–1)kl$ Weissenberg photographs, $0kl$ and $hk(0–1)$ precession photographs, *a*- and *b*-axis rotation photographs, and a *c*-axis cone-axis photograph (all taken with Cu Kα radiation; λ 1.5418 Å) revealed the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, $hk0$ for $h = 2n + 1$—compatible only with the centrosymmetric orthorhombic space group *Pbca* (D_{2h}^{15}, No. 61).

Unit cell parameters, from calibrated ($Pb(NO_3)_2$, $a = 7.8566$ Å) precession photographs, taken with Cu Kα radiation at 24 ± 2°, are $a = 8.111 \pm 0.007$, $b = 17.10 \pm 0.02$, and $c = 34.53 \pm 0.05$ Å. The unit cell volume is 4789 Å^3. The observed density, $\rho_{obsd} = 1.63 \pm 0.01$ g cm^{-3} (by flotation in aqueous BaI_2 solution) is consistent with the value calculated for $M = 591.72$ and $Z = 8$ (*i.e.*, $\rho_{calcd} = 1.641$ g cm^{-3}).

No crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of the X-Ray Data.—The complex crystallizes as colorless thin rectangular plates. Three crystals were used during the course of the analysis. Dimensions, referred sequentially to **a**, **b**, **c**, were as follows: crystal I (aligned along its *b* axis) 0.30 × 0.36 × 0.06 mm; crystal II (*a*-mounted) 0.18 × 0.40 × 0.06 mm; crystal III (*a*-mounted) 0.26 × 0.50 × 0.06 mm.

Intensity data were collected using a scintillation counter attached to a 0.01°-incrementing Supper-Pace Buerger Automated Diffractometer, using the "stationary-background, ω-scan, stationary background" counting sequence that we have described at length previously.[12] Details specific to the present analysis are as follows: (i) Cu Kα radiation (*i.e.*, Cu radiation filtered through a 3.0-mil Ni filter) was used;[13] (ii) the X-ray generator was operated at 49 kV/18 mA; (iii) the scan angle was $\omega(hkl) = [1.70 + 0.80L^{-1}(hkl)]°$, where $L(hkl)$ is the Lorentz factor for the reflection hkl; (iv) $d\omega/dt = 2°$ min^{-1}; (v) the count associated with the ω scan was $C(hkl)$, and initial and final backgrounds $[B_i(hkl), B_f(hkl)]$ were each counted for one-fourth the time of the ω scan; (vi) standard reflections within a given

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[1] E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

[2] F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

[3] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

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[13] Cu radiation was used rather than the less absorbed Mo radiation, because it allows better resolution of adjacent reflections—important with the present 34.5-Å *c* axis.

Weissenberg level were measured after each 40 reflections in order to monitor the stability of the entire configuration—the maximum deviation from the mean was ~2%; (vii) $I(hkl)$, the net intensity of the reflection hkl, was calculated as $I(hkl) = C(hkl) - 2[B_1(hkl) + B_f(hkl)]$.

Based on our previous experience with the Supper-Pace diffractometer and the ω-scan technique, reflections were weighted according to the following scheme.

$$I(hkl) > 4900,\ \sigma\{I(hkl)\} = 0.1[I(hkl)]$$

$$I(hkl) \leq 4900,\ \sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$$

Data were subsequently rejected on two bases: (i) $I(hkl) < 3[C(hkl) + 4B_1(hkl) + 4B_f(hkl)]^{1/2}$, *i.e.*, reflection not significantly (3σ) above background; (ii) $B_1(hkl)/B_f(hkl)$ or $B_f(hkl)/B_1(hkl) > 3.0$, symptomatic of overlap of adjacent reflections or of high λ "streaking" from an adjacent lower-angle reflection.

A total of 1937 reflections in levels $h(0\text{–}9)l$ were collected from crystal I, 1243 reflections in levels $(0\text{–}2)kl$ were collected from crystal II, and 310 reflections from the $3kl$ level were collected from crystal III. Each level is complete to $\sin\theta = 0.80$, save for data in the sphere $0 < \theta < 4°$, which are obscured from the counter by a Pb backstop. All data were corrected for Lorentz and polarizations effects and absorption corrections were applied.[14] With $\mu(\text{Cu K}\alpha) = 119.8\ \text{cm}^{-1}$, transmission factors were 0.056–0.509 for data from crystal I (volume 5.4×10^{-6} cm^3), 0.060–0.463 for crystal II (4.3×10^{-6} cm^3), and 0.041–0.480 for crystal III (7.1×10^{-6} cm^3). [We should note that, while the transmission factors demonstrate large variations, (i) the crystal habit and mechanical properties made it impossible for us to obtain an essentially cylindrical specimen, and (ii) crystal dimensions were measured accurately.]

