Inorganica Chimica Acta, 29 (1978) 273–277

The Crystal and Molecular Structure of an Iridium(I) Complex containing a Large Ring formed from Diacetylene Diphosphine

RONALD MASON and GEOFFREY A. WILLIAMS

School of Molecular Sciences, University of Sussex, Falmer, Brighton, BN1 9QJ, U.K.

Received December 28, 1977

The crystal and molecular structure of [IrCl(CO)L] (where L is $Bu^t_2PC{\equiv}C(CH_2)_5C{\equiv}CPBu^t_2$*) has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in the orthorhombic space group* Pbca *with eight molecules in a cell of dimensions* a *15.297(6)* b *30.72(1),* c *12.309(4)* Å*. Automatic diffractometry provided significant Bragg intensities of 3085 independent reflections and the structure, determined by conventional heavy atom methods, was refined by least-squares methods to* R *0.026. In the discrete [IrCl(CO)L] molecules, the iridium atom has a distorted planar coordination geometry with* trans *phosphorus atoms.*

Introduction

It has been shown by Shaw and his co-workers [1, 2] that long chain diphosphines of the type $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 9, 10, 12) form large chelate rings (12- to 45-membered). The stability of these macrocyclic complexes, relative to open chain structures, has been explained in terms of favourable conformational and entropy effects [3]. It is now well established that acetylenic groups promote the formation of large rings and this has been explained in parallel terms [4]. It is not unexpected therefore that diacetylenic diphosphines of the type $Bu^t_2PC{\equiv}C(CH_2)_nC{\equiv}CPBu^t_2$ would form large chelate rings with metals [5], and the structural chemistry of [IrCl(CO)L] (L = $Bu^t_2PC{\equiv}C(CH_2)_5C{\equiv}CPBu^t_2$), reported here, confirms this to be the case.

Experimental

Crystals of [IrCl(CO)L] suitable for X-ray study were grown from ethanol solution. Oscillation, Weissenberg and precession photographs showed the crystals to be orthorhombic, with the systematic absences $0kl$ with k odd, $h0l$ with l odd and $hk0$ with h odd uniquely determining the space group to be the centrosymmetric *Pbca*. Accurate unit cell parameters, together with their estimated standard deviations (e.s.d.'s), were derived by a least-squares analysis of the setting angles determined for 12 angularly well separated reflections each with a 2θ value greater than 40°. All data were obtained at 21 °C from a Hilger and Watts automatic four-circle diffractometer (Y290) using graphite monochromatised MoKα radiation (λ 0.70926 Å). Intensities were measured via an ω–2θ scan regime. The crystal, a lozenge of dimensions 0.30 by 0.34 by 0.37 mm, was mounted with its a axis coincident with the ϕ diffractometer axis. The intensities of all 6344 independent reflections having $\sin\theta/\lambda \leqslant 0.618°$ were measured and 3085 independent, statistically significant $[I \geqslant 3\sigma(I)]$ reflections formed the basis for the structure determination and refinement. No significant variations in the intensities of 3 standard reflections were observed, and geometrical and absorption corrections [6] were applied to the integrated intensities.

Crystal Data

[IrCl(CO)L] : $C_{26}H_{46}OP_2ClIr$, M 664.3, orthorhombic, a 15.297(6), b 30.72(1), c 12.309(4) Å, U 5784.4 Å^3, D_m (by flotation, using n-heptane/carbon tetrachloride) 1.51, Z 8, D_c 1.525 g cm^{-3}, space group *Pbca* (D_{2h}^{15}; No. 61), λ (MoKα, graphite crystal monochromator) 0.70926 Å, μ 51.0 cm^{-1}.

Structure Determination and Refinement

A three-dimensional Patterson synthesis and two consecutive Fourier syntheses demonstrated the positions of all the non-hydrogen atoms. Least-squares refinement of atomic coordinates and individual isotropic temperature factors was performed by use of the program CRYLSQ [7] in the full-matrix mode, the function minimised being $\Sigma w \Delta F^2$ where w is the weight assigned to the $|F_o|$ values and $\Delta F = ||F_o| - |F_c||$. After four cycles using unit weights, refinement converged with R, defined as $\Sigma\Delta F/\Sigma|F_o|$, 0.057.

