Structural Studies of Steric Effects in Phosphine Complexes. Part 4.[1] Synthesis and Crystal and Molecular Structure of *trans*-Di-iodobis(tri-*o*-tolylphosphine)platinum(II)–Dichloromethane (1/1)

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The title complex has been synthesized and crystallizes in a 1 : 1 ratio with dichloromethane in the monoclinic space group *C*2/*c* with $a = 22.100(3)$, $b = 9.961(3)$, $c = 21.516(3)$ Å, $\beta = 113.19(1)°$, and $Z = 4$. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final *R* of 0.036 for 3 073 observed reflections measured by diffractometer. The dichloromethane is disordered over three equally populated sites around the crystallographic two-fold axis. The *trans*-$[PtI_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ molecule resides on a crystallographic centre of symmetry with Pt–I and Pt–P distances of 2.622(1) and 2.348(2) Å respectively. The failure of this complex to undergo intramolecular metallation can be explained by the steric effects of the $P(C_6H_4Me\text{-}o)_3$ ligand, which are described by cone-angle calculations ($\theta = 183°$) and a 'ligand profile'.

THE steric effects of phosphorus ligands, described in terms of a ligand cone angle θ,[2] have recently been documented by Tolman.[3] His estimates of θ for bulky phosphines such as tri-t-butylphosphine ($\theta = 182 \pm 2°$), tricyclohexylphosphine ($\theta = 179 \pm 10°$, revised[3] to 170°), and tri-*o*-tolylphosphine ($\theta = 194 \pm 6°$) were based on CPK (Corey–Pauling–Koltun) molecular models.[2] Calculations using ^1H n.m.r. chemical-shift information have recently led Trogler and Marzilli[4] to postulate a value of 170° for $P(C_6H_{11})_3$ in the over-crowded system $[Co(Hdmg)_2(HOMe)\{P(C_6H_{11})_3\}]^+$ (Hdmg = monoanion of dimethylglyoxime). *X*-Ray structural determinations of $[PBu^t_3H][NiBr_3(PBu^t_3)]$,[5] $[Hg(O_2CMe)_2(PBu^t_3)]$,[1] $[Cu(ClO_4)\{P(C_6H_{11})_3\}_2]$,[6] $[\{Hg(NO_3)_2[P(C_6H_{11})_3]\}_2]$,[7] and $[Hg(SCN)_2\{P(C_6H_{11})_3\}]$[8] in our laboratory have established[9] experimental θ values for PBu^t_3 and $P(C_6H_{11})_3$ and led us to define 'ligand profiles'[1,7,9] to describe the bulkiness of the phosphorus ligands. For both ligands the values of θ are far from constant; they range from 176 to 187°, and 163 to 181° respectively.

As an extension of these structural studies of steric effects in phosphine complexes, we report the *X*-ray single-crystal analysis of *trans*-$[PtI_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ (1), which was undertaken for a comparison of steric interactions involving the phosphorus ligands with those previously reported for *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ (2)[10] and other bulky phosphine complexes.

TABLE 1

Selected * bond lengths (Å) and angles (°) with standard deviations in parentheses

Pt–I	2.622(1)	P–C(11)	1.841(9)
Pt–P	2.348(2)	P–C(21)	1.846(8)
		P–C(31)	1.845(8)
C(1)–Cl(1)	1.69(2)		
C(1)–Cl(2)	1.93(2)	mean P–C	1.844(1)
C(1)–Cl(3)	1.42(2)	mean C–C (phenyl)	1.40(1)
I–Pt–P	93.3(1)	mean $C(sp^2)$–$C(sp^3)$	1.49(1)
Pt–P–C(11)	116.7(3)		
Pt–P–C(21)	107.4(3)		
Pt–P–C(31)	117.4(3)	C(11)–P–C(21)	107.4(4)
		C(11)–P–C(31)	100.9(4)
		C(21)–P–C(31)	106.1(4)

* Other geometric data have been deposited as supplementary material.

RESULTS AND DISCUSSION

Table 1 contains selected bond lengths and angles and their standard deviations calculated using the covariance matrix. The crystal structure (Figure 1) consists of discrete centrosymmetric molecules of *trans*-$[PtI_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ [(1), Figure 2] with the platinum co-ordination necessarily planar because of space-group requirements. Each dichloromethane solvent molecule is disordered over three sites around a crystallographic two-fold axis. The pattern of contacts between the disordered solvent and the molecules of (1) corresponds to normal van der Waals contacts with the shortest being a Cl ··· H distance of 2.73 Å.

