molecular contacts are collected in Table VI. The individual molecules of $(C_7H_6CH_2)Fe(CO)_3$ are separated by normal van der Waals distances, closest approaches (of each type) being as follows: oxygen· · ·oxygen, 3.374 (4) Å; oxygen· · ·carbon, 3.261 (4) Å; oxygen· · ·hydrogen, 2.50 (3) Å; carbon· · ·hydrogen, 3.02 (5) Å; hydrogen· · ·hydrogen, 2.81 (6) Å.

Registry No. $(C_8H_8)Fe(CO)_3$, 12559-94-3.

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X-Ray Crystallographic Studies on Fluxional Pentacoordinate Transition Metal Complexes.
III.[1,2] (Cycloocta-1,5-diene)[1,3-bis(diphenylphosphino)propane]methyliridium(I)

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The fluxional pentacoordinate complex (cycloocta-1,5-diene)[1,3-bis(diphenylphosphino)propane]methyliridium(I), $(C_8H_{12})[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Ir(CH_3)$, crystallizes in the centrosymmetric monoclinic space group $C2/c$ ($C_{2h}{}^6$; No. 15) with $a = 23.92$ (3), $b = 18.44$ (2), $c = 15.77$ (1) Å, and $\beta = 119.80$ (8)°. Observed and calculated densities are 1.61 (2) and 1.601 g cm^{-3} (respectively) for $M = 727.8$ and $Z = 8$. X-Ray diffraction data were collected with a Supper–Pace automated diffractometer and the structure was solved using a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 7.6\%$ for the 3573 independent nonzero reflections out to $\sin\theta = 0.86$ (Cu Kα radiation). The iridium atom is in a slightly distorted trigonal-bipyramidal coordination environment, with the chelating 1,3-bis(diphenylphosphino)propane ligand occupying two equatorial sites, the methyl ligand being in an axial site, and with the cycloocta-1,5-diene ligand spanning the remaining axial and equatorial positions. Important bond distances include: Ir–P = 2.309 (4) and 2.337 (4), Ir–CH_3 = 2.153 (18), Ir–olefin(equatorial) = 2.033 (12), and Ir–olefin(axial) = 2.127 (12) Å. The diequatorial angle P(1)–Ir–P(2) is 93.4 (1)°.

Introduction

We have previously reported crystallographic studies on the fluxional pentacoordinate iridium(I) species $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$[1] and $(C_8H_{12})[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Ir(CH_3)$[2] which have been synthesized (and their variable-temperature ^{1}H nmr spectra investigated) by Shapley and Osborn.[3,4] In the present paper we report the results of a crystallographic study of $(C_8H_{12})[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Ir(CH_3)$. Correlations between molecular geometry and fluxional behavior[3,4] are interpreted in terms of stereoisomeric interconversions *via* the Berry ("pseudorotation") mechanism.[5]

Unit Cell and Space Group

Crystals of (cycloocta-1,5-diene)[1,3-bis(diphenylphosphino)propane]methyliridium(I), hereafter referred to as (C_8H_{12})(DPPP)Ir(CH_3), were supplied by Dr. J. R. Shapley and Professor J. A. Osborn of Harvard University. In the crystalline state the complex is air stable for several months and does not decompose upon irradiation with X-rays. Examination of the crystal form and the reciprocal lattice symmetry of $2/m$ (C_{2h}) indicated that the crystals belonged to the monoclinic system.

Sets of $h'k'(0\text{-}1)$ and $h'(0\text{-}1)l'$ Weissenberg photographs, along with c'- and b'-axis oscillation photographs, were taken with Cu Kα radiation; $(0\text{-}1)k'l'$, $h'k'(0\text{-}1)$, and $h'0l'$ precession photographs along with a'-, b'-, and c'-cone-axis photographs were taken with Mo Kα radiation. The systematic absences thus identified were $h'k'l'$ for $h' + k' + l' = 2n + 1$ and $h'0l'$ for $h' = 2n + 1$, consistent with space groups $I2/a$ or Ia.[6]

Unit cell parameters, obtained from calibrated (lead nitrate, $a_{24°} = 7.8566$ Å) precession photographs taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) at 24 ± 2° are $a' = 15.77$ (1), $b' = 18.44$ (2), $c' = 21.12$ (3) Å; and $\beta' = 100.60$ (8)°.

These (primed) parameters were those used during data collection. They were later transformed to conform to the standard setting for space group $C2/c$ ($C_{2h}{}^6$; No. 15) by the transformation

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix}$$

The new cell thus defined has the parameters $a = 23.92$ (3), $b = 18.44$ (2), $c = 15.77$ (1) Å; and $\beta = 119.80$ (8)°.

The volume of the unit cell is 6037 Å^3; the observed density, $\rho_{\text{obsd}} = 1.61$ (2) g cm^{-3} (by neutral buoyancy in aqueous zinc iodide solution), indicates eight molecules per unit cell. The calculated density is $\rho_{\text{calcd}} = 1.601$ g cm^{-3} for $M = 727.8$ and $Z = 8$.

The satisfactory solution of the crystal structure confirms the true space group to be the centrosymmetric $C2/c$ with one molecule in the asymmetric unit rather than the noncentrosymmetric possibility, Cc. No crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of the X-Ray Diffraction Data

The complex crystallizes as colorless parallelepipeds. Two crystals were used during the analysis. Crystal I (0.23 × 0.23 × 0.30 mm, referred to a′, b′, c′) was aligned along the b' axis; crystal II (0.28 × 0.18 × 0.38 mm, with respect to a′, b′, c′) was aligned along its c' axis.

Intensity data were collected with Cu Kα radiation ($\bar{\lambda}$ 1.5418 Å) on a 0.01°-incrementing Supper-Pace "Buerger Automated diffractometer" using a stationary-background, ω-scan, stationary-background counting sequence and equiinclination Weissenberg geometry.

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(2) Part II: M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 12, 260 (1973).

(3) J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, 92, 6976 (1970).

