Pyramidal Five-co-ordination with Flattened Tetrahedral Basal Bonds. Crystal and Molecular Structures of Dibromotris-(5-ethyl-5*H*-dibenzophosphole)palladium(II)–Chlorobenzene, Dibromotris-(5-ethyl-5*H*-dibenzophosphole)platinum(II)–Bromobenzene, and Dibromotris-(5-methyl-5*H*-dibenzophosphole)platinum(II)–Bromobenzene

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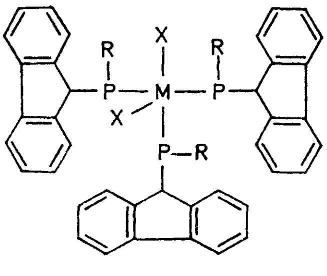
In the molecules of the title compounds one bromine atom is at the apex of a distorted tetragonal pyramid which has the five-co-ordinate metal atom in the centre of the base. The other bromine atom and the three phosphorus atoms lie in basal positions. The angle between apical and basal bonds is greater than 90° for the bromine atom (mean 100°) and for the phosphorus atom *trans* to it (mean 108°). The similar angles for the other two phosphorus atoms are less than 90° (both mean 86°). The basal bonds are directed to the corners of a flattened and distorted tetrahedron.

The apical bond is always longer by at least 0·4 Å than the metal–bromine basal bond. Differences in apical bond length between the closely related Pd and Pt compounds (1) and (2) with identical ligands, and between the two platinum compounds (2) and (3) which differ only in alkyl substituent (Me or Et) are discussed. The former is a chemical effect, the latter may, in part, arise from intermolecular effects. The bond from M to the phosphorus atom *trans* to the basal bromine is *ca.* 0·06 Å shorter than the other M–P bonds.

The plane of one phosphole ligand L(I) is steeply inclined to those of the others L(II), L(III). An interaction is found between L(II), *trans* to the basal bromine, and L(III) which brings them parallel plane-to-plane and makes the angle P(II)–M–P(III) < P(II)–M–P(I) by *ca.* 5·4°.

The detailed stereochemistry of the metals is explained in terms of steric effects and ligand interaction.

FIVE-co-ordinate complexes $NiL_3(CN)_2$,[1] [L = 5-R-5*H*-dibenzophosphole, (4*a*), (4*b*) R = Me,† (5) R = Et], show either trigonal bipyramidal or tetragonal pyramidal bonds for the nickel atom and one compound has been obtained in both sterochemical forms. The proximity and parallelism of two of the ligands L suggests a possible interaction between them, but this does not determine the stereochemistry of the nickel atom. A crystal structure investigation of other members of the general series ML_3X_2, in which M and X are varied, has been undertaken in order to determine whether the ligand interaction persists and whether the stereochemistry of the metal is affected. In this paper X = Br and M = Pd or Pt.



	R	M	X	Solvent
(1)	Et	Pd	Br	PhCl
(2)	Et	Pt	Br	PhBr
(3)	Me	Pt	Br	PhBr
(4*a*),(4*b*)	Me	Ni	CN	
(5)	Et	Ni	CN	

The structures of the ethyl-substituted palladium compound (1) and the ethyl-substituted platinum compound (2) are very closely related in cell constants and molecular positions, and, although the methyl-substituted platinum compound (3) shows greater differences in cell constants, all three could be described as being isostructural. Intramolecularly (2) and (3) are very closely alike, more so than (1) and (2). Figures 1 and 2 show the asymmetric unit for compounds (1) and (3) respectively. This unit consists of one molecule of the metal complex and one molecule of chlorobenzene or bromobenzene. The three organic ligands

