X-Ray Crystallographic Studies on Fluxional Pentacoordinate Transition Metal Complexes. II.[1] (Cycloocta-1,5-diene)[1,2-bis(diphenylphosphino)ethane]methyliridium(I), (C_8H_{12})(diphos)Ir(CH_3)

MELVYN ROWEN CHURCHILL* and SUSAN A. BEZMAN

The stereochemically nonrigid complex (cycloocta-1,5-diene)[1,2-bis(diphenylphosphino)ethane]methyliridium(I), $(C_8H_{12})[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Ir(CH_3)$, crystallizes in the centrosymmetric orthorhombic space group *Pnma* $(D_{2h}{}^{16}$; No. 62) with $a = 10.13$ (1), $b = 21.33$ (3), and $c = 13.70$ (2) Å; $\rho_{obsd} = 1.58 \pm 0.02$ and $\rho_{calcd} = 1.602$ g cm^{-3} for $M = 713.8$ and $Z = 4$. X-Ray diffraction data to sin $\theta = 0.78$ (Cu Kα radiation) were collected on a Supper-Pace automated diffractometer, and the structure was solved using Patterson, Fourier, and least-squares refinement methods. All nonhydrogen atoms were accurately located, the final unweighted discrepancy index being $R_F = 5.6\%$ for the 1698 symmetry-independent nonzero reflections. The central iridium(I) atom has a (distorted) trigonal-bipyramidal coordination environment, with the chelating 1,2-bis(diphenylphosphino)ethane ligand occupying two equatorial sites and the methyl group occupying an axial position, while the cycloocta-1,5-diene ligand takes up the remaining two coordination positions (*i.e.*, one axial and one equatorial). The molecule possesses a crystallographically imposed mirror plane, which necessitates that the P–C–C–P framework of the 1,2-bis(diphenylphosphino)ethane moiety be planar. Important distances and angles in the metal coordination sphere include Ir–P = Ir–P' = 2.308 (3) Å, Ir–CH$_3$ = 2.133 (16) Å, Ir–olefin (equatorial) = 2.011 (9) Å, Ir–olefin (axial) = 2.106 (9) Å, and P–Ir–P' = 84.9 (2)°. The molecular geometry and fluxional behavior of (C_8H_{12})-$[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Ir(CH_3)$ are compared with those of $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$.

Introduction

Stereochemical nonrigidity of pentacoordinate transition metal complexes has been the subject of some recent mechanistic studies.[2-5] Shapley and Osborn[2] have reported the temperature-dependent ^1H nmr spectra of the compounds $(C_8H_{12})[(C_6H_5)_{3-n}(CH_3)_nP]_2Ir(R)$, where R = CH$_3$ or H and $0 \leqslant n \leqslant 2$; a trigonal-bipyramidal ground state was proposed, and a Berry "pseudorotation" process[6] was suggested as a possible mechanism for the interconversion of stereoisomers.[2] Extension of these studies to complexes of the type (C_8H_{12})-$(P\frown P)Ir(R)$, where P P is a chelating diphosphine, have yielded some unusual results.[7] Thus, the bis-phosphine complex $(C_8H_{12})[(C_6H_5)_2(CH_3)P]_2Ir(CH_3)$ has a ^1H nmr spectrum in which there are two separate vinylic (C_8H_{12}) resonances at temperatures as high as 80°;[2] however, the electronically equivalent complex $(C_8H_{12})[(C_6H_5)_2P(CH_2)_2P$-$(C_6H_5)_2]Ir(CH_3)$, hereafter called (C_8H_{12})(diphos)Ir(CH_3), shows a single vinylic resonance at temperatures as low as $-60°$ (the limit imposed by solubility).[7] Interconversion of pentacoordinate stereoisomers is thus very much affected by chelation and (in the species studied thus far) occurs more rapidly in chelated than in the analogous nonchelated complexes. We have previously reported the results of a crystallographic study of $(C_8H_{12})[(C_6H_5)(CH_3)_2P]Ir(CH_3)^{1,8}$ and now provide details of our subsequent examination of (C_8H_{12})(diphos)Ir(CH_3). This present X-ray structural analysis is the second in a series undertaken with a view toward ascertaining relationships between molecular geometry and intramolecular rearrangements (*i.e.*, "fluxional behavior") in certain classes of pentacoordinate transition metal derivatives.

Unit Cell and Space Group

A quantity of (C_8H_{12})(diphos)Ir(CH_3) was kindly donated by Dr. J. R. Shapley of Harvard University. Crystals suitable for an X-ray structural analysis were grown (over a 24-hr period) at the interface of a saturated solution of the complex in deoxygenated CH$_2$Cl$_2$ and a layer of cyclohexane. The complex is air stable for several months in the crystalline state and is not X-ray sensitive. Examination of the crystal habit and of the reciprocal lattice symmetry suggested that the crystals belonged to the orthorhombic system (*i.e.*, diffraction symmetry D_{2h}; *mmm*). A systematic survey of (0-1)kl and hk(0-1) Weissenberg photographs, h(0-1)l and hk(0-1) precession photographs, a- and c-axis oscillation photographs, and b and c cone-axis photographs (all taken with Cu Kα radiation, $\bar{\lambda}$ 1.5418 Å) revealed the systematic absences 0kl for $k + 1 = 2n + 1$ and $hk0$ for $h = 2n + 1$—consistent with the centrosymmetric space group *Pnma* $(D_{2h}{}^{16}$; No. 62) or with the noncentrosymmetric space group $Pn2_1a$ $(C_{2v}{}^9$; No. 33). The accurate solution of the crystal structure revealed the true space group to be the centrosymmetric possibility.

