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Crystal and Molecular Structure of (Methyl isocyanide)bis[1,2-bis(diphenylphosphino)ethane]iridium(I) Perchlorate, [Ir(CNMe)(diphos)$_2$](ClO$_4$)

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The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. Cell dimensions are $a = 13.004$ (7) Å, $b = 17.224$ (11) Å, $c = 12.127$ (7) Å, $\alpha = 106.57$ (5)°, $\beta = 109.71$ (5)°, $\gamma = 79.71$ (4)°, $V = 2440.6$ (27) Å^3. The observed and calculated densities are 1.542 (7) and 1.537 g/cm^3, respectively. Refinement on F for 6313 reflections with $F_o^2 > 3\sigma(F_o^2)$ converged to conventional and weighted R factors of 0.0460 and 0.0531. The cation has a trigonal bipyramidal geometry with the isocyanide ligand in an equatorial site and each chelate bridging one axial and one equatorial position. The mean Ir–P distance is 2.328 (9) Å. The isocyanide is coordinated in a linear fashion and the Ir–C bond length is 1.945 (8) Å. Both five-membered chelate rings exhibit similar conformations which are of an unsymmetrical type. The details of the coordination geometry are compared with those of a number of other [ML(diphos)$_2$]$^+$ systems and discussed with regard to nonbonded interactions and electronic effects. The stereochemical nonrigidity of the molecule is also considered.

Introduction

Isocyanide complexes of the platinum group elements have been the focus of recent research activities because of the interesting chemistry which these systems exhibit, both at the metal center and the carbon donor atom of the isocyanide ligand. In 1972, Bedford and Rouschias[1] reported that methyl isocyanide reacts with IrCl(CO)(PPh$_3$)$_2$ to yield the blue-black complex [Ir(CNMe)$_4$]X (X = Cl) which in turn undergoes photosubstitution with 1,2-bis(diphenylphosphino)ethane, diphos, to produce a stable, yellow five-coordinate cationic species of formula [Ir(CNMe)(diphos)$_2$]$^+$. The ^{1}H NMR spectrum of this latter species, which was isolated as its ClO$_4^-$ salt, shows a quintet for the methyl resonance because of coupling with four equivalent phosphorus donor atoms ($^5J_{\text{P-H}} = 1.6$ Hz). This observation aroused our interest since it meant that the complex either adopted a square pyramidal structure with an apical methyl isocyanide ligand or was stereochemically nonrigid.

The latter explanation seemed more plausible in view of the reported structure of [Ir(CO)(diphos)$_2$]$^+$,[2] and the structure of [Ru(NO)(diphos)$_2$]$^+$ which was then being completed in our laboratory.[3] Both of these systems showed a trigonal bipyramidal coordination geometry with diphos ligands spanning axial and equatorial positions and the monodentate ligand occupying the remaining equatorial site. Based on bonding considerations in nitrosyl chemistry,[3-6] it was thought that [Ru(NO)(diphos)$_2$]$^+$ should be stereochemically nonrigid, a proposal confirmed by Caulton,[7] and that nitrosyl bending should help lower the energy of the square pyramidal transition state proposed for the rearrangement process in this system. However, since methyl isocyanide exhibits no tendency toward bent coordination, stabilization of an analogous square pyramidal transition state through apical ligand bending should not occur in the isoelectronic system [Ir(CNMe)(diphos)$_2$]$^+$.

In order to unequivocally establish the molecular structure of [Ir(CNMe)(diphos)$_2$]$^+$ and to possibly shed light on the dynamics of bis chelated five-coordinate complexes, a single crystal structure determination of this complex as its perchlorate salt has been performed.

Collection and Reduction of the X-Ray Data

Single crystals of [Ir(CNMe)(diphos)$_2$]ClO$_4$ were provided by Dr. George Rouschias. Zero and upper level precession photographs revealed that the Laue symmetry was $\bar{1}$. Reflections with $h + k$, $k + l$, and $h + l = 2n + 1$ were systematically absent, thus indicating that a face-centered cell had been chosen. A cell reduction was carried out[8] to obtain the primitive reduced cell. The cell reduction confirmed the triclinic symmetry of the lattice. All further work was performed in the primitive reduced cell.

The crystal was transferred to the diffractometer for the precise determination of lattice constants and data collection. The original mounting was such that b^* was nearly parallel to the diffractometer ϕ axis but prior to further examination the goniometer head arcs were adjusted to reduce the danger of collisions. In the final orientation the b^* axis was *offset* from ϕ by about 7.5°. Precise cell constants at 22°C were determined from a least-squares refinement[9] of the setting angles of 12 well-resolved reflections ($\sin\theta/\lambda > 0.34$) which were carefully centered (using Mo$K\alpha_1$ radiation, $\lambda = 0.709261$ Å) on a Picker FACS-I diffractometer equipped with a graphite monochomator. The lattice constants are $a = 13.004$ (7) Å, $b = 17.224$ (11) Å, $c = 12.127$ (7) Å, $\alpha = 106.57$ (5)°, $\beta = 109.71$ (5)°, $\gamma = 79.71$ (4)°, $V = 2440.6$ (27) Å^3. The experimental density of 1.542 (7) g/cm^3 as determined by flotation in CCl$_4$–petroleum ether is in excellent agreement with a value of 1.537 g/cm^3 calculated for two molecules of [Ir(CNMe)(diphos)$_2$]ClO$_4$ per unit cell.