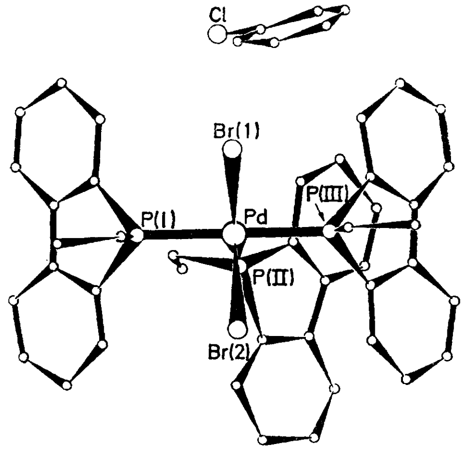


FIGURE 1 The molecules of the structure (1) projected on the best plane through C(α,I), C(α′,I), C(α,III), and C(α′,III)

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† *a* And *b* denote different stereochemistries, for definition, see p. 1882.

[1] H. M. Powell, D. J. Watkin, and J. B. Wilford, *J. Chem. Soc.* (*A*), 1971, 1803.

in each complex are labelled (I), (II), (III) and this labelling, as well as the modification of the normal chemical numbering for the ligand molecule (Figure 3), corresponds with that used for the nickel complexes.

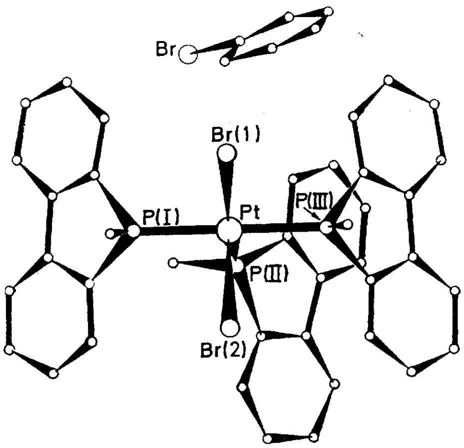

FIGURE 2 The molecules of the structure (3) projected on the best plane through atoms C(α,I), C(α′,I), C(α,III), and C(α′,III)

Ligands (II) and (III) are always nearly parallel plane-to-plane with a separation of 3·35—3·50 Å. Ligands (II) and (III) are distinguished by the choice of angle P(II)–M–P(I) < P(III)–M–P(I), which does not require angle P(II)–M–P(III) to be greater than P(II)–M–P(I) or the converse, but ensures that these two angles are stereochemically comparable.

The arrangement of metal bonds is much the same in all three compounds. It is derivable by small distortions from a square pyramid having the metal atom and four of its attached atoms in the base and one of the bromide atoms at the apex. Independently of valency angles the apex is always distinguishable by a M–Br(2) distance at least 0·4 Å greater than the other metal-bromine distance in the same molecule. The bond arrangement differs from the tetragonal pyramidal form in the nickel complex (4*a*) [1] in two ways. In (4*a*) one phosphorus atom is at the apex and the other two are mutually *trans* in the base, but in the palladium and platinum compounds (1)—(3), three phosphorus atoms are in basal positions; in (4*a*) all four angles, α, between the apical bond and the basal bonds are greater than 90° by 10° or more, but for (1)—(3) they are not.

The stereochemical form differs also from tetragonal pyramids in general found in a variety of complexes formed by nickel and other metals. These usually have all angles α greater than 90°, though in a small group all are less than 90°. In the present compounds the basal bromine atom and the phosphorus atom P(II) *trans* to it have α greater than 90°, the atoms P(I) and P(III) have α less than 90°. The four basal bonds point to the corners of a very flattened tetrahedron. Table 1 summarises this stereochemistry.