It was evident, from the calculated bond lengths, that one of the methylene chain carbon atoms (C6)

TABLE I. Final Atomic Parameters for [IrCl(CO)L]. E.s.d. values (in parentheses) refer to the least significant digits. U-tensors in Å^2. Anisotropic thermal parameters are defined by $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U^{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Atom	x/a	y/b	z/c	$10^4\ U_{11}$	$10^4\ U_{22}$	$10^4\ U_{33}$	$10^4\ U_{12}$	$10^4\ U_{13}$	$10^4\ U_{23}$
Ir	0.31904(1)	0.35253(1)	-0.00315(3)	328(1)	356(1)	352(1)	33(1)	29(2)	51(2)
Cl	0.43435(14)	0.30418(7)	0.03977(17)	621(12)	709(12)	693(13)	280(11)	122(10)	244(10)
P1	0.23555(11)	0.33280(6)	0.14756(14)	422(10)	346(8)	375(9)	25(8)	87(8)	10(7)
P2	0.39995(10)	0.39126(5)	-0.13199(14)	292(8)	367(8)	377(9)	16(7)	12(7)	43(7)
O	0.1622(3)	0.3950(2)	-0.0927(5)	423(29)	760(36)	766(36)	106(26)	-77(26)	81(30)
C1	0.1629(4)	0.3765(2)	0.1717(6)	406(40)	403(36)	524(40)	96(31)	91(32)	24(32)
C2	0.1225(5)	0.4090(3)	0.1778(7)	469(44)	560(47)	786(58)	27(38)	127(42)	-53(44)
C3	0.0740(6)	0.4496(3)	0.1802(9)	592(54)	479(46)	1285(86)	178(42)	46(56)	29(54)
C4	0.0866(7)	0.4755(3)	0.0783(10)	1001(79)	531(53)	1292(91)	416(55)	-556(74)	-277(59)
C5	0.1792(8)	0.4888(3)	0.0529(7)	1301(87)	523(47)	616(46)	436(61)	208(64)	-5(39)
C6A[a]	0.1713(9)	0.5075(4)	-0.0635(11)	782(90)	599(72)	792(83)	405(70)	284(79)	215(66)
C6B[b]	0.2291(16)	0.5252(8)	-0.0397(25)	412(139)	466(142)	1274(266)	7(113)	-632(156)	-152(144)
C7	0.2455(9)	0.5121(3)	-0.1252(10)	1430(100)	932(78)	1317(94)	770(75)	939(87)	641(72)
C8	0.3028(5)	0.4731(3)	-0.1395(7)	710(59)	609(49)	824(59)	229(44)	403(50)	325(46)
C9	0.3464(5)	0.4421(2)	-0.1456(6)	499(41)	435(39)	606(45)	50(34)	140(36)	74(37)
C10	0.2952(5)	0.3315(3)	0.2817(6)	723(55)	564(43)	407(39)	93(40)	69(37)	-1(34)
C11	0.3654(6)	0.3673(3)	0.2772(7)	836(61)	871(63)	527(50)	-169(52)	-112(47)	-153(44)
C12	0.3402(6)	0.2876(3)	0.3001(7)	825(67)	937(67)	596(51)	277(54)	4(48)	200(49)
C13	0.2340(7)	0.3416(3)	0.3772(7)	1018(75)	1121(81)	427(43)	238(64)	93(50)	-86(49)
C14	0.1595(5)	0.2861(2)	0.1273(7)	547(47)	409(38)	674(49)	-139(34)	157(40)	-75(36)
C15	0.2132(7)	0.2461(3)	0.0920(9)	1110(72)	363(42)	1101(78)	-175(48)	127(66)	-131(48)
C16	0.1023(7)	0.2752(3)	0.2261(8)	940(70)	742(61)	932(74)	-247(56)	457(62)	-10(56)
C17	0.1000(6)	0.2970(3)	0.0346(8)	780(59)	739(58)	987(81)	-246(49)	-133(54)	-39(51)
C18	0.3987(5)	0.3683(2)	-0.2719(5)	515(40)	545(41)	379(38)	-36(35)	-13(33)	-55(31)
C19	0.4401(6)	0.3958(3)	-0.3576(6)	775(58)	759(56)	494(44)	72(48)	172(45)	76(43)
C20	0.4390(7)	0.3235(3)	-0.2720(6)	1345(92)	550(47)	508(54)	218(56)	139(58)	-115(39)
C21	0.3009(5)	0.3642(3)	-0.3008(7)	618(55)	1145(80)	554(47)	-204(50)	-47(42)	-97(49)
C22	0.5123(5)	0.4100(3)	-0.0889(6)	456(43)	555(45)	540(47)	-91(36)	-21(39)	24(38)
C23	0.5792(5)	0.3732(3)	-0.1023(8)	464(49)	1090(75)	936(71)	157(49)	-72(49)	217(61)
C24	0.5026(6)	0.4224(4)	0.0306(7)	572(49)	1241(83)	597(65)	-364(53)	-68(42)	-118(51)
C25	0.5412(6)	0.4494(3)	-0.1539(8)	605(52)	868(65)	861(64)	-223(49)	152(52)	65(55)
C26	0.2235(4)	0.3802(2)	-0.0553(6)	369(35)	613(45)	402(35)	-77(34)	99(31)	-9(35)