Unit cell parameters from calibrated zero-level precession photographs [Pb(NO$_3$)$_2$, $a = 7.8566$ Å] taken with Cu Kα radiation at $24 \pm 2°$ are $a = 10.13$ (1), $b = 21.33$ (3), and $c = 13.70$ (2) Å. The volume of the unit cell is 2960 Å^3. The observed density of 1.58 ± 0.02 g cm^{-3} (by flotation in aqueous BaI$_2$) indicates four molecules per unit cell. The calculated density is 1.602 g cm^{-3} for $M = 713.8$ and $Z = 4$. For space group *Pnma* (in the absence of disorder) the molecule is required to have crystallographic C_s (*m*) or C_i (Ī) symmetry. The latter symmetry is, however, impossible for the molecule.

Collection and Unification of the X-Ray Diffraction Data

The complex crystallizes as thin pale yellow rectangular plates. Two crystals were used in the collection of intensity data. Crystal C (0.80 × 0.04 × 0.52 mm, referred to $\vec{a}, \vec{b}, \vec{c}$) was mounted along its c axis and crystal A (0.68 × 0.09 × 0.50 mm) was aligned along its a axis.

Diffraction data were collected with Cu Kα radiation on a Supper-Pace Buerger automated diffractometer using equiinclination Weissenberg geometry and a stationary-background, ω-scan, stationary-background counting sequence. The apparatus and experimental precautions have been described previously.[9] Details of the present analysis are as follows. (i) The X-ray generator was operated at 49 kV/18 mA. (ii) The scan angle (ω) was chosen as [1.70 +

* Address correspondence to this author at the University of Illinois at Chicago Circle.

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

(3) D. P. Rice and J. A. Osborn, *J. Organometal. Chem.*, 30, C84 (1971).

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(5) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 93, 1797 (1971).

(6) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960).

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Table I. Final Parameters for (C_8H_{12})(diphos)Ir(CH_3)

(A) Atomic Coordinates and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
Ir	0.20073 (5)	$^1/_4$	0.01690 (4)	
P	0.3016 (2)	0.1770 (1)	−0.0825 (2)	
Me	0.0476 (15)	$^1/_4$	−0.0900 (12)	4.6 (3)
C(1)	0.2102 (8)	0.1077 (5)	−0.1247 (7)	3.7 (2)
C(2)	0.0943 (9)	0.0897 (5)	−0.0797 (8)	4.3 (2)
C(3)	0.0272 (10)	0.0390 (6)	−0.1122 (8)	5.3 (2)
C(4)	0.0670 (11)	0.0049 (5)	−0.1926 (9)	5.4 (2)
C(5)	0.1871 (12)	0.0219 (7)	−0.2364 (9)	6.1 (3)
C(6)	0.2559 (11)	0.0736 (5)	−0.2034 (8)	5.2 (2)
C(7)	0.4560 (9)	0.1415 (5)	−0.0461 (8)	3.6 (2)
C(8)	0.5752 (14)	0.1640 (8)	−0.0762 (13)	8.9 (4)
C(9)	0.6962 (21)	0.1375 (14)	−0.0304 (14)	11.6 (7)
C(10)	0.6879 (13)	0.0935 (9)	0.0337 (12)	7.7 (6)
C(11)	0.5740 (13)	0.0682 (7)	0.0576 (11)	6.7 (3)
C(12)	0.4555 (13)	0.0918 (7)	0.0183 (7)	5.2 (3)
C(13)	0.3445 (9)	0.2153 (5)	−0.2014 (7)	4.5 (2)
C(14)	0.0532 (9)	0.2158 (6)	0.1151 (7)	4.7 (2)
C(15)	0.1011 (10)	0.1746 (6)	0.1971 (9)	5.9 (3)
C(16)	0.2427 (12)	0.1766 (6)	0.2124 (8)	5.4 (2)
C(17)	0.3229 (8)	0.2178 (5)	0.1413 (7)	3.7 (2)
H(2)	0.0606	0.1136	−0.0240	4.3
H(3)	−0.0528	0.0260	−0.0773	5.3
H(4)	0.0136	−0.0298	−0.2181	5.4
H(5)	0.2221	−0.0030	−0.2907	6.1
H(6)	0.3379	0.0861	−0.2360	5.2
H(8)	0.5811	0.1965	−0.1265	8.9
H(9)	0.7830	0.1538	−0.0491	11.6
H(10)	0.7685	0.0784	0.0654	7.7
H(11)	0.5716	0.0328	0.1031	6.7
H(12)	0.3714	0.0725	0.0371	5.2
H(14)	0.0190	0.1948	0.0566	4.7
H(15a)	0.0729	0.1260	0.1807	5.9
H(15b)	0.0524	0.1898	0.2649	5.9
H(16a)	0.2603	0.1943	0.2867	5.4
H(16b)	0.2802	0.1283	0.2064	5.4
H(17)	0.3778	0.1965	0.0926	3.7

(B) Anisotropic Thermal Parameters ($\times 10^5$) for Iridium and Phosphorus Atoms[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	415 (7)	218 (2)	303 (5)	0	19 (6)	0
P	659 (24)	223 (6)	369 (13)	11 (20)	77 (28)	−15 (16)