Table 1 also reveals regularity in bond lengths. Discussion of apical bond lengths is given on page **1885** in the light of conformational and environmental details. Change from palladium to platinum makes little difference in basal bond lengths, as shown by approximate constancy of values in each of the first four rows of the Table. The distances metal to P(I), P(II), and P(III) are distinguishable, the means being **2·336**, **2·266**, and **2·306** Å. A M–P(II) distance smaller than M–P(I) or M–P(III) is understandable as being mainly a *trans* effect, this phosphorus being *trans* to Br(1). The atoms P(I) and P(III) are not in exactly equivalent chemical situations because of the L(II) · · · L(III) interaction so a difference in bond length could be explained. The observed difference is small but consistent, and might be real; it is in the right sense for an additional attraction affecting L(III), *i.e.* M–P(III) is shorter than M–P(I). However, if real, the effect should occur in all members of the series though its magnitude could vary with the stereochemistry. In the nickel compounds of ref. 1 and in other compounds,[2] all different stereochemically from (1)—(3), a difference is not observed. A difference in bond length for P(I) and P(III) is therefore much less certain than the difference for P(II) and the others.

TABLE 1

Bond lengths (Å) and angles (°) at the metal atom, with estimated standard deviations in parentheses

	(1)	(2)	(3)
(*a*) Bond lengths			
M–P(I)	2·355(9)	2·342(5)	2·312(5)
M–P(II)	2·294(9)	2·257(5)	2·248(6)
M–P(III)	2·303(9)	2·309(5)	2·306(6)
M–Br(1)	2·555(5)	2·542(3)	2·534(3)
M–Br(2)(apical)	2·936(4)	3·143(3)	3·026(3)
(*b*) Bond angles			
P(I)–M–P(II)	97·95(32)	98·55(18)	98·40(19)
P(I)–M–P(III)	168·67(33)	166·87(17)	168·57(19)
P(II)–M–P(III)	92·79(32)	93·01(17)	92·62(20)
Br(1)–M–P(I)	86·11(24)	85·32(14)	84·86(14)
Br(1)–M–P(II)	147·78(26)	154·56(14)	156·44(15)
Br(1)–M–P(III)	86·73(25)	86·90(13)	86·26(15)
Br(2)–M–P(I)	87·20(23)	86·21(13)	85·90(14)
Br(2)–M–P(II)	108·67(25)	106·47(13)	108·34(15)
Br(2)–M–P(III)	85·94(24)	84·55(12)	88·09(15)
Br(1)–M–Br(2)	103·43(14)	98·85(8)	97·15(8)

The stereochemical behaviour is considered first by reference to the metal atom and its immediate neighbours only. A model of C_{2v} symmetry which retains the pseudo-tetragonal pyramidal angles of (4*a*) but substitutes palladium for nickel and Br for CN, with bond lengths Pd–Br 2·55 and Pd–P(basal) 2·317, has four equal non-bonded distances P · · · Br(basal) 3·37 Å. This calculated value is very close to the distance observed in the different type of tetragonal pyramid actually found for the compound. There is, therefore, no steric factor involving only the basal bromine and phosphorus atoms which could destabilise the form

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[2] H. M. Powell, K. M. Chui, and D. J. Watkin, unpublished work.

having the angles of (4*a*). Other possible steric effects are between the bromine atoms and some of the carbon atoms of the ligands. The shortest contact is calculated at 3·31 Å between Br(2) and carbon atom C(γ) of ligand (I) (Figure 3). In the real structure the distances Br · · · C atoms are $\geqslant$3·8 Å. This may explain why the form of (4*a*), the tetragonal pyramid, is not adopted by the bromides. Similar calculations show a shortest Br · · · C distance of 3·05 Å for a trigonal bipyramidal form with the metal valency angles of the complex (5).[1] Although such considerations may eliminate hypothetical molecular forms obtained by atomic substitution into those already known, they do not cover possible conformational variations and the basic stereochemistry may not be determined by such steric restrictions.