The quality of the crystal was checked by means of narrow source, open counter ω scans.[10] The full widths at half-maximum for typical strong reflections were in the range 0.05–0.08°. Intensities were measured by the θ–2θ scan technique. The takeoff angle for the X-ray tube was set at 1.5° so that the intensities of typical strong reflections were roughly 80% of their maximum value as a function of takeoff angle. Data were collected at a scan rate of 2°/min with scans being made from 0.75° below the $K\alpha_1$ peak to 0.75° above the $K\alpha_2$ peak. Background counts of 4 sec were made at each end of the scan. Attenuator foils were automatically inserted when the intensity of the diffracted beam reached 10,000 counts/sec. The pulse height analyzer was set for a 90% window centered on Mo $K\bar{\alpha}$ radiation.

Data were collected for the hemisphere with $l \geq 0$ for $3 \leq 2\theta \leq 50°$. Three standards were monitored after every 60 observations. The standards showed no change in intensities during data collection. A total of 9190 reflections were measured. The values of I and $\sigma^2(I)$ were obtained using the expressions previously described.[11] The value of p used in the expression for the variance was chosen as 0.05. Values of I and $\sigma^2(I)$ were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections.[8]

Since the absorption coefficient for Mo $K\bar{\alpha}$ radiation is 31.35 cm^{-1}, an absorption correction was made. The crystal faces were indexed by a comparison of diffractometer setting angles with optical goniometric measurements. Crystal dimensions were carefully measured with a Zeiss travelling hairline eyepiece.[12] The absorption correction was made analytically using the method of De Meulenaer and Tompa.[8,13] Transmission coefficients ranged from 0.265 to 0.766 with the mean being 0.644. On the assumption that the correct space group was $P\bar{1}$ equivalent reflections (those with $l = 0$) were averaged. The R factor for averaging was 2.4%. The final data set consisted of 8667 independent reflections of which only the 6313 with $F_o^2 > 3\sigma(F_o^2)$

Table I. Positional and Thermal Parameters for $[Ir(CNMe)(diphos)_2](ClO_4)$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.229319 (25)[b]	0.254595 (19)	0.067264 (30)	34.34 (21)	18.52 (12)	41.44 (27)	−1.48 (10)	11.64 (17)	5.14 (12)
Cl(1)	0.7168 (7)	0.3182 (6)	0.4721 (8)	8.33 (20)[c]					
Cl(2)	0.7731 (7)	0.3457 (5)	0.5320 (8)	8.99 (23)					
P(1)	0.21122 (16)	0.16127 (12)	0.16166 (18)	37.3 (14)	23.4 (8)	46.0 (18)	−2.8 (8)	10.5 (13)	6.6 (10)
P(2)	0.30706 (16)	0.14143 (12)	−0.04553 (19)	43.2 (15)	22.2 (8)	52.7 (19)	−0.7 (8)	18.3 (14)	6.6 (10)
P(3)	0.25568 (18)	0.35332 (13)	−0.01643 (20)	54.8 (17)	22.2 (8)	57.5 (20)	−4.3 (9)	18.3 (15)	8.4 (11)
P(4)	0.04261 (17)	0.29764 (13)	−0.00405 (20)	41.2 (15)	28.5 (9)	66.9 (21)	2.3 (9)	14.7 (14)	17.2 (11)
C(1)	0.2879 (7)	0.3270 (5)	0.2248 (8)	65 (7)	24 (3)	59 (8)	−5 (4)	20 (6)	8 (4)
C(2)	0.3816 (12)	0.4228 (8)	0.4318 (10)	190 (16)	65 (7)	63 (10)	−60 (8)	6 (10)	−22 (7)
C(3)	0.2253 (6)	0.0584 (5)	0.0655 (7)	49 (6)	24 (3)	51 (7)	−4 (3)	18 (5)	7 (4)
C(4)	0.3247 (6)	0.0554 (5)	0.0245 (7)	55 (6)	23 (3)	69 (8)	4 (3)	28 (6)	10 (4)
C(5)	0.1301 (7)	0.4235 (5)	−0.0337 (8)	70 (7)	25 (3)	86 (9)	6 (4)	27 (7)	17 (5)
C(6)	0.0300 (7)	0.3767 (5)	−0.0843 (8)	50 (6)	36 (4)	100 (10)	10 (4)	28 (7)	32 (5)
N	0.3211 (7)	0.3698 (5)	0.3201 (7)	104 (8)	34 (3)	67 (8)	−18 (4)	22 (6)	0 (4)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Anisotropic thermal parameters have been multiplied by 10^4. [b] In this and subsequent tables the estimated standard deviations of the least significant figures are given in parentheses. [c] The disordered Cl atom was refined isotropically with 50% occupancy at each of two sites. The parameter given is B in the expression $\exp[-B(\sin\theta/\lambda)^2]$.

Table II. Group Parameters[a] for $[Ir(CNMe)(diphos)_2](ClO_4)$

Group	X_c	Y_c	Z_c	ϕ	θ	ρ
PH(11)[b]	0.4022 (3)	0.1303 (2)	0.4012 (3)	−0.736 (4)	2.742 (3)	0.699 (4)
PH(12)	0.0013 (3)	0.1717 (2)	0.2501 (3)	2.754 (4)	2.488 (3)	0.893 (4)
PH(21)	0.5564 (3)	0.1467 (2)	−0.0423 (3)	2.302 (12)	1.861 (3)	1.107 (12)
PH(22)	0.1802 (3)	0.0677 (3)	−0.3278 (4)	0.554 (4)	−3.003 (4)	−2.085 (4)
PH(31)	0.2985 (3)	0.3098 (2)	−0.2753 (4)	1.256 (4)	2.990 (3)	−1.450 (4)
PH(32)	0.4471 (4)	0.4722 (3)	0.1372 (4)	0.592 (4)	2.808 (4)	0.334 (5)
PH(41)	−0.0715 (4)	0.3963 (3)	0.2013 (4)	2.212 (4)	2.932 (4)	1.121 (4)
PH(42)	−0.1363 (3)	0.1796 (3)	−0.2042 (4)	−2.460 (4)	3.159 (4)	−0.568 (4)
GP(1)[c]	0.7168[d]	0.3182	0.4721	2.586 (14)	3.390 (16)	−1.049 (13)
GP(2)	0.7731	0.3457	0.5320	1.322 (14)	2.676 (12)	1.513 (14)