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

Atom	B_{maj} (dc's major axis)	B_{med} (dc's median axis)	B_{min} (dc's minor axis)
Ir	3.97 (0.000, 1.000, 0.000)	2.28 (0.092, 0.000, 0.996)	1.70 (0.996, 0.000, −0.092)
P	4.07 (0.024, 0.998, −0.064)	2.95 (−0.655, −0.033, −0.755)	2.52 (−0.755, 0.060, 0.65)

[a] The anisotropic thermal parameter is defined by $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$. [b] Direction cosines (dc's) are referred to the natural crystal axes. The major, median, and minor axes of the vibration ellipsoids are defined in terms of B (the isotropic thermal parameter), since this is a quantity familiar to crystallographers. The transformation to root-mean-square displacement, $(\overline{U^2})^{1/2}$, is $(\overline{U^2})^{1/2} = (B/8\pi^2)^{1/2}$.

$0.80L(hkl)]$,[10,11] where $L^{-1}(hkl)$ is the multiplicative Lorentz factor for the reflection hkl. (iii) The scan speed $(d\omega/dt)$ was $2°$ min⁻¹. (iv) The count associated with the ω scan is $C(hkl)$; the initial and final backgrounds, $B_i(hkl)$ and $B_f(hkl)$, were each counted for one-fourth the time of the main scan. (v) Standard reflections, within a given Weissenberg level, were measured after each 40 reflections in order to monitor the stability of the crystal and apparatus. The maximum deviation from the mean was less than 2%. (vi) $I(hkl)$, the integrated intensity of the reflection hkl, was calculated as $I(hkl) = C(hkl) - 2[B_i(hkl) + B_f(hkl)]$.

Reflections were weighted according to the scheme $I(hkl) \geqslant 4900$, $\sigma[I(hkl)] = 0.1[I(hkl)]$; $I(hkl) > 4900$, $\sigma[I(hkl)] = 7.0 \cdot$

(10) This scan angle is chosen by examining the width of reflections at various Υ angles (*i.e.*, vertical Weissenberg coordinate) on Weissenberg photographs.

(11) The term involving $L^{-1}(hkl)$ allows for extension of reflections at low angles on upper Weissenberg levels; this is a result of the divergence of the X-ray beam: D. C. Phillips, *Acta Crystallogr.*, **7**, 746 (1954).

$[I(hkl)]^{1/2}$. All data were subjected to two tests and retained only if (a) $B_i(hkl)/B_f(hkl)$ and $B_f(hkl)/B_i(hkl)$ were <3.0 and (b) $I(hkl) > 3.0[C(hkl) + 4B_i(hkl) + 4B_f(hkl)]^{1/2}$. The first of these tests eliminates reflections that are subject to overlap or to asymmetric "streaking" (*i.e.*, white radiation associated with a lower angle reflection); the second criterion rejects reflections that are 3σ or less above background, based on counting statistics alone.

A total of 1585 reflections in levels $hk(0-8)$ were collected from crystal C; 1480 reflections in levels $(0-7)kl$ were collected from crystal A. Each level is complete to $\sin \theta = 0.78$, save for data in the sphere $0 \leqslant \theta \leqslant 4°$, which are shielded from the scintillation counter by a Pb backstop. All data were corrected for Lorentz and polarization effects $[(Lp)^{-1} = 2 \cos^2 \bar{\mu} \sin \Upsilon/(1 + \cos^2 2\theta)]$ and absorption corrections were applied[12] ($\mu = 97.95$ cm⁻¹). Transmission factors

(12) Using IMBIBE, a Fortran IV program for the IBM 360 computer, written by Dr. J. Wormald. This program uses a gaussian quadrature numerical integration technique: C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

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ranged from 0.0763 to 0.6746 for data from crystal C (volume 11.3×10^{-6} cm^3) and from 0.0964 to 0.4127 for data from crystal A (volume 23.1×10^{-6} cm^3). All data were placed on a common scale *via* a least-squares procedure which minimizes a sum of residuals linear in the logarithms of the individual scale factors.[13] The resulting 1698 independent nonzero reflections were placed on an (approximately) absolute scale by means of a Wilson plot,[14] which also yielded the overall isotropic thermal parameter, $\bar{B} = 1.94$ Å^2.

Solution of the Crystal Structure

Crystallographic computations were carried out under the CRYM system, *i.e.*, the set of crystallographic programs which was written under the direction of Dr. R. E. Marsh of the California Institute of Technology.

A three-dimensional Patterson synthesis (from which the origin peak had been removed and which was "sharpened" such that the average intensity was no longer θ dependent) revealed a set of vectors consistent with an iridium atom at $x = 0.200$ and $z = 0.016$. [The y coordinate was set at $^1/_4$; it is required to have this value if the true space group is *Pnma* and is arbitrary if the space group is the polar *Pn2$_1$a*.] A three-dimensional Fourier synthesis, phased only by the iridium atom ($R_F = 27.5\%$),[15] revealed the locations of the two phosphorus and 16 carbon atoms and strongly suggested that the molecule possessed a crystallographic mirror plane. The analysis was continued assuming the space group to be *Pnma*. A second Fourier synthesis ($R_F = 19.9\%$) quickly led to the location of all remaining nonhydrogen atoms.