Data were placed on a common scale by a least-squares process which minimizes a set of residuals linear in the logarithms of the individual scale factors.[15] The resulting 1724 independent nonzero reflections were placed on an (approximately) absolute scale by means of a Wilson plot,[16] which indicated an average overall thermal parameter of $\bar{B} = 2.24$ Å^2.

Elucidation and Refinement of the Structure.—Unless stated otherwise, all crystallographic calculations were performed with the CRYM system[17] on the Harvard University IBM 360/65 computer. Scattering curves for neutral iridium,[18a] phosphorus,[18b] carbon,[18b] and hydrogen[18b] were used; values for iridium and phosphorus were corrected for both the real and for the imaginary components of dispersion [$\Delta f'(\text{Ir}) = -5 \rightarrow -6$ e, $\Delta f''(\text{Ir}) = +7 \rightarrow +6$ e; $\Delta f'(\text{P}) = +0.2$ e, $\Delta f''(\text{P}) = +0.5$ e].[18c,19]

The residual minimized during least-squares refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$ and where $\sigma\{F^2(hkl)\}$ is derived from $\sigma\{I(hkl)\}$ by appropriate propagation of Lorentz, polarization, absorption, and scale factors. Discrepancy indices used below are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

The iridium position was located from a three-dimensional Patterson map from which the origin had been removed and which had been "sharpened" so that the average intensity was no longer θ dependent. A three-dimensional Fourier synthesis, phased only by the iridium atom ($R_F = 68.3\%$), revealed the location of both phosphorus atoms and of five carbon atoms. A second Fourier map ($R_F = 39.3\%$) revealed a further ten carbon atoms, and a third such map ($R_F = 29.8\%$) led to the location of all remaining nonhydrogen atoms. Six cycles of full-matrix least-squares refinement of individual atomic positional and isotropic thermal parameters (along with an overall scale factor) led smoothly to convergence at $R_F = 7.8\%$ and $R_{wF^2} = 3.8\%$. Hydrogen atoms (other than those of the methyl groups, which are indeterminate) were now included in calculated positions

TABLE I

FINAL ATOMIC PARAMETERS FOR $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$

(A) Fractional Positional Parameters and Isotropic Thermal Parameters[a]