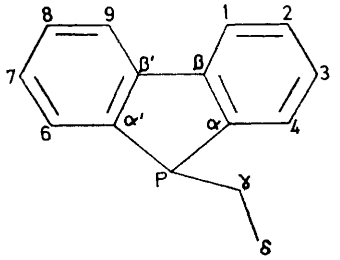

FIGURE 3 The ligand numbering system

If it is assumed that for these compounds the stable form, whether or not steric factors are involved, is basically a tetragonal pyramid with one bromine atom at the apex, the stereochemistry proves to be explicable in great detail in terms of steric effects of the five ligands and the ligand–ligand interaction which has been postulated. First it is necessary to consider the non-bonded P · · · P separation possible in such a compound. Accurate values for observed distances are listed in Table 2. The largest values are in the nickel compounds[1] (4*b*) and (5) although the smallest might be expected since nickel is the smallest of the central atoms. The greater distances arise because the trigonal bipyramidal bonds to phosphorus are equatorial and the angles between them are all greater than 110°. The short distances in the palladium and platinum compounds are accompanied by unusual distortions of angles which increase the distances between basal atoms. This has the appearance of a relief of potential overcrowding. If the overcrowding is a direct effect between phosphorus atoms it is possible to derive an empirical radius for phosphorus atoms applicable to internal contacts. If, however, the overcrowding involves ligand atoms more remote from the central metal, the argument which follows will still hold if the contact radii derived for the phosphorus and bromine are regarded as effective values applicable when these more remote interactions occur.

TABLE 2

P · · · P and P · · · Br distances (Å) with estimated standard deviations in parentheses

Complex	Stereochemistry *	P(I) · · · P(II)	P(III) · · · P(II)	P(I) · · · Br(1)	P(III) · · · Br(1)
(1)	(*c*)	3·508(12)	3·329(12)	3·355(11)	3·341(11)
(2)	(*c*)	3·486(7)	3·313(7)	3·313(6)	3·341(5)
(3)	(*c*)	3·452(8)	3·293(8)	3·274(6)	3·313(6)
(5)	(*b*)	3·940	3·741		
(4*b*)	(*b*)	4·076	3·721		
(4*a*)	(*a*)	3·466(3)	3·401(3)		

* See page 1882 for definition.

When there is overcrowding, as is evident from bond-angle distortion, it is reasonable to take the effective contact radius as half the distance corresponding to minimum overcrowding, *i.e.* the largest distance between two similar atoms which are seen to be displaced so as to increase their separation. This distance for P · · · P is taken as 3·48 Å (the mean of three close values in Table 2); P · · · Br is slightly less (3·36 Å) than this.

The detailed stereochemistry for the palladium compound may now be considered. In the discussion which follows, substitution of platinum for palladium makes only minor changes of detail in the conclusion. From the bond lengths and the empirical contact distances the angles required between adjacent basal bonds are calculated as P–Pd–P 97° 20′ and P–Pd–Br 86° 51′. The sum of the four angles is $8\frac{1}{2}$° greater than 360° and is incompatible with coplanar bonds. Various deviations from coplanarity which allow all the basal angles to take up the required values may be imagined. They will be restricted initially to those which preserve a plane of symmetry relating the bond angles, *e.g.* P(I)–Pd–P(II) and P(III)–Pd–P(II). If the three phosphorus atoms remain in the plane at right angles to the apical bond, the bond to Br(1) must be bent $64\frac{1}{2}$° away from the plane. This gives a stereochemical form which is no longer approximately a tetragonal pyramid.

Any set of small displacements of all four atoms to one side of the plane will make the sum of the angles less than 360° and so will worsen the overcrowding. A large deviation of the Pd–Br(1) bond from the tetragonal pyramidal is avoided only if P(I) and P(III) are on the opposite side of the plane to Br(1). Displacement of P(II) to the same side as P(I) and P(III) causes P(I) and P(III) to move in the direction of the fourth basal position and so forces further deviation of the

Pd-Br bond. Displacement of P(II) to the opposite side to P(I) and P(III) has the opposite effect. The overcrowding may therefore be relieved by allowing the four bonds to displace so that they point towards the corners of a flat tetrahedron. If all bonds were inclined at the *same* angle to the basal plane, either above or below, their directions would be defined and the calculated values for α would be 101 and 79°.