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(6) Apart from an origin shift of 1/4 in y, $I2/a$ is identical to $I2/c$ and Ia is identical to Ic.

Table I. Final Atomic Parameters for $(C_8H_{12})(DPPP)Ir(CH_3)$

(A) Positional and Isotropic Thermal Parameters, with Esd's[a]

Atom	*x*	*y*	*z*	*B*, Å²
Ir	0.23620 (2)	0.11247 (3)	0.24520 (3)	
P(1)	0.3118 (2)	0.1955 (2)	0.3481 (3)	
P(2)	0.1515 (2)	0.1957 (2)	0.1890 (2)	
Me	0.2147 (7)	0.0923 (9)	0.3605 (12)	3.3 (3)
C(1)	0.3466 (6)	0.2642 (8)	0.3021 (9)	2.3 (2)
C(2)	0.3112 (7)	0.2825 (8)	0.2041 (12)	2.9 (3)
C(3)	0.3325 (7)	0.3401 (10)	0.1685 (14)	3.5 (3)
C(4)	0.3891 (9)	0.3777 (9)	0.2306 (13)	3.5 (3)
C(5)	0.4230 (9)	0.3596 (10)	0.3299 (15)	3.9 (4)
C(6)	0.4022 (8)	0.3041 (9)	0.3651 (11)	3.4 (3)
C(7)	0.3828 (6)	0.1547 (8)	0.4496 (9)	2.3 (2)
C(8)	0.3837 (9)	0.1356 (9)	0.5366 (14)	4.0 (3)
C(9)	0.4358 (10)	0.0986 (14)	0.6096 (14)	5.2 (5)
C(10)	0.4887 (9)	0.0765 (12)	0.5972 (14)	5.2 (4)
C(11)	0.4870 (9)	0.0972 (11)	0.5146 (13)	4.6 (4)
C(12)	0.4362 (8)	0.1349 (9)	0.4400 (12)	3.7 (3)
C(13)	0.1272 (6)	0.2503 (9)	0.0788 (10)	2.6 (3)
C(14)	0.1515 (8)	0.3188 (10)	0.0792 (12)	3.7 (3)
C(15)	0.1316 (8)	0.3566 (12)	−0.0085 (13)	4.3 (4)
C(16)	0.0901 (9)	0.3262 (12)	−0.0951 (15)	4.5 (4)
C(17)	0.0647 (8)	0.2556 (10)	−0.0985 (12)	4.0 (3)
C(18)	0.0822 (8)	0.2192 (11)	−0.0131 (12)	3.9 (3)
C(19)	0.0713 (6)	0.1591 (8)	0.1590 (9)	2.6 (2)
C(20)	0.0220 (8)	0.2047 (10)	0.1467 (12)	3.6 (3)
C(21)	−0.0392 (7)	0.1785 (9)	0.1256 (11)	3.3 (3)
C(22)	−0.0481 (9)	0.0986 (13)	0.1167 (15)	4.3 (4)
C(23)	0.0007 (9)	0.0588 (12)	0.1279 (14)	4.8 (5)
C(24)	0.0612 (8)	0.0848 (10)	0.1483 (12)	3.9 (3)
C(25)	0.2832 (7)	0.2562 (9)	0.4121 (10)	2.7 (3)
C(26)	0.2267 (7)	0.3029 (10)	0.3402 (11)	3.1 (3)
C(27)	0.1606 (8)	0.2659 (10)	0.2796 (11)	3.1 (3)
C(28)	0.2778 (7)	0.0048 (9)	0.2819 (12)	3.3 (3)
C(29)	0.2091 (7)	0.0005 (10)	0.2065 (11)	3.1 (3)
C(30)	0.1884 (8)	−0.0197 (10)	0.1021 (11)	3.4 (3)
C(31)	0.1806 (9)	0.0444 (9)	0.0361 (11)	3.7 (4)
C(32)	0.2228 (6)	0.1086 (8)	0.0969 (11)	2.5 (2)
C(33)	0.2892 (8)	0.1033 (9)	0.1591 (12)	3.4 (3)
C(34)	0.3271 (9)	0.0355 (11)	0.1799 (13)	4.3 (4)
C(35)	0.3349 (8)	−0.0067 (10)	0.2667 (14)	3.5 (3)
H(2)	0.2719	0.2558	0.1601	2.9
H(3)	0.3074	0.3539	0.0995	3.5
H(4)	0.4048	0.4162	0.2049	3.5
H(5)	0.4618	0.3868	0.3745	3.9
H(6)	0.4263	0.2921	0.4349	3.4
H(8)	0.3473	0.1486	0.5457	4.0
H(9)	0.4365	0.0873	0.6709	5.2
H(10)	0.5245	0.0477	0.6467	5.2
H(11)	0.5239	0.0849	0.5062	4.6
H(12)	0.4375	0.1479	0.3808	3.7
H(14)	0.1827	0.3411	0.1414	3.7
H(15)	0.1482	0.4055	−0.0068	4.3
H(16)	0.0773	0.3528	−0.1559	4.5
H(17)	0.0349	0.2332	−0.1615	4.0
H(18)	0.0636	0.1714	−0.0152	3.9
H(20)	0.0296	0.2571	0.1527	3.6
H(21)	−0.0738	0.2114	0.1174	3.3
H(22)	−0.0890	0.0763	0.1030	4.3
H(23)	−0.0058	0.0062	0.1213	4.8
H(24)	0.0951	0.0516	0.1548	3.9
H(25a)	0.3230	0.2919	0.4616	2.7
H(25b)	0.2678	0.2231	0.4548	2.7
H(26a)	0.2399	0.3262	0.2883	3.1
H(26b)	0.2207	0.3467	0.3824	3.1
H(27a)	0.1488	0.2400	0.3316	3.1
H(27b)	0.1253	0.3089	0.2395	3.1
H(28)	0.2874	0.0163	0.3485	3.3
H(29)	0.1762	0.0110	0.2245	3.1
H(30a)	0.1418	−0.0480	0.0712	3.4
H(30b)	0.2248	−0.0565	0.1028	3.4
H(31a)	0.1298	0.0614	−0.0030	3.7
H(31b)	0.1952	0.0279	−0.0171	3.7
H(32)	0.2020	0.1555	0.0915	2.5
H(33)	0.3125	0.1477	0.1915	3.4
H(34a)	0.3755	0.0498	0.1931	4.3
H(34b)	0.3030	0.0004	0.1152	4.3
H(35a)	0.3388	−0.0648	0.2544	3.5
H(35b)	0.3790	0.0113	0.3323	3.5