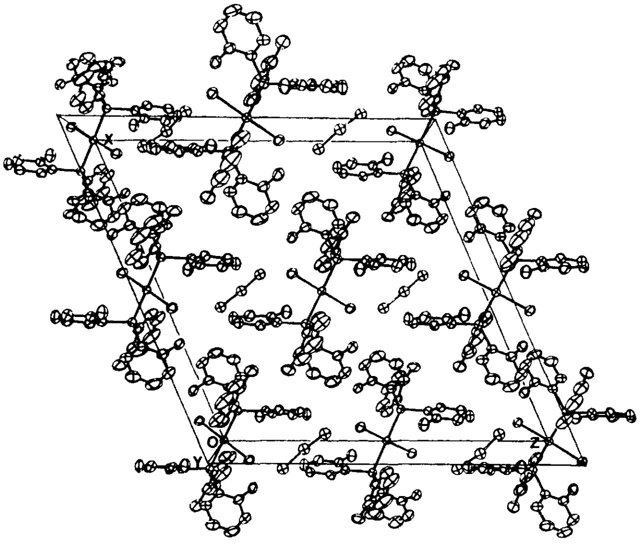

FIGURE 1 A view of the crystal packing viewed down *b*. For clarity only one of the disordered dichloromethane molecules is shown

The molecular structure of (1) has several features in common with *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ (2)[10] and *trans*-$[IrCl(CO)\{P(C_6H_4Me\text{-}o)_3\}_2]$ (3).[11] In both platinum complexes (1) and (2), crowding of the bulky co-ordinated ligands causes the Pt–P distances [2.371(2) and 2.348(2) Å in (2) and (1) respectively] to be larger than the corresponding distances found in the uncrowded, unstrained, *trans* complexes $[PtBr_2(PEt_3)_2]$ [2.315(4) Å] [12] and $[PtH_2\{P(C_6H_{11})_3\}_2]$ [2.25(1) Å].[13] The Pt–I distances [2.612(1) and 2.622(1) Å in (2) and (1) respectively] are larger than 2.598 Å, a value calculated [10] from covalent radii. No significant deviations from previously reported values are observed for the remaining bond lengths and angles.

From the co-ordinates of Table 1 we have calculated the cone angle θ for this overcrowded tri-*o*-tolylphosphine to be 183°, a value identical to that which we obtained from the published co-ordinates of (3), but 15° smaller than the 198° value found for this ligand in the less crowded $[\{HgCl(ClO_4)[P(C_6H_4Me\text{-}o)_3]\}_2]$ structure.[9] In the corresponding isostructural tricyclohexylphosphine complex (2) similar overcrowding by the bulky iodine atoms also causes the $P(C_6H_{11})_3$ cone angle (163°) to be 15° smaller than the value found for the uncrowded ligand.[9]

The steric requirements of phosphine ligands are more adequately represented by ligand profiles,[1,7,9] examples of which, from (1) and (3) for the $P(C_6H_4Me\text{-}o)_3$ ligand, are shown in Figure 3. From the similarity of the two profiles, the conformations of the ligands are seen to be essentially identical in the two complexes (1) and (3). Also obvious from this representation is the way in which the iodine atoms fit in the gaps between the *o*-tolyl groups. The departure of the I–Pt–P angles from 90° (to 93.3 and 86.7°) is simply a consequence of intramolecular packing.

The i.r. and ^{31}P n.m.r. spectroscopic data for (1) and $[PtCl_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ (4) are consistent with the structure shown in Figure 2. A far-i.r. band at 345 cm^{-1} may be assigned to ν(Pt–Cl) of (4). The absence of an i.r. band due to ν(Pt–Cl) is noteworthy for the iodo-complex; the assignment of a ν(Pt–I) stretching frequency [14] was precluded by the 200-cm^{-1} limitation of our spectrometer. The values of $^1J(^{195}Pt\text{–}^{31}P)$ are also in the range expected for *trans*-$[PtX_2(PR_3)_2]$ complexes.[15,16] According to the bond length–coupling constant correlation described by Pidcock and his co-workers,[16] complex (1) would be expected to have a Pt–P distance of 2.26 Å. The longer observed distance is attributable (see above) to the steric effect of the bulky phosphine.

