Crystal Structures of Three Palladium Complexes with *ortho*-Phenylenebis(methylphenylarsine) Ligands

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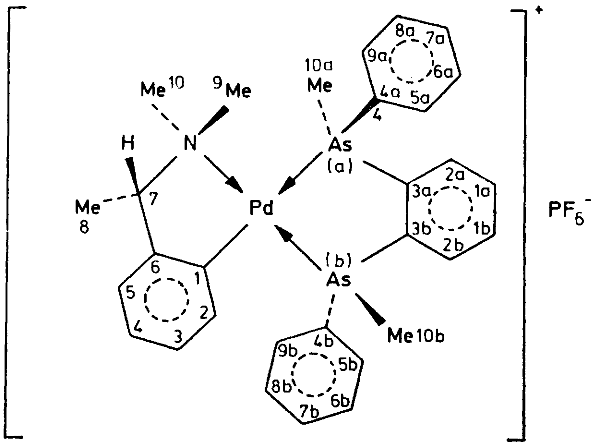
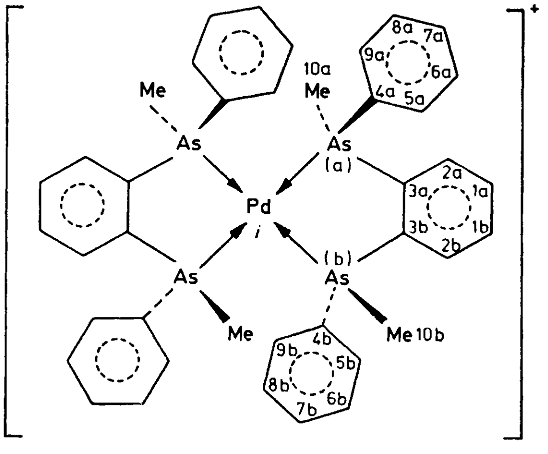
The absolute configuration of $(+)_{589}$-(*RR*)-*ortho*-phenylenebis(methylphenylarsine) has been determined from the crystal and molecular structure of the internal diastereoisomer $(+)_{589}$-[*S*-dimethyl(α-methylbenzyl)aminato-C^2,*N*][*SS*-*ortho*-phenylenebis(methylphenylarsine)]palladium(II) hexafluorophosphate, (1). The absolute configuration of the parent *S*-dimethyl(α-methylbenzyl)amine previously assigned spectroscopically is incidentally confirmed also. Also reported are the structure determinations of *meso*-bis[*RR*,*SS*-*ortho*-phenylenebis(methylphenylarsine)]palladium(II)-dichloride and -di-iodide [(2) and (3) respectively], the former as its ethane-1,2-diol solvate. Crystals of (1) are orthorhombic, space group $P2_12_12_1$, a = 18.309(7), b = 15.376(6), c = 11.333(4) Å, Z = 4; those of (2) are monoclinic, space group $C2/c$, a = 27.467(7), b = 9.573(2), c = 21.067(4) Å, β = 125.39(1)°, Z = 4, while those of (3) are monoclinic, space group $P2_1/c$, a = 9.689(2), b = 22.006(4), c = 10.007(1) Å, β = 108.23(1)°, and Z = 2.

A PREVIOUS paper[1] has described the resolution of the chelating ditertiary arsine *racemic-ortho*-phenylenebis-(methylphenylarsine) into its enantiomers by fractional crystallisation of internal diastereoisomeric palladium(II) complexes containing optically active *ortho*-metallated dimethyl(α-methylbenzyl)amines; the free arsine ligand can then be obtained by cyanolysis of the palladium complex. In order to establish the absolute configuration of the dissymmetric tertiary arsines, the *X*-ray crystal-structure determination of the complex $(+)_{589}$-[*S*-dimethyl(α-methylbenzyl)aminato-C^2,*N*][*SS*-*ortho*-phenylenebis(methylphenylarsine)]palladium(II) hexafluorophosphate,(1),† has been carried out and is reported in this paper. (As well as determining the arsenic chirality absolutely by this method, that chirality has also been determined relative to that of the amine moiety; the chirality of the latter has been previously established spectroscopically,[2] so that the present result also confirms that assignment independently and consistently.)

The *racemic* ditertiary arsine reacts with solutions of palladium(II) chloride to give an equilibrium mixture of the internally diastereoisomeric complexes [Pd(ditertiary arsine)$_2$]Cl$_2$.[1] Isolation of the internally compensated *meso* form and crystallization from aqueous ethanol yielded the dihydrate in a form unsuitable for *X*-ray structure determination; subsequently a more suitable form was obtained as the bis(ethane-1,2-diol) solvate from ethylene glycol solution. Both the chloride (2) and the iodide (3) yielded conductivities and n.m.r. spectra in solution indicative of associated chloride and iodide species; accordingly the present report also describes the structure determination of *meso*-bis[*RR*,*SS*-*ortho*-phenylenebis(methylphenylarsine)]palladium(II)-dichloride–ethane-1,2-diol (1/2) and -di-iodide, (2) and (3), in order to confirm the assignment of configuration and ascertain the extent of any palladium–anion interaction.



(1)



Cl⁻ (2)
I⁻ (3)

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For all three compounds, data were measured at 295(1) K using a Syntex $P\bar{1}$ four-circle diffractometer, equipped with a monochromatic Mo-K_α radiation source (λ 0.710 69 Å), and using a conventional θ—2θ scan mode. Unique data sets were measured to within a preset $2\theta_{max.}$ limit, except in the case of (1) where an independent set of ' Friedel pairs ' was measured as well to $2\theta_{max.}$ 20° to support assignment of the absolute configuration. The unique data sets each com-

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† $(^+)_{589}$-[*S*-2-(1′-Dimethylaminoethyl)phenyl-C^1N][*SS*-*ortho*-phenylenebis(methylphenylarsine)]palladium(II) hexafluorophosphate.

prised $n(I)$ independent intensities; of these $n(I_0)$ with $I > 3\sigma(I)$ were considered ' observed ' and used in the structure determination and refinement after absorption correction. All structures were solved by the heavy-atom method. Refinement of the structures was basically by 9 × 9 block-diagonal least squares; however, the parameters of the palladium atoms and their immediate environment were refined jointly as single blocks. Hydrogen atoms were included in the refinement with constrained positional parameters corresponding to trigonal or tetrahedral sites, and thermal parameters as isotropic estimates. Non-hydrogen atom thermal parameters were refined anisotropically throughout, except for one of the glycol molecules in (2) which was found to have the carbon atoms disordered equally over two orientations; the thermal parameters of the disordered carbon atoms were refined isotropically. Reflection weights used in the refinements were $[\sigma^2(F_0) + 0.000\,5(F_0)^2]^{-1}$. Neutral-atom scattering factors were used

TABLE 1

Individual crystal data

Compound	(1)	(2)	(3)
Formula	$C_{30}H_{34}As_2F_6NPPd$	$C_{44}H_{52}As_4Cl_2O_4Pd$	$C_{40}H_{40}As_4I_2Pd$
M	809.8	1 121.9	1 180.6
Symmetry	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P2_1/c$
a/Å	18.309(7)	27.467(7)	9.689(2)
b/Å	15.376(6)	9.573(2)	22.006(4)
c/Å	11.333(4)	21.067(4)	10.007(1)
β/°		125.39(1)	108.23(1)
U/Å^3	3 190(2)	4 516(2)	2 026.4(6)
D_m/g cm^{-3}	1.69(1)	1.66(1)	1.95(1)
D_c/g cm^{-3}	1.69	1.65	1.94
Z	4	4	2
F(000)	1 608	2 240	1 128
μ_{Mo} (cm^{-1})	26.6	33.7	50.6
R	0.050 *	0.051	0.065
R'	0.060 *	0.055	0.074
S	1.44	1.41	1.9
Specimen size/mm	0.50 × 0.32 × 0.37	0.07 × 0.30 × 0.10	0.15 × 0.11 × 0.30
$n(I)$	4 070	3 014	3 662
$n(I_o)$	2 384	1 648	1 903
$2\theta_{max.}$/°	55	45	50

* R,R' (alternative hand): 0.065, 0.071.