Table I (*Continued*)

(B) Anisotropic Thermal Parameters (with Esd's) for Iridium and Phosphorus 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	125 (1)	134 (2)	233 (4)	−17 (2)	219 (3)	31 (3)
P(1)	112 (6)	243 (10)	219 (13)	−26 (14)	197 (12)	13 (21)
P(2)	139 (7)	165 (8)	303 (16)	−1 (16)	238 (18)	10 (20)

(C) Direction Cosines for Vibration Ellipsoids of Iridium and Phosphorus Atoms[c]

Atom	B_{max} (dc's major axis)	B_{med} (dc's median axis)	B_{min} (dc's minor axis)
Ir	2.22	1.94	1.21
	(0.755, −0.209, 0.164)	(−0.119, 0.889, 0.443)	(−0.645, −0.408, 0.881)
P(1)	3.35	1.97	1.25
	(−0.153, 0.988, 0.081)	(0.670, 0.099, 0.306)	(−0.727, −0.117, 0.949)
P(2)	2.47	2.25	1.93
	(0.607, 0.067, 0.385)	(−0.192, 0.979, 0.152)	(−0.771, −0.192, 0.910)

[a] Estimated standard deviations, esd's, 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) are referred to the monoclinic axes. The magnitudes of the major, median, and minor axes of the atomic vibration ellipsoids are defined in terms of B (the normal isotropic thermal parameter, having units of Å^2). The transformation to root-mean-square displacement, $(\bar{U}^2)^{1/2}$, is $(\bar{U}^2)^{1/2} = (B/8\pi^2)^{1/2}$.

The apparatus and experimental technique have been described in a previous publication.[7]

Details applying to the present analysis include the following. (i) The X-ray generator was operated at 49 kV and 18 mA. (ii) The scan range was set at $\omega(hkl) = [1.7 + 0.8/L(hkl)]°$. Here, $L(hkl)$ is the Lorentz factor for the reflection hkl and is given by $\cos^2 \bar{\mu} \sin \Upsilon$, where $\bar{\mu}$ is the equiinclination angle and Υ the vertical Weissenberg coordinate. (iii) The scan speed was $d\omega/dt = 2°\ \text{min}^{-1}$. (iv) The count associated with the ω scan is $C(hkl)$ and the initial and final backgrounds, $B_1(hkl)$ and $B_2(hkl)$, were each counted for one-fourth the time of the ω scan. (v) Standard reflections within each level were collected after each batch of 40 reflections in order to monitor the stability of the crystal and apparatus. Deviations were statistical only, the maximum deviation from the mean being less than 1%. (vi) $I(hkl)$, the integrated intensity of the reflection hkl, was calculated by $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$. (vii) Reflections were weighted according to the following scheme, which has consistently proved successful for data collected *via* the ω-scan technique: $I(hkl) > 4900$, $\sigma[I(hkl)] = 0.1[I(hkl)]$; $I(hkl) \leqslant 4900$, $\sigma[I(hkl)] = 7.0 \cdot [I(hkl)]^{1/2}$. (viii) Data were subsequently rejected on two bases—overlap of (or streaking from) an adjacent reflection, as indicated by the criterion $[B_1(hkl)/B_2(hkl)]$ or $[B_2(hkl)/B_1(hkl)] \geqslant 3.0$, and reflection not significantly above background, as indicated by the inequality $I(hkl) < 3.0[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$.

With crystal I mounted on its b' axis, 3981 reflections from levels $h'(0\text{–}20)l'$ were collected; 4426 reflections from levels $h'k'(0\text{–}8)$ were collected from the c'-mounted crystal II. Data are complete to $\sin \theta = 0.86$, save for the few reflections in the sphere $0 \leqslant \theta \leqslant 4°$, which are shielded from the counter by a lead backstop. All data were corrected for Lorentz and polarization effects [by multiplying by $2 \cos^2 \bar{\mu} \sin \Upsilon/(1 + \cos^2 2\theta)$] and an absorption correction was applied.[8] With μ (Cu Kα) = 96.11 cm^{-1}, transmission factors ranged from 0.0870 to 0.2627 for data from crystal I (volume 15.9×10^{-6} cm^3) and from 0.1100 to 0.2789 for data from crystal II (volume 17.4×10^{-6} cm^3).

All reflection indices were now transformed to the standard setting ($C2/c$), as described above. Data from the 30 Weissenberg levels were placed on a common scale by a least-squares procedure which minimizes a set of residuals linear in the logarithms of the individual scale factors.[9] The resulting 3573 independent nonzero reflections were placed on an (approximately) absolute scale by means of a Wilson plot,[10] which also yielded the overall isotropic thermal parameter, $\bar{B} = 1.52\ \text{Å}^2$.

Solution and Refinement of the Structure

All crystallographic calculations were, unless otherwise indicated, carried out using the CRYM system[11] on the Harvard University IBM 360/65 computer. Scattering factors for neutral carbon and hydrogen were taken from ref 12. Scattering factor curves for phosphorus and iridium are the Hartree–Fock–Slater values of Hanson, *et al.*;[13] these were corrected for both the real and imaginary components of anomalous dispersion [$\Delta f'(\text{P}) = +0.2$, $\Delta f''(\text{P}) = +0.5$, $\Delta f'(\text{Ir}) = -5$ to -6, and $\Delta f''(\text{Ir}) = +7$ to $+6$ e].[14]

The residual minimized during least-squares refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where the sum is over all reflections hkl, and $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$, where $\sigma[\{F^2(hkl)\}] = \sigma[I(hkl)]F^2(hkl)/I(hkl)$. Discrepancy indices are defined as

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

$$R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^4$$

A three-dimensional Patterson synthesis, which had been "sharpened" such that the average coefficient was no longer θ dependent and from which the origin peak had been removed, revealed a set of vectors consistent with an iridium atom in the general (eightfold) position of the centrosymmetric space group $C2/c$, with coordinates $x \approx 0.235$, $y \approx 0.114$, $z \approx 0.245$.

