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Solid-state structures of $(C_8H_{12})(PhMe_2P)_2Ir(Me)$ and (C_8H_{12})(diphos)Ir(Me). Two stereochemically non-rigid pentacoordinate Ir^I species

MELVYN R. CHURCHILL★ and SUZAN A. BEZMAN

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138 (U.S.A.)

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It has been known, for some time, that certain pentacoordinate phosphorus(V) derivatives undergo rapid intramolecular rearrangements in the liquid phase or in solution[1,2] and a mechanism (termed "pseudorotation") has been proposed[3] and confirmed for these rearrangements[4–6]. While pentacoordination is well established for transition metal complexes, there have been only a few reports of fluxional behaviour in these compounds (see ref. 7 and references therein) and only recently have any mechanistic studies been reported[7–9]. The problem, here, is more complex than for main-group elements since the idealized ground-state geometry may be square-pyramidal (C_{4v}) or trigonal-bipyramidal (D_{3h}) or even some distortion therefrom.

Shapley and Osborn have described the temperature-dependent ^{1}H NMR spectrum of $(C_8H_{12})(Ph_{3-n}Me_nP)_2Ir(R)$ complexes (C_8H_{12} = 1,5-cyclooctadiene; $0 \leqslant n \leqslant 2$, R = H or Me) and have discussed the possible mechanisms of intramolecular rearrangement in some detail[7]. We now report the results of an X-ray diffraction study on $(C_8H_{12})(PhMe_2P)_2Ir(Me)$ which confirm the proposed[7] trigonal-bipyramidal ground state and provide detailed information on the geometry within the iridium(I) coordination sphere.

Crystals were obtained by evaporation, under reduced pressure, of a deoxygenated benzene solution of the compound. Unit cell data are: orthorhombic, space group *Pbca* (D_{2h}^{15}; No. 61), with $a = 8.11$ (1), $b = 17.10$ (2), $c = 34.53$ (5) Å, $V = 4789$ Å^3, $\rho_{obsd} = 1.63 \pm 0.01$, $\rho_{calcd} = 1.641$ g·cm^{-3} for $M = 591.7$ and $Z = 8$.

X-ray diffraction data to $\sin\theta = 0.80$ (Cu-Kα radiation, $\lambda = 1.5418$ Å) were collected with a 0.01°-incrementing Supper-Pace diffractometer using equi-inclination Weissenberg geometry and a 'stationary-background, ω-scan, stationary-background' counting sequence. A total of 3390 reflections were collected from the levels $h(0\text{-}9)\ell$ and $(0\text{-}3)k\ell$ and were corrected for Lorentz, polarization and absorption ($\mu = 119.8$ cm^{-1}) effects. All data were placed on a common scale and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R = 6.8\%$ for the 1724 independent non-zero reflections. (Anisotropic thermal parameters applied only to Ir and P atoms; all non-methyl hydrogens located in calculated positions.)

The structure of the molecule is shown in Fig.1. The iridium(I) atom is in

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★Address correspondence to this author at: Department of Chemistry, University of Illinois at Chicago Circle, Box 4348, Chicago, Illinois 60680 (U.S.A.)

essentially trigonal-bipyramidal coordination, with a methyl [Me(1)] and an olefinic group [C(17)–C18)] in axial positions, the remaining olefinic residue [C(13)–C(14)] and two phenyldimethylphosphine ligands occupying the three equatorial sites. The iridium–methyl linkage is 2.202 (22) Å; rather longer than values found for octahedral Ir^{III}–Me linkages[10] The iridium–phosphorus distances are equivalent: Ir–P(1) = 2.316 (5) and Ir–P(2) = 2.329 (5) Å. The iridium atom is not coplanar with P(1), P(2) and A but is displaced (towards B) by 0.208Å. Angles within the equatorial plane are irregular, the smallest being P(1)–Ir–P(2) = 101.5 (0.2)°, with P(1)–Ir–A = 130.4 (0.6)° and P(2)–Ir–A = 125.4 (0.6)°. Angles from the coordinated methyl group are: Me(1)–Ir–P(1) = 87.0 (0.6)°, Me(1)–Ir–P(2) = 84.5 (0.6)°, Me(1)–Ir–A = 82.8 (0.8)° and Me(1)–Ir–B = 168.7 (0.8)°; those from the axial olefinic group are: B–Ir–P(1) = 97.9 (0.6)°, B–Ir–P(2) = 104.3 (0.6)° and B–Ir–A = 86.4 (0.8)°.