[a] C6A occupancy factor 0.7. [b] C6B occupancy factor 0.3.

was severely disordered. A difference synthesis indicated two alternative positions for this carbon atom, both positions persisting throughout the refinement. Hence further refinement was based on partial occupancy, by C6, of these positions, the occupancy factors being determined as 0.7 and 0.3 from the difference synthesis.

All non-hydrogen atoms were then refined anisotropically; at convergence R had the value 0.038. Absorption corrections were now applied to the intensity data, and two further cycles of refinement with unit weighting of reflections provided R = 0.033. A parabolic weighting scheme of the form

$$w = (a + b\,|F_o| + c\,|F_o|^2)^{-1}$$

was then applied, the parameters being revised after an analysis of observed and calculated structure factors to final values of a 35.0, b −0.38, c 0.0012 for $|F_o|$ on absolute scale. A difference synthesis at this stage yielded the positions of all hydrogen atoms, but including only those in higher occupancy positions bonded to the disordered methylene carbon atom and its adjacent neighbouring carbon atoms. These hydrogen positions were included in the scattering model but were not refined, each hydrogen atom being given an isotropic temperature factor equal to that of the carbon atom to which it was bonded. Refinement converged to R 0.026 and R_w, defined as $(\Sigma w \Delta F^2/\Sigma w\,|F_o|^2)^{1/2}$, 0.026. The maximum shift/error at convergence was 0.29 associated with the alternative positions of the disordered C6, and 0.15 for the positional parameters and 0.27 for the thermal parameters of all other atoms. An inspection of the data showed no evidence for secondary extinction. A final difference synthesis was essentially flat and showed no peaks larger than $|0.5|$ $e\text{Å}^{-3}$, with the exception of one peak of height $|1.0|$ $e\text{Å}^{-3}$ in the vicinity of the iridium atom. Final atomic parameters and their e.s.d. values are listed in Table I.

Atomic scattering factor curves for non-hydrogen atoms were taken from ref. 8, with those for Ir, Cl and P modified for the real and imaginary anomalous dispersion corrections [9]. The scattering factor curve for H was taken from ref. 10. All computations were performed on the Atlas Computer Laboratory's ICL 1906A computer. Initial data processing used the University of Sussex computer programs, and structure determination and refinement used the 'X-Ray 74' program system [7]. Listings of the final values of $|F_o|$ and F_c, and of the hydrogen atom parameters, are available on request.

Results and Discussion

The discrete [IrCl(CO)L] units are seen to contain a twelve-membered ring with a *trans* arrangement of the phosphorus atoms about the iridium atom. In previous structural studies of related macrocyclic tertiary phosphine complexes [1, 11, 12], the phosphorus atoms have also been *trans* bonding, as expected on steric grounds. The distorted planar environment of the iridium atom is completed by carbonyl- and chloro-ligands. The molecular geometry and atom numbering are shown in Figure 1. Interatomic distances, angles and correlated e.s.d. values are given in Tables II and III.