A three-dimensional Fourier synthesis, phased only by the iridium atom ($R_F = 51.1\%$), revealed the locations of all nonhydrogen atoms. Full-matrix least-squares refinement of all positional and isotropic thermal parameters led to convergence at $R_F = 9.9\%$ and $R_{wF^2} = 6.4\%$. Subsequent refinement of the scale factor, positional parameters for all nonhydrogen atoms, anisotropic thermal parameters for iridium and phosphorus atoms, and isotropic thermal parameters for carbon atoms led to convergence at $R_F = 8.3\%$ and $R_{wF^2} = 4.8\%$. Hydrogen atoms (other than those of the methyl group, which are indeterminant) were now included in calculated positions with their isotropic thermal parameters set equal to those of the carbon atoms to which they were bonded. Neither the hydrogen atom positions nor their thermal parameters were refined; they were, however, redefined with respect to the refined carbon atom parameters. Convergence, with $(\Delta/\sigma)_{\text{max}} < 0.1$, was obtained with $R_F = 7.6\%$ and $R_{wF^2} = 4.2\%$. A final difference-Fourier map showed no significant features other than slight residuals around the iridium and phosphorus atom positions.

Anisotropic thermal parameter refinement of the carbon atoms was not attempted, since refinement of these parameters in the presence of a third-row transition metal atom is likely to yield results that are not physically meaningful.

Final positional and thermal parameters for all atoms are collected in Table I. A list of observed and calculated structure factor amplitudes is available elsewhere.[15]

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(7) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 7, 1123 (1968).

(8) Using IMBIBE, a Fortran IV program for the IBM 360, by Dr. J. Worwald. This is based on the gaussian quadrature numerical integration technique: see C. W. Burnham, *Amer. Mineral.*, 51, 159 (1966).

(9) A. D. Rae, *Acta Crystallogr.*, 19, 683 (1965).

(10) A. J. C. Wilson, *Nature (London)*, 150, 152 (1942).

(11) CRYM is an integrated sequence of crystallographic routines for the IBM 360/65 computer, compiled under the direction of Dr. R. E. Marsh at the California Institute of Technology.

(12) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 202.

(13) H. P. Hanson, F. Herman, J. D. Lea, and S. Skellman, *Acta Crystallogr.*, 17, 1040 (1964).

(14) See ref 12, pp 214–215.

(15) 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. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-531

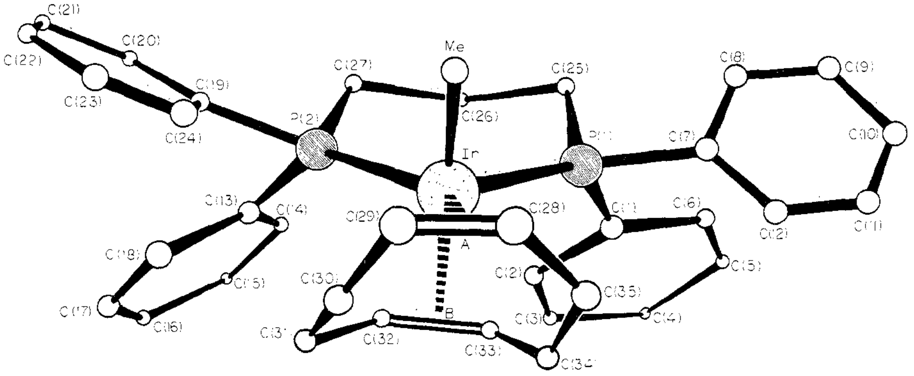

Figure 1. Stereochemistry of the $(C_8H_{12})(DPPP)Ir(CH_3)$ molecule. *Hydrogen atoms, which are omitted for the sake of clarity, are numbered the same as the carbon atoms to which they are attached.* Note that A is the midpoint of C(28)-C(29) and that B is the midpoint of C(32)-C(33).

Description of the Molecular Structure

Interatomic distances and bond angles are shown in Tables II and III, respectively. The molecular geometry and labeling of atoms is depicted in Figure 1.

The Iridium(I) Coordination Sphere. The overall geometry of the iridium(I) coordination sphere is similar to that found previously for $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$[1] and $(C_8H_{12})(\text{diphos})Ir(CH_3)$[2] (diphos = 1,2-bis(diphenylphosphino)ethane)—*i.e.*, a trigonal-bipyramidal environment with the two axial sites occupied by a methyl group and one olefinic arm [C(32)-C(33)] of the cycloocta-1,5-diene ligand and with the three equational sites occupied by the chelating phosphine ligand and the remaining olefinic residue [C(28)-C(29)] of the cycloocta-1,5-diene ligand.

The iridium atom is not coplanar with the equatorial donor atoms [P(1), P(2), and A] but is displaced toward B by 0.189 Å—see Table IV.

Angles within the iridium(I) coordination sphere deviate from those of idealized trigonal-bipyramidal (D_{3h}) symmetry. Angles from the axial methyl group are Me-Ir-P(1) = 87.3 (5), Me-Ir-P(2) = 84.7 (5), and Me-Ir-A = 83.8 (7)°. From the axial olefinic ligand, angles are B-Ir-P(1) = 102.3 (5), B-Ir-P(2) = 103.5 (5), and B-Ir-A = 83.2 (7)°. [The smaller value of this last angle represents geometric constraints within the chelating cycloocta-1,5-diene ligand.] The trans angle, Me-Ir-B, is 166.8 (6)°. Angles within the trigonal plane exhibit rather more significant deviations from D_{3h} symmetry, with P(1)-Ir-A = 128.7 (5), P(2)-Ir-A = 135.4 (5), and P(1)-Ir-P(2) = 93.4 (1)°. The small P-Ir-P angle presumably reflects the spanning limitations of the chelating DPPP ligand.