We have recently extended our studies to (C_8H_{12})(diphos)Ir(Me) (diphos = 1,2-bis-(diphenylphosphino)ethane). This complex undergoes intramolecular rearrangement at even lower temperatures than does $(C_8H_{12})(PhMe_2P)_2Ir(Me)$; no limiting spectrum has been observed, but the complex has a proton magnetic resonance spectrum consistent with molecular C_s symmetry[11]. Thus, magnetic resonance studies do not allow a distinction between a square-pyramidal or trigonal-bipyramidal ground state.

Crystal data for (C_8H_{12})(diphos)Ir(Me) are: orthorhombic, space group *Pnma* (D_{2h}^{16}; No. 62), with $a = 10.13$ (1), $b = 21.33$ (3), $c = 13.70$ (2) Å, $V = 2960$ Å^3, $\rho_{obsd} = 1.58 \pm 0.02$, $\rho_{calcd} = 1.602$ g · cm^{-3} for $M = 713.8$ and $Z = 4$. Data to $\sin\theta = 0.86$ Cu-Kα) were collected (as described above) for levels *hk*(0-8) and (0-7)*kℓ*. The corrected, correlated data ($\mu = 97.95$ cm^{-1}) have allowed refinement to $R = 6.1\%$ for the 1698 independent non-zero reflections. (Anisotropic thermal parameters for Ir and P only.) The Ir^I center has a trigonal

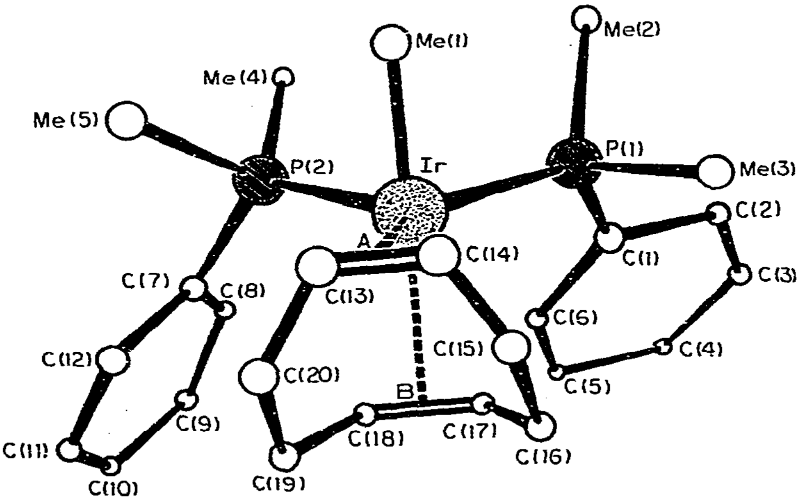

Fig.1. The $(C_8H_{12})(PhMe_2P)_2Ir(Me)$ molecule, viewed down '*b*'. (Note that A and B refer to the mid-points of the olefin residues defined by C(13)–C(14) and C(17)–C(18), respectively.) Iridium to olefin distances are: Ir–A = 2.078 (11), Ir–B = 2.117 (10) Å. Corresponding distances in (C_8H_{12})(diphos)Ir(Me) are: Ir–A = 2.008 (11), Ir–B = 2.090 (10) Å.

bipyramidal stereochemistry and the molecule has precise C_s symmetry (with the mirror plane containing the iridium atom and methyl group, and bisecting the diphos and the 1,5-cyclooctadiene ligands. The relative orientation of ligands is the same as in $(C_8H_{12})(PPhMe_2)_2Ir(Me)$, with Ir–Me = 2.126 (17) and Ir–P = 2.308 (3) Å. Angles around the metal atom (in deg.) are P–Ir–P′ = 84.9 (2), P–Ir–A = P′–Ir–A = 136.3 (4); Me–Ir–P = Me–Ir–P′ = 84.7 (3), Me–Ir–A = 85.7 (5), Me–Ir–B = 170.4 (5); B–Ir–P = B–Ir–P′ = 102.2 (3) and B–Ir–A = 84.7 (4).

It is tempting to speculate that (as is the case with phosphorus compounds[2]) the extra strain associated with the small equatorial P–Ir–P angle of 84.9 (2)° in (C_8H_{12})-(diphos)Ir(Me), as opposed to that of 101.5 (2)° in $(C_8H_{12})(PPhMe_2)_2Ir(Me)$, is responsible for the greater ease of intramolecular rearrangement (probably 'pseudorotation') in the former complex.

Finally, it should be noted that NMR studies and crystallographic results suggest that in HML_4 complexes a different mode of intramolecular rearrangement is operative; Muetterties and coworkers[12] have concluded that non-rigidity in these species arises from 'hydrogen atom traverse of MP_4 "tetrahedral" faces'.

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