Crystal and Molecular Structure of *trans*-Di-iodobis(tricyclohexylphosphine)platinum(II): An Overcrowded Molecule

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The crystal and molecular structure of the title compound has been determined. Crystals are triclinic, space group $P\bar{1}$, a = 11·139(2), b = 10·235(2), c = 10·269(2) Å, α = 90·85(2), β = 113·84(2), γ = 110·91(2)°, Z = 1·3533 observed intensities were measured by diffractometer; the structure was solved by the heavy-atom method and refined to a final R of 0·041. The crystal contains discrete *trans*-$[PtI_2\{(C_6H_{11})_3P\}_2]$ molecules, which show considerable evidence of overcrowding, most apparent in the Pt–P [2·371(2) Å] and the Pt–I distances [2·612(1); expected values 2·32 and 2·60 Å]. This is correlated with the ready elimination of tricyclohexylphosphine from the title compound.

THE di-iodobis(phosphine)-platinum(II) complexes of bulky phosphines have been found [1] to eliminate one mole of phosphine ligand per mole of platinum on heating, giving di-iodo-bridged diplatinum species. It was suspected that this might be caused by ligand–ligand steric interactions. To investigate this, a single-crystal X-ray structure determination was performed on the title compound (II), *trans*-$[PtI_2\{(C_6H_{11})_3P\}_2]$, in which these interactions should be particularly marked. The unit cell of the corresponding dichloride (I) was also determined.

EXPERIMENTAL

(II) was crystallized by slow evaporation of a solution of the complex [1] in dichloromethane–ethanol as orange parallelepipeds, (I) separated too rapidly from dichloromethane and chloroform solutions for suitably sized crystals to be obtained; by heating under reflux in dichloromethane–ethanol larger crystals were formed but they were still too small. It was reasoned that the size was being limited by the agitating effect of the boiling liquid shattering them. A sample of (I) was therefore suspended in 2 : 1 ethanol–dichloromethane, sealed in a glass tube, and kept at 90° for 2 weeks. The crystals formed were then a suitable size and very similar in form to those of (II).

TABLE 1

Unit-cell constants of the compounds *trans*-$[MX_2\{(C_6H_{11})_3P\}_2]$

	M	X	a/Å	b/Å	c/Å	α	β	γ	U/Å^3
(I) *	Pt	Cl	10·608	10·257	9·998	91·72°	109·47°	112·74°	929·92
(II) *	Pt	I	11·139	10·235	10·269	90·85	113·84	110·91	988·77
(III) †	Ni	Cl	10·5	10·3	10·0	91·05	110·20	113·05	925

* Determined from the reflecting positions measured on a PW 1100 diffractometer; calc. σ: ±0·002 Å and 0·002°. † From ref. 2.

Crystal Data.—$C_{36}H_{66}I_2P_2Pt$ (II), Triclinic, for unit-cell dimensions see Table 1. D_c = 1·69, Z = 1, D_m = 1·66 (by flotation in benzene–methylene iodide), $F(000)$ = 496, Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 53 cm^{-1}. Spacegroup $P\bar{1}$, with the molecule occupying a centre of symmetry, was assumed because of the isomophism with the corresponding Ni compound,[2] and proved satisfactory.

Data for layers $hk0$—10 were collected on a Stoe Weissenberg diffractometer (graphite monochromator, ω scan no attenuators) to 2θ maximum 60°. Data about a crossing axis were later collected, but had to be discarded because they gave unsatisfactory interlayer scaling, perhaps due to slight crystal decomposition. For this reason the absolute values of the B_{33} terms of the anisotropic temperature factors are not known. Lorentz and polarisation corrections (monochromator assumed ideally mosaic) were applied and the data corrected for absorption with the program ABSCOR.[3] Crystal dimensions are in Table 2. 3533 Reflections having $I/\sigma(I) > 3$ were considered observed.

The iodine and phosphorus atoms were readily located on a Patterson synthesis and the light atoms found by Fourier methods. Refinement by least-squares methods reached R 0·053 with all atoms isotropic, 0·046 with Pt, I, and P anisotropic, and finally 0·041 with all atoms anisotropic. Hydrogen atoms were excluded because a final difference-Fourier synthesis showed only random low electron density. Anomalous dispersion by Pt, I, and P was allowed for, and scattering factors were from ref. 4. Computation was with the programs of Dr. D. R. Russell on an ICL 4130 computer.