The iridium-methyl distance, Ir-Me, is 2.153 (18) Å. Iridium-phosphorus distances, Ir-P(1) = 2.309 (4) and Ir-P(2) = 2.337 (4) Å, are clearly not equivalent since they differ by 0.028 Å or ~5σ. The longer iridium-phosphorus bond, Ir-P(2), is that which is more nearly trans to the Ir-A bond [A-Ir-P(2) = 135.4 (5)°, while A-Ir-P(1) = 128.7 (5)°].

The axial iridium-olefin distance (Ir-B) is 2.127 (12) Å, while the corresponding equatorial distance (Ir-A) is only 2.033 (12) Å. The difference of 0.094 Å represents 5.5σ and is highly significant. This pattern of iridium-olefin distances appears to be general for trigonal-bipyramidal iridium(I) species containing a cycloocta-1,5-diene ligand which spans an axial and an equatorial coordination site.[1,2,16]

The DPPP Ligand. The phosphorus-phenyl bond distances range from 1.818 (14) to 1.861 (17) Å and average 1.841 ± 0.018 Å,[17] in good agreement with results from similar complexes.[1,2,18] The phosphorus-methylene linkages are 1.852 (18) and 1.859 (17) Å, the mean value being 1.856 ± 0.005 Å. The difference between P-C(sp^2) and P-C(sp^3) bond lengths, while of low significance, is in keeping with the variation in covalent radius of carbon with change of hybridization (*i.e.*, ~0.77 Å for C(sp^3) and ~0.74 Å for C(sp^2)).

The C-P-C angles range from 99.1 (7) to 102.9 (7)° and average 100.7°—significantly lower than the theoretical regular tetrahedral value of 109.47°. However, contraction of C-P-C angles appears to be a characteristic both of phosphine complexes of the transition metals and of free phosphines.[19]

The CH_2-CH_2 distances within the DPPP ligand are 1.526 (24) and 1.542 (25) Å, the mean being 1.534 ± 0.011 Å—in excellent agreement with the accepted C(sp^3)-C(sp^3) distance of 1.537 ± 0.005 Å.[20]

The six-membered chelate ring defined by Ir-P(1)-C(25)-C(26)-C(27)-P(2) adopts a "chair" conformation, presumably to minimize ring strain (by analogy with the cyclohexane molecule). Although this conformation is not shown clearly in Figure 1, it is evident from Table IV(B) that the iridium atom lies 0.853 Å *above* and C(26) lies 0.685 Å *below* the plane defined by P(1), P(2), C(25), and C(27).

Dihedral angles within the six-membered chelate ring are collected in Table V. The ring is ordered, thermal parameters for the methylene carbons [C(25), C(26), C(27)] being normal and essentially equivalent (*B* = 2.7 (3), 3.1 (3), 3.1 (3) Å^2, respectively—see Table I).

The 24 independent carbon-carbon bonds within the phenyl rings vary from 1.315 (33) to 1.487 (29) Å and average 1.395 ± 0.034 Å, a value which is in good agreement with the accepted C-C(aromatic) distance of 1.394 ± 0.005 Å.[21]

The Cycloocta-1,5-diene Ligand. This ligand has a rather irregular geometry which only approximately corresponds to the expected "tub" conformation. Dihedral angles within this system are collected in Table V(A).

The mean C(sp^2)-C(sp^3) and C(sp^3)-C(sp^3) bond lengths are, respectively, 1.513 ± 0.021 and 1.514 ± 0.015 Å—as compared with the accepted values of 1.510 ± 0.005 and 1.537 ± 0.005 Å.[20] The axially bonded olefinic residue, C(32)-C(33), is 1.394 (25) Å, while the equatorially bonded olefinic

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(16) P. Porta, H. M. Powell, R. J. Mawby, and L. M. Venanzi, *J. Chem. Soc. A*, 455 (1967).

(17) Within the text, esd's on individual bond distances are given in parentheses. Esd's on mean values, calculated by the "scatter" formula given in footnote *a* to Table II, are shown as ±*X.XXX* Å.

(18) J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and K. A. Taylor, *Chem. Commun.*, 906 (1966).

(19) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2980 (1968); see, especially, Table 7.

(20) *Chem. Soc., Spec. Publ.*, No. 18, S14s (1965).

(21) *Chem. Soc., Spec. Publ.*, No. 18, S16s (1965).

Table II. Interatomic Distances (with Esd's) for the $(C_8H_{12})(DPPP)Ir(CH_3)$ Molecule