Full-matrix least-squares refinement of positional and individual isotropic thermal parameters, along with the overall scale factor, led to convergence at $R_F = 11.5\%$ and $R_{wF^2} = 8.1\%$. A further four cycles of full-matrix least-squares refinement of positional parameters (save for the y coordinates of atoms lying in the molecular mirror plane), of isotropic thermal parameters for all carbon atoms, of anisotropic thermal parameters for iridium and phosphorus atoms (with β_{12} and β_{23} of the iridium atom constrained to zero), and of an overall scale factor led to convergence at $R_F = 6.5\%$ and $R_{wF^2} = 3.2\%$. At this point a secondary extinction factor[16,17] was included in the refinement; all hydrogen atoms (other than those of the methyl and methylene groups) were included in calculated positions with isotropic thermal parameters set equal to those of the carbon atoms to which they were bonded. Although no hydrogen atom parameters were refined, they were redefined relative to the updated carbon atom positions and thermal parameters. Refinement terminated with $R_F = 5.6\%$ and $R_{wF^2} = 2.2\%$. The final value for the extinction factor was $\chi = 3.69$ (34) $\times 10^{-6}$. A final difference Fourier showed no significant residual electron density except in the immediate vicinity of the iridium atom, thereby validating the results of the least-squares refinement procedure and confirming the correctness of the molecular structure.

Throughout the analysis, scattering factors for neutral iridium, phosphorus, carbon, and hydrogen were used;[18a] the "heavy-atom" values were corrected for dispersion [$\Delta f'$(Ir) = $-5 \rightarrow -6$ e, $\Delta f''$(Ir) = $+7$e, $\Delta f'$(P) = $+0.2$ e, $\Delta f''$(P) = $+0.5$ e].[18b] 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 $\sigma[F^2(hkl)] = \sigma[I(hkl)]|F^2(hkl)|/ [I(hkl)]$.

Final atomic parameters are collected in Table I. Observed and calculated structure factor amplitudes are available.[19]

Molecular Structure

Interatomic distances and angles, with their estimated

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

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

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

(16) The secondary extinction factor (χ) modifies the calculated structure factor amplitude, according to the expression F^2(cor) = F^2(uncor)[1 + $\chi\beta F^2$(uncor)], where β = (1 + cos^4 2θ)/[sin 2θ(1 + cos^2 2θ)].

(17) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963); A. Larson, *ibid.*, 23, 664 (1967).

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

(19) 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-73-260.

Table II. Interatomic Distances (with Esd's) within the (C_8H_{12})(diphos)Ir(CH$_3$) Molecule

Atoms	Dist, Å	Atoms	Dist, Å
(A) Distances from Central Iridium Atom			
Ir–P	2.308 (3)	Ir---A^b	2.011 (9)
Ir–Me	2.133 (16)	Ir---B^b	2.106 (9)
(B) Phosphorus–Phenyl Distances			
P–C(1)	1.837 (10)	P–C(7)	1.808 (10)
		Mean P–C(phenyl)	1.823 (21)^a
(C) Phosphorus–Methylene Distance			
P–C(13)	1.874 (10)		
(D) Carbon–Carbon Distances within C$_8$H$_{12}$ Ligand			
C(14)–C(14')	1.459 (21)	C(17)–C(17')	1.374 (21)
		Mean C(sp^2)–C(sp^2)	1.416 (59)^a
C(14)–C(15)	1.507 (15)	C(16)–C(17)	1.543 (15)
		Mean C(sp^2)–C(sp^3)	1.525 (25)^a
C(15)–C(16)	1.451 (16)		
(E) Carbon–Carbon Distances within the Phenyl Rings			
C(1)–C(2)	1.381 (13)	C(7)–C(8)	1.364 (18)
C(2)–C(3)	1.352 (15)	C(8)–C(9)	1.487 (27)
C(3)–C(4)	1.381 (16)	C(9)–C(10)	1.289 (32)
C(4)–C(5)	1.404 (16)	C(10)–C(11)	1.314 (20)
C(5)–C(6)	1.381 (18)	C(11)–C(12)	1.408 (19)
C(6)–C(1)	1.381 (15)	C(12)–C(7)	1.380 (17)
		Mean C–C	1.377 (49)^a
(F) C(sp^3)–C(sp^3) Distance in diphos Ligand			
C(13)–C(13')	1.481 (21)		
(G) Intramolecular Interligand Contacts			
P$\cdots$P'	3.114	C(8)$\cdots$C(13)	3.099
P$\cdots$Me	3.009	C(12)$\cdots$H(17)	2.578
P$\cdots$C(14)	3.787	C(13)$\cdots$H(6)	2.797
P$\cdots$H(14)	3.460	C(13)$\cdots$H(8)	2.638
P$\cdots$C(17)	3.194	C(14)$\cdots$H(2)	2.896
P$\cdots$H(17)	2.554	H(2)$\cdots$H(14)	2.097

a Esd's for mean bond distances are calculated from the equation $\sigma = [[\Sigma_{i=1}^{i=N} (x_i - \bar{x})^2]/(N - 1)]^{1/2}$, where x_i is the ith bond length and $\bar{x}$ is the mean of the N equivalent bond lengths. b A is the midpoint of C(14)–C(14') and B is the midpoint of C(17)–C(17').

standard deviations, are shown in Tables II and III (respectively). The molecular geometry is shown in Figure 1. Hydrogen atoms, which are excluded from this figure for the sake of clarity, are numbered the same as the carbon atoms to which they are bonded.