Atom	x	y	z	B, Å^2 [a]
Ir	0.30931 (9)	0.51177 (6)	0.12651 (2)	
P(1)	0.2278 (6)	0.5833 (4)	0.1802 (2)	
P(2)	0.2604 (6)	0.6005 (4)	0.0766 (2)	
Me(1)	0.0477 (27)	0.4808 (14)	0.1189 (6)	5.1 (5)
Me(2)	0.0104 (21)	0.6211 (13)	0.1829 (6)	4.3 (4)
Me(3)	0.2369 (36)	0.5281 (18)	0.2269 (8)	8.0 (7)
Me(4)	0.1063 (23)	0.6798 (14)	0.0840 (6)	5.0 (5)
Me(5)	0.1763 (23)	0.5498 (15)	0.0326 (7)	5.5 (5)
C(1)	0.3413 (24)	0.6707 (14)	0.1926 (6)	4.7 (5)
C(2)	0.3027 (22)	0.7126 (14)	0.2274 (6)	4.9 (5)
C(3)	0.3904 (21)	0.7819 (13)	0.2358 (6)	4.0 (4)
C(4)	0.5049 (24)	0.8125 (14)	0.2107 (6)	5.2 (5)
C(5)	0.5463 (26)	0.7707 (17)	0.1763 (7)	6.3 (6)
C(6)	0.4643 (23)	0.7042 (14)	0.1688 (6)	4.4 (5)
C(7)	0.4272 (22)	0.6519 (13)	0.0555 (6)	4.2 (4)
C(8)	0.4618 (22)	0.7338 (14)	0.0663 (6)	4.5 (5)
C(9)	0.5978 (26)	0.7760 (16)	0.0539 (7)	6.1 (6)
C(10)	0.6990 (22)	0.7363 (14)	0.0288 (6)	4.7 (5)
C(11)	0.6751 (24)	0.6608 (15)	0.0159 (7)	5.8 (6)
C(12)	0.5403 (22)	0.6242 (13)	0.0299 (5)	3.9 (4)
C(13)	0.3523 (22)	0.3968 (13)	0.0999 (6)	4.1 (5)
C(14)	0.3325 (22)	0.3873 (14)	0.1395 (6)	4.0 (5)
C(15)	0.4717 (30)	0.3652 (17)	0.1643 (8)	7.5 (7)
C(16)	0.5911 (24)	0.4304 (15)	0.1738 (7)	5.7 (5)
C(17)	0.5579 (22)	0.5114 (13)	0.1550 (6)	3.8 (4)
C(18)	0.5764 (23)	0.5240 (13)	0.1163 (6)	3.8 (4)
C(19)	0.6389 (23)	0.4645 (14)	0.0899 (6)	4.5 (5)
C(20)	0.5209 (26)	0.3943 (15)	0.0810 (7)	6.6 (6)
H(2)	0.2153	0.6931	0.2454	6.0
H(3)	0.3685	0.8096	0.2608	6.0
H(4)	0.5589	0.8637	0.2166	6.0
H(5)	0.6337	0.7903	0.1584	6.0
H(6)	0.4926	0.6760	0.1443	6.0
H(8)	0.3814	0.7607	0.0837	6.0
H(9)	0.6204	0.8308	0.0626	6.0
H(10)	0.7985	0.7645	0.0189	6.0
H(11)	0.7527	0.6349	−0.0026	6.0
H(12)	0.5212	0.5698	0.0202	6.0
H(13)	0.2528	0.4056	0.0833	6.0
H(14)	0.2214	0.3956	0.1513	6.0
H(15)	0.4260	0.3447	0.1892	6.0
H(15′)	0.5345	0.3229	0.1508	6.0
H(16)	0.5897	0.4377	0.2025	6.0
H(16′)	0.7033	0.4130	0.1655	6.0
H(17)	0.5219	0.5557	0.1719	6.0
H(18)	0.5458	0.5763	0.1055	6.0
H(19)	0.7423	0.4426	0.1014	6.0
H(19′)	0.6652	0.4907	0.0648	6.0
H(20)	0.5042	0.3922	0.0523	6.0
H(20′)	0.5770	0.3453	0.0899	6.0

(B) Anisotropic Thermal Parameters for Ir and P Atoms[a,b]

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Ir	1332 (18)	240 (5)	68 (1)	−113 (14)	−37 (6)	−13 (4)
P(1)	1580 (82)	448 (32)	73 (5)	−218 (102)	77 (37)	−60 (25)
P(2)	1523 (79)	294 (29)	77 (5)	21 (87)	−68 (37)	−54 (23)

(C) Direction Cosines for Atomic Vibration Ellipsoids[c]

Atom	B_{max} (dc's major axis)	B_{med} (dc's median axis)	B_{min} (dc's minor axis)
Ir	3.67 (−0.905, 0.266, 0.333)	3.26 (−0.197, 0.433, −0.880)	2.61 (−0.378, −0.861, −0.340)
P(1)	5.79 (0.403, −0.853, 0.332)	3.90 (−0.878, −0.462, −0.124)	3.16 (−0.259, 0.242, 0.935)
P(2)	4.46 (−0.609, −0.448, 0.654)	3.80 (−0.771, 0.528, −0.356)	2.86 (−0.186, −0.721, −0.667)

[a] Esd's, shown in parentheses, are right adjusted to the least significant digit of the preceding number. [b] The anisotropic thermal parameter is defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [c] Direction cosines (dc's) refer to the orthorhombic axes. The major, median, and minor axes of the atomic vibration ellipsoids are defined in terms of B (the normal isotropic thermal parameter, units Å^2). The transformation to root-mean-square displacement is $(\overline{U^2})^{1/2} = [B/8\pi^2]^{1/2}$.

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[14] Using IMBIBE, a Fortran IV program for the IBM 360, by Dr. J. Wormald. This program is based on a Gaussian quadrature numerical integration technique; see C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

[15] A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[16] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

[17] CRYM is an integrated sequence of crystallographic routines for the IBM 360 computer and was written under the direction of Dr. R. E. Marsh at the California Institute of Technology.