Figure 1 gives the atomic numbering, Table 3 the atomic positions and temperature factors, Tables 4 and 5 bond lengths and angles. Final structure factors are listed in Supplementary Publication No. SUP 21043 (18 pp., 1 microfiche).†

TABLE 2

Crystal dimensions * of (II)

Face	A	B	C	$D \times 10^3$ cm
1	0·612	−0·790	0·000	5·153
2	−0·612	0·790	0·000	4·294
3	0·999	0·048	0·000	9·370
4	−0·999	−0·048	0·000	1·085
5	0·346	0·938	1·804	0·816
6	−0·346	−0·938	−1·804	50·502

* According to the equations $Ax + By + Cz = D$.

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[1] P. G. Leviston and M. G. H. Wallbridge, to be published.

[2] P. L. Bellon, V. Albano, V. D. Bianco, F. Pompa, and V. Scatturin, *Ricerca Sci.*, 1963, **3**, 1213.

[3] 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

[4] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

TABLE 3

Atomic co-ordinates (× 10^4) and anisotropic * temperature factors (× 10), with standard deviations in parentheses

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pt	0	0	0	18·3(2)	16·0(1)	25·2(2)	9·0(1)	0·5(1)	5·5(1)
I	1655·0(5)	−1053·1(5)	698·6(8)	27·0(2)	28·3(2)	62·4(4)	23·2(2)	−2·1(2)	9·3(2)
P	2005(2)	2071(2)	325(2)	22·3(6)	18·6(6)	25·5(9)	9·6(6)	0·6(6)	4·0(5)
C(1)	1692(8)	3732(7)	1115(10)	27(3)	21(2)	33(4)	9(3)	3(3)	7(2)
C(2)	2946(9)	5109(8)	1296(12)	35(3)	20(3)	57(5)	17(3)	5(3)	6(2)
C(3)	2397(11)	6310(9)	1644(13)	49(4)	25(3)	62(6)	20(4)	5(4)	10(3)
C(4)	1758(11)	6573(9)	3005(13)	52(5)	29(3)	60(6)	9(3)	−3(4)	19(3)
C(5)	554(11)	5198(11)	2891(13)	45(4)	42(4)	57(6)	14(4)	12(4)	24(4)
C(6)	1076(10)	3966(9)	2517(11)	43(4)	31(3)	35(4)	12(3)	14(3)	18(3)
C(7)	2522(9)	1941(8)	−1442(9)	33(3)	31(3)	22(4)	11(3)	3(3)	10(3)
C(8)	1439(11)	1974(12)	−2483(11)	45(4)	59(5)	33(4)	27(4)	3(3)	19(4)
C(9)	2031(14)	1943(14)	−3860(13)	63(6)	68(7)	36(5)	30(5)	13(4)	22(5)
C(10)	2336(13)	595(13)	−4648(12)	58(6)	57(5)	33(5)	10(4)	4(4)	10(4)
C(11)	3385(13)	506(13)	−3620(12)	59(6)	62(6)	35(5)	15(4)	16(4)	25(5)
C(12)	2816(12)	572(11)	−2216(11)	62(5)	42(4)	45(4)	76(3)	11(4)	26(4)
C(13)	3707(8)	2377(8)	1395(9)	21(3)	31(3)	27(4)	14(3)	−2(2)	4(2)
C(14)	3680(9)	2845(10)	3003(10)	28(3)	49(4)	29(4)	18(3)	1(3)	16(3)
C(15)	4955(10)	2753(13)	3726(12)	31(4)	78(6)	42(5)	34(5)	−1(3)	15(4)
C(16)	6369(10)	3725(12)	3514(12)	29(3)	75(6)	41(5)	26(5)	−3(3)	12(3)
C(17)	6378(9)	3339(12)	1908(13)	23(3)	62(5)	48(5)	19(4)	6(3)	13(3)
C(18)	5108(8)	3415(10)	1178(12)	21(3)	48(4)	40(5)	24(3)	3(3)	2(3)

* In the form: $\exp\{-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}klb^*c^* + 2B_{13}hla^*c^* + 2B_{12}hka^*b^*)\}$.