Iridium(I) Coordination Sphere

The metal coordination sphere is essentially a trigonal bipyramid in which axial sites are occupied by a methyl (Me) and an olefin [C(17)–C(17')] group, while the three equatorial positions are taken up by the bidentate chelating diphos ligand and the remaining olefinic residue [C(14)–C(14')]. The iridium–methyl linkage of 2.133 (16) Å may be compared with the Ir(I)–CH$_3$ distance of 2.202 (22) in (C$_8$H$_{12}$)- [(C$_6$H$_5$)(CH$_3$)$_2$P]$_2$Ir(CH$_3$)[1] and with Ir(III)–carbon bonds which range from 2.05 (2) Å in [(2,2'-bipy)(CO)Ir(CO$_2$CH$_3$)- I$_2$]^{20} up to 2.16 (2) Å in (C$_6$H$_5$CHCH$_2$COC$_6$H$_5$)IrCl$_2$[(CH$_3$)$_2$- SO]$_2$.[21]

The iridium–phosphorus distances of 2.308 (3) Å in the present compound are somewhat shorter than those reported previously for pentacoordinate trigonal-bipyramidal iridium-(I)-phosphine derivatives; *cf.* Ir–P(equatorial) = 2.316 (5) and 2.329 (5) Å in (C$_8$H$_{12}$)[C$_6$H$_5$(CH$_3$)$_2$P]$_2$Ir(CH$_3$),[1] Ir–P- (axial) = 2.36 (1) and 2.38 (1) Å in Ir(O$_2$)Cl(CO)[P-

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

(21) M. McPartlin and R. Mason, *Chem. Commun.*, 545 (1967).

Table III. Interatomic Angles (Deg) within the
$(C_8H_{12})(diphos)Ir(CH_3)$ Molecule

Atoms	Angle	Atoms	Angle
(A) Angles around Iridium Atom			
P–Ir–P'	84.9 (2)	Me–Ir–P	85.2 (3)
P–Ir–A	136.4 (3)	Me–Ir–A	85.3 (5)
		B–Ir–P	102.6 (3)
Me–Ir–B	169.4 (5)	B–Ir–A	84.0 (3)
(B) Angles around Phosphorus Atom			
Ir–P–C(1)	120.4 (3)	C(1)–P–C(7)	100.7 (4)
Ir–P–C(7)	120.2 (4)	C(1)–P–C(13)	101.2 (5)
Ir–P–C(13)	108.8 (3)	C(7)–P–C(13)	102.8 (4)
(C) Angles within the C_8H_{12} Ligand			
C(14')–C(14)–C(15)	125.6 (9)	C(15)–C(16)–C(17)	116.5 (9)
C(14)–C(15)–C(16)	114.2 (9)	C(16)–C(17)–C(17')	124.7 (8)
(D) Angles within Phenyl Rings			
C(1)–C(2)–C(3)	120.3 (10)	C(7)–C(8)–C(9)	118.0 (16)
C(2)–C(3)–C(4)	122.5 (10)	C(8)–C(9)–C(10)	120.6 (18)
C(3)–C(4)–C(5)	117.3 (10)	C(9)–C(10)–C(11)	121.8 (16)
C(4)–C(5)–C(6)	120.2 (11)	C(10)–C(11)–C(12)	120.4 (14)
C(5)–C(6)–C(1)	120.5 (10)	C(11)–C(12)–C(7)	121.0 (12)
C(6)–C(1)–C(2)	119.1 (9)	C(12)–C(7)–C(8)	117.8 (11)
		Mean	120.0 (16)[a]
(E) Angle within diphos Chelate Ring			
P–C(13)–C(13')	115.8 (7)		

[a] See footnote *a* to Table II

Figure 1. The stereochemistry of the $(C_8H_{12})(diphos)Ir(CH_3)$
molecule. The *b* direction is horizontal and the molecule is
viewed from a direction in the *ac* plane that is 30° from −*a*,
toward +*c*.

Table IV. Least-Squares Plane within $(C_8H_{12})(diphos)Ir(CH_3)$[a,b]
Equation of Plane: $0.7323X + 0.0000Y + 0.6809Z - 1.4680 = 0$

Atom	Dev, Å	Atom	Dev, Å
P[b]	0.000	C(13)	−0.791
P'[b]	0.000	C(13')	−0.791
C(14)[b]	0.000	Ir	+0.179
C(14')[b]	0.000		
A	0.000		

[a] The plane is expressed in cartesian coordinates such that [*X, Y,
Z*] = [*xa, yb, zc*]. [b] The plane was calculated using unit weights
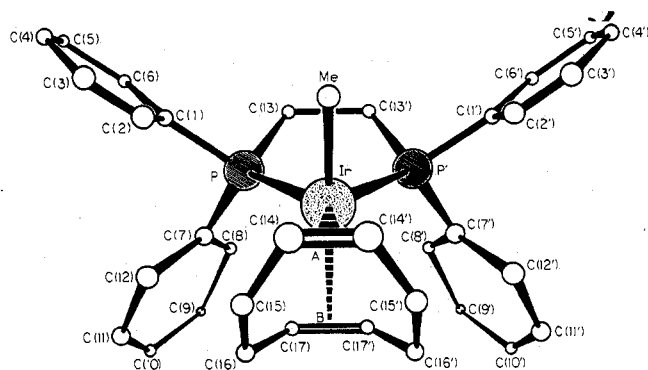for these atoms and zero weights for all other atoms.