[18] "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962: (a) pp 202–203; (b) p 211; (c) p 216.

[19] The CRYM system allows for the variation of $\Delta f'$ and $\Delta f''$ as a function of $\sin\theta/\lambda$.

TABLE II

DISTANCES (WITH ESD'S) WITHIN THE $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ MOLECULE

Atoms	Dist, Å	Atoms	Dist, Å
I. Distances from Iridium Atom			
Ir–P(1)	2.316 (5)	Ir–Me(1)	2.202 (22)
Ir–P(2)	2.329 (5)	Ir···A[b]	2.078 (14)
Ir–P(av)	2.323 (9)[a]	Ir···B[b]	2.117 (14)
II. Phosphorus–Methyl Distances			
P(1)–Me(2)	1.880 (20)	P(2)–Me(4)	1.861 (22)
P(1)–Me(3)	1.871 (29)	P(2)–Me(5)	1.878 (23)
		P–Me (av)	1.873 (9)[a]
III. Phosphorus–Phenyl Distances			
P(1)–C(1)	1.806 (22)	P(2)–C(7)	1.770 (20)
		P–Ph (av)	1.788 (25)[a]
IV. Carbon–Carbon Double-Bond Distances within 1,5-Cyclo-C_8H_{12} Ligand			
C(13)–C(14)	1.386 (28)	C(17)–C(18)	1.362 (27)
		C–C (av)	1.374 (17)[a]
V. $C(sp^3)$–$C(sp^2)$ Distances in C_8H_{12} Ligand			
C(13)–C(20)	1.514 (31)	C(17)–C(16)	1.553 (30)
C(14)–C(15)	1.465 (33)	C(18)–C(19)	1.456 (28)
		C–C (av)	1.497 (45)[a]
VI. $C(sp^3)$–$C(sp^3)$ Distances in C_8H_{12} Ligand			
C(15)–C(16)	1.512 (35)	C(19)–C(20)	1.565 (31)
		C–C (av)	1.539 (37)[a]
VII. Carbon–Carbon Distances in the Phenyl Rings			
C(1)–C(2)	1.434 (30)	C(7)–C(8)	1.474 (28)
C(2)–C(3)	1.413 (29)	C(8)–C(9)	1.385 (31)
C(3)–C(4)	1.373 (29)	C(9)–C(10)	1.374 (31)
C(4)–C(5)	1.426 (33)	C(10)–C(11)	1.377 (31)
C(5)–C(6)	1.343 (32)	C(11)–C(12)	1.349 (30)
C(6)–C(1)	1.414 (29)	C(12)–C(7)	1.359 (27)
		C–C (av)	1.393 (39)[a]
VIII. Intramolecular Interligand Interactions			
P(1)···P(2)	3.598		
P(1)···Me(1)	3.111	P(2)···Me(1)	3.050
P(1)···C(14)	3.733	P(2)···C(13)	3.651
P(1)···H(14)	3.361	P(2)···H(13)	3.342
P(1)···C(17)	3.072	P(2)···C(18)	3.187
P(1)···H(17)	2.448	P(2)···H(18)	2.554

[a] Esd's on mean bond lengths are calculated from the equation $\sigma = \{[\Sigma_{i=1}^{i=N}(\chi_i - \bar{\chi})^2]/(N - 1)\}^{1/2}$, where χ_i is the ith bond length and $\bar{\chi}$ is the mean of N equivalent bond lengths. [b] A is the midpoint of C(13)–C(14) and B is the midpoint of C(17)–C(18); see Figure 1.

with $d(C\text{–}H) = 1.00$ Å[20] and with isotropic thermal parameters of 6.0 Å^2, but were not permitted to refine. Their positions were, however, up-dated with respect to the subsequent refined positions of their attached carbon atoms. Four cycles of full-matrix refinement of all nonhydrogen positional parameters, of anisotropic thermal parameters for iridium and phosphorus atoms, and of isotropic thermal parameters for all carbon atoms led to final convergence at $R_F = 6.8\%$ and $R_{wF^2} = 3.0\%$. In the final cycle of refinement no parameter varied by more than 20% of its standard deviation. Anisotropic thermal parameter refinement of carbon atoms was thought to be unwise and was not attempted.

A final difference Fourier synthesis showed no significant residual electron density save in the immediate vicinity of the iridium atom, thus validating the results of the least-squares refinement process and confirming the correctness of the refined molecular structure.