[a] X_c, Y_c, and Z_c are the coordinates of the group centers. The angles ϕ, θ, and ρ are in radians and have been previously defined (see R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965)). [b] The first digit indicates the P atom to which the phenyl group is bound. [c] GP(1) and GP(2) are the tetrahedra of oxygen atoms associated with Cl(1) and Cl(2). [d] Positional parameters for the oxygen tetrahedra were constrained to be those of the Cl with which they are associated.

were used in the refinement of the structure.

Solution and Refinement of the Structure

The structure was solved and refined using standard Patterson, Fourier, and least-squares methods.[8] In all least-squares refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights, w, were taken as $(1/\sigma(F_o))^2 = 4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Ir, Cl, P, O, N, and C were taken from the tabulation of Cromer and Mann.[14] Corrections for anomolous dispersion of Ir, Cl, and P were made using the $\Delta f'$ and $\Delta f''$ values of Cromer and Lieberman.[15] The hydrogen scattering factor was that of Stewart et al.[16]

The three-dimensional Patterson map could be interpreted in space group $P\bar{1}$ and the successful refinement confirms this choice. The positions of the Ir atom and the four phosphorus atoms were deduced from the Patterson map, and a difference Fourier map phased by the five-atom model revealed the remaining nonhydrogen atoms of the cation. A model was adopted in which the phenyl rings were treated as rigid groups (D_{6h} symmetry, C–C = 1.392 Å). Each group atom was refined isotropically and the nongroup atoms were refined with anisotropic thermal parameters. This model of the cation refined to convergence with $R_1 = 0.098$ and $R_2 = 0.147$.[17]

The major feature of a difference Fourier computed at this point was the presence of two strong (equally intense) peaks surrounded by a number of weaker peaks. The two intense peaks were interpreted as resulting from partial Cl atoms of a disordered perchlorate. The model developed for the disordered perchlorate involved refinement of two Cl sites, each with 50% occupancy. Associated with each Cl site was a tetrahedron of oxygen atoms (each oxygen with 50% occupancy). The center of the tetrahedra were constrained to be at the Cl sites, and the Cl–O distance was set at 1.45 Å. Inclusion of the ClO_4^-, as just described, in the model yielded $R_1 = 0.077$ and $R_2 = 0.096$.

Prior to this point refinement had been carried out with data that had not been corrected for absorption. The use of the corrected data lowered R_1 and R_2 to 0.051 and 0.062, respectively. Idealized positions were now calculated for the phenyl and methylene protons (C–H = 1.00 Å, trigonal or tetrahedral geometry as appropriate at C), but the methyl groups of the isocyanide ligand were omitted from consideration. The thermal parameters for hydrogen atoms were chosen to be 1 Å^2 larger than those of the carbon atom to which the hydrogen is bound. Two additional cycles of refinement yielded $R_1 = 0.0460$ and $R_2 = 0.0531$. On the final cycle of refinement no parameter associated with the cation shifted by more than half of its estimated standard deviation. Despite the low final R factors the model for the disordered ClO_4^- group is inadequate as judged by the large thermal parameters of some of the oxygen atoms, as well as a tendency for the orientational parameters to oscillate during the final cycles of refinement. A more extended treatment of the anion disorder was not attempted since the structural parameters of the cation were insensitive to inclusion of the anion in the model.

A final difference Fourier map showed no peaks larger than 1.4 $e^-/Å^3$ or 20% of the height of a typical carbon atom in this structure. The major peaks in the final difference map were all in the vicinity of the perchlorate. The estimated standard deviation of an observation of unit weight[17] was 1.32 e^- for 6313 reflections and 227 variables. The quantity $\sum w(|F_o| - |F_c|)^2$ showed no trends as a function of either $|F_o|$ or $\sin\theta/\lambda$. A listing of the observed and calculated structure factors for those reflections used in the refinement is available.[18]

The positional and thermal parameters obtained from the final cycle of least-squares refinement are given in Tables I and II. The derived positional parameters for the atoms of the rigid groups are given in Table III, along with the isotropic thermal parameters of these atoms. A table of the parameters used in calculating the hydrogen contributions to the calculated structure factors, F_c, is available.[18]

Description of the Structure

The crystal structure consists of discrete $[Ir(CNMe)(diphos)_2]^+$ cations and disordered perchlorate anions. The cation is illustrated in Figures 1 and 2, and the unit cell is shown in Figure 3.