Atoms	Dist, Å	Atoms	Dist, Å
(A) Distances from Iridium Atom			
Ir–P(1)	2.309 (4)	Ir–A[b]	2.033 (12)
Ir–P(2)	2.337 (4)	Ir–B[b]	2.127 (12)
Ir–P(mean)	2.323 (20)[a]	Ir–Me	2.153 (18)
(B) Phosphorus–Phenyl Distances			
P(1)–C(1)	1.850 (15)	P(2)–C(13)	1.835 (15)
P(1)–C(7)	1.818 (14)	P(2)–C(19)	1.861 (17)
		$P-C_6H_5$(mean)	1.841 (18)[a]
(C) Phosphorus–Methylene Distances			
P(1)–C(25)	1.852 (18)	P(2)–C(27)	1.859 (17)
		$P-CH_2$(mean)	1.856 (5)[a]
(D) Carbon–Carbon Distances within C_8H_{12} Ligand			
C(28)–C(29)	1.475 (25)	C(32)–C(33)	1.394 (25)
		C(sp^2)–C(sp^2)(mean)	1.434 (57)[a]
C(29)–C(30)	1.511 (22)	C(33)–C(34)	1.483 (28)
C(31)–C(32)	1.543 (24)	C(35)–C(28)	1.516 (29)
		C(sp^3)–C(sp^2)(mean)	1.513 (21)[a]
C(30)–C(31)	1.524 (24)	C(34)–C(35)	1.503 (27)
		C(sp^3)–C(sp^3)(mean)	1.514 (15)[a]
(E) Carbon–Carbon Distances in Phenyl Rings of DPPP Ligand			
C(1)–C(2)	1.386 (21)	C(13)–C(14)	1.389 (25)
C(2)–C(3)	1.409 (25)	C(14)–C(15)	1.404 (25)
C(3)–C(4)	1.398 (27)	C(15)–C(16)	1.347 (28)
C(4)–C(5)	1.400 (27)	C(16)–C(17)	1.428 (29)
C(5)–C(6)	1.370 (27)	C(17)–C(18)	1.370 (24)
C(6)–C(1)	1.409 (23)	C(18)–C(13)	1.428 (22)
C(7)–C(8)	1.406 (24)	C(19)–C(20)	1.381 (25)
C(8)–C(9)	1.385 (30)	C(20)–C(21)	1.414 (27)
C(9)–C(10)	1.433 (35)	C(21)–C(22)	1.487 (29)
C(10)–C(11)	1.338 (28)	C(22)–C(23)	1.315 (33)
C(11)–C(12)	1.387 (27)	C(23)–C(24)	1.400 (31)
C(12)–C(7)	1.408 (26)	C(24)–C(19)	1.387 (24)
		C–C(mean)	1.395 (34)[a]
(F) C(sp^3)–C(sp^3) Distances within DPPP Ligand			
C(25)–C(26)	1.526 (24)	C(26)–C(27)	1.542 (25)
		C(sp^3)–C(sp^3)(mean)	1.534 (11)[a]
(G) Selected Intramolecular Nonbonding Contacts			
P(1)···P(2)	3.382	P(1)···C(33)	3.235
P(1)···C(28)	3.643	P(2)···C(32)	3.173
P(2)···C(29)	3.815	P(1)···H(28)	3.356
P(1)···Me	3.083	P(2)···H(29)	3.455
P(2)···Me	3.028	H(28)···Me	2.313
C(28)···Me	2.876	H(29)···Me	2.394
C(29)···Me	2.908	P(1)···H(33)	2.629
		P(2)···H(32)	2.494

[a] Esd's on mean bond lengths are calculated by the "scatter" equation

$$\sigma = \left\{ \left[\sum_{i=1}^{i=N} (\chi_i - \overline{\chi})^2 \right] / (N-1) \right\}^{1/2}$$

Here, χ_i is the value for the ith bond length, and $\overline{\chi}$ is the mean of N equivalent bond lengths. [b] A is the midpoint of C(28)–C(29) and B is the midpoint of C(32)–C(33)–see Figure 1.

linkage is 1.475 (25) Å. While the esd's on these distances are high, this pattern of the longer carbon-carbon bond being associated with the shorter metal-olefin bond is consistent with previous studies[2] and with the recognized mode of interaction of an olefin with a transition metal involving d_π-π^* metal→olefin back-donation (*cf.* ref 22).

Intermolecular Contacts. Those contacts which approach the sum of the van der Waals radii of the atoms involved are given in Table VI. Shortest contacts of each type are 2.75 Å for carbon···hydrogen and 2.15 Å for hydrogen···hydrogen. There are no abnormally short intermolecular distances.

Table III. Bond Angles (deg) within the $(C_8H_{12})(DPPP)Ir(CH_3)$ Molecule

Atoms	Angle	Atoms	Angle
(A) Angles around Iridium Atom			
P(1)–Ir–P(2)	93.4 (1)	Me–Ir–A	83.8 (7)
P(1)–Ir–A	128.7 (5)	B–Ir–P(1)	102.3 (5)
P(2)–Ir–A	135.4 (5)	B–Ir–P(2)	103.5 (5)
Me–Ir–P(1)	87.3 (5)	B–Ir–A	83.2 (7)
Me–Ir–P(2)	84.7 (5)	Me–Ir–B	166.8 (6)
(B) Angles around Phosphorus Atoms			
Ir–P(1)–C(1)	121.8 (4)	Ir–P(2)–C(13)	121.7 (6)
Ir–P(1)–C(7)	114.0 (5)	Ir–P(2)–C(19)	116.6 (5)
Ir–P(1)–C(25)	114.3 (6)	Ir–P(2)–C(27)	114.7 (6)
C(1)–P(1)–C(7)	102.9 (7)	C(13)–P(2)–C(19)	99.1 (7)
C(1)–P(1)–C(25)	99.2 (7)	C(13)–P(2)–C(27)	102.0 (7)
C(7)–P(1)–C(25)	101.9 (7)	C(19)–P(2)–C(27)	99.2 (8)
(C) Angles within the C_8H_{12} Ligand			
C(35)–C(28)–C(29)	126.5 (15)	C(31)–C(32)–C(33)	123.2 (15)
C(28)–C(29)–C(30)	121.5 (16)	C(32)–C(33)–C(34)	125.0 (16)
C(29)–C(30)–C(31)	114.6 (15)	C(33)–C(34)–C(35)	115.0 (17)
C(30)–C(31)–C(32)	110.5 (13)	C(34)–C(35)–C(28)	111.0 (16)
(D) Angles within Phenyl Groups of DPPP Ligand			
C(6)–C(1)–C(2)	119.9 (14)	C(18)–C(13)–C(14)	118.2 (14)
C(1)–C(2)–C(3)	119.1 (16)	C(13)–C(14)–C(15)	120.7 (15)
C(2)–C(3)–C(4)	120.8 (16)	C(14)–C(15)–C(16)	120.7 (19)
C(3)–C(4)–C(5)	119.1 (18)	C(15)–C(16)–C(17)	120.2 (18)
C(4)–C(5)–C(6)	120.5 (19)	C(16)–C(17)–C(18)	119.5 (16)
C(5)–C(6)–C(1)	120.6 (15)	C(17)–C(18)–C(13)	120.6 (17)
C(12)–C(7)–C(8)	117.7 (15)	C(24)–C(19)–C(20)	120.0 (16)
C(7)–C(8)–C(9)	120.4 (20)	C(19)–C(20)–C(21)	122.5 (16)
C(8)–C(9)–C(10)	121.2 (19)	C(20)–C(21)–C(22)	116.3 (17)
C(9)–C(10)–C(11)	116.8 (20)	C(21)–C(22)–C(23)	117.6 (21)
C(10)–C(11)–C(12)	123.9 (22)	C(22)–C(23)–C(24)	126.0 (21)
C(11)–C(12)–C(7)	120.0 (16)	C(23)–C(24)–C(19)	117.5 (18)
(E) Angles within Chelating Bridge of DPPP Ligand			
P(1)–C(25)–C(26)	111.5 (10)	C(26)–C(27)–P(2)	118.4 (13)
C(25)–C(26)–C(27)	117.9 (15)		