Final positional and thermal parameters for all atoms are collected in Table I. Observed and calculated structure factor amplitudes are available elsewhere.[21]

The Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are shown in Table II; bond angles, with esd's, are presented in Table III. Figure 1 shows the molecule viewed down b along with the atomic numbering scheme. (Hydrogen atoms, not included in the figure, are numbered identically with their attached carbon atoms.)

TABLE III

BOND ANGLES (DEG) WITHIN THE $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ MOLECULE

Atoms	Angle	Atoms	Angle
I. Around Iridium Atom			
P(1)–Ir–P(2)	101.5 (2)	Me(1)–Ir–P(1)	87.0 (6)
P(1)–Ir–A	130.4 (6)	Me(1)–Ir–P(2)	84.5 (6)
P(2)–Ir–A	125.4 (6)	Me(1)–Ir–A	82.8 (8)
		B–Ir–P(1)	97.9 (6)
Me(1)–Ir–B	168.7 (8)	B–Ir–P(2)	104.3 (5)
		B–Ir–A	86.4 (8)
II. Around Phosphorus Atoms			
Ir–P(1)–Me(2)	114.3 (9)	Ir–P(2)–Me(4)	119.1 (7)
Ir–P(1)–Me(3)	119.3 (6)	Ir–P(2)–Me(5)	111.1 (7)
Ir–P(1)–C(1)	118.8 (7)	Ir–P(2)–C(7)	119.8 (7)
Me(2)–P(1)–Me(3)	99.6 (11)	Me(4)–P(2)–Me(5)	101.8 (10)
Me(2)–P(1)–C(1)	100.5 (9)	Me(4)–P(2)–C(7)	102.0 (10)
Me(3)–P(1)–C(1)	101.1 (12)	Me(5)–P(2)–C(7)	100.0 (10)
III. Within C_8H_{12} Ligand			
C(20)–C(13)–C(14)	121.6 (19)	C(16)–C(17)–C(18)	122.1 (18)
C(13)–C(14)–C(15)	121.2 (20)	C(17)–C(18)–C(19)	122.8 (19)
C(14)–C(15)–C(16)	115.5 (21)	C(18)–C(19)–C(20)	116.4 (18)
C(15)–C(16)–C(17)	117.0 (19)	C(19)–C(20)–C(13)	116.5 (19)
IV. Within the Phenyl Rings			
C(6)–C(1)–C(2)	116.1 (19)	C(12)–C(7)–C(8)	111.5 (18)
C(1)–C(2)–C(3)	118.8 (19)	C(7)–C(8)–C(9)	124.7 (19)
C(2)–C(3)–C(4)	122.1 (19)	C(8)–C(9)–C(10)	114.3 (21)
C(3)–C(4)–C(5)	119.6 (20)	C(9)–C(10)–C(11)	125.6 (21)
C(4)–C(5)–C(6)	118.0 (22)	C(10)–C(11)–C(12)	115.7 (21)
C(5)–C(6)–C(1)	125.4 (21)	C(11)–C(12)–C(7)	128.1 (20)

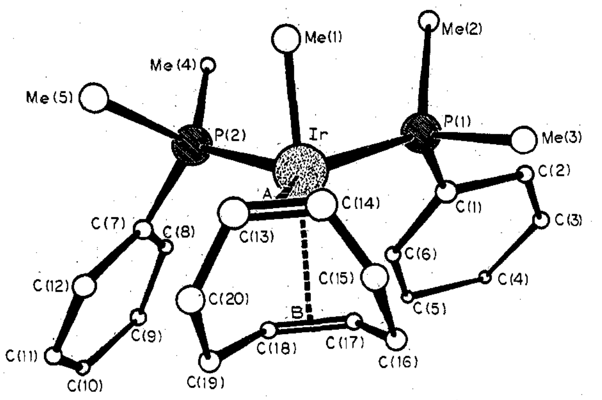

Figure 1.—The $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ molecule, projected on (010). Note that A and B are the midpoints of C(13)–C(14) and C(17)–C(18), respectively.

The Metal Coordination Sphere.—The central iridium(I) atom has an essentially trigonal-bipyramidal

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[20] The true internuclear C–H distance is, of course, 1.08 Å. However, X-ray diffraction studies show the centroid of the electron density around hydrogen to be systematically displaced along the C–H bond toward carbon. The present C–H bond distance of 1.00 Å allows for this systematic error.