The geometry of the cation is that of a somewhat distorted trigonal bipyramid. Each diphos ligand bridges an axial and equatorial coordination site with the isocyanide ligand occupying the remaining equatorial position. Tables III and IV

Table III. Derived Positional Parameters for Group Atoms

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
PH(11)					PH(31)				
C(111)	0.3182 (4)	0.1484 (3)	0.3022 (4)	2.68 (14)	C(311)	0.2779 (4)	0.3293 (4)	−0.1647 (4)	3.17 (16)
C(112)	0.2990 (3)	0.1038 (3)	0.3715 (5)	3.52 (17)	C(312)	0.3811 (4)	0.2949 (4)	−0.1733 (4)	3.68 (17)
C(113)	0.3830 (5)	0.0858 (3)	0.4705 (5)	3.97 (18)	C(313)	0.4017 (4)	0.2755 (4)	−0.2839 (5)	4.62 (21)
C(114)	0.4861 (4)	0.1123 (4)	0.5002 (4)	4.48 (20)	C(314)	0.3190 (5)	0.2903 (4)	−0.3860 (4)	4.95 (22)
C(115)	0.5053 (3)	0.1569 (4)	0.4308 (5)	4.49 (20)	C(315)	0.2158 (4)	0.3247 (4)	−0.3774 (4)	5.21 (22)
C(116)	0.4214 (4)	0.1749 (3)	0.3318 (5)	3.19 (16)	C(316)	0.1953 (3)	0.3441 (4)	−0.2667 (5)	4.42 (20)
PH(12)					PH(32)				
C(121)	0.0881 (4)	0.1672 (3)	0.2050 (5)	2.39 (14)	C(321)	0.3644 (4)	0.4206 (3)	0.0725 (5)	3.28 (16)
C(122)	0.0744 (4)	0.2315 (3)	0.3005 (5)	3.63 (17)	C(322)	0.4579 (5)	0.3948 (3)	0.1562 (6)	4.00 (19)
C(123)	−0.0124 (5)	0.2360 (3)	0.3456 (4)	4.00 (18)	C(323)	0.5406 (4)	0.4464 (4)	0.2209 (5)	4.89 (21)
C(124)	−0.0854 (4)	0.1761 (4)	0.2952 (5)	4.66 (21)	C(324)	0.5298 (5)	0.5238 (4)	0.2020 (6)	6.05 (26)
C(125)	−0.0717 (4)	0.1118 (3)	0.1997 (5)	4.75 (21)	C(325)	0.4364 (6)	0.5496 (3)	0.1183 (7)	7.33 (31)
C(126)	0.0150 (4)	0.1073 (3)	0.1546 (4)	3.78 (18)	C(326)	0.3536 (5)	0.4980 (4)	0.0535 (6)	5.45 (23)
PH(21)					PH(41)				
C(211)	0.4495 (3)	0.1408 (3)	−0.0475 (5)	2.72 (15)	C(411)	−0.0247 (5)	0.3529 (4)	0.1115 (5)	3.64 (17)
C(212)	0.4819 (4)	0.1118 (3)	−0.1513 (4)	3.77 (18)	C(412)	0.0294 (4)	0.4146 (4)	0.2038 (6)	4.71 (21)
C(213)	0.5889 (5)	0.1177 (4)	−0.1462 (4)	4.25 (19)	C(413)	−0.0174 (6)	0.4581 (4)	0.2937 (5)	6.29 (27)
C(214)	0.6634 (3)	0.1526 (4)	−0.0372 (5)	4.36 (20)	C(414)	−0.1184 (6)	0.4398 (4)	0.2912 (6)	6.97 (30)
C(215)	0.6310 (4)	0.1815 (4)	0.0666 (4)	4.42 (20)	C(415)	−0.1725 (5)	0.3781 (5)	0.1988 (7)	6.89 (29)
C(216)	0.5240 (4)	0.1756 (3)	0.0615 (4)	3.56 (17)	C(416)	−0.1256 (5)	0.3346 (4)	0.1090 (6)	5.37 (23)
PH(22)					PH(42)				
C(221)	0.2351 (4)	0.0974 (3)	−0.2062 (4)	3.10 (16)	C(421)	−0.0622 (4)	0.2310 (3)	−0.1150 (5)	3.30 (16)
C(222)	0.2592 (5)	0.0173 (3)	−0.2641 (5)	4.28 (20)	C(422)	−0.1615 (5)	0.2635 (3)	−0.1822 (6)	5.04 (22)
C(223)	0.2042 (6)	−0.0124 (3)	−0.3858 (5)	5.73 (25)	C(423)	−0.2356 (4)	0.2121 (4)	−0.2714 (6)	5.22 (23)
C(224)	0.1252 (5)	0.0381 (4)	−0.4495 (4)	5.72 (24)	C(424)	−0.2103 (5)	0.1282 (4)	−0.2934 (5)	5.14 (22)
C(225)	0.1011 (5)	0.1182 (4)	−0.3916 (5)	5.55 (24)	C(425)	−0.1110 (5)	0.0957 (2)	−0.2262 (6)	4.95 (22)
C(226)	0.1561 (5)	0.1479 (3)	−0.2699 (5)	4.09 (19)	C(426)	−0.0369 (4)	0.1471 (3)	−0.1370 (5)	3.75 (17)
GP(1)					GP(2)				
O(11)	0.6531 (14)	0.3084 (14)	0.3459 (5)	24.8 (19)	O(21)	0.7231 (14)	0.3855 (9)	0.6266 (11)	13.8 (7)
O(12)	0.7954 (12)	0.3771 (9)	0.5044 (21)	25.3 (13)	O(22)	0.8868 (4)	0.3190 (11)	0.5858 (14)	12.4 (7)
O(13)	0.7746 (14)	0.2407 (7)	0.4916 (19)	13.0 (8)	O(23)	0.7675 (13)	0.4024 (8)	0.4614 (14)	10.6 (5)
O(14)	0.6447 (13)	0.3465 (10)	0.5464 (15)	10.1 (6)	O(24)	0.7149 (14)	0.2760 (7)	0.4543 (14)	26.0 (22)