These angles are derived from a consideration of the overcrowding of the four basal atoms only. When the apical Br(2) is taken into account two effects arise. First, since the repulsion will be greater for Br · · · Br than for Br to the neutral phosphorus, the basal bromine and consequently P(II) are the pair below the basal plane; secondly, the repulsion will tend to increase α for every basal bond. Angles α for the bonds to the four atoms are: 103 [Br(1)], 86 [P(I)], 108½ [P(II)], and 86° [P(III)]. They differ by a few degrees, always in the correct sense, from the hypothetical values calculated. To this extent the general explanation based on overcrowding is satisfactory. However, the bond angles as observed are not related by a plane of symmetry. This may be seen from the stereographic projections in Figure 4. The palladium atoms and atoms Br(1), Br(2), and P(II) lie very close to a plane but P(I) and P(III) are not exactly in mirror-image positions relative to this plane. The deviation is not attributable to any effect confined to the metal and its immediate five attached atoms but it can be explained by an interaction of ligands (II) and (III).

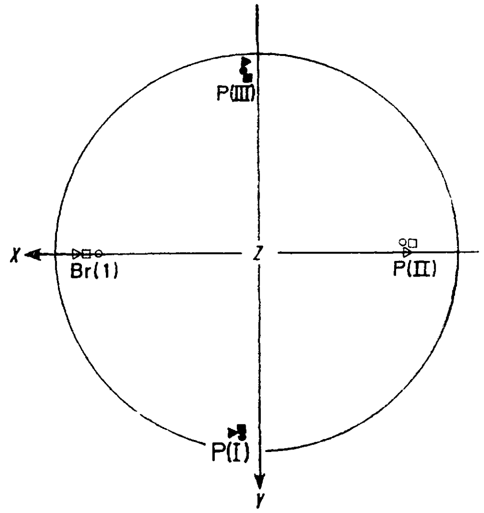

FIGURE 4 Open circle α > 90°, filled circle α < 90° for (1); open triangle α > 90°, filled triangle α < 90° for (3); open square α > 90°, filled square α < 90° for (2); α is the angle between a bond and the *Z* axis

In each of the three nickel compounds $NiL_3(CN)_2$ previously examined[1] two of the dibenzophosphole ligands are arranged close to each other plane-to-plane. The angle P(II)-Ni-P(III) (*A*) of the bonds which link the two ligands concerned is smaller than the angle (*B*) P(II)-Ni-P(I) between the bonds that join non-parallel ligands. The values (*A*) and (*B*) are given in Table 3 together with corresponding angles for the new members of the series ML_3X_2. Among the six compounds the stereochemistry has three different forms: (*a*) distorted tetragonal pyramidal with P(II) apical and P(I) and P(III) *trans* basal, (*b*) distorted trigonal bipyramidal with all phosphorus atoms equatorial, and (*c*) distorted tetragonal pyramidal with all phosphorus atoms basal. If no selective interaction between ligands L is assumed exact equality of (*A*) and (*B*) is still not to be expected since in the polyatomic molecule a particular angle may be influenced by many factors. The difference Δ might be expected to be one or two orders of magnitude less than (*A*) and, for a series of such molecules, to be distributed around zero. Instead the invariable negative values shown in the Table establish the attraction between (II) and (III). The energy of the interaction is small and so the difference in the two angles is relatively small. For the trigonal bipyramidal form (*b*) all three P-M-P angles are stereochemically comparable (ideally 120°).

TABLE 3

Values (°) of angles (*A*) P(II)-M-P(III) and (*B*) P(II)-M-P(I), and (*A*)-(*B*) (=Δ)

Complex	Stereo-chemistry	(*A*)	(*B*)	Δ
(4*a*)	(*a*)	98·1	100·7	−2·6
(4*b*)	(*b*)	110·8	116·3	−5·5
			(132·8) *	(−22·0) *
(5)	(*b*)	111·8	121·6	−10·0
			(126·4) *	(−14·6) *
(1)	(*c*)	92·8	98·0	−5·2
(2)	(*c*)	93·0	98·6	−5·6
(3)	(*c*)	92·6	98·4	−5·3

* Values in parentheses are for angles P(I)-M-P(III) and the difference between (*A*) and this angle.