[21] A compilation of observed and calculated 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-72-2243. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

coordination environment, with axial sites occupied by a methyl [Me(1)] ligand and an olefinic arm [C(17)–C(18)] of the cycloocta-1,5-diene ligand; equatorial sites are occupied by two dimethylphenylphosphine ligands and by the remaining olefinic linkage [C(13)–C(14)] of the cycloocta-1,5-diene ligand.

The iridium–methyl distance, Ir–Me(1) = 2.202 (22) Å, is rather longer than known values for iridium(III)–carbon bonds, *viz.*, 2.16 (2) Å for Ir–CH< in $(C_6H_5CHCH_2COC_6H_5)IrCl_2[(CH_3)_2SO]_2$,[22] 2.10 Å for $Ir–CH_3$ in $(Ir(CH_3)Cl_2(CO)_2]_2$,[23] 2.05 (4) Å for $Ir–CH_3$ in $Ir(CH_3)I(NO)[P(C_6H_5)_3]_2$,[24] and 2.05 (2) Å for $Ir–CO_2CH_3$ in $[(bipy)(CO)Ir(CO_2CH_3)I_2]$[25] (where bipy = 2,2′-bipyridyl).

The iridium–phosphorus distances, Ir–P(1) = 2.316 (5) Å and Ir–P(2) = 2.329 (5) Å, are equivalent, the mean value being 2.323 ± 0.009 Å.[26]

The axial iridium–olefin distance, Ir–B, is 2.117 (14) Å while the corresponding equatorial distance, Ir–A, is 2.078 (14) Å. The difference of 0.039 ± 0.20 Å is significant only at the 2σ level. We may note, however, that longer axial than equatorial iridium–olefin linkages have previously been observed in the trigonal-bipyramidal species $[(C_8H_{12})_2Ir(SnCl_3)]$.[27]

The iridium atom is not coplanar with P(1), P(2), and A, but is displaced out of this equatorial plane toward B, by 0.208 Å; see Table IV. Angles within the iridium(I) coordination sphere are somewhat distorted from those of an idealized trigonal bipyramid (*i.e.*, perfect D_{3h} symmetry). Thus, angles from the axial methyl group are Me(1)–Ir–P(1) = 87.0 (6)°, Me(1)–Ir–P(2) = 84.5 (6)°, and Me(1)–Ir–A = 82.8 (8)°. Fom the axial olefinic bond we have B–Ir–P(1) = 97.9 (6)°, B–Ir–P(2) = 104.3 (5)°, and B–Ir–A = 86.4 (8)°; this last angle is due to the geometry of the chelating diolefin. The trans angle, Me(1)–Ir–B, is 168.7 (8)°.

TABLE IV

DEVIATIONS OF ATOMS (IN Å) FROM THE EQUATORIAL COORDINATION PLANE[a]

P(1)[b]	0.000	C(13)	+0.034
P(2)[b]	0.000	C(14)	−0.034
A[b]	0.000	Ir	+0.208

[a] Equation of plane: $0.9716X + 0.2188Y + 0.0897Z - 4.5360 = 0$. The plane is expressed in Cartesian coordinates, such that $[X, Y, Z] = [xa, yb, zc]$. [b] The plane was calculated using unit weights for these atoms, and zero weights for all other atoms.

Angles within the equatorial plane are also irregular, with A–Ir–P(1) = 130.4 (6)° and A–Ir–P(2) = 125.4 (6)°. Most noteworthy, however, is the angle P(1)–Ir–P(2) = 101.5 (2)°, which is 18.5° (or over 90σ) smaller than that expected in an idealized trigonal bipyramid. The reasons for this are almost certainly associated with close *intra*molecular contacts. Thus, as can be seen from section VIII of Table II, interligand contacts between the axial olefinic moiety [H(17)–C(17)–C(18)–H(18)] and the two phosphorus atoms are already short [*viz.*, P(1)···C(17) = 3.072 and P(2)···C(18) = 3.187 Å, while P(1)···H(17) = 2.448 and P(2)···H(18) = 2.554 Å] and are certain to *decrease* as the P(1)–Ir–P(2) angle is opened to the ideal trigonal value of 120°.