Table IV. Least-Squares Planes within the $(C_8H_{12})(DPPP)Ir(CH_3)$ Molecule[a,b]

Atom	Dev, Å	Atom	Dev, Å
(A) Equatorial Coordination Plane			
Equation: $0.6361X + 0.1552Y - 0.7558Z - 0.0320 = 0$			
P(1)*	0.000	C(25)	+1.242
P(2)*	0.000	C(26)	+0.867
A*	0.000	C(27)	+1.050
Ir	−0.189	C(28)	+0.050
		C(29)	−0.050
(B) Plane within Six-Membered Chelate Ring			
Equation: $0.4564X + 0.7446Y - 0.4872Z + 2.4640 = 0$			
P(1)*	+0.058	C(27)*	+0.076
P(2)*	−0.059	Ir	−0.853
C(25)*	−0.075	C(26)	+0.685

[a] Planes are in cartesian coordinates such that $[X, Y, Z] = [xa + zc \cos\beta, yb, zc \sin\beta]$. [b] Planes are derived using unit weights for atoms marked with asterisks and zero weight for all other atoms.

Table V. Dihedral Angles (deg)

Atoms	Angle	Atoms	Angle
(A) For C_8H_{12} Ligand			
C(35)–C(28)–C(29)–C(30)	2.5	C(31)–C(32)–C(33)–C(34)	3.9
C(28)–C(29)–C(30)–C(31)	90.0	C(32)–C(33)–C(34)–C(35)	91.3
C(29)–C(30)–C(31)–C(32)	25.1	C(33)–C(34)–C(35)–C(28)	29.5
C(30)–C(31)–C(32)–C(33)	56.1	C(34)–C(35)–C(28)–C(29)	47.9
(B) For Chelate Ring			
Ir–P(1)–C(25)–C(26)	62.2	C(26)–C(27)–P(2)–Ir	44.3
P(1)–C(25)–C(26)–C(27)	73.5	C(27)–P(2)–Ir–P(1)	30.9
C(25)–C(26)–C(27)–P(2)	65.5	P(2)–Ir–P(1)–C(25)	39.6

Discussion

Shapley and Osborn[3,4] have shown that the temperature at

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(22) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

Table VI. Intermolecular Contacts between $(C_8H_{12})(DPPP)Ir(CH_3)$ Molecules[a]

Old atom	New atom	Transformn	Dist, Å
H(6)	C(21)	$x + 1/2, -y + 1/2, z + 1/2$	2.75
H(30a)	C(22)	$-x, -y, -z$	2.84
H(30b)	C(26)	$-x + 1/2, y - 1/2, -z + 1/2$	2.80
H(35a)	C(26)	$-x + 1/2, y - 1/2, -z + 1/2$	2.88
H(17)	H(17)	$-x, y, -z - 1/2$	2.44
H(18)	H(5)	$x - 1/2, -y + 1/2, z - 1/2$	2.43
H(23)	H(5)	$-x + 1/2, y - 1/2, -z + 1/2$	2.43
H(25a)	H(21)	$x + 1/2, -y + 1/2, z + 1/2$	2.47
H(25b)	H(25b)	$-x + 1/2, -y + 1/2, -z + 1$	2.22
H(26b)	H(8)	$-x + 1/2, -y + 1/2, -z + 1$	2.40
H(27a)	H(21)	$-x, y, -z + 1/2$	2.36
H(30a)	H(22)	$-x, -y, -z$	2.44
H(30b)	H(26b)	$-x + 1/2, y - 1/2, -z + 1/2$	2.15
H(34a)	H(16)	$-x + 1/2, -y + 1/2, -z$	2.35
H(35a)	H(27b)	$-x + 1/2, y - 1/2, -z + 1/2$	2.47
H(35b)	H(10)	$-x + 1, -y, -z$	2.42

[a] Only those contacts which closely approach the sum of van der Waals radii for the atoms involved have been included.

which compounds of the type $(C_8H_{12})(phosphine)_2Ir(CH_3)$ begin to exhibit fluxional behavior is a sensitive function of the nature of the phosphine ligands. Thus, the "coalescence temperature" (which is defined[3] as that temperature at which the vinylic proton resonances of the C_8H_{12} ligand coalesce to a single signal in the ^1H nmr spectrum) changes from 67° for $(C_8H_{12})(PPhMe_2)_2IrMe$ to 12° for $(C_8H_{12})(DPPP)IrMe$ to <−60° for $(C_8H_{12})(diphos)IrMe$; the free energy of activation for the intramolecular rearrangement ($\Delta G^{\ddagger}$) ranges from 16.3 kcal/mol for $(C_8H_{12})(PPhMe_2)_2IrMe$ to 13.4 kcal/mol for $(C_8H_{12})(DPPP)IrMe$ to <9.2 kcal/mol for $(C_8H_{12})(diphos)IrMe$.