RESULTS AND DISCUSSION

The complex is confirmed to have a *trans*-square-planar geometry about the platinum. The structure is shown in Figure 1 viewed down the x axis. The phosphine substituents are staggered about the P–Pt–P axis. The cyclohexane rings are all in the ' chair ' conformation and the bond lengths and angles agree, within 2σ, with the mean values for each ring.

TABLE 4

Distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Distances

Pt–I	2·612(1)	C(7)–C(8)	1·548(15)
Pt–P	2·371(2)	C(8)–C(9)	1·539(20)
P–C(1)	1·844(8)	C(9)–C(10)	1·538(19)
P–C(7)	1·861(10)	C(10)–C(11)	1·551(20)
P–C(13)	1·891(9)	C(11)–C(12)	1·547(19)
Mean P–C	1·865	C(12)–C(7)	1·550(14)
		Mean	1·546
C(1)–C(2)	1·546(12)		
C(2)–C(3)	1·546(14)	C(13)–C(14)	1·522(14)
C(3)–C(4)	1·517(18)	C(14)–C(15)	1·547(16)
C(4)–C(5)	1·543(16)	C(15)–C(16)	1·548(17)
C(5)–C(6)	1·555(15)	C(16)–C(17)	1·529(18)
C(6)–C(1)	1·543(14)	C(17)–C(18)	1·535(15)
Mean	1·541	C(18)–C(13)	1·575(13)
		Mean	1·543
		Overall mean	1·543

(*b*) Angles

I–Pt–P	90·62(5)	C(12)–C(7)–C(8)	109·5(8)
Pt–P–C(1)	113·76(27)	C(7)–C(8)–C(9)	109·8(9)
Pt–P–C(7)	111·00(27)	C(8)–C(9)–C(10)	111·3(12)
Pt–P–C(13)	115·51(28)	C(9)–C(10)–C(11)	110·4(11)
P–C(1)–C(2)	116·0(6)	C(10)–C(11)–C(12)	110·8(10)
P–C(1)–C(6)	113·9(6)	C(11)–C(12)–C(7)	110·0(10)
P–C(7)–C(8)	115·1(7)	Mean	110·5
P–C(7)–C(12)	109·8(7)		
P–C(13)–C(14)	113·0(6)	C(18)–C(13)–C(14)	110·0(7)
P–C(13)–C(18)	114·6(6)	C(13)–C(14)–C(15)	109·2(8)
		C(14)–C(15)–C(16)	110·0(10)
C(6)–C(1)–C(2)	111·0(7)	C(15)–C(16)–C(17)	110·9(10)
C(1)–C(2)–C(3)	108·7(8)	C(16)–C(17)–C(18)	112·1(10)
C(2)–C(3)–C(4)	111·2(10)	C(17)–C(18)–C(13)	107·7(9)
C(3)–C(4)–C(5)	111·8(9)	Mean	110·0
C(4)–C(5)–C(6)	111·2(9)	Overall mean	110·3
C(5)–C(6)–C(1)	109·1(9)		
Mean	110·5		

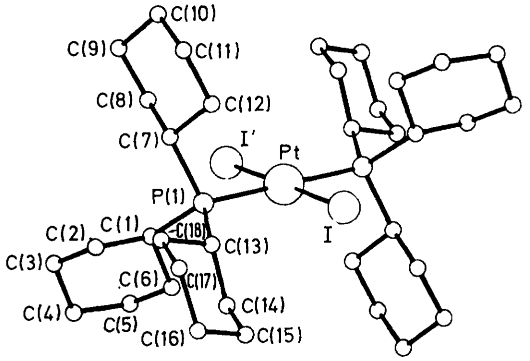

FIGURE 1 The structure of (II) showing the atomic numbering system used in the analysis

TABLE 5

Non-bonded iodine–carbon distances (Å). Primed atoms are related to unprimed ones by the centre of symmetry at the origin

I···C(13)	3·396(8)	I···C(6′)	3·719(9)
I···C(14)	3·725(9)	I···C(8′)	3·716(9)
I···C(1′)	3·483(8)		

As was expected from the cell constants the complex is isostructural with (III), *trans*-$[\mathrm{NiCl_2}\{(\mathrm{C_6H_{11}})_3\mathrm{P}\}_2]$. However, the determination of the latter compound, in two dimensions only, is not sufficiently accurate for comparisons to be made. The most useful structure for comparison and examination of the interactions is the accurate determination (R 0·077) of (IV), *trans*-$[\mathrm{PtBr_2(Et_3P)_2}]$,[5] which allowed much more meaningful discussion of the interactions caused by increasing the bulk

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[5] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1966, **10**, 1775.

of the phosphine ligand. Some comparative data are given in Table 6.