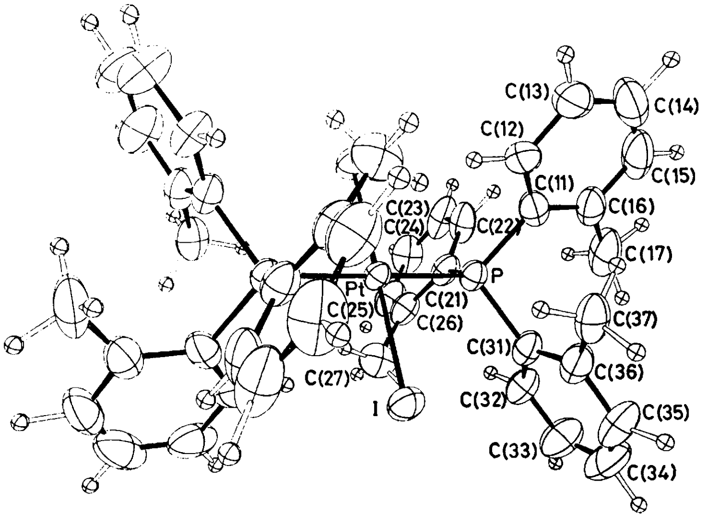

FIGURE 2 The molecular structure of complex (1)

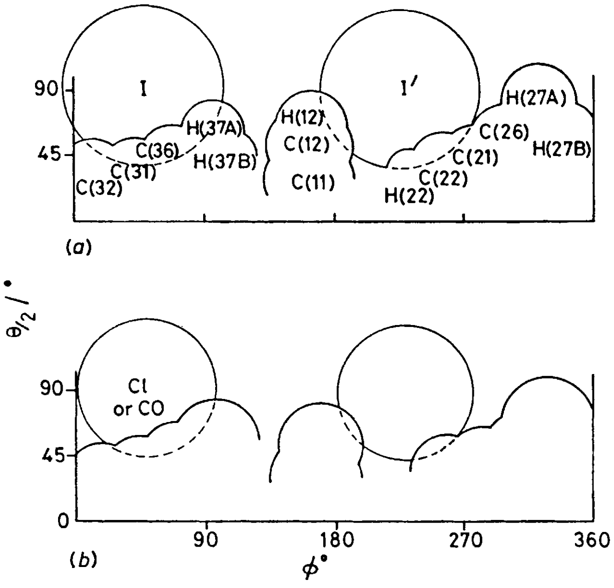

FIGURE 3 Ligand profiles for (*a*) *trans*-$[PtI_2\{P(C_6H_4Me\text{-}o)_3\}_2$ (*b*) *trans*-$[IrCl(CO)\{P(C_6H_4Me\text{-}o)_3\}_2]$. For details of construction, see ref. 1 and 9

Shaw and his co-workers [15] have shown that t-butyl and *o*-tolyl substituents on tertiary phosphine ligands promote internal metal–carbon bond formation in platinum(II) and palladium(II) complexes, with the rate of ring formation increasing in the order Pt > Pd and I > Br > Cl. The ready intramolecular metallation of PBu^t_3 with platinum(II) and palladium(II) [17] is in accord with the bulkiness of the phosphine being an important factor in such metallations. However, Bennett and Longstaff [18] apparently did not observe similar ring formation in the reactions of $P(C_6H_4Me\text{-}o)_3$ with Pt^{II} and Pd^{II} [in contrast to ring-closure reactions with rhodium(III) chloride]. Cheney and Shaw [15b] observed that $PBu^t_2(C_6H_4Me\text{-}o)$ is bulkier and metallates more readily than $PBu^t(C_6H_4Me\text{-}o)_2$.

In the present work our attempts to observe metallated products from *trans*-$[PtX_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ were unsuccessful and it is not clear which of the thermodynamic or kinetic effects important in metallation reactions [15] is the dominant factor. The orientation of the *o*-tolyl substituents and resulting barrier to rotation, as described by the 'ligand profile,' is presumably a major factor in the inability of these complexes to undergo intramolecular metallation.