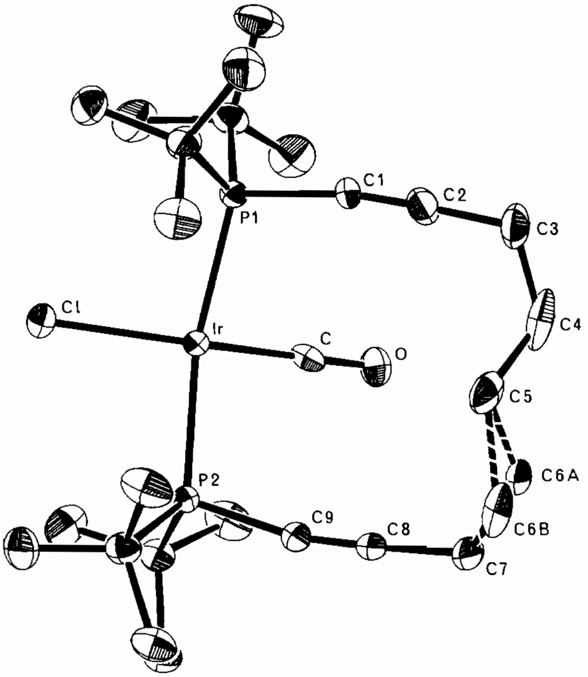

Figure 1. Molecular geometry of [IrCl(CO)L] perpendicular to the 12-atom ring.

The X-ray and ^{31}P n.m.r. data for each of the related macrocyclic tertiary phosphine complexes [IrCl(CO{$Bu^t_2P(CH_2)_{10}PBu^t_2$}] [1], [RhCl(CO){$Bu^t_2P(CH_2)_{10}PBu^t_2$}]$_2$, [1], and [RhCl(CO){$Bu^t_2P(CH_2)_4C{\equiv}C(CH_2)_4PBu^t_2$}] [11] show the presence of two conformers (rotamers), one with the carbonyl function in the *gauche* position with respect to the four t-butyl groups, the other with the ligand *gauche* to the t-butyl groups. In contrast, only one rotamer can be detected in the ^{31}P n.m.r. spectrum of [IrCl(CO)L], and there is no evidence, from our X-ray analysis, for any configurational disorder of the carbonyl- and chloro-ligands. The observed rotamer with the chloride *gauche* to the t-butyl groups is stabilized by having adjacent carbonyl and acetylenic functions (Figure 1).

The torsion angles within the ring (Table IV) are close to the 'normal' values of 180° or 60° and do not demonstrate any substantial degree of ring strain. Equally, the intracyclic carbon–carbon bond lengths are quite normal, save for those bond lengths associated with the disordered methylene carbon atom which

TABLE II. Interatomic Distances (Å).

(a) Intramolecular Distances:

Ir–Cl	2.366(2)	C8–C9	1.165(11)
Ir–P1	2.332(2)	C10–C11	1.536(12)
Ir–P2	2.337(2)	C10–C12	1.530(12)
Ir–C26	1.808(7)	C10–C13	1.534(12)
P1–C1	1.767(7)	C14–C15	1.542(12)
P1–C10	1.887(7)	C14–C16	1.535(13)
P1–C14	1.863(7)	C14–C17	1.497(12)
P2–C9	1.772(7)	C18–C19	1.493(11)
P2–C18	1.861(7)	C18–C20	1.506(11)
P2–C22	1.889(8)	C18–C21	1.543(11)
O–C26	1.140(8)	C22–C23	1.535(12)
C1–C2	1.177(10)	C22–C24	1.526(11)
C2–C3	1.453(11)	C22–C25	1.516(12)
C3–C4	1.498(15)	O···Cl	3.304(9)
C4–C5	1.507(16)	O···C2	3.411(10)
C5–C6A	1.549(16)	O···C8	3.274(10)
C5–C6B	1.769(30)	O···C9	3.234(9)
C6A–C7	1.372(19)	C26···C1	2.946(10)
C6B–C7	1.155(33)	C26···C2	3.376(11)
C7–C8	1.495(14)	C26···C8	3.272(11)
		C26···C9	2.897(10)