TABLE 2

Non-hydrogen atom fractional cell parameters (× 10^4) of complex (1)

Atom	x	y	z
Pd	3 042.5(5)	2 600.8(6)	1 265.3(9)
(a) Ligand 1, part a			
As	4 229.7(7)	2 015.2(9)	625.7(12)
C(1)	4 528(9)	−609(10)	−342(15)
C(2)	4 659(9)	281(11)	−157(16)
C(3)	4 099(7)	787(8)	281(13)
C(4)	4 946(6)	1 940(8)	1 894(11)
C(5)	4 723(7)	2 052(8)	3 023(12)
C(6)	5 212(8)	1 996(9)	3 946(13)
C(7)	5 942(8)	1 798(8)	3 724(14)
C(8)	6 166(8)	1 688(8)	2 598(16)
C(9)	5 700(7)	1 741(8)	1 655(12)
C(10)	4 803(9)	2 440(12)	−675(16)
(b) Ligand 1, part b			
As	2 659.7(7)	1 149.6(8)	1 250.5(13)
C(1)	3 869(9)	−958(9)	36(15)
C(2)	3 323(7)	−485(8)	480(12)
C(3)	3 443(7)	406(8)	599(11)
C(4)	1 830(7)	876(7)	267(11)
C(5)	1 769(8)	1 342(8)	−806(12)
C(6)	1 207(8)	1 106(11)	−1 576(14)
C(7)	766(8)	391(11)	−1 312(17)
C(8)	847(8)	−39(11)	−286(16)
C(9)	1 389(7)	154(10)	482(15)
C(10)	2 467(10)	591(10)	2 739(12)
(c) Ligand 2			
N	3 313(6)	3 947(7)	1 357(11)
C(1)	2 084(6)	3 051(8)	1 893(11)
C(2)	1 501(7)	2 644(9)	2 454(11)
C(3)	929(7)	3 084(10)	2 946(12)
C(4)	876(8)	3 959(11)	2 853(13)
C(5)	1 420(8)	4 388(8)	2 255(13)
C(6)	2 017(7)	3 980(7)	1 789(11)
C(7)	2 592(7)	4 433(8)	1 161(15)
C(8)	2 406(9)	4 474(11)	−174(15)
C(9)	3 560(8)	4 125(8)	2 567(15)
C(10)	3 873(8)	4 258(12)	516(17)
(d) The anion			
P	8 344(2)	2 330(3)	3 719(5)
F(1)	7 809(8)	1 637(9)	4 072(20)
F(2)	8 956(10)	1 782(12)	3 997(34)
F(3)	8 292(12)	1 953(14)	2 488(15)
F(4)	8 888(11)	3 016(12)	3 355(17)
F(5)	8 377(10)	2 804(12)	4 915(14)
F(6)	7 694(9)	2 880(9)	3 444(21)

TABLE 3

Non-hydrogen atom co-ordinates (× 10^4) for complex (2)

	Ligand part a			Ligand part b		
Atom	x	y	z	x	y	z
As	1 857.0(6)	2 568(2)	417.6(7)	1 965.2(6)	4 558(2)	−735.4(8)
C(1)	850(6)	6 113(16)	197(8)	929(6)	6 962(16)	−263(9)
C(2)	1 144(5)	4 837(15)	428(6)	1 269(6)	6 589(13)	−518(7)
C(3)	1 484(5)	4 402(14)	169(6)	1 535(5)	5 247(13)	−317(6)
C(4)	2 187(6)	2 304(14)	1 494(7)	1 307(5)	4 369(13)	−1 833(7)
C(5)	2 747(6)	2 797(14)	2 056(8)	1 011(7)	3 127(16)	−2 091(8)
C(6)	2 995(7)	2 558(21)	2 827(8)	520(7)	3 012(18)	−2 860(8)
C(7)	2 689(8)	1 932(16)	3 065(9)	328(6)	4 124(17)	−3 346(8)
C(8)	2 125(8)	1 467(18)	2 519(9)	639(7)	5 355(18)	−3 085(9)
C(9)	1 864(6)	1 618(18)	1 723(8)	1 113(7)	5 483(16)	−2 326(7)
C(10)	1 173(6)	1 354(15)	−141(8)	2 421(6)	6 093(14)	−734(8)
Pd	2 500(—)	2 500(—)	0 000(—)			
Cl	1 683(2)	−257(5)	−1 227(2)			
Glycol molecules						
O	336(5)	1 249(16)	758(7)	497(5)	906(14)	2 192(7)
C	216(8)	−106(20)	435(10)	11(19)	480(39)	2 267(19) *
				90(16)	1 551(34)	2 324(19) *

* Population 0.5.

throughout, Cl^- and I^- excepted, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[3-5] Computation was carried out using the '*X*-Ray '76 ' program system implemented on a CYBER 73 computer.[6] The assignment of absolute configuration of (1) is made on the basis of a ratio test on the residuals (Table 1). Individual crystallographic data specific to each compound are given in Table 1. Carbon-atom numbering for the complex ion in each compound is given above; hydrogen-atom numbering follows that of the present carbon in each case, with suffixes α, β, and γ where necessary for distinguishing purposes. Non-hydrogen atom parameters are given in Tables 2, 3, and 4 for complexes (1), (2), and (3) respectively. Material deposited comprises tables of structure factor amplitudes, thermal parameters, and hydrogen-atom parameters.*

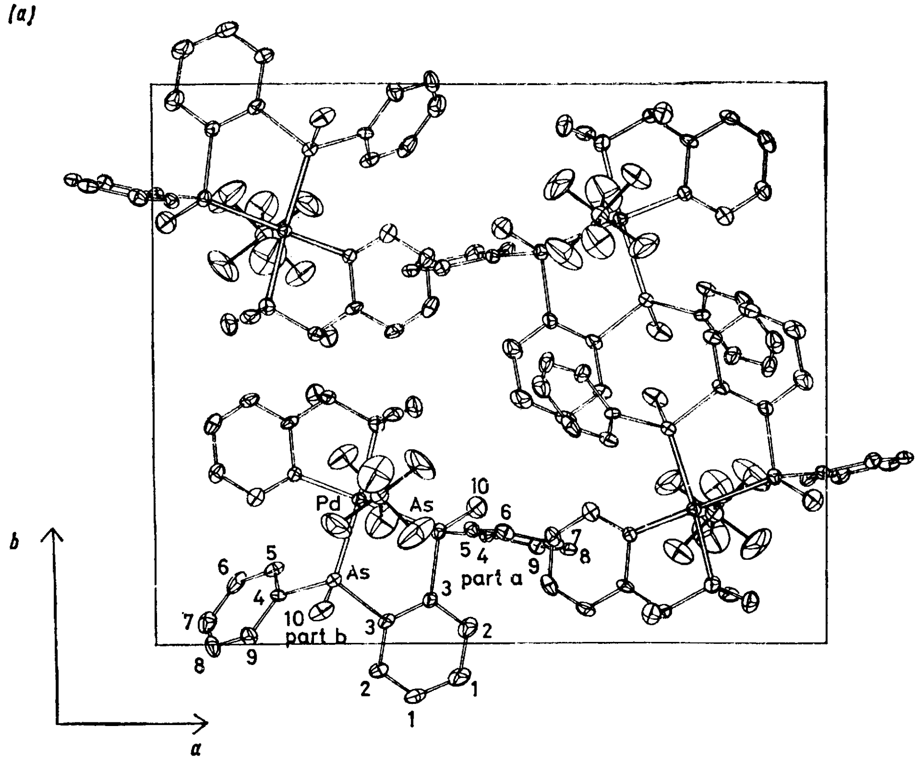
TABLE 4

Non-hydrogen atom co-ordinates (× 10^4) for complex (3)