TABLE 6

Comparison of geometry of (IV), *trans*-[$PtBr_2(Et_3P)_2$], and (II), *trans*-[$PtI_2\{(C_6H_{11})_3P\}_2$]

	(IV)	(II)
Pt–P	2·315(4) Å	2·371(2) Å
P–Pt–X	92·8(1)°	90·63(5)°
Pt–P–C(1) *	119·3(8)	113·80(27)
Pt–P–C(7) *	111·1(10)	111·03(27)
Pt–P–C(13) *	114·8(6)	115·48(28)
Mean Pt–P–C	115·1	114·43

* Atom numbering for (II); corresponding numbers for (IV) (ref. 5) are: C(1), C(3), C(5).

The Pt–P bond length of 2·315(4) in (IV) is 0·056 Å shorter than that reported here. This value is highly significant in terms of the errors quoted. Messmer and Amma [5] quote Pt–P bond lengths of 2·16—2·26 Å from earlier literature but regard the errors (up to ±0·07 Å) as too great to be readily interpreted. It is significant that even in (II) reported here the bond length does not reach 2·41 Å, the sum of the single bond covalent radii of Pt and P; [5] the shortening has been used as evidence of Pt–P double, *i.e.* d_π–d_π, bonding from the nonbonding *d* orbitals on platinum to the empty phosphorus *d* orbitals.[5] The present results lend weight to this hypothesis.

It has not proved possible to find a Pt–I bond length with which to make a valid comparison with the value of 2·612 Å reported here. Applying the difference of 0·17 Å between the covalent radii of I and Br (Table 1 of ref. 6, subtracting 0·76 Å from r_b) to the Pt–Br distance of 2·428(2) found by Messmer and Amma gives a value of 2·598 Å, which is 0·014 Å shorter than in (II). Although this procedure is not particularly reliable it still indicates a lengthening of the Pt–I bond.

The Pt–P–C(n) (n = 1,7,13) angles are all significantly greater than the value for a tetrahedral angle of 109·47° but not significantly different from the values found in (IV), possibly indicating that neither ligand can ' fold back ' to relieve the carbon–halogen interactions because of intraligand repulsions.

In (IV), there is only one short, *i.e.* <4 Å, bromine to carbon distance, of 3·32(2), whereas in (II) there are five such short interactions between carbon and iodine. The P–Pt–Br angle is increased by 2·8(1)° on the side of the unfavourable interaction; in (II) the degree of opening is only 0·63°, and Figure 2 shows that the interactions are spread over both phosphine ligands, three on one side, two on the other; it is suggested therefore that the P–Pt–I angle more closely approaches 90° because the two sets of interactions are more nearly balanced. Here, however, the angle is opened up on the side having the two, rather than the three, unfavourable interactions. A model shows that, using predicted positions, both hydrogen atoms on C(14) closely approach the iodine atom, whereas the other approaches involve only one hydrogen atom each.

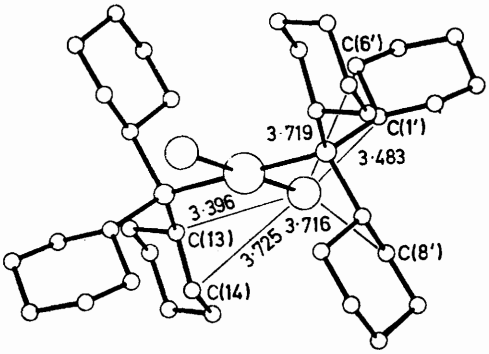

FIGURE 2 Short iodine–carbon contacts

Conclusions.—It is clear that complex (II) is very highly crowded, resulting in great interligand repulsions and an increase in the phosphorus platinum distance with respect to the analogue (IV). This is therefore in agreement with the proposed hypothesis that the bridged Pt–I–Pt complex is formed by elimination of the phosphine because it is significantly less strained than is (II). {The As–Pt–Cl(b) angle in [$Pt_2Cl_4(Me_3As)_2$] is 95° (ref. 7).}

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