(b) Intermolecular Contacts[a] within the Limits of the Contact Radii: Ir, Cl, P, 2.2 Å; O, C, 1.9 Å:

C4···C4$^{\mathrm{I}}$	3.606(16)	Cl···C16$^{\mathrm{IV}}$	3.962(10)
C13···C15$^{\mathrm{II}}$	3.787(13)	C19···O$^{\mathrm{V}}$	3.451(10)
C3···C8$^{\mathrm{III}}$	3.756(13)	C23···C21$^{\mathrm{V}}$	3.606(12)
C23···C13$^{\mathrm{IV}}$	3.771(13)		

[a] Roman numeral superscripts refer to the following co-ordinate transformations:

I	$-x, 1-y, -z$	IV	$\frac{1}{2}+x, y, \frac{1}{2}-z$
II	$x, \frac{1}{2}-y, \frac{1}{2}+z$	V	$\frac{1}{2}+x, y, -\frac{1}{2}-z$
III	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$		

must suffer from systematic errors reflecting our approximate scattering model. Although only the one atom (C6) in the methylene chain is significantly disordered, occupying partially each of the two positions C6A, C6B [C6A···C6B, 1.08(3)Å], the thermal parameters observed for the remaining methylene carbon atoms indicate considerable thermal motion of these atoms.

TABLE III. Bond Angles (Degrees).

Cl–Ir–C26	167.6(2)	C6B–C7–C8	121.0(16)
Cl–Ir–P1	93.87(7)	C7–C8–C9	176.7(10)
Cl–Ir–P2	94.38(7)	C8–C9–P2	168.4(7)
P1–Ir–P2	164.15(6)	P1–C10–C11	106.9(5)
P1–Ir–C26	87.8(2)	P1–C10–C12	111.4(5)
P2–Ir–C26	87.0(2)	P1–C10–C13	111.8(6)
Ir–C26–O	175.1(7)	C11–C10–C12	108.7(7)
Ir–P1–C1	106.3(2)	C11–C10–C13	108.1(7)
Ir–P1–C10	115.9(3)	C12–C10–C13	109.8(7)
Ir–P1–C14	115.8(3)	P1–C14–C15	108.6(5)
C1–P1–C10	99.9(3)	P1–C14–C16	114.7(6)
C1–P1–C14	102.4(3)	P1–C14–C17	108.0(5)
C10–P1–C14	113.8(4)	C15–C14–C16	110.6(7)
Ir–P2–C9	105.5(3)	C15–C14–C17	106.7(7)
Ir–P2–C18	115.4(2)	C16–C14–C17	107.8(7)
Ir–P2–C22	116.5(2)	P2–C18–C19	115.8(5)
C9–P2–C18	104.0(3)	P2–C18–C20	110.1(5)
C9–P2–C22	100.3(3)	P2–C18–C21	104.7(5)
C18–P2–C22	112.6(3)	C19–C18–C20	110.0(7)
P1–C1–C2	170.2(7)	C19–C18–C21	107.1(6)
C1–C2–C3	177.3(9)	C20–C18–C21	108.8(7)
C2–C3–C4	111.9(8)	P2–C22–C23	110.6(6)
C3–C4–C5	116.1(9)	P2–C22–C24	105.0(5)
C4–C5–C6A	102.7(9)	P2–C22–C25	111.1(6)
C4–C5–C6B	135.2(11)	C23–C22–C24	110.6(7)
C5–C6A–C7	119.1(11)	C23–C22–C25	109.7(7)
C5–C6B–C7	117.4(19)	C24–C22–C25	109.7(7)
C6A–C7–C8	117.9(10)		

TABLE IV. Torsion Angles (Degrees)[a,b] for [IrCl(CO)L].