	Ligand part a			Ligand part b		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
As	2 027(2)	673.7(7)	771(2)	931(2)	−440.7(7)	2 301(2)
C(1)	4 305(20)	971(8)	5 028(20)	3 861(17)	491(8)	5 678(16)
C(2)	3 779(16)	1 034(7)	3 587(18)	2 855(16)	63(7)	4 922(16)
C(3)	2 758(14)	609(6)	2 806(15)	2 329(14)	137(6)	3 438(14)
C(4)	1 804(15)	1 531(6)	338(15)	2 027(15)	−1 173(6)	2 442(14)
C(5)	2 706(28)	1 818(9)	−243(35)	1 995(19)	−1 622(8)	3 363(20)
C(6)	2 529(40)	2 391(11)	−605(44)	2 708(24)	−2 172(9)	3 366(23)
C(7)	1 448(25)	2 732(8)	−452(27)	3 555(22)	−2 245(9)	2 484(21)
C(8)	485(21)	2 453(9)	34(27)	3 623(22)	−1 788(9)	1 630(22)
C(9)	660(19)	1 845(8)	436(25)	2 852(20)	−1 258(7)	1 575(17)
C(10)	3 711(16)	422(8)	199(19)	−374(17)	−621(8)	3 375(19)
Pd	0 000(—)	0 000(—)	0 000(—)			
I	−1 896(2)	974.8(7)	2 293(2)			

DISCUSSION

(*a*) *Overall Structural Features.—Complex* (1). The asymmetric unit of the structure comprises the formula unit consisting of an anion-cation pair; although Figure 1(*a*) suggests the possibility of a close interaction between the two species, this is illusory and there is no close Pd · · · F contact less than 4.3 Å. The thermal motion of the PF_6^- species is high and may account for the distortions observed from ideal octahedral geometry (Table 5); the latter, however, may also be a consequence to some extent of close hydrogen contacts [F(2) · · · H(11a)($\frac{3}{2} - x$, $\bar{y}$, $\frac{1}{2} + z$), 2.5 Å; F(6) · · · H(12b) ($1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$), 2.4 Å]. This appears unlikely, however, as there is no evidence from the thermal parameters that the amplitudes of vibration of F(2,6) are at all diminished by these ' interactions.' The absolute chirality of the



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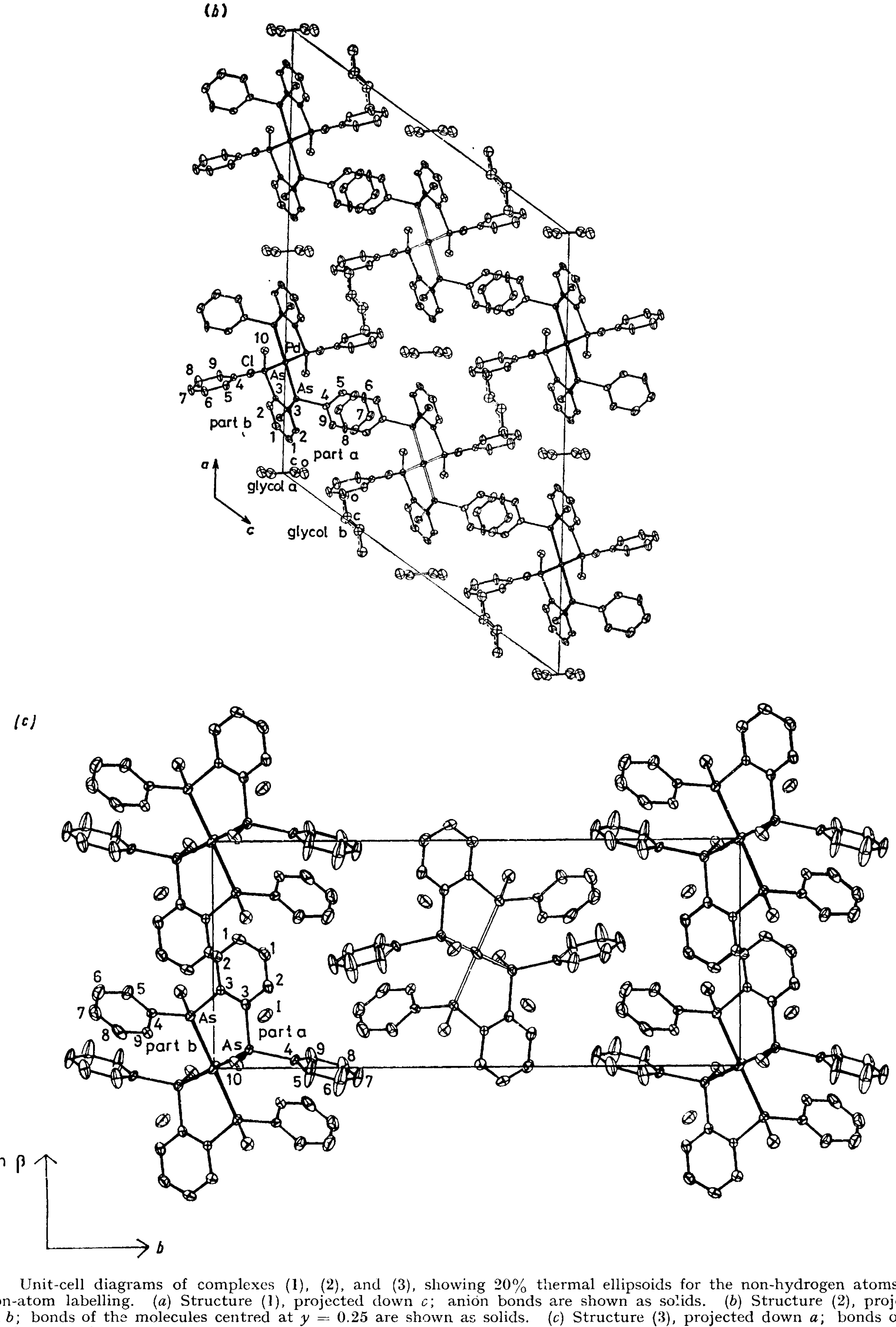
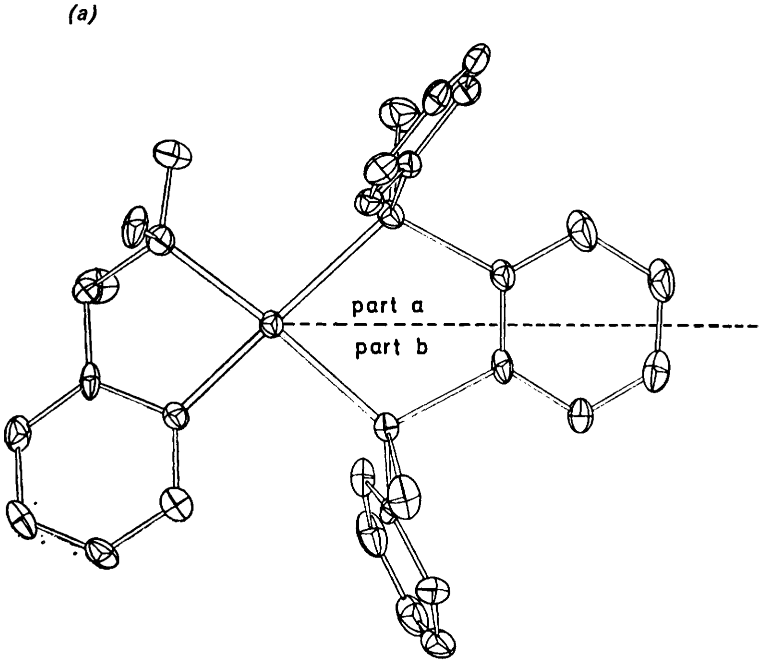
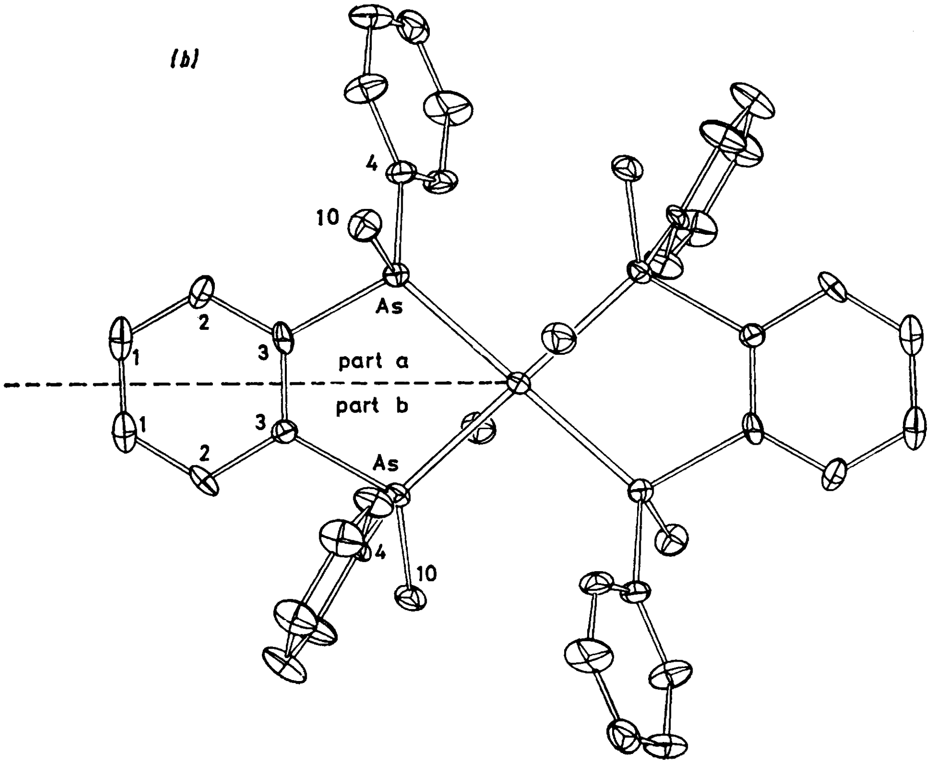