EXPERIMENTAL

The title complex (1) was obtained by metathesis from the chloro-complex (4) using NaI. Since repeated attempts to prepare (4) by the literature method [18] were unsuccessful, two new synthetic routes were developed. In the first,

$P(C_6H_4Me\text{-}o)_3$ and $PtCl_2$ were heated under reflux under dinitrogen in a 2 : 1 mol ratio for 18 h in dry degassed chloroform. The pale yellow precipitate was washed with diethyl ether and recrystallized from dichloromethane (Found: C, 57.8; H, 4.80. $C_{42}H_{42}Cl_2P_2Pt$ requires C, 57.65; H, 4.85%), m.p. (decomp.) 266—272 °C; ν(Pt–Cl) at 345 cm^{-1} (Nujol mull, CsI plates). N.m.r. spectra: $\delta(^{31}P)$ 17.0 p.p.m. (downfield relative to 85% H_3PO_4, dimethyl sulphoxide and chloroform solutions), $^1J(^{195}Pt\text{–}^{31}P)$ 2 603 Hz; $\delta(^1H)$ 1.25 (Me), 7.0—7.7 p.p.m. (aromatic) (deuteriochloroform solution).

The second method involved heating $P(C_6H_4Me\text{-}o)_3$ and $[PtCl_2(NCPh)_2]$ under reflux in a 2.25 : 1 mol ratio under dinitrogen for 20 h in dry degassed benzene. The pale yellow solid which had precipitated after 2 h was collected on a frit, washed with benzene and diethyl ether, and dried *in vacuo*. Purification was effected by Soxhlet extraction with chloroform. This product was shown to be (4) by elemental analysis, a mixed m.p. with the product of the first method, and ^{31}P n.m.r. spectroscopy. Using dichloromethane rather than benzene as the solvent in the second method led to the isolation of $[PtCl_2(NCPh)\{P(C_6H_4Me\text{-}o)_3\}]$ and starting materials.

The metathetical reaction was effected in dry acetone from (4) using a two-fold excess of anhydrous NaI and a reflux time of 4 h. Concentration of the reaction mixture to dryness left a yellowish orange residue (1.28 g) which on Soxhlet extraction with dichloromethane deposited orange crystals of (1) (Found: C, 46.55; H, 4.15. $C_{42}H_{42}I_2P_2Pt$ requires C, 47.7; H, 4.00%), m.p. (decomp.) 255—258 °C. The *X*-ray analysis subsequently revealed the presence of dichloromethane solvent molecules in the crystal lattice; the analytical data are consistent with the presence of 0.4—0.6 mol of solvent per mol of platinum complex in the material analysed. N.m.r. spectra: $\delta(^{31}P)$ 3.7 p.p.m. (in $CHCl_3$), $^1J(^{195}Pt\text{–}^{31}P)$ 2 502 Hz; $\delta(^1H)$ 1.58 (Me), 6.8—7.7 p.p.m. (aromatic) (in $CDCl_3$).

Attempts to induce metallation of (1) or (4) by refluxing in 2,2-dimethoxypropane solution (8 h), bis(2-methoxyethyl) ether (24 h), ethylene glycol (24 h), water containing 1 mol equivalent of sodium acetate (18 h), and, for (4), ethylene glycol (7 d) led only to reduction to Pt^0 and/or recovery of starting material.

Crystal Data.—$C_{42}H_{42}I_2P_2Pt\cdot CH_2Cl_2$, $M = 1\,142.5$, Monoclinic, $a = 22.100(3)$, $b = 9.961(3)$, $c = 21.516(3)$ Å, $\beta = 113.19(1)°$, $U = 4\,354$ Å^3, $Z = 4$, $D_c = 1.74$ g cm^{-3}, $F(000) = 2\,200$, space group Cc (C_s^4, no. 9) or $C2/c$ (C_{2h}^6, no. 15) from systematic absences $h0l$ when $l = 2n + 1$ and hkl when $h + k = 2n + 1$ ($C2/c$ from successful refinement), Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 46.2$ cm^{-1}.