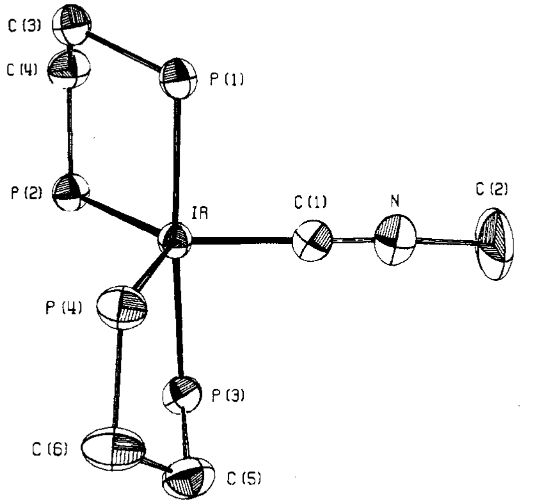


Figure 1. A perspective drawing of the inner coordination sphere of $[Ir(CNMe)(diphos)_2]^+$. The thermal ellipsoids enclose 50% of the electron distribution.

Table IV. Bond Distances for $[Ir(CNMe)(diphos)_2](ClO_4)$

Atoms	Distance, Å	Atoms	Distance, Å
Ir–C(1)	1.945 (8)	P(1)–C(3)	1.838 (8)
		P(2)–C(4)	1.853 (8)
Ir–P(1)	2.306 (3)	P(3)–C(5)	1.838 (8)
Ir–P(2)	2.324 (3)	P(4)–C(6)	1.843 (9)
Ir–P(3)	2.338 (3)		Av 1.843 (4)
Ir–P(4)	2.345 (3)		
	Av[a] 2.328 (9)	P(1)–C(111)	1.843 (5)[b]
		P(1)–C(121)	1.825 (6)
C(1)–N	1.166 (10)	P(2)–C(211)	1.858 (5)
N–C(2)	1.456 (11)	P(2)–C(221)	1.851 (5)
		P(3)–C(311)	1.836 (6)
C(3)–C(4)	1.522 (11)	P(3)–C(321)	1.830 (6)
C(5)–C(6)	1.508 (12)	P(4)–C(411)	1.845 (7)
	Av 1.515 (7)	P(4)–C(421)	1.851 (5)
			Av 1.842 (4)

[a] Average values are computed from the expressions $\bar{x} = \Sigma x_i/n$; $\sigma(\bar{x}) = [\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$, where n is the number of chemically equivalent values. [b] Estimates of the errors in distances involving group atoms were obtained using the variances only; estimates for other bond distances were obtained from the full variance-covariance matrix.

present important intramolecular distances and angles for the structure. The geometry found for the cation is similar to that observed for a number of bis(diphos) complexes of the group 8 elements including $[M(O_2)(diphos)_2]^+$ (M = Rh, Ir),[19] $[Ir(CO)(diphos)_2]^+$,[2] $[Ir(S_2)(diphos)_2]^+$,[20] and $[Ru(NO)(diphos)_2]^+$.[3]

The Ir–P bond lengths range from 2.306 (3) to 2.345 (3) Å without apparent correlation between the nature of the coordination site and the length of the metal–phosphorus bond. A similar variation of M–P bond lengths has also been found in other bis(diphos) chelates.[3,19] The mean Ir–P bond length in the present structure is 2.328 (9) Å which compares favorably with corresponding values in the other $[IrL(diphos)_2]^+$ complexes (L = CO, Ir–P = 2.37 (2);[2] L = O_2, Ir–P = 2.36 (4);[19] L = S_2, Ir–P = 2.351 (10)[20]).

The Ir–C bond length of 1.945 (8) Å is significantly longer than the value of 1.82 (2) Å observed in the closely related carbonyl system $[Ir(CO)(diphos)_2]^+$. As expected, the isocyanide ligand coordinates in a linear fashion with an Ir–C–N bond angle of 178.3 (8)°. The angle at the N atom of the isocyanide ligand is 168.7 (11)° but it should be noted that the methyl carbon shows considerable thermal motion normal to the N–Me bond. Distances within the ligand are normal, 1.166 (10) and 1.456 (11) Å for the C≡N and N—Me bonds, respectively.

Distortions within the coordination sphere arise from constraints of the metal–ligand chelate rings, and from minimization of nonbonded interactions between the isocyanide ligand and the phenyl rings bonded to the phosphine donors. The angles formed by the chelating diphos ligands are 84.59 (9) and 83.23 (9)° (Table V). There is a nearly linear axial

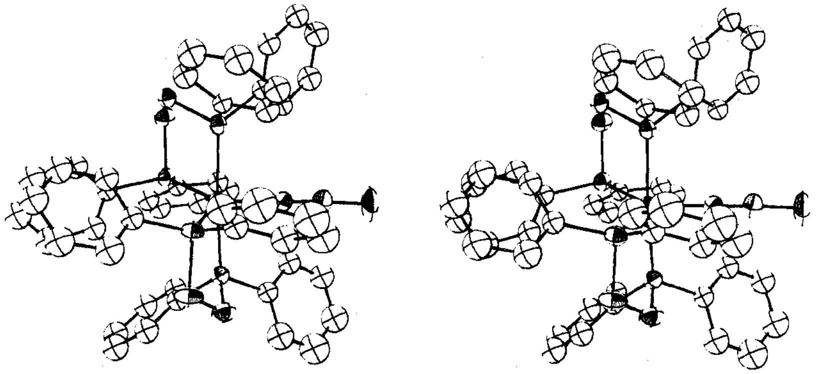


Figure 2. A stereoscopic view of the entire $[Ir(CNMe)(diphos)_2]^+$ complex. The orientation is the same as in Figure 1. The thermal ellipsoids enclose 50% of the electron distribution.