FIGURE 1 Unit-cell diagrams of complexes (1), (2), and (3), showing 20% thermal ellipsoids for the non-hydrogen atoms and carbon-atom labelling. (*a*) Structure (1), projected down *c*; anion bonds are shown as solids. (*b*) Structure (2), projected down *b*; bonds of the molecules centred at $y = 0.25$ are shown as solids. (*c*) Structure (3), projected down *a*; bonds of the molecules centred at (0,0,0) are shown as solids. All axial systems are right-handed


(a)
part a
part b


(b)
4
10
As
2
1
3
part a
part b
3
1
2
As
4
10

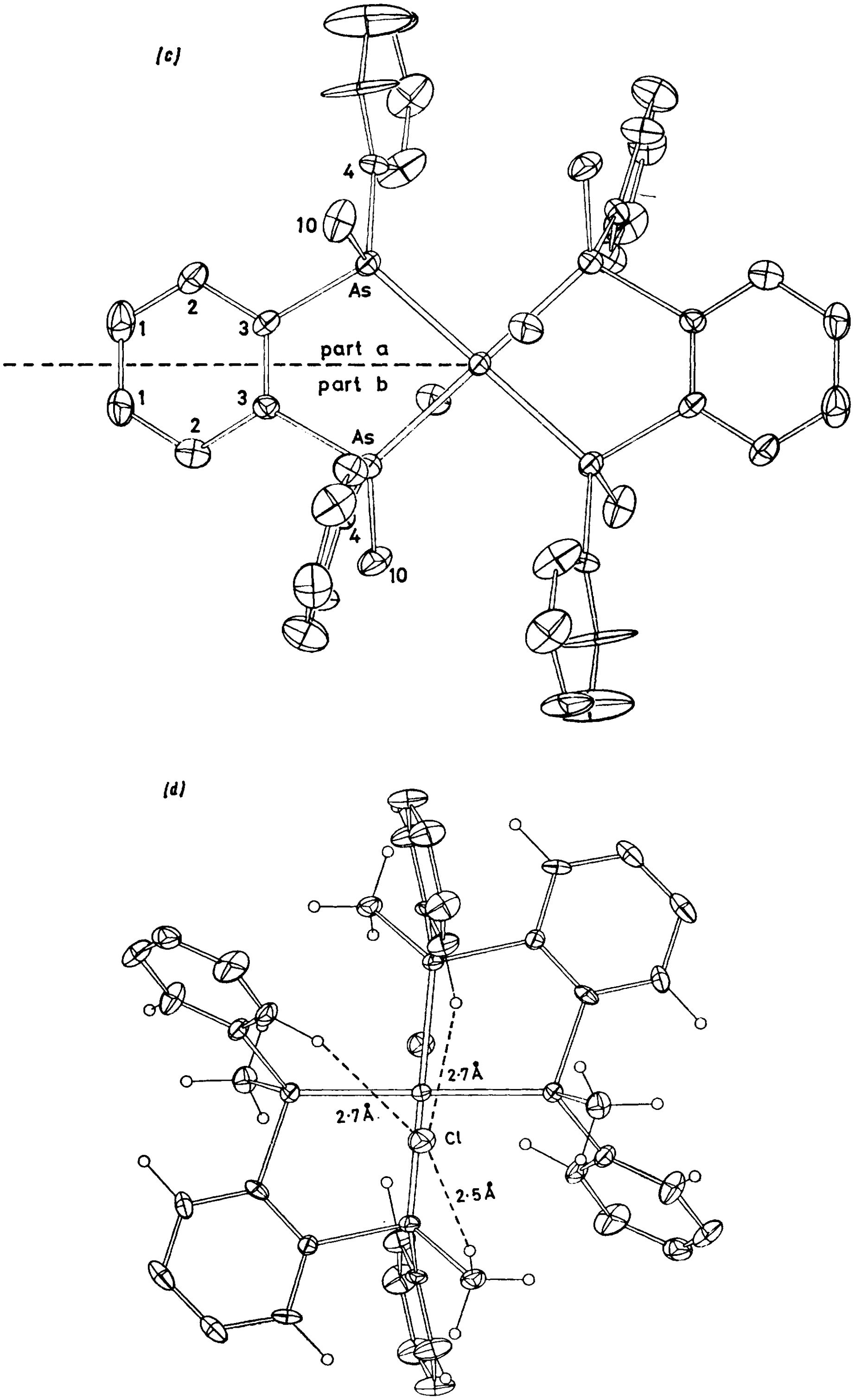


FIGURE 2 Projections of the palladium-containing complex species [(1), (*a*); (2), (*b*) and (*d*); and (3), (*c*)] normal to the plane defined by the palladium atom and its co-ordination environment. In (*b*), (*c*), and (*d*) the pair of nearby halide counter-ions are also shown. In (*d*) the phenyl *ortho*- and the methyl-hydrogen atoms are shown as circles of radius 0.1 Å

cation has been established to be that shown above and in the Figures, confirming that of the amine (previously assigned by spectroscopic means[2]) and establishing that of the arsine ligand both absolutely and relative to that proposed for the amine. The chirality of both arsenic atoms is, of course, the same (*S*).