A	−60(1)
B	171(1)
C	−168(1)
D	−162(1)
E	−87(3)
F	53(2)
G	−57(3)

[a] E.s.d. values in parentheses. [b] Torsion angles A·····G refer to the sequences:

A B D F
C2–C3–C4–C5–C6A–C7–C8
C E G
C2–C3–C4–C5–C6B–C7–C8

The iridium–phosphorus bond lengths in $[\mathrm{IrCl(CO)}[\mathrm{Bu^t_2P(CH_2)_{10}PBu^t_2}]]$ [1], which contains a thirteen-membered saturated ring, are 2.365(3) and 2.359(3) Å. These are significantly larger than the iridium–phosphorus bond lengths of 2.332(2) and 2.337(2) Å observed in [IrCl(CO)L] which contains a twelve-membered unsaturated ring. The shorter metal–phosphorus bond lengths are associated with the more rigid ring system, and this follows the trend we discuss for several macrocyclic tertiary phosphine complexes of rhodium(I) [12]. Our view is that the small variations reflect the changing metal–phosphorus σ-bond in these systems: in the large rings the σ-bonding orbital of the phosphorus atom will be essentially that of simple tertiary phosphine ligands; decreasing ring size implies more 's' bond character in the metal–phosphorus bond, given the relatively poor orbital overalp of the metal with the phosphorus 'p' orbitals which is consequent upon ring and substituent steric constraints.

The equation to the mean plane [7] passing through the atoms P1, P2, C1, C2, C8 and C9 is

$$0.6425X + 0.3884Y + 0.6605Z = 7.5023$$

where X, Y and Z are coordinates in Å with respect

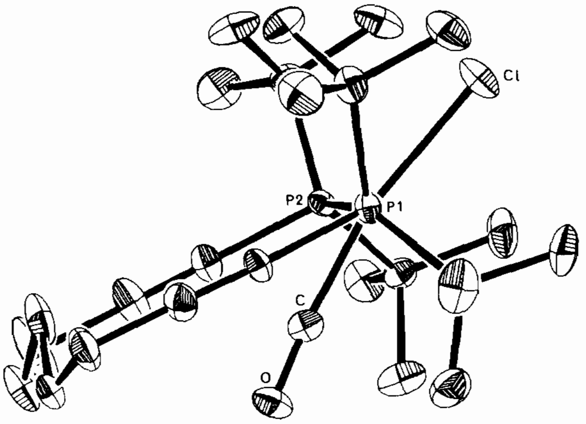

Figure 2. Molecular geometry of [IrCl(CO)L] looking exactly along the P1–Ir vector (partial atom C6B has been omitted for clarity, and the iridium atom is hidden behind P1).

to the orthogonal axis set a, b, c. None of the atoms is more than 0.027 Å away from the plane. The iridium atom is displaced 0.186 Å from the plane in the direction of displacement of the carbonyl ligand (Figure 2). The angle between this plane and (i) the Ir–Cl bond is 22.5°, and (ii) the mean line through Ir–C26–O is 36.6°. The coordination geometry about the iridium atom is distorted significantly away from planarity (Figure 2).

Acknowledgements

We thank the S.R.C. for support, and the University of Melbourne for a Travelling Scholarship (G.A.W.).

References

1 F. C. March, R. Mason, K. M. Thomas, and B. L. Shaw, *Chem. Comm.*, 584 (1975).
2 A. Pryde, B. L. Shaw, and B. Weeks, *J. Chem. Soc. Dalton*, 322 (1976).
3 B. L. Shaw, *J. Am. Chem. Soc.*, *97*, 3856 (1975).
4 J. Dale, A. J. Hubert and G. S. D. King, *J. Chem. Soc.*, *73 (1963).*
5 *H. D. Empsall, E. Mentzer, D. Pawson, B. L. Shaw, R. Mason and G. A. Williams, Chem. Comm.*, 311 (1977).
6 "International Tables for X-ray Crystallography", Vol. 3, p. 162, Kynoch Press, Birmingham (1962).
7 J. M. Stewart, "The X-ray System, Version of July" (1972), Technical Report TR 72-192 of the Computer Science Centre, University of Maryland (X-ray 74 version implemented at Atlas Computer Laboratory).
8 D. T. Cromer and J. T. Waber, *Acta Cryst.*, *18*, 104 (1965).
9 D. T. Cromer, *Acta Cryst.*, *18*, 17 (1965).
10 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, *42*, 3175 (1965).
11 R. Mason, G. Scollary, B. Moyle, K. I. Hardcastle, B. L. Shaw and C. J. Moulton, *J. Organometal. Chem.*, *113*, C49 (1976).
12 R. Mason and G. Scollary, submitted to Austr. J. Chem.