Preliminary Weissenberg and precession photographs provided unit-cell dimensions which were refined by least-squares treatment of the diffractometer co-ordinates of 12 reflections for which θ(Mo-K_α) was between 10 and 20°. Three-dimensional diffractometer data for all reflections with $\theta \leqslant 25°$ were collected by our standard method.[19] Lorentz and polarization corrections were applied, but not absorption corrections since the square cross-section of the particular crystal used would minimize intensity losses due to absorption. 3 074 Independent reflections had $I \geqslant 3\sigma(I)$ and were retained as the observed data.

The non-hydrogen atoms were located by Patterson and Fourier methods and refined * by full-matrix techniques using anisotropic temperature factors, weights derived from counting statistics, and the scattering factors of ref. 20. All hydrogen atoms were located from a difference synthesis at $R = 0.043$ and were included in the subsequent calculations with scattering factors from ref. 21. The phenyl hydrogens were constrained to ride with the carbon atoms to which they are bonded (C–H 1.08 Å) and were given a single overall isotropic temperature factor U which refined to 0.10(1) Å^2. The methyl hydrogens were refined as fixed groups (C–H 1.08 Å, H–C–H 109.5°) with an overall temperature factor U which refined to 0.13(2) Å^2.

The dichloromethane solvent molecules are disordered equally over three sites such that the carbon atom is located on the crystallographic two-fold axis surrounded by chlorine atoms. After elimination of the 002 reflection because of suspected extinction problems, final values of R and R' [$= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$] are 0.036 and 0.048 respectively.

TABLE 2

Final co-ordinates (fractional, × 10^5 for Pt and I; × 10^4 for P and C; × 10^3 for Cl and H) with standard deviations in parentheses

	x/a	y/b	z/c
Pt	0	0	0
I	5 421(3)	−15 656(6)	−6 159(3)
P	1 016(1)	595(2)	852(1)
C(11)	1 250(5)	2 379(9)	902(4)
C(12)	800(5)	3 226(9)	410(5)
C(13)	949(7)	4 594(11)	375(8)
C(14)	1 560(9)	5 045(13)	842(10)
C(15)	2 002(7)	4 228(15)	1 306(8)
C(16)	1 865(5)	2 881(11)	1 349(5)
C(17)	2 400(6)	2 075(14)	1 874(6)
C(21)	987(4)	131(9)	1 670(4)
C(22)	1 061(5)	1 159(12)	2 142(4)
C(23)	990(5)	884(15)	2 739(5)
C(24)	853(6)	−405(13)	2 879(5)
C(25)	788(5)	−1 423(12)	2 422(5)
C(26)	823(4)	−1 176(10)	1 798(4)
C(27)	678(6)	−2 303(10)	1 317(5)
C(31)	1 761(4)	−211(9)	834(4)
C(32)	2 078(5)	−1 208(11)	1 304(5)
C(33)	2 641(6)	−1 810(14)	1 297(6)
C(34)	2 879(6)	−1 491(14)	832(7)
C(35)	2 564(6)	−485(14)	351(6)
C(36)	2 001(5)	187(10)	338(5)
C(37)	1 706(5)	1 255(11)	−186(5)
C(1)	5 000	−811(37)	2 500
Cl(1)	422(1)	−34(2)	233(1)
Cl(2)	445(1)	8(2)	168(1)
Cl(3)	466(1)	−45(2)	291(1)
H(12)	34	280	8
H(13)	60	520	−2
H(14)	168	608	81
H(15)	246	464	166
H(17A)	222	161	221
H(17B)	269	139	172
H(17C)	269	295	211
H(22)	118	216	203
H(23)	102	169	309
H(24)	80	−62	33
H(25)	71	−243	255
H(27A)	22	−217	90
H(27B)	107	−251	117
H(27C)	64	−306	165
H(32)	188	−147	167
H(33)	288	−259	166
H(34)	331	−199	82
H(35)	276	−20	−1
H(37A)	120	106	−47
H(37B)	177	225	3
H(37C)	198	119	−50

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* Fourier and least-squares calculations were performed using the program system SHELX written by G. M. Sheldrick, University Chemical Laboratory, Cambridge.

Atomic co-ordinates and their standard deviations are given in Table 2. A list of calculated and observed structure factors, thermal parameters, bond lengths and angles in the phenyl rings, and an analysis of variance calculated after the final refinement cycle have been deposited as Supplementary Publication No. 22470 (26 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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