TABLE 5

Interatomic distances and angles for complex (1) *

Ligand 1		Ligand 2	
(*a*) Distances (Å)			
Pd–As	2.462(2), 2.339(2)	Pd–C(1)	2.02(1)
C(1)–C(1′)	1.39(2)	Pd–N	2.13(1)
C(1)–C(2)	1.41(2), 1.34(2)	C(1)–C(2)	1.39(2)
C(2)–C(3)	1.38(2), 1.39(2)	C(2)–C(3)	1.37(2)
C(3)–C(3′)	1.38(2)	C(3)–C(4)	1.35(2)
C(3)–As	1.94(1), 1.98(1)	C(4)–C(5)	1.37(2)
As–C(10)	1.92(2), 1.93(1)	C(5)–C(6)	1.37(2)
As–C(4)	1.95(1), 1.93(1)	C(1)–C(6)	1.44(2)
C(4)–C(5)	1.35(2), 1.42(2)	C(6)–C(7)	1.45(2)
C(5)–C(6)	1.38(2), 1.40(2)	C(7)–C(8)	1.55(2)
C(6)–C(7)	1.39(2), 1.40(2)	C(7)–N	1.53(2)
C(7)–C(8)	1.35(2), 1.35(3)	N–C(9)	1.47(2)
C(8)–C(9)	1.37(2), 1.35(2)	N–C(10)	1.48(2)
C(9)–C(4)	1.44(2), 1.40(2)		
The anion			
P–F(1)	1.50(2)	P–F(4)	1.51(2)
P–F(2)	1.44(2)	P–F(5)	1.54(2)
P–F(3)	1.51(2)	P–F(6)	1.49(2)
(*b*) Angles (°)			
As–Pd–As′	85.04(6)	C(1)–Pd–N	81.5(4)
C(1′)–C(1)–C(2)	119(1), 124(1)	Pd–C(1)–C(2)	132(1)
C(1)–C(2)–C(3)	118(1), 117(1)	Pd–C(1)–C(6)	113(1)
C(2)–C(3)–C(3′)	120(1), 122(1)	C(2)–C(1)–C(6)	115(1)
C(2)–C(3)–As	122(1), 119(1)	C(1)–C(2)–C(3)	123(1)
C(3′)–C(3)–As	118(1), 119(1)	C(2)–C(3)–C(4)	121(1)
Pd–As–C(3)	107.8(4), 109.7(4)	C(3)–C(4)–C(5)	118(1)
Pd–As–C(4)	113.5(4), 116.6(3)	C(4)–C(5)–C(6)	123(1)
Pd–As–C(10)	125.6(5), 118.3(4)	C(5)–C(6)–C(1)	120(1)
C(3)–As–C(4)	100.0(5), 103.2(5)	C(5)–C(6)–C(7)	123(1)
C(3)–As–C(10)	104.1(7), 101.7(6)	C(1)–C(6)–C(7)	117(1)
C(4)–As–C(10)	102.6(6), 105.3(6)	C(6)–C(7)–N	109(1)
As–C(4)–C(5)	119(1), 117(1)	C(6)–C(7)–C(8)	110(1)
As–C(4)–C(9)	121(1), 122(1)	N–C(7)–C(8)	110(1)
C(5)–C(4)–C(9)	120(1), 120(1)	C(7)–N–Pd	105.5(7)
C(4)–C(5)–C(6)	121(1), 118(1)	C(7)–N–C(9)	108(1)
C(5)–C(6)–C(7)	120(1), 120(1)	C(7)–N–C(10)	110(1)
C(6)–C(7)–C(8)	119(1), 121(2)	Pd–N–C(9)	107.3(8)
C(7)–C(8)–C(9)	123(1), 122(1)	Pd–N–C(10)	116.3(9)
C(8)–C(9)–C(4)	118(1), 119(1)	C(9)–N–C(10)	109(1)
Other angles about the palladium atom			
As(a)–Pd–C(21)	176.4(3)	As(b)–Pd–C(21)	94.0(3)
As(a)–Pd–N	99.5(3)	As(b)–Pd–N	175.3(3)
Anion angles			
F(1)–P–F(2)	92(1)	F(2)–P–F(6)	178(1)
F(1)–P–F(3)	86(1)	F(3)–P–F(4)	93(1)
F(1)–P–F(4)	179(1)	F(3)–P–F(5)	174(1)
F(1)–P–F(5)	97(1)	F(3)–P–F(6)	89(1)
F(1)–P–F(6)	86(1)	F(4)–P–F(5)	83(1)
F(2)–P–F(3)	92(2)	F(4)–P–F(6)	94(1)
F(2)–P–F(4)	87(1)	F(5)–P–F(6)	87(1)
F(2)–P–F(5)	93(2)		

* For ligand 1, the two entries are for parts a and b respectively; primed atoms lie in the other half of the molecule.

Complex (2). The asymmetric unit of the structure is comprised of one half of the formula unit. The complex palladium species lies with the palladium situated on a crystallographic inversion centre so that the two ligands are centrosymmetrically related and of opposite chirality, consistent with the formulation of the complex as *meso*. A pair of symmetry-related chlorine species lie above and below the co-ordination plane of the palladium. Two independent glycol molecules are found, only one half of each being crystallographically independent. One is ordered and lies with the centre of the C–C bond at a crystallographic inversion centre; the other is disordered, and lies located about a crystallographic two-fold axis. The one independent oxygen of the latter glycol molecule is well defined as occupying only a single site, but the

TABLE 6

Interatomic distances and angles *

	(2)		(3)	
	a	b	a	b
(*a*) Distances (Å)				
Pd–X	3.459(4)		3.985(2)	
Pd–As	2.387(2)	2.409(1)	2.388(2)	2.399(2)
As–C(10)	1.92(1)	1.93(2)	1.97(2)	1.94(2)
As–C(3)	1.95(1)	1.95(2)	1.94(1)	1.94(1)
As–C(4)	1.91(1)	1.95(1)	1.93(1)	1.91(1)
C(3)–C(3′)	1.37(2)		1.35(2)	
C(2)–C(3)	1.39(3)	1.42(2)	1.41(2)	1.42(2)
C(1)–C(2)	1.39(2)	1.37(3)	1.38(3)	1.40(2)
C(1)–C(1′)	1.38(3)		1.38(3)	
C(4)–C(5)	1.37(2)	1.36(2)	1.35(4)	1.36(2)
C(5)–C(6)	1.37(2)	1.39(2)	1.31(3)	1.39(3)
C(6)–C(7)	1.34(3)	1.35(2)	1.34(4)	1.39(4)
C(7)–C(8)	1.36(2)	1.37(2)	1.33(4)	1.33(3)
C(8)–C(9)	1.40(2)	1.36(2)	1.39(3)	1.38(3)
C(4)–C(9)	1.39(3)	1.36(2)	1.34(3)	1.36(3)
As(a) · · · As(b)	3.234(3)		3.241(2)	
(*b*) Angles (°)				
As(a)–Pd–As(b)	84.78(6)		85.23(5)	
Pd–As–C(10)	115.2(6)	117.9(4)	113.8(5)	120.0(4)
Pd–As–C(4)	119.4(5)	119.2(4)	120.7(4)	116.5(4)
Pd–As–C(3)	108.2(5)	106.8(4)	106.7(4)	106.4(4)
C(10)–As–C(4)	105.7(7)	103.2(6)	104.7(7)	103.3(7)
C(10)–As–C(3)	101.9(5)	107.7(3)	102.8(7)	105.4(7)
C(3)–As–C(4)	104.6(6)	100.3(6)	106.6(6)	103.8(5)
As–C(3)–C(3′)	118(1)	119(1)	119(1)	119(1)
As–C(3)–C(2)	122(1)	121(1)	120(1)	120(1)
C(3′)–C(3)–C(2)	120(1)	120(2)	121(1)	121(1)
C(1)–C(2)–C(3)	121(2)	118(1)	119(2)	117(1)
C(1′)–C(1)–C(2)	118(2)	123(1)	120(2)	122(1)
As–C(4)–C(5)	120(1)	119(1)	121(1)	122(1)
As–C(4)–C(9)	121(1)	121(1)	122(1)	119(1)
C(5)–C(4)–C(9)	119(1)	120(1)	117(2)	118(1)
C(4)–C(5)–C(6)	120(2)	119(1)	122(3)	121(2)
C(5)–C(6)–C(7)	122(1)	121(1)	123(4)	119(2)
C(6)–C(7)–C(8)	119(2)	120(1)	117(2)	119(2)
C(7)–C(8)–C(9)	121(2)	120(2)	121(2)	122(2)
C(8)–C(9)–C(4)	118(1)	121(1)	120(2)	121(2)
X–Pd–As	89.9(1)	104.68(7)	87.74(5)	76.56(5)