We may note that other trigonal-bipyramidal iridium species which contain two equatorial phosphine ligands and an equatorial olefin ligand also show a reduction from 120° in their P–Ir–P angles. Thus P–Ir–P = 114.1 (1)° in IrH(CO)[*trans*-(NC)CH=CH(CN)]$[P(C_6H_5)_3]_2$,[28,29] 111.6 (1)° in $Ir(C_6N_4H)(CO)[C_2(CN)_4][P(C_6H_5)_3]_2$,[30] and 110.4 (1)° in $IrBr(CO)[C_2(CN)_4][P(C_6H_5)_3]_2$.[28,31]

The Phosphine Ligands.—The phosphorus–methyl distances are equivalent within the limits of experimental error and range from P(2)–Me(4) = 1.861 (22) to P(1)–Me(2) = 1.880 (20), averaging 1.873 ± 0.009 Å. Phosphorus–phenyl distances are P(1)–C(1) = 1.806 (22) and P(2)–C(7) = 1.770 (20) Å, the mean value being 1.788 ± 0.025 Å. Carbon–carbon bond lengths within the phenyl rings vary from 1.343 (32) to 1.474 (28) Å, with an average value of 1.393 ± 0.039 Å, in agreement with the recognized C–C (aromatic) distance of 1.394 ± 0.005 Å.[32]

Angles about the phosphorus atom are distorted from T_d toward C_{3v} symmetry (with the Ir–P bond defining the pseudo threefold axis); Ir–P–C and Ir–P–Me angles range from 111.1 (7) to 119.8 (7)°, while Me–P–Me and Me–P–C angles vary from 99.6 (11) to 102.0 (10)°.

The Cycloocta-1,5-diene Ligand.—The cycloocta-1,5-diene ligand takes up its customary "tub" (C_{2v}) conformation. The coordinated double bonds, C(13)–C(14) and C(17)–C(18), have lengths of 1.386 (28) and 1.362 (27) Å, respectively, as compared to an uncoordinated olefinic distance of ~1.34 Å. The four $C(sp^3)–C(sp^2)$ distances range from 1.456 (28) to 1.553 (30) Å, averaging 1.497 ± 0.045 Å, in reasonable agreement with the accepted value of 1.51 Å; similarly, the two $C(sp^3)–C(sp^3)$ bonds average 1.539 ± 0.037 Å in length, indistinguishable from the recognized distance of 1.54 Å.

The dihedral angles collected in Table V show the essential twofold symmetry of the cycloocta-1,5-diene ligand.

TABLE V

DIHEDRAL ANGLES (DEG) IN THE CYCLOOCTA-1,5-DIENE LIGAND

Atoms	Angle	Atoms	Angle
C(20)–C(13)–C(14)–C(15)	7.3	C(16)–C(17)–C(18)–C(19)	4.2
C(13)–C(14)–C(15)–C(16)	77.4	C(17)–C(18)–C(19)–C(20)	71.6
C(14)–C(15)–C(16)–C(17)	2.7	C(18)–C(19)–C(20)–C(13)	1.7
C(15)–C(16)–C(17)–C(18)	69.1	C(19)–C(20)–C(13)–C(14)	69.6

Intermolecular Contacts.—Intermolecular contacts, to 3.0 Å, are collected in Table VI. As can be seen from this list, the individual molecules are separated by normal van der Waals distances, closest approaches of each type being: hydrogen···hydrogen = 2.47

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TABLE VI

INTERMOLECULAR CONTACTS, TO 3.0 Å[a]

Atom 1	Atom 2	Transformation	Dist, Å
H(15)	H(3)	$-x + 1, y - {}^1/_2, -z + {}^1/_2$	2.47
H(16′)	H(5)	$-x + {}^3/_2, y - {}^1/_2, z$	2.49
H(16)	H(3)	$-x + 1, y - {}^1/_2, -z + {}^1/_2$	2.55
H(19)	H(9)	$-x + {}^3/_2, y - {}^1/_2, z$	2.59
H(20)	H(12)	$-x + 1, -y + 1, -z$	2.60
H(19)	Me(1)	$x + 1, y, z$	2.63
H(20′)	H(9)	$-x + {}^3/_2, y - {}^1/_2, z$	2.64
H(13)	H(8)	$-x + {}^1/_2, y - {}^1/_2, z$	2.71
H(20)	H(11)	$-x + 1, -y + 1, -z$	2.74
H(16′)	H(4)	$-x + {}^3/_2, y - {}^1/_2, z$	2.75
H(15′)	H(5)	$-x + {}^3/_2, y - {}^1/_2, z$	2.76
H(3)	H(4)	$x - {}^1/_2, y, -z + {}^1/_2$	2.79
H(12)	H(12)	$-x + 1, -y + 1, -z$	2.79
H(13)	H(11)	$-x + 1, -y + 1, -z$	2.87
H(20)	C(12)	$-x + 1, -y + 1, -z$	2.88
H(20)	C(11)	$-x + 1, -y + 1, -z$	2.91
H(20)	H(10)	$-x + {}^3/_2, y - {}^1/_2, z$	2.94
H(20′)	H(10)	$-x + {}^3/_2, y - {}^1/_2, z$	2.99