$(C_6H_5)_3]_2$,[22] Ir–P(axial) = 2.386 (8) and 2.391 (8) Å in Ir-
$(O_2)I(CO)[P(C_6H_5)_3]_2$,[23] Ir–P(axial) = 2.328 (8) and 2.359
(9) Å in $Ir(SO_2)Cl(CO)[P(C_6H_5)_3]_2$,[24] Ir–P = 2.37 (2) Å
(average of two axial and two equatorial) in [Ir(CO)-
$(diphos)_2^+]Cl^-$,[25] and Ir–P(axial) = 2.336 (7) and 2.349 (7) Å,
while Ir–P(equatorial) = 2.283 (7) and 2.452 (9) Å in $[Ir(O_2)$-
$(diphos)_2^+] [PF_6^-]$.[26]

The slightly longer Ir(I)–P distance in $(C_8H_{12})[(C_6H_5)$-
$(CH_3)_2P]_2Ir(CH_3)$ [*i.e.*, 2.323 ± 0.009 Å (average) as
compared to the present value of 2.308 (3) Å] may be a
result of the $[(C_6H_5)(CH_3)_2P]$ ligands' having poorer π-
acceptor properties than the diphos ligand.

Axial and equatorial Ir–olefinic linkages are 2.106 (9) and
2.011 (9) Å, respectively; the difference of 0.095 Å is
significant at the 7σ level. This trend has previously been
observed in other trigonal-bipyramidal Ir(I) species where
cycloocta-1,5-diene spans an axial and an equatorial site
[*cf.* $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$[1] and $(C_8H_{12})_2Ir$-
$(SnCl_3)$[27]], but never at such high level of significance.

The iridium atom is not coplanar with atoms of the
equatorial coordination plane [*i.e.*, P, P', C(14), and C(14')]
but is displaced toward B by 0.179 Å—see Table IV.

Angles within the coordination sphere are somewhat
distorted from idealized D_{3h} symmetry but are not distorted
systematically toward C_{4v} symmetry as has been observed in
certain other five-coordinate transition metal species.[28]
Angles from the coordinated methyl group are Me–Ir–P =
Me–Ir–P' = 85.2 (3)° and Me–Ir–A = 85.3 (5)°, with the trans
angle, Me–Ir–B, being 169.4 (5)°. From the axial olefinic

ligand, angles are B–Ir–P = B–Ir–P' = 102.6 (3)° and B–Ir–A =
84.0 (3)°. The above-noted distortions of cis angles from 90°
and of the trans angle from 180° are probably due to intra-
molecular repulsions, coupled with the restriction of the
"bite" distance of the cycloocta-1,5-diene ligand.

Angular distortions within the trigonal plane are, however,
significantly greater, with P–Ir–A = P'–Ir–A = 136.4 (3)° and
P–Ir–P' = 84.9 (2)°! The small P–Ir–P' angle is presumably
due to the spanning limitations of the chelating diphos
ligand, since it is very similar to the bite angle of 82–84°
exhibited by diphos in other trigonal-bipyramidal transition
metal complexes[25-26] wherein the diphos ligand is char-
acterized by its spanning one axial and one equatorial
position. The present complex represents the first report
of a pentacoordinate complex in which a diphos ligand
chelates diequatorially.

diphos Ligand

The P–C(sp²) bond lengths are P–C(1) = 1.837 (10) Å and
P–C(17) = 1.808 (10) Å, the mean value of 1.823 ± 0.021 Å
being in good agreement with the corresponding P–C distance
of 1.83 Å in $[Ir(CO)(diphos)_2^+]Cl^-$.[25] The P–C(sp³) distance,
P–C(13) = 1.874 (10) Å, is some 0.05 Å longer—in keeping
with the difference of ~0.03 Å in the covalent radii of sp²-
and sp³-hybridized carbon atoms. The C–P–C angles range
from 100.7 (4) to 102.8 (4)°, the mean value of 101.6° being
significantly lower than the ideal tetrahedral angle of 109.47°.
This pattern of low C–P–C angles is general both for free
phosphines and for phosphine complexes of the transition
metals and has been noted by Churchill and O'Brien.[29] The
Ir–P–C angles are correspondingly larger, with values ranging
from Ir–P–C(13) = 108.8 (3)° to Ir–P–C(1) = 120.4 (3)°.

The CH_2–CH_2 distance within the diphos ligand is C(13)–
C(13') = 1.481 (21) Å. This value is slightly, but not

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(1968); see, especially, Table 7.

Table V. Dihedral Angles within the Cyclooocta-1,5-diene Ligand

Atoms	Angle, deg
C(15')–C(14')–C(14)–C(15)	0.0
C(14')–C(14)–C(15)–C(16)	68.8
C(14)–C(15)–C(16)–C(17)	2.2
C(15)–C(16)–C(17)–C(17')	72.2
C(16)–C(17)–C(17')–C(16')	0.0
C(17)–C(17')–C(16')–C(15')	72.2
C(17')–C(16')–C(15')–C(14')	2.2
C(16')–C(15')–C(14')–C(14)	68.8

Table VI. Intermolecular Contacts, to 3.0 Å

Atom 1	Atom 2	Transformation	Dist, Å
H(15a)	H(4)	$-x, -y, -z$	2.29
H(11)	H(4)	$-x + 1/2, -y, z + 1/2$	2.60
H(3)	H(3)	$-x, -y, -z$	2.62
H(17)	H(15b)	$x + 1/2, y, -z + 1/2$	2.64
H(16b)	H(5)	$-x + 1/2, -y, z + 1/2$	2.67
H(15b)	C(17)	$x - 1/2, y, -z + 1/2$	2.72
H(10)	H(3)	$x + 1, y, z$	2.89
H(14)	H(9)	$x - 1, y, z$	2.93
H(12)	H(5)	$-x + 1/2, -y, z + 1/2$	2.94
H(3)	C(3)	$-x, -y, -z$	2.95
H(9)	H(2)	$x + 1, y, z$	2.96
H(5)	H(3)	$x + 1/2, y, -z - 1/2$	2.98
H(10)	C(4)	$-x + 1, -y, -z$	2.99

significantly, lower than the accepted $C(sp^3)$–$C(sp^3)$ distance of 1.537 Å.