(*c*) The glycol molecules in complex (2)

(*i*) Molecule (a)

C(a)–C(a′)	1.51(2)	C(a)–O(a)	1.41(2)
C(a′)–C(a)–O(a)	105(1)		

(*ii*) Molecule (b)

O(b)–C(b)	1.49(6)	O(b)–C(bb)	1.44(5)
C(b)–C(bb′)	1.46(6)		

(*d*) Interspecies contacts

(*i*) Complex (2): Cl · · · H(b5), 2.6_5; Cl · · · H(2b) $(x, y - 1, z)$, 2.8_0; Cl · · · H(5a) $(\frac{1}{2} - x, \frac{1}{2} - y, \bar{z})$, 2.7_0; Cl · · · H(10γb) $(\frac{1}{2} - x, \frac{1}{2} - y, \bar{z})$, 2.5_1; Cl · · · H(8a) $(x, \bar{y}, z - \frac{1}{2})$, 2.6_5; Cl · · · H_0 (3′bb) $(x, \bar{y}, z - \frac{1}{2})$, 2.0_4

(*ii*) Complex (3): I · · · H(9a), 2.8_9; I · · · H(10βb), 2.8_8; I · · · H(2b) $(\bar{x}, \bar{y}, 1 - z)$, 2.9_1; I · · · H(9b), $(\bar{x}, \bar{y}, \bar{z})$, 3.0_0

* Primes denote atoms in the other part (a or b) of the molecule or ligand as appropriate.

carbon atom appears to be equally disposed between a pair of sites 1.04(5) Å apart.

Complex (3). Again the asymmetric unit of the structure is comprised of one-half of the formula unit, the palladium atom lying on a crystallographic centre of symmetry, so that the second ligand is inversion related to the first, and the complex *meso*. Again a pair of symmetry-related halide species lie nearby above and below the co-ordination plane of the palladium atom. Because of the *meso* disposition of the two ligands about the palladium atom in (2) and (3), the PdL_2 systems, as well as having exact *i* symmetry, also have pseudo-*m* internal symmetry [Figure 2 (*b*) and (*c*)]. Interatomic distances and angles are given in Table 6.

TABLE 7

Comparison of the arsenic atom environments in complexes (1), (2), and (3) (distances in Å, angles in degrees)

	(1)		(2)		(3)	
	a	b	a	b	a	b
Pd–As	2.462(2)	2.339(2)	2.387(2)	2.409(1)	2.388(2)	2.399(2)
As–Pd–As	85.04(6)		84.78(6)		85.23(5)	
Pd–As–C(3)	107.8(4)	109.7(4)	108.2(5)	106.8(4)	106.7(4)	106.4(4)
Pd–As–C(4)	113.5(4)	116.6(4)	119.4(5)	119.2(4)	120.7(4)	116.5(4)
Pd–As–C(10)	125.6(5)	118.3(4)	115.2(6)	117.9(4)	113.8(5)	120.0(4)
C(3)–As–C(4)	100.0(5)	103.2(5)	104.6(6)	100.3(6)	106.6(6)	103.8(5)
C(3)–As–C(10)	104.1(7)	101.7(6)	101.9(5)	107.7(3)	102.8(9)	105.4(7)
C(4)–As–C(10)	102.6(5)	105.3(6)	105.7(5)	103.2(6)	104.7(7)	103.3(7)

(*b*) *The Palladium Co-ordination Environment.*—In (2) and (3), ⟨Pd–As⟩ are 2.39_8 and 2.39_4 Å respectively, similar to the value determined previously in $[Pd\{C_6H_4(AsMe_2)_2\}_2]I_2$[7] ($2.4_0$ Å). Within each compound, however, the two distances differ significantly: 2.387(2), 2.409(1) Å for (2); 2.388(2), 2.399(2) Å for (3). Although it is tempting to dismiss the differences as trivial, it is nevertheless interesting to observe that in each complex, although the halide species approach the fifth and sixth co-ordination positions they do not do so in a strictly axial sense but instead are offset towards one of the arsenic atoms [As(b)] in each case; it is, in each ligand, the corresponding Pd–As(b) distance which is the longer. It therefore appears likely that the Pd–As(b) distance may be elongated because of partial bond formation *or* charge-transfer interaction between the arsenic atom and the iodine, *or* that some other effect responsible for displacing the iodine from a truly axial position also perturbs the arsenic atom position; the latter appears the more likely and is elaborated below.

In (1), the Pd–As distances are grossly different both from each other and from the values observed in (2) and (3), one bond being very long [2.462(2) Å] and the other very short [2.339(2) Å]; the deviations far exceed any reasonable correction to the geometry for the effects of libration and must, presumably, be ascribed as resulting from the substituent effects of the carbon and nitrogen ligand atoms in the co-ordination sphere of the palladium atom.

(*c*) *The Arsenic Atom Environment.*—In the three complexes considerable variation is found in the palladium–arsenic distances; the precision of determination of the remaining distances about each arsenic atom is much lower, since carbon atoms are involved in each case, and it would be unwise to attribute much significance to any differences observed. By contrast, the differences in the angular geometries about the arsenic atoms are considerable and highly significant; these are compared in Table 7. The variation in any given angular parameter however, does not depend monotonically upon the variation in the most obvious bonding variable, namely the length of the Pd–As bond. This suggests the source of the variations in the angular geometry about the arsenic atom to lie in steric effects associated with the substituents and, possibly, the counter-ion, rather than electronic effects originating in or transmitted by the palladium atom. In all three of the present compounds studied, a number of substantial and significant deviations of the arsenic atom from the associated phenyl–phenylene ring planes are observed (Tables 8, 9), further suggestive of the presence of steric strain or interaction of the system with the counter-ion.

TABLE 8

Phenyl ring planes in complex (1)

Least-squares planes in the form $pX + qY + rZ = s$; the right-hand orthogonal (Å) frame is defined by $X = ax$, $Y = by$, $Z = cz$. Planes are defined by the six carbon atoms of the ring

	Ligand 1			
Phenyl	a	b	Central	Ligand 2
10^4p	1 972	6 382	3 572	4 934
10^4q	9 774	−6 166	−1 597	1 029
10^4r	−757	−4 610	9 203	8 637
s	4.536	1.197	2.787	4.200
σ/Å [a]	0.01	0.02	0.02	0.02
Deviations, δ(*n*), of the defining atoms [b]				
	0.00(4)	−0.03(4)	−0.03(1a)	0.02(1)
	−0.01(5)	0.02(5)	0.03(2a)	−0.02(2)
	0.01(6)	−0.01(6)	−0.01(3a)	0.01(3)
	−0.01(7)	0.01(7)	0.02(1b)	0.01(4)
	0.00(8)	−0.02(8)	0.01(2b)	−0.02(5)
	−0.00(9)	0.03(9)	−0.01(3b)	0.00(6)
Deviations of other atoms				
Pd	0.36	−0.77	−0.12	0.20
As(a)	−0.03	(1.51)	0.14	0.55
As(b)	(−1.96)	0.17	−0.03	−0.39
θ [c]	83.1	79.8	4.6	17.2

[a] Estimated standard deviation of defining atom. [b] δ(*n*) is the deviation from the plane of carbon atom C(*n*) in Å. [c] Angle with the $PdAs_2CN$ plane.