Table V. Selected Bond Angles for $[Ir(CNMe)(diphos)_2](ClO_4)$

Atoms	Angle, deg	Atoms	Angle, deg
C(1)-Ir-P(1)	89.3 (3)	Ir-C(1)-N	178.3 (8)
C(1)-Ir-P(2)	132.7 (2)	C(1)-N-C(2)	168.7 (11)
C(1)-Ir-P(3)	87.2 (3)		
C(1)-Ir-P(4)	106.9 (3)		
P(1)-Ir-P(2)	83.23 (9)	Ir-P(1)-C(3)	108.9 (3)
P(1)-Ir-P(3)	176.24 (8)	Ir-P(2)-C(4)	107.9 (3)
P(1)-Ir-P(4)	97.59 (9)	Ir-P(3)-C(5)	106.2 (3)
P(2)-Ir-P(3)	98.34 (9)	Ir-P(4)-C(6)	108.0 (3)
P(2)-Ir-P(4)	120.36 (9)	Av	107.7 (5)
P(3)-Ir-P(4)	84.59 (9)		
		P(1)-C(3)-C(4)	106.0 (5)
Ir-P-C(phenyl), av[a]	120.3 (9)	P(2)-C(4)-C(3)	109.0 (5)
		P(3)-C(5)-C(6)	110.5 (6)
C(methylene)-P-C(phenyl), av	102.2 (8)	P(4)-C(6)-C(5)	111.7 (6)
		Av	109.3 (12)
C(phenyl)-P-C(phenyl), av	101.4 (7)		

[a] See footnote *a* in Table IV.

Table VI. Root Mean Square Amplitudes of Vibration (Å × 10^3)[a]

Atom	Min	Inter	Max
Ir	154.8 (5)	161.0 (5)	168.1 (5)
P(1)	165 (3)	173 (4)	183 (3)
P(2)	166 (3)	183 (3)	186 (3)
P(3)	173 (3)	188 (4)	203 (3)
P(4)	167 (3)	193 (3)	213 (4)
C(1)	181 (13)	192 (13)	222 (12)
C(2)	146 (18)	318 (17)	413 (16)
C(3)	173 (13)	183 (13)	193 (11)
C(4)	167 (13)	197 (13)	219 (11)
C(5)	171 (13)	226 (14)	242 (12)
C(6)	167 (13)	203 (14)	267 (12)
N	185 (12)	233 (11)	286 (10)

[a] Calculated along the principal axes of thermal motion.

Table VII. Equations of Planes and Deviations of Atoms from Their Respective Planes (Referred to Triclinic Coordinates)

Atom	Distance, Å	Atom	Distance, Å
Plane through Ir, P(1), P(2)			
$9.73x + 2.43y + 4.27z = 3.14$			
C(3)	−0.52	P(3)	0.14
C(4)	0.26	P(4)	−2.02
Plane through Ir, P(3), P(4)			
$-1.54x + 7.836y + 8.75z = 2.23$			
C(5)	0.59	P(1)	0.12
C(6)	−0.06	P(2)	−1.99
Plane through P(2), P(4), C(1)			
$6.80x + 13.93y - 9.08z = 4.47$			
Ir	0.02	C(3)	−2.72
P(1)	−2.26	C(4)	−1.71
P(3)	2.34	C(5)	2.62
N	−0.04	C(6)	1.74
C(2)	0.09		

Table VIII. Torsional Angles within the Chelate Rings

Atoms	Angle, deg
P(2)-Ir-P(1)-C(3)[a]	−17.5 (3)
Ir-P(1)-C(3)-C(4)	46.0 (5)
P(1)-C(3)-C(4)-P(2)	−53.6 (6)
C(3)-C(4)-P(2)-Ir	39.5 (6)
C(4)-P(2)-Ir-P(1)	−8.5 (3)
P(4)-Ir-P(3)-C(5)	19.6 (3)
Ir-P(3)-C(5)-C(6)	−43.7 (7)
P(3)-C(5)-C(6)-P(4)	47.6 (8)
C(5)-C(6)-P(4)-Ir	−29.4 (7)
C(6)-P(4)-Ir-P(3)	2.1 (3)

[a] If atoms are considered as being numbered 1, 2, 3, 4 going from left to right, a positive angle means that when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

P–Ir–P arrangement, and consequently, the nonchelating P_{eq}–Ir–P_{ax} angles are found to be 97.59 (9) and 98.34 (9)°. The major distortion in the coordination geometry occurs in the trigonal plane with P_{eq}–Ir–C bond angles of 132.7 (2) and 106.9 (3)°. The cause of this distortion relates to the orientation of the phenyl rings attached to the phosphine donors and their nonbonded interactions with the isocyanide ligand. In particular, the phenyl ring designated as PH(32) is oriented such that C(322) and H(322) are situated 3.107 and 2.682 Å away from the isocyanide donor atom. Any movement of the MeNC ligand to equalize the P–Ir–C bond angles in the trigonal plane will increase the repulsions from these nonbonding contacts. Other close C(1)···H contacts are 2.633 and 2.697 Å associated with hydrogens H(116) and H(412), respectively. The remaining angle in the trigonal plane of the coordination polyhedron is the angle trans to the isocyanide ligand, P(2)–Ir–P(4), which has a value of 120.36 (9)°. This angle compares with corresponding values of 108 (1)° and 99.3 (2)° in $[Ir(CO)(diphos)_2]^+$,[2] and $[Ru(NO)(diphos)_2]^+$,[3] respectively, and reasons for the observed trend are discussed below.