The five-membered chelate ring Ir–P–C(13)–C(13')–P' is not planar but adopts a hinged (or "envelope") conformation with strictly planar P–Ir–P' and P–C(13)–C(13')–P' moieties, the dihedral angle between these planes being 21.9°. The C(13)–C(13') bridging system lies 0.791 Å below the trigonal coordination plane and is displaced in the opposite direction to the iridium atom (see Table IV).

Since the diphos ligand has crystallographically imposed C_s (m) symmetry, the torsional angle about the CH_2–CH_2 bond is precisely zero. This situation appears to be unique, since previous studies of five-membered chelate rings involving a metal atom and a bidentate diphosphine group show fairly large torsional angles, ranging from 36 to 55°.[30] We emphasize that the possibility of disorder within the five-membered chelate ring in the present structure has been considered and rejected. The thermal parameter of C(13) is reasonable ($B = 4.5$ (2) Å^2), both P–C(13) and C(13)–C(13') bond distances are reasonable, and neither observed nor difference Fourier syntheses provide any evidence for such an occurrence.

The 12 independent carbon–carbon bonds within phenyl rings of the diphos ligand vary from 1.289 (32) to 1.487 (27) Å and average 1.377 ± 0.049 Å. This value may be compared to the accepted C–C(aromatic) distance of 1.394 ± 0.005 Å.[31]

Cyclooocta-1,5-diene Ligand

The coordinated cycloocta-1,5-diene ligand possesses precise (*i.e.*, crystallographically imposed) C_s symmetry and approximate C_{2v} symmetry (see Figure 1). Carbon–carbon single-bond distances range from 1.451 (16) to 1.543 (15) Å—results typical for cycloocta-1,5-diene bonded to a heavy metal.[27,32,33] The dihedral angles collected in Table V indicate the "tub" conformation of this ligand.

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Table VII. Comparison of the Iridium(I) Coordination Spheres in $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ and $(C_8H_{12})(diphos)Ir(CH_3)$

Atoms	$[(C_6H_5)(CH_3)_2P]_2$ derivative	diphos derivative	Diff^a
I. Iridium–Ligand Distances (Å)			
Ir–P	2.316 (5)	2.308 (3)	−0.008 (6)
Ir–P'	2.329 (5)	2.308 (3)	−0.021 (6)
Ir–Me	2.202 (22)	2.133 (16)	−0.069 (27)
Ir- - -A(eq)	2.078 (14)	2.011 (9)	−0.067 (17)
Ir- - -B(ax.)	2.117 (14)	2.106 (9)	−0.011 (17)
II. Angles (Deg) between Axial and Equatorial Ligands			
Me–Ir–P	87.0 (6)	85.2 (3)	−1.8 (7)
Me–Ir–P'	84.5 (6)	85.2 (3)	+0.7 (7)
Me–Ir–A	82.8 (8)	85.3 (5)	+2.5 (9)
B–Ir–P	97.9 (6)	102.6 (3)	+4.7 (7)
B–Ir–P'	104.3 (5)	102.6 (3)	−1.7 (6)
B–Ir–A	86.4 (8)	84.0 (3)	−2.4 (9)
III. Angles (Deg) between Equatorial Ligands			
P–Ir–P'	101.5 (2)	84.9 (2)	−16.6 (3)
P–Ir–A	130.4 (6)	136.4 (3)	+6.0 (7)
P'–Ir–A	125.4 (6)	136.4 (3)	+11.0 (7)
IV. Angles (Deg) between Axial Ligands			
Me–Ir–B	168.7 (8)	169.4 (5)	+0.7 (9)

^{a} The difference is defined as (value for diphos derivative) − (value for $[(C_6H_5)(CH_3)_2P]_2$ derivative). The estimated standard deviation on the difference is calculated by the normal statistical expression $\sigma(A-B) = [\sigma^2(A) + \sigma^2(B)]^{1/2}$.

The axially bonded olefinic residue [C(17)–C(17')] has a carbon–carbon distance of 1.374 (21) Å, while the equatorially bonded olefinic linkage C(14)–C(14') is 1.459 (21) Å in length. While the estimated standard deviations on these distances are unfortunately high, it is interesting to note that the longer olefinic linkage is associated with the shorter metal–olefin interaction.

Intermolecular Contacts

Intermolecular contacts to 3.0 Å are collected in Table VI. Molecules are separated by normal van der Waals' distances, with the shortest hydrogen·· ·hydrogen distance being 2.29 Å and the shortest carbon·· ·hydrogen contact being 2.72 Å.

Discussion

The tendency of ligands (in the absence of overriding steric constraints) to occupy preferentially either axial or equatorial positions has previously been noted in stereochemical considerations of trigonal-bipyramidal species.[34,35] These site preferences must surely play an important part in the stereochemistry of the present (solid-state *and ground-state*) structure, since, in their absence, the diphos ligand would be expected to span an axial and an equatorial position in order to avoid gross P–Ir–P' angular distortions and simultaneously to maximize overlap with the d_{z^2} sp^3 hybrid orbitals of the metal atom.