This appears to be a manifestation of a more general phenomenon. In all metal complexes so far studied crystallographically in which the metal atom is chelated by a diarsine-type ligand, it has been found that the metal atom deviates from the ligand plane by an amount which varies; a dihedral angle significantly different from zero has been found in all cases between the MAs_2 plane and the phenylene-ring plane. The origin of this distortion is somewhat obscure; in bis[*o*-phenylenebis(dimethylarsine)] metal derivatives it has been thought to possibly arise from interactions between the methyl groups of the opposed ligands where these are co-ordinated in a square or equatorial plane about the metal; if this were so, it might be expected that the magnitude of the dihedral angle might correlate with some parameter of the system relating to the distance apart of these groups (such as the metal–arsenic distance or As • • • As distance) but in the examples so far available, no such correlation appears to exist (Table 10).

In the present examples, similar dihedral angles are found. That for (1) is rather smaller than that of the others [6.1°; *cf.* 13.0(2), 16.3(3)°], and in view of the nature of the second ligand in that complex, would tend to support the above hypothesis. In (2) and (3), however, given the potential *2* symmetry of each ligand, rather than the *mm* symmetry of those previously studied, it might be expected that interligand inter-

TABLE 9

Phenyl ring least-squares planes of complexes (2) and (3)

The form of the plane is $pX + qY + rZ = s$; the right-hand orthogonal (Å) frame is defined by $X = ax + cz \sin \beta$, $Y = by$, $Z = cz \sin \beta$

	(2)			(3)		
Defining atoms	C(1a)—(3a) C(1b)—(3b)	C(4a)—(9a)	C(4b)—(9b)	C(1a)—(3a) C(1b)—(3b)	C(4a)—(9a)	C(4b)—(9b)
10^4p	4 185	4 795	9 208	−8 228	2 761	6 046
10^4q	4 129	−8 773	−2 858	5 594	2 710	3 842
10^4r	8 089	−234	−2 656	1 002	9 222	6 977
s	3.587	0.006	5.003	−0.467	1.634	1.365
σ/Å [a]	0.02	0.02	0.01	0.01	0.02	0.02
δ (defining atoms)/Å						
C(1a), (4a), (4b)	−0.02	0.01	0.00	0.00	0.03	−0.01
C(2a), (5a), (5b)	0.02	−0.02	0.00	−0.01	−0.02	0.03
C(3a), (6a), (6b)	0.01	0.02	0.01	0.01	−0.01	−0.02
C(1b), (7a), (7b)	0.00	0.00	−0.02	0.00	0.03	0.00
C(2b), (8a), (8b)	0.02	−0.01	0.02	0.00	−0.01	0.02
C(3b), (9a), (9b)	−0.03	0.01	−0.01	−0.01	−0.01	−0.01
δ (other atoms)/Å						
As(a)	−0.07	0.02		−0.05	−0.08	
As(b)	−0.17		−0.11	−0.01		−0.10
Pd	0.27	1.19	0.64	0.47	−1.63	−1.36
C(10)		0.49	0.61		−0.23	−0.51
θ [b]	13.0			16.3		

[a] Estimated standard deviation of defining atom. [b] Dihedral angle of the $PdAs_4$ plane with the central aromatic ring.

TABLE 10

Dihedral angles (θ/°) between the MAs_2 and phenylene-ring planes for square-planar bis(diarsine ligand)–metal arrays, together with mean metal–arsenic distance and intra- and inter-ligand As • • • As distances, r and s (Å). Distances to the fifth and sixth ligand atoms, X, are also given (Å)

Compound	θ	⟨M–As⟩	r	s	M–X
$[PdI_2\{C_6H_4(AsMe_2)_2\}_2]$ [a]	2.7	2.40	3.25	3.53	3.40
$[PtI_2\{C_6H_4(AsMe_2)_2\}_2]$ [b]	12.5	2.38	3.25	3.47	3.50
$[PtCl_2\{C_6H_4(AsMe_2)_2\}_2]$ [c]	9.0	2.38	3.19	3.52	4.16
$[NiI_2\{C_6H_4(AsMe_2)_2\}_2]$ [d]	10.4	2.29	3.17	3.31	3.22
$[Co(ClO_4)_2\{C_6H_4(AsMe_2)_2\}_2]$ [e]	12	2.30	3.14	3.36	3.30
$[AuI_3\{C_6H_4(AsMe_2)_2\}_2]$ [f]	28	2.45			3.35
$[CoCl_2\{C_6H_4(AsMe_2)_2\}_2][ClO_4]$ [g]		2.34	3.25	3.37	2.22
$[NiCl_2\{C_6H_4(AsMe_2)_2\}_2]Cl$ [h]		2.36			2.43
$[NiCl_2\{C_6H_4(AsMe_2)_2\}_2]Cl$ [i]	9	2.34	3.21	3.40	2.43
$[CoCl_2\{C_6H_4(AsMe_2)_2\}_2]Cl$ [i]	9	2.33	3.20	3.40	2.26
$[Co\{C_6H_4(AsMe_2)_2\}_2(NO)(NCS)][NCS]$ [j]	15	2.35	3.18	3.42	1.87 (NO) 2.13 (NCS)
$[PdCl_2\{C_6H_4(AsMePh)_2\}_2]\cdot 2C_2H_6O_2$ [k]	13.0	2.40	3.23	3.54	3.46
$[PdI_2\{C_6H_4(AsMePh)_2\}_2]$ [k]	16.3	2.39	3.24	3.52	3.99

[a] Ref. 7. [b] N. C. Stephenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 791. [c] N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 1517. [d] N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 592. [e] F. W. B. Einstein and G. A. Rodley, *J. Inorg. Nuclear Chem.*, 1967, **29**, 347. [f] V. F. Duckworth, C. M. Harris, and N. C. Stephenson, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 419. [g] P. J. Pauling, D. W. Porter, and G. B. Robertson, *J. Chem. Soc. (A)*, 1970, 2728. [h] P. Kreisman, R. Marsh, J. R. Preer, and H. B. Gray, *J. Amer. Chem. Soc.*, 1968, **90**, 1067. [i] P. K. Bernstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 3040. [j] J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, 1975, **14**, 624. [k] This work [compounds (2) and (3)].

actions might cause a twisting of the arsenic atoms relative to the phenylene ring so that they or their substituents distort alternate sides of the ring plane. That this does not occur may not be strange in view of the overall potential pseudo-*m* symmetry of the complex, and its inversion symmetry, but the approach of the nearby halide ions is also unsymmetric. In short, given the unsymmetric nature of the substituents and their possible interactions it is perhaps significant that the distortion of the ligand–metal system is of the type already observed in more symmetrical systems.

TABLE 11

Least-squares planes in the forms and frames defined, for the palladium atom and the four near, square-planar co-ordinating atoms of complexes (1)—(3). Deviations of the arsenic substituent atoms are given

	(1)	(2)	(3)
10^4p	2 997	2 611	−6 923
10^4q	−1 100	5 735	6 366
10^4r	9 477	7 765	3 398
s	2.623	3.166	0.000
δC(3a)	−0.21	0.49	0.52
δC(4a)	1.80	1.18	1.12
δC(10a)	−1.12	−1.72	−1.79
δC(3b)	−0.16	0.49	0.48
δC(4b)	−1.48	−1.69	−1.68
δC(10b)	1.57	1.17	1.20

(*d*) *The Arsenic Substituent Dispositions.*—In the following paper,[8] we have reported the structure determinations of some related *ortho*-phenylenebis(methylphenylphosphine) ligand species; the disposition of the phenyl groups has been examined and related to the deviation of the methyl groups from the plane of the central aromatic ring by way of the torsion angle about the arsenic–phenyl bond, a close correlation existing between the two. For the present compounds, these and related relevant parameters are given in Tables 8—12. The following features are noted.