Form and Disposition of the Phosphole Ligand.—The form of the phosphole ligand is very nearly the same in all positions of all three compounds. To a first approximation it can be related to a best plane through the carbon atoms of the aromatic system. For any one ligand the displacements of individual atoms from the best plane are small and within the range of the standard deviation. However, when all nine indedependent ligands are considered the displacements indicate a slight folding towards a butterfly form. This is apparent also when the planes of the two six-membered rings are considered separately. The angles between the normals to the best planes through them are given in Table 4. This shows a mean value of 3° 49′ with a standard deviation of *ca.* 1° 30′. For the individual ligand the displacement of the phosphorus atom from the best plane through all the non-alkyl carbon atoms is within the standard deviations, but for all nine ligands it is consistently to the side opposite to the wings of the butterfly. The alkyl group is always placed so that there is approximately a plane of symmetry through the whole ligand.

The disposition of the ligands as a whole is next considered. For the nickel compounds it was possible to discuss the ligand positions in relation to a plane in which the three phosphorus atoms lie, either the equatorial plane of a trigonal bipyramid or a plane containing the apical bond and two basal bonds of the tetragonal pyramid. In the present case the distortions make it more convenient to refer the geometry to the apical bond direction, which is completely defined, and a basal plane through the metal atom at right angles to this bond. The apical bond direction is taken as the Z axis. If there were a plane of symmetry of the molecule through Br(1), Br(2), and P(II) the intersection of this with the basal plane would have provided a fixed axis of reference in the plane. In the absence of such symmetry the plane through Br(1), Br(2), and the metal atom is arbitrarily chosen to contain the X axis at right angles to Z. The positive direction of the axes are from the metal atom towards Br(1) and Br(2); Y is taken perpendicular to X and Z in a right-handed system. The directions of the phosphorus–metal bonds are defined by the angles (α, ϕ) of Table 5 where α is the angle between the bond and the Z axis and ϕ is the angle between the XZ plane and the plane containing Z and the bond.

TABLE 4

Inclination of the two six-membered rings

Complex	(I)	(II)	(III)
(1)	0° 36′	4° 24′	5° 54′
(2)	4° 15′	4° 27′	3° 3′
(3)	3° 6′	3° 34′	5° 3′

TABLE 5

Angles defining metal bond directions

Complex		P(I)–M	P(II)–M	P(III)–M
(1)	α	87° 12′	108° 40′	85° 56′
	ϕ	85° 20′	182° 49′	274° 20′
(2)	α	86° 13′	106° 29′	84° 33′
	ϕ	84° 41′	182° 24′	274° 0′
(3)	α	85° 54′	108° 20′	88° 5′
	ϕ	84° 17′	180° 0′	274° 0′

TABLE 6

Rotation angle

Complex	L(I)	L(II)	L(III)
(1)	53° 52′	101° 23′	310° 49′
(2)	48° 47′	112° 7′	307° 37′
(3)	45° 32′	104° 41′	307° 52′

For the phosphole ligands a rotation angle is stated. The plane through the metal, Br(2), and the P atom is imagined as the plane of symmetry of the ligand in a reference position, with P–C(γ) of the alkyl group pointing upwards towards Br(2). The rotation angle given in Table 6 for the ligand is that through which the ligand must then be rotated from the reference position about the metal–phosphorus bond in order that the symmetry plane may reach its observed position.