[a] Note that hydrogen atoms of methyl groups have not been included in this computation.

Å for H(15)···H(3) $[-x + 1, y - {}^1/_2, -z + {}^1/_2]$ and carbon···hydrogen = 2.63 Å for H(19)···Me(1) $[x + 1, y, z]$.

Discussion

The present X-ray structural analysis confirms the ground-state stereochemistry of $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ as originally assigned by Shapley and Osborn.[7] On cooling solutions of this complex, the limiting low-temperature ^1H nmr spectrum is first observed at 0°. The coalescence of the cycloocta-1,5-diene vinylic resonances and of the methylenic signals (and other spectral characteristics) observed upon warming the solution can be explained in terms of a series of pseudorotations using the P(1)–Ir, P(2)–Ir, and Me(1)–Ir bonds as pivots (*cf.* scheme 1 of Figure 2 in ref 7).[33] These pseudorotations involve, *inter alia,* the transit of a phosphine ligand into an axial position. Thus, the value of the P–Ir–P angle is an important consideration in the pseudorotation of these pentacoordinate species. It is thus comforting to note that the P–Ir–P angle in (C_8H_{12})(diphos)$Ir(CH_3)$, a species which exhibits fluxional behavior at temperatures as low as −60°, has the extremely low value of ∼85°.[11,34] Furthermore, the equatorial P–Ir–P and P–Ir–A angles are the only angles about iridium that show drastic changes in going from $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ to (C_8H_{12})(diphos)$Ir(CH_3)$.

Subsequent papers in this series will report the crystal structures of further molecules in this class, with particular attention being paid to correlations between fluxional behavior and geometry within the metal coordination sphere.

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(33) Note the pseudorotation is not the only mechanism that explains the detailed features of the temperature-dependent ^1H nmr spectrum of the complex under discussion (*cf.* ref 7). It is, however, the most *probable* mechanism.

(34) The crystal structure of (C_8H_{12})(diphos)$Ir(CH_3)$ has been undertaken. Details will be reported at a later date.

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Molecular Bromine Bridging of $Sb^{III}{}_2Br_9{}^{3-}$ Anions and the Crystal Structure of Tetramethylammonium Nonabromodiantimonate(III)–Dibromine

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Tetramethylammonium nonabromodiantimonate(III)–dibromine, $[(CH_3)_4N]_3Sb_2Br_9 \cdot Br_2$, crystallizes in space group $P6_3/mmc$ with $a = 9.585$ (5) Å, $c = 22.667$ (3) Å, and $Z = 2$. The observed and calculated densities are 2.55 and 2.48 g/cm³. The 289 independent reflections, significantly above background, were measured on a four-circle diffractometer equipped with a scintillation counter and were used for anisotropic, full-matrix least-squares refinement of the heavy-atom parameters to a conventional $R = 0.137$. The structure contains $Sb_2Br_9{}^{3-}$ anions bridged by Br_2 molecules. The cations as well as the Br_2 molecules are disordered. Only one-third of the terminal bromines are bridged. The $Sb^{III}{}_2Br_9$ moiety consists of two $SbBr_6$ octahedra sharing a face. The Br–Sb–Br···Br–Br···Br–Sb–Br chain is nearly linear. The Br···Br_2 distance is 2.89 (1) Å, which is indicative of important bridging interactions.

Introduction

The crystal structure of tetramethylammonium nonabromodiantimonate(III)–dibromine, $[(CH_3)_4N]_3Sb_2Br_{11}$, was undertaken as part of a series of structure investigations of halo-coordinated antimony compounds.[1–10] Numerous intensely colored compounds of the type $R_xSb_yBr_z$, where R is an aliphatic amine,

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