(i) Because of chelation of the palladium atom in each complex by the arsenic atoms of the ligand, the tetrahedral lone-pair sites of the arsenic atoms will be closely constrained towards the plane of the central aromatic ring in the present compounds; in the phosphines, it has been argued that substituent and lone-pair interaction in the absence of the metal is minimized by the molecule adopting a conformation in which the substituents are unsymmetrically disposed. It is noteworthy in *all* of the present examples that the methyl and phenyl carbon atoms associated with any given arsenic are not evenly disposed on either side of the central-ring plane but are skewed. In (2) and (3), in part a, the methyl lies closer to the plane than the phenyl, while the converse is true for part b (Table 9). In (1) the situation is more involved; the palladium atom is not located on a crystallographic symmetry element and is chelated by only one diarsine ligand, and a large *trans* effect is observed. The disposition of the substituent atoms on the two arsenics about the central plane differs, and it is not clear at this stage which factors predominate in causality. However, it would be expected that, for those arsenic atoms for which the substituent carbons lie evenly disposed relative to the central-ring plane, the lone pair should lie in that plane also and be ascribed with a stronger Pd–As bond; this is in fact true of part b of compound (1), the only segment for which this disposition is found, and in which Pd–As is the shortest observed.

TABLE 12

Deviations of C(10) from the central phenylene-ring plane (δ/Å), together with the torsion angles τ = C(10)–As–C(4)–C(5,9)(°)

Molecule/ part	δC(10)	τ
(1a)	−0.95	150.1, −31.9
(1b)	1.54	168.5, −22.9
(2a)	−1.83	166.6, −13.8
(2b)	0.96	158.0, −26.7
(3a)	−1.90	0.5, 172.2
(3b)	1.19	−12.0, 166.7

(ii) For the present diarsine ligands, the substituent carbon atom dispositions are such that all methyl-carbon atoms are well out of the central-ring plane; the C(10)–As–C(4)–C(5,9) torsion angles should thus be nearer 0 or 180 than 90°; this is in fact so. Given the fact that in (2) and (3) the palladium is co-ordinated by a pair of ligands of opposite chirality, we find that the substituent protrusion from the molecular plane is such that, whereas the same substituents of the two halves of the same ligand lie on opposite sides of the plane, the same substituents from adjacent arsenic atoms of different ligands lie on the same side of the plane and adjacent to each other. Given the constraints already operative within the isolated ligand (*cf.* ref. 8), we find that the As–C(4) bonds from the different ligands must run parallel to each other (or nearly so); for (2) and (3), this As · · · As separation is 3.542(2), 3.523(2) Å and it also follows that, irrespective of the methyl dispositions, the two associated phenyl rings must lie nearly parallel to each other and normal to the molecular plane (Figure 2), and should play a considerable part in dictating the methyl disposition and the deviation of the arsenic-atom lone pairs from that plane (Figure 2).

(*e*) *Interactions between the Halide Species and the Palladium Complex.*—As indicated above, the n.m.r. spectra of (2) and (3) in solution are indicative of strong association between the halide and the complex species. It is common in cation–anion systems of the present type, involving a 'square-planar' cation, for the anion to approach the fifth and sixth co-ordination sites of the metal, and the present study was undertaken to ascertain whether the spectroscopic perturbations could be accounted for simply on the basis of a weak interaction of a van der Waals or ion-pairing type or whether a stronger interaction involving a genuinely higher co-ordination number is involved. Relevant is the previous structure determination of di-iodobis[*o*-phenylenebis(dimethylarsine)]palladium(II) (4).[7] In the latter, as in (2) and (3), the palladium atom lies on a crystallographic inversion centre, with close, centrosymmetrically related, halide contacts in the fifth and sixth co-ordination positions (Pd · · · I, 3.40 Å); in the latter, the species is referred to as the ' di-iododi[*o*-phenylenebis(dimethylarsine)]palladium(II) *molecule* ' (our italics) on the grounds of this interaction and the assignment of the species in nitrobenzene solution as $[Pd(diarsine)_2I]^+$ on the basis of conductivity measurements. In the present studies, we find no significant anion–palladium interaction in (1). In (2) and (3), the palladium atoms, sited on crystallographic inversion centres, are approached in the fifth and sixth co-ordination positions by halide species at distances Pd • • • Cl, 3.459(4) (2) and Pd • • • I, 3.985(2) Å.

The interaction of the halide ions with the ligand substituents is of interest in (2) and (3). As noted above, the substituent groups at the arsenic atoms do not dispose themselves equally about the ligand plane; on one side of the plane C(4b) and C(10a) stand well out at distances greater than 1.7 Å, while on the other C(4a) and C(10b) lie closer to the plane at distances between 0.9 and 1.2 Å. Inspection of Figure 2 shows the halide ion in projection above and below the plane of the four arsenic atoms. It lies almost within the $PdAs_2$ angle of one ligand on the side of those substituents that lie nearer the plane; its position is biased towards the methyl group of part b of the ligand and almost coincides in projection with the Pd–As(b) bond. Of the four substituents, two methyl and two phenyl groups which surround it, only three have significant hydrogen-atom contacts to it: two come from the methyl and phenyl *ortho* hydrogens of the ligand containing it in projection, and the other from the nearby phenyl group of the other ligand. The halide ion rests above this tripod array of hydrogen atoms, the two phenyl hydrogen legs being close together (Table 13), and well removed from the fourth (methyl) substituent on that side; its position is essentially the approximate centre of gravity of the three interactions, and it is the ligand with only one interaction rather than two in which the substituents stand well out of the plane. Seemingly, the interspecies interactions, here with halide ions, may be determinants to some extent of the distortions observed in the metal–ligand systems. Conversely, they also preclude a closer approach of the halide in (2) and (3), although the results for complex (4) indicate that in a less sterically hindered system a stronger interaction is possible.

TABLE 13

Anion–cation hydrogen interactions (Cl,I • • • H < 3.0 Å) for complexes (2) and (3). Only the hydrogen atom is specified

(2) *		(3)	
H(5b)	2.6_5	H(9a)	2.8_9
H(2b^{I}))	2.8_0	H(10βb)	2.8_8
H(5a^{II})	2.7_0	H(2b^{I})	2.9_1
H(10γb^{II})	2.5_1	H(9b^{II})	3.0_0
H(8a^{III})	2.6_6		

Angles(°) subtended by the intermolecular hydrogen contacts

H(10γb^{II}) · · · H(5b)	126	H(10βb) · · · H(9b^{II})	111
H(10γb^{II}) · · · H(5a^{II})	132	H(10βb) · · · H(9a)	119
H(5b) · · · H(5a^{II})	58	H(9b^{II}) · · · H(9a)	63

Transformations of the asymmetric unit:

I	$(x, y - 1, z)$	$(\bar{x}, \bar{y}, 1 - z)$
II	$(\frac{1}{2} - x, \frac{1}{2} - y, \bar{z})$	$(\bar{x}, \bar{y}, \bar{z})$
III	$(x, \bar{y}, z - \frac{1}{2})$	

* Also: H_0 (3bb'^{II}) 2.0_4 (one of the disordered glycol hydrogen atoms; estimated).

(f) *Substituent Interactions within the One Ligand.*—Interactions between the substituent hydrogen atoms are presumed to be of the type discussed at greater length in the following paper;[8] the phenyl *o*-hydrogen nearest the methyl is assumed to be straddled by two of the methyl-hydrogen atoms, the net interaction being insufficient to cause abnormal enlargement of the C(4)–As–C(10) angles or of the *o*–C–C(4)–As angle. In the case of the methyl groups in (2) and (3) which do not interact with the halogen, it is a consequence of this methyl orientation which does not permit direct confrontation of the remaining hydrogen with the halide; in the case of the methyl group which *does* interact, the hydrogen is directed immediately towards the halide.

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REFERENCES

[1] N. K. Roberts and S. B. Wild, *J.C.S. Dalton*, 1979, 2015.

[2] J. C. Craig, R. P. K. Chan, and S. K. Roy, *Tetrahedron*, 1967, **23**, 3573.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] ' The *X*-Ray System—Version of March, 1976,' ed. J. M. Stewart, Technical Report, TR–446, Computer Science Centre, University of Maryland, U.S.A.

[7] N. C. Stephenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 797.

[8] N. K. Roberts, B. W. Skelton, and A. H. White, following paper.