TABLE 7

Complex	∠ of inclination	Mean sep./Å	∠ of twist
(1)	1° 0′	3·354	22° 0′
(2)	3° 3′	3·387	22° 9′
(3)	5° 45′	3·441	22° 29′

TABLE 8

Atomic co-ordinates for (1), with estimated standard deviations in parentheses

	x/a	y/b	z/c
Pd	0·0267(2)	0·2454(1)	0·0338(3)
Br(2)	0·0981(4)	0·1470(2)	−0·1120(4)
Br(1)	0·1857(4)	0·3632(2)	0·0301(4)
Cl(1)	0·9498(23)	0·4564(16)	0·3215(39)
P(I)	0·1837(9)	0·2301(5)	0·2252(9)
P(II)	−0·1490(9)	0·1853(5)	0·0902(9)
P(III)	−0·0947(9)	0·2653(5)	−0·1717(9)
C(α,I)	0·2228(36)	0·2810(19)	0·3782(32)
C(4,I)	0·2501(34)	0·3592(18)	0·4084(40)
C(3,I)	0·2830(31)	0·3897(22)	0·5343(33)
C(2,I)	0·2750(37)	0·3401(23)	0·6344(35)
C(1,I)	0·2440(38)	0·2714(25)	0·6123(44)
C(9,I)	0·1745(31)	0·1094(24)	0·5295(40)
C(8,I)	0·1319(40)	0·0416(20)	0·4673(55)
C(7,I)	0·1132(40)	0·0219(26)	0·3237(54)
C(6,I)	0·1272(40)	0·0840(17)	0·2499(39)
C(α',I)	0·1550(33)	0·1473(19)	0·3059(39)
C(β',I)	0·1847(32)	0·1642(16)	0·4388(29)
C(β,I)	0·2149(36)	0·2372(19)	0·4788(33)
C(γ,I)	0·3260(28)	0·2420(16)	0·1793(29)
C(δ,I)	0·4418(34)	0·2269(18)	0·2981(39)
C(α,II)	−0·2442(33)	0·0956(16)	0·0054(31)
C(4,II)	−0·2009(36)	0·0410(18)	0·0102(36)
C(3,II)	−0·2965(36)	−0·0256(19)	−0·0623(47)
C(2,II)	−0·4183(35)	−0·0204(17)	−0·1395(38)
C(1,II)	−0·4611(29)	0·0363(17)	−0·1244(32)
C(9,II)	−0·5035(31)	0·1804(16)	−0·0679(29)
C(8,II)	−0·5153(35)	0·2495(25)	−0·0412(38)
C(7,II)	−0·3927(39)	0·3085(23)	0·0434(38)
C(6,II)	−0·2821(32)	0·2852(21)	0·0699(38)
C(α',II)	−0·2865(34)	0·2131(15)	0·0372(36)
C(β',II)	−0·3938(26)	0·1656(16)	−0·0322(30)
C(β,II)	−0·3762(31)	0·0983(17)	−0·0512(33)
C(γ,II)	−0·1179(39)	0·1775(22)	0·2765(31)
C(δ,II)	−0·2453(42)	0·1463(22)	0·3097(43)
C(α,III)	−0·2339(25)	0·1995(18)	−0·2613(30)
C(4,III)	−0·2460(32)	0·1348(15)	−0·3138(31)
C(3,III)	−0·3626(43)	0·0861(19)	−0·3838(42)
C(2,III)	−0·4609(42)	0·1139(17)	−0·4212(35)
C(1,III)	−0·4591(30)	0·1803(20)	−0·3900(33)
C(9,III)	−0·3909(47)	0·3391(27)	−0·2836(41)
C(8,III)	−0·3439(47)	0·4099(23)	−0·2316(43)
C(7,III)	−0·2171(41)	0·4421(20)	−0·1636(41)
C(6,III)	−0·1314(36)	0·4001(18)	−0·1338(53)
C(α',III)	−0·1837(36)	0·3297(20)	−0·1884(34)
C(β',III)	−0·3172(37)	0·2944(20)	−0·2645(37)
C(β,III)	−0·3344(27)	0·2263(16)	−0·3043(30)
C(γ,III)	0·0020(28)	0·2902(15)	−0·2793(33)
C(δ,III)	−0·0728(42)	0·3074(24)	−0·4283(41)
C(1)	0·8015(58)	0·4562(33)	0·2859(65)
C(2)	0·7337(93)	0·4245(30)	0·3813(47)
C(3)	0·5975(91)	0·4171(31)	0·3553(90)
C(4)	0·5476(55)	0·4488(42)	0·2483(87)
C(5)	0·6130(78)	0·4832(29)	0·1704(54)
C(6)	0·7366(62)	0·4889(26)	0·1760(64)