The iridium–diphos chelate rings are distinctly nonplanar, and both possess similar conformations which are of an unsymmetrical type. Gollogly and Hawkins[21] have analyzed the conformations of five-membered chelate rings in metal–diamine systems and their conclusions can be extrapolated to analogous metal–diphos ring systems. Several essentially equienergetic conformations are possible including one having C_2 symmetry and two unsymmetrical types. In one of these, both carbon atoms lie on the same side of a plane defined by the metal and donor atoms of the chelate, while in the other type the carbon atoms lie on opposite sides of this plane. The results presented in Table VII clearly show that the chelate ring conformations in $[Ir(CNMe)(diphos)_2]^+$ are of the latter type. Torsional angles associated with the chelate rings are given in Table VIII and these values may be compared with the tabulation given by Hall et al.[22] for metal–diphos

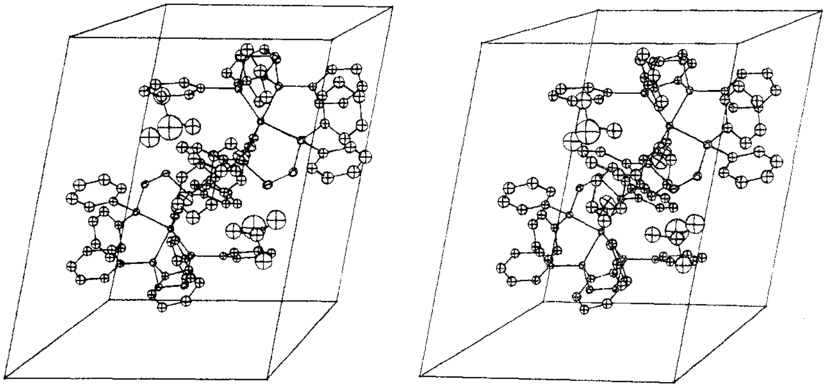


Figure 3. The crystallographic unit cell for $[Ir(CNMe)(diphos)_2](ClO_4)$. The viewing direction is along c^* and the a axis is horizontal. Only the disordered perchlorate centered at Cl(1) is shown.

structures. The torsional angles in the present study agree most closely with those in one of the chelate rings in $[Ir(CO)(diphos)_2]^{+2}$ and with those in the mixed donor atom chelate structure $[Pt(SCH_2CH_2PEt_2)_2]\cdot AgNO_3$.[23]

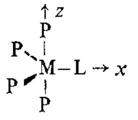
Bond distances and angles within the chelate rings are normal. The average P–C and C–C distances are 1.843 (4) and 1.515 (7) Å, respectively, and the P atoms exhibit approximate tetrahedral stereochemistry. The largest angular deviation from the tetrahedral angle at phosphorus is the average Ir–P–C(phenyl) angle of 120.3 (9)°.

Discussion

The trigonal bipyramidal structure of $[Ir(CNMe)(diphos)_2]^+$ is thus very similar to those of $[Ir(CO)(diphos)_2]^+$ [2] and $[Ru(NO)(diphos)_2]^+$ [3] and it permits a direct structural comparison of isocyanide, carbonyl, and nitrosyl coordination in these d^8 complexes of the platinum group metals. The key structural parameter in this comparison, in addition to the metal–ligand bond length, is the angle in the trigonal plane trans to the unique ligand.

In a discussion of the bonding in pentacoordinate coordinate complexes, Rossi and Hoffmann[24] have considered the effects of π acceptor orbitals on substituents in the different positions of a trigonal bipyramid. For d^8 complexes, they conclude that the π interaction is greatest when the substituent is in the equatorial position, as the unique ligand L is constrained to be in the present discussion, and that the interaction is greater in the equatorial plane than perpendicular to it.

The π acceptor orbital in the trigonal plane interacts strongly with the metal d_{xy} orbital, assuming structure I, leading to



I

stabilization of the d_{xy} level which acquires metal–ligand π bonding character. This molecular orbital is spatially extended toward ligand L as a π orbital and away from the phosphine donor atoms in the trigonal plane. The degree of π acidity of L directly influences the extent of this interaction which is therefore presumed to be in the order $NO^+ > CO > CNMe$.

The d_{xy} orbital, however, also interacts with the phosphine donors in the trigonal plane and it becomes weakly σ^* in character. Similarly, σ^* character is found in the other d orbital in the trigonal plane, $d_{x^2-y^2}$. As the P_{eq}–M–P_{eq} bond angle decreases from 120 to 90° the σ^* interaction of the phosphine donor orbitals with the metal d_{xy} function increases as that with the metal $d_{x^2-y^2}$ orbital decreases. However, as the d_{xy} orbital becomes more polarized toward ligand L through π bonding, its spatial extent toward the phosphine donors decreases, thus diminishing this σ^* interaction. The phosphine donors move to achieve the most stable structures in these systems in which the antibonding character of occupied, primarily metal-based orbitals is minimized. If the d_{xy} level is most polarized toward the unique ligand when L is NO^+ then the P_{eq}–M–P_{eq} angle in $[Ru(NO)(diphos)_2]^+$ should be the smallest of those under consideration. Conversely, if the d_{xy} level is least polarized toward L when L = CNMe then $[Ir(CNMe)(diphos)_2]^+$ should show the largest P–M–P bond angle. The observed structural results are entirely consistent with these bonding considerations: L = NO^+, P–Ru–P = 99.3 (2)°;[3] L = CO, P–Ir–P = 108 (1)°;[2] and L = CNMe, P–Ir–P = 120.36 (9)°.