Distances and angles within the iridium(I) coordination sphere of $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)^1$ and (C_8H_{12})-(diphos)Ir(CH$_3$) are compared in Table VII. It can quickly be ascertained that the most significant differences involve the angular distribution of the equatorial ligands—in particular the P–Ir–P' angle in $(C_8H_{12})(diphos)Ir(CH_3)$ is 16.6° (or about 55σ !) smaller than the corresponding angle in $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$.

It now becomes apparent that the large observed differences in the rate of steroisomeric interconversion for (C_8H_{12})-

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Scheme I
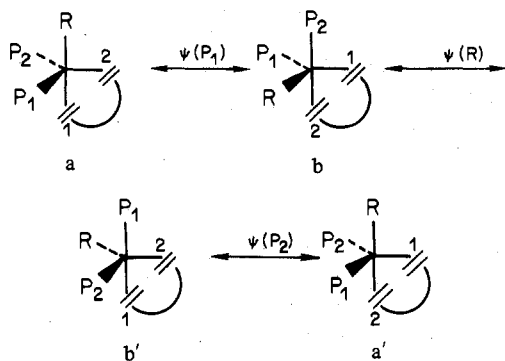
(diphos)Ir(CH$_3$) and for $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ are entirely consonant with the mechanism suggested by Shapley and Osborn (see Scheme I) in which there are successive "pseudorotations" about P_1, R, and P_2. For equilibration of vinyls 1 and 2 to occur, the reaction must proceed from ground state a, through the high-energy intermediates b and b', back to ground state a'. In the high-energy inter-

mediate, a methyl group occupies an equatorial position and the two phosphine groups occupy an equatorial and an axial position. Since ground state a is of higher energy for the diphos compound, due to extra strain associated with a small equatorial P-Ir-P' angle, the diphos compound is expected (*as observed*) to undergo the intramolecular interconversion a → a' at a greater rate than the analogous bis-(monodentate)phosphine complex in which the P-Ir-P' angle is not strained by chelation and is closer to the ideal equatorial value of 120°.

Further information on these systems is expected to be obtained from current X-ray structural analyses on the species $(C_8H_{12})[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]Ir(CH_3)$ in which n has values other than 2. (The case with $n = 2$, of course, is covered by the present article.)

Contribution from the Departments of Chemistry, Montgomery College, Takoma Park, Maryland 20012 and University of Maryland, College Park, Maryland 20742

Crystal and Molecular Structures of Pentacarbonyltriphenylphosphinechromium(0) and Pentacarbonyl(triphenyl phosphite)chromium(0)[1]

HAROLD J. PLASTAS, JAMES M. STEWART, and SAMUEL O. GRIM*

The crystal and molecular structures of pentacarbonyltriphenylphosphinechromium(0), $(C_6H_5)_3PCr(CO)_5$, and pentacarbonyl(triphenyl phosphite)chromium(0), $(C_6H_5O)_3PCr(CO)_5$, have been determined by single-crystal X-ray diffraction techniques. Both crystals belong to the triclinic system, space group $P\bar{1}$, with cell dimensions $a = 9.709$ (3), $b = 11.942$ (2), $c = 9.559$ (2) A; $\alpha = 91.73$ (1), $\beta = 95.58$ (2), $\gamma = 74.17$ (1)° for the phosphine complex and $a = 11.212$ (2), $b = 11.497$ (5), $c = 10.695$ (3) A; $\alpha = 114.33$ (2), $\beta = 105.58$ (2), $\gamma = 66.50$ (3)° for the phosphite complex. The calculated densities, assuming $Z = 2$, are 1.422 and 1.459 g cm^{-3}; the observed densities are 1.416 and 1.446 g cm^{-3} for the phosphine and phosphite complexes, respectively. For the phosphine complex the final value of the conventional R factor is 4.3% for 3450 independent reflections observed to be greater than three standard deviations above the background. For the phosphite complex the final value of the conventional R factor is 4.8% for 3573 independent reflections observed to be greater than three standard deviations above the background. Both structures exhibit slightly distorted octahedral geometry about the chromium with phosphorus and five carbons occupying the coordinate positions. In the phosphine compound, the chromium–phosphorus distance is 2.422 (1) A; the trans chromium–carbon distance is 1.845 (4) A, and the four cis chromium–carbon distances are 1.878 (4), 1.894 (4), 1.882 (5), and 1.867 (4) A, respectively. In the phosphite compound, the corresponding bond lengths are as follows: Cr-P, 2.309 (1) A; trans Cr-C, 1.861 (4) A; cis Cr-C, 1.892 (5), 1.895 (4), 1.904 (6), and 1.892 (4) A, respectively.

Introduction

There have been numerous X-ray structural determinations of coordination compounds in which phosphorus ligands have been present.[2-4] In most cases these were carried out mainly to prove the stereochemistry about the metal atom

or to ascertain the bonding characteristics of other ligands, such as organic moieties or inorganic ligands attached to the metal. In view of the high interest in metal carbonyls and their derivatives and the physical data published on substituted metal carbonyls, such as infrared spectra,[5] equilibrium constants,[6] and nmr data[7] it seemed that X-ray structural data on some fairly simple related compounds would be very

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