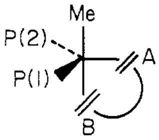
It can quickly be ascertained from Table VII (*quod vide*) that there are no significant changes in bond distances from one complex to another. Similarly, a survey of the bond angles reveals that only the diequatorial P(1)-Ir-P(2) angle [and, consequently the diequatorial P(1)-Ir-A and P(2)-Ir-A angles] varies widely within the three complexes investigated.

Clearly the rates at which the three compounds undergo fluxional behavior must, primarily, be due to the spanning limitations of the diequatorially coordinated phosphines.[23] Substantiating this hypothesis is the positive correlation of $\Delta G^{\ddagger}$ with the P(1)-Ir-P(2) angle—*i.e.*, the smaller this angle, then the more readily interconversion of isomers occurs. This is precisely the trend expected if the Berry pseudorotation mechanism is operative and the ground-state complex Ia proceeds *via* a rate-limiting Berry pseudorotation (using P(1) as a "pivot") to the higher energy isomer IIa in which the more electronegative methyl group[24-26] is in an equatorial position and a phosphorus atom occupies an axial site. Equilibration of the vinylic protons of the C_8H_{12} ligand then occurs as the net result of pseudorotations about P(1), Me (leading to IIb), and P(2) (leading back to Ib, which is indistinguishable from Ia).

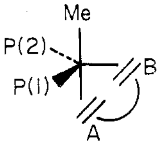
Table VII. Comparison of Molecular Properties of Closely Related Trigonal-Bipyramidal Iridium(I) Complexes

	(C_8H_{12})-$(PPhMe_2)_2$-IrMe[a]	(C_8H_{12})-(DPPP)IrMe	(C_8H_{12})-(diphos)-IrMe[b]
	(A) Bond Lengths, Å		
Ir-Me	2.202 (22)	2.153 (18)	2.133 (16)
Ir-P(1)	2.316 (5)	2.309 (4)	2.308 (3)
Ir-P(2)	2.329 (5)	2.337 (4)	2.308 (3)
Ir-A	2.078 (14)	2.033 (12)	2.011 (9)
Ir-B	2.117 (14)	2.127 (12)	2.106 (9)
C=C(eq)	1.386 (28)	1.475 (25)	1.459 (21)
C=C(ax)	1.362 (27)	1.394 (25)	1.374 (21)
Ir· · ·(trigonal plane)	0.208	0.189	0.179
	(B) Bond Angles, Deg		
P(1)-Ir-P(2)	101.5 (2)	93.4 (1)	84.9 (2)
P(1)-Ir-A	130.4 (6)	128.7 (5)	136.4 (3)
P(2)-Ir-A	125.4 (6)	135.4 (5)	136.4 (3)
Me-Ir-P(1)	87.0 (6)	87.3 (5)	85.2 (3)
Me-Ir-P(2)	84.5 (6)	84.7 (5)	85.2 (3)
Me-Ir-A	82.8 (8)	83.8 (7)	85.3 (5)
B-Ir-P(1)	97.9 (6)	102.3 (5)	102.6 (3)
B-Ir-P(2)	104.3 (5)	103.5 (5)	102.6 (3)
B-Ir-A	86.4 (8)	83.2 (7)	84.0 (3)
Me-Ir-B	168.7 (8)	166.8 (6)	169.4 (5)
	(C) Fluxional Properties		
Coalescence temp, °C	67[c]	12[d]	<−60[d]
$\Delta G^{\ddagger}$, kcal/mol	16.3[c]	13.4[d]	<9.2[d]

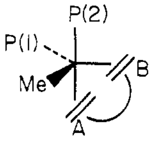
[a] See ref 1. [b] See ref 2. [c] See ref 3. [d] See ref 4.



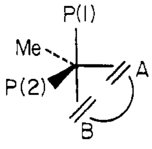
Ia



Ib



IIa



IIb

Of the three complexes in Table VII, the ground state (I) is expected to be higher in energy for the diphos than for the DPPP complex due to the extra strain associated with the smaller Ir-P-C-C-P chelate ring of the former and the concomitantly larger distortion of the P(1)-Ir-P(2) angle from the ideal diequatorial angle of 120°. By the same token, the $(PPhMe_2)_2$ complex should have the lowest ground state energy and largest $\Delta G^{\ddagger}$ because of its lack of ring strain and a P(1)-Ir-P(2) angle closer to 120°.

We may note that temperature-dependent ^1H nmr studies[3] on the species $(C_8H_{12})(phosphine)_2IrH$ [where phosphine = PPh_3, PPh_2Me, $PPhMe_2$] may be interpreted similarly. The "coalescence temperature" for the complex with the most bulky phosphine, PPh_3, is the highest (70°); the PPh_2Me complex has a coalescence temperature of 10° and the $PPhMe_2$-containing species has one of −2°. However, electronic effects could also play a role, since the basicities of PPh_3, PPh_2Me, and $PPhMe_2$ are different.

Further studies in this series will concentrate on (diolefin)-$(phosphine)_2IrX$ species where X = $SnCl_3$ or H.

Registry No. $(C_8H_{12})[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Ir(CH_3)$, 37540-76-4.

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(23) Note that the diphos and DPPP ligands have essentially identical basicities. Changes in fluxional behavior are thus not due to changes in the character of the metal-phosphine bonds.

(24) The Allred-Rochow electronegativities are 2.50 for carbon and 2.06 for phosphorus: A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

(25) While preference rules for ligand occupation of axial or equatorial sites are not yet tabulated for pentacoordinate transition metal species, we may assume that factors such as electronegativity and π-acceptor capability will be important. Assuming a trigonal-bipyramidal stereochemistry, we tentatively suggest that highly electronegative ligands prefer to occupy axial sites (*cf.* ref 26) while strong π-acceptor ligands prefer to occupy equatorial sites.

(26) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968); this review article includes some rules for preferential occupation of sites in trigonal-bipyramidal phosphorus(V) derivatives.