The room-temperature equivalence of the phosphine donor atoms on the NMR time scale first attracted our attention to the $[Ir(CNMe)(diphos)_2]^+$ cation.[1] Bedford and Rouschias[25] have recently listed the following alternatives as possible rationalizations of this observation: (a) a square pyramidal (SP) structure with four equivalent phosphorus nuclei; (b) a rigid trigonal bipyramidal (TBP) structure with coupling constants such that the ^1H resonance of the CNMe ligand would appear as a quintet from an overlapping triplet of triplets; and (c) a stereochemically nonrigid TBP structure. The present structural results show that the solid state structure has a TBP coordination geometry, thus eliminating (a). Possibility (b) is highly unlikely, and in view of the established nonrigidity of pentacoordinate frameworks,[26] (c) appears to be the most reasonable explanation.

In light of the structural similarities of $[Ru(NO)(diphos)_2]^+$ and $[Ir(CNMe)(diphos)_2]^+$, and the fact that Caulton[7] has established Berry pseudorotation as the mechanism by which the phosphorus nuclei equilibrate in $M(NO)(diphos)_2^+$ systems (M = Fe, Ru), it is appealing to consider the stereochemical nonrigidity of $[Ir(CNMe)(diphos)_2]^+$ in terms of pseudorotation. This would require, however, a square-pyramidal transition state with the CNMe ligand in the apical position. Caulton has suggested[7] that M–NO bending might help stabilize the SP transition state in the $[M(NO)(diphos)_2]^+$ systems, but this would not be operative in the CNMe complex.

An alternative rearrangement mechanism might involve dissociation of one end of the diphos ligand followed by recombination in an equilibrating manner. This is similar to the proposal put forth by Stalick, Corfield, and Meek[27] for the structurally related $[CoCl(diphos)_2]^+$ cation. These investigators argued against a nondissociative mechanism for interconverting the Co complex from its TBP isomer to its SP isomer, both of which are isolable, because of steric hindrance. The same steric factors may also be important in $[Ir(CNMe)(diphos)_2]^+$. It seems clear that a detailed NMR analysis similar to that done by Caulton[7] must be performed on $[Ir(CNMe)(diphos)_2]^+$ in order to unequivocally answer the question of its fluxionality.

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Registry No. $[Ir(CNMe)(diphos)_2]ClO_4$, 40226-65-1.

Supplementary Material Available: Tables of the observed and calculated structure factor amplitudes, and of the parameters used in calculating the hydrogen atom contributions to the F_c, 40 pages. Ordering information is given on any current masthead page.

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Structural and Carbon-13 Nuclear Resonance Studies of a Compound Containing the $Fe_2(CO)_6$ Entity. Hexacarbonyl[μ-(1,2,5-η:1,4,5-η)-3-oxo-1,2,4,5-tetraphenyl-1,4-pentadiene-1,5-diyl]diiron(*Fe–Fe*)

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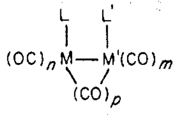
Diphenylacetylene reacts with diiron nonacarbonyl in tetrahydrofuran to produce a compound of empirical formula $Fe_2(CO)_7(PhCCPh)_2$, identical with a product obtained some years ago by W. Hübel and coworkers. An x-ray crystallographic study has shown that the compound consists of an $(OC)_3Fe–Fe(CO)_3$ unit to which is bonded $–CPh{=}CPhC(O)CPh{=}CPh–$ in such a way that each terminal carbon atom forms a σ bond to one iron atom while the π bond in which it is involved forms a donor bond to the other iron atom. The entire structure then possesses only one symmetry element, a twofold axis of symmetry passing through the CO group of the ligand and bisecting the Fe–Fe bond. The three CO groups on each iron atom are nonequivalent. The structure is analogous to that previously determined by Piron, Piret, Meunier-Piret, and van Meersche for the tetramethyl compound. The Fe–Fe distance is 2.536 (1) Å. Crystal data: space group $P2_1/n$; $a = 13.167$ (5), $b = 11.535$ (3), $c = 21.787$ (8) Å; $\beta = 95.11$ (2)°; $Z = 4$. The ^{13}C NMR spectrum was recorded at various temperatures from −25 to +85°. At the lowest temperatures three separate, equally intense, equally narrow signals are observed, in accord with the molecular structure. These begin to broaden at about −10° and coalesce at about +30° to a single broad resonance which sharpens as the temperature is raised further. There is no indication of preferential collapse of any two signals. From line shape analysis, the activation parameters for carbonyl scrambling have been estimated to be $\Delta G^\ddagger(300\ K) = 15.1$ (2) kcal mol^{-1}, $\Delta H^\ddagger = 14.1$ (1) kcal mol^{-1}, $\Delta S^\ddagger = -3.2$ (5) cal mol^{-1} deg^{-1}, $E_a = 14.7$ (2) kcal mol^{-1}, and $A = 3.4$ (8) $\times 10^{12}$ sec^{-1}.

Introduction

Let us begin by indicating the context of the work reported here, which is but one small contribution to a very large field. There exists a vast number of dinuclear metal carbonyls of the type **1**. The two characteristic features are (1) the presence of terminal CO groups, on both metal atoms, and (2) the existence of a single bond between the metal atoms. The variable features are (1) the identity of the metal atoms, which may be identical or different, (2) the number of CO groups on each metal atom, which can range from 1 to 5 and may be the same or different for the two metal atoms when the metal atoms are different or even when they are the same, (3) the nature of L and L′ which may themselves be CO groups, which may be bridging groups such as RS, S_2, R_2P, R_2N, R_2Ge, $RC{\equiv}CR$, etc., which may be polyene or polyenyl groups, or which may be different regions of one large polyene



$$\overset{L}{(OC)_nM}{-}\overset{L'}{M'(CO)_m}\quad (CO)_p$$

1