The observed symmetry plane is defined as the ' best ' plane through the metal atom, the phosphorus atom,

TABLE 9

Anisotropic temperature factors (Å^2 $\times 10^3$) * for (1), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Pd	43(2)	45(2)	41(2)	18(3)	7(3)	20(3)
Br(2)	67(3)	56(3)	63(3)	5(4)	17(4)	40(4)
Br(1)	59(3)	51(3)	86(3)	44(4)	5(5)	−5(4)
Cl(1)	145(20)	257(31)	474(52)	−47(62)	117(51)	13(39)
P(III)	49(6)	56(6)	36(6)	32(10)	13(9)	31(10)
P(II)	48(6)	54(6)	32(5)	2(9)	−7(9)	7(10)
P(I)	48(6)	44(6)	55(6)	30(10)	−2(10)	54(10)
C(γ,III)	37(20)	19(18)	71(25)	39(34)	−10(35)	2(31)
C(δ,III)	101(36)	109(38)	74(32)	24(54)	−26(53)	103(60)
C(γ,II)	100(32)	111(34)	13(20)	108(43)	−18(40)	24(54)
C(δ,II)	106(37)	84(33)	95(36)	107(55)	144(61)	−11(56)
C(γ,I)	43(21)	50(22)	42(21)	84(35)	63(34)	47(35)
C(δ,I)	67(26)	58(25)	104(31)	153(47)	110(47)	92(43)
C(1)	165(58)	157(60)	153(62)	−263(103)	−304(104)	125(95)
C(2)	373(118)	110(51)	43(34)	55(62)	29(100)	224(132)
C(3)	256(106)	71(44)	239(97)	−116(104)	−137(151)	68(110)
C(4)	100(47)	180(84)	197(89)	−251(135)	19(108)	10(97)
C(5)	218(78)	86(44)	114(46)	−71(71)	−23(102)	225(110)
C(6)	141(54)	70(38)	178(63)	−138(77)	−95(100)	2(75)
C(α,III)	1(16)	79(28)	37(20)	7(38)	−20(29)	−12(34)
C(4,III)	65(25)	15(19)	52(24)	−49(35)	−30(38)	31(36)
C(3,III)	124(39)	40(26)	108(36)	109(51)	51(60)	105(54)
C(2,III)	135(38)	13(20)	59(26)	−55(37)	53(51)	6(45)
C(1,III)	33(21)	86(31)	48(23)	−24(41)	6(35)	34(41)
C(9,III)	127(40)	121(41)	58(29)	14(53)	59(56)	106(67)
C(8,III)	131(42)	83(34)	85(33)	51(54)	41(60)	145(64)
C(7,III)	90(34)	63(29)	82(32)	01(48)	32(53)	22(53)
C(6,III)	70(30)	22(23)	211(54)	51(56)	−28(62)	79(46)
C(α′,III)	83(30)	68(29)	50(25)	85(43)	−1(43)	72(49)
C(β′,III)	83(31)	73(30)	72(28)	103(49)	97(49)	91(51)
C(β,III)	27(19)	44(22)	54(22)	67(36)	52(33)	42(34)
C(α,II)	71(26)	24(20)	48(23)	−3(35)	73(40)	−1(38)
C(4,II)	87(31)	40(26)	66(27)	48(43)	53(46)	26(46)
C(3,II)	59(29)	42(26)	150(42)	72(54)	68(59)	45(46)
C(2,II)	64(28)	26(22)	90(32)	−62(43)	19(48)	−56(42)
C(1,II)	38(21)	34(21)	53(23)	35(37)	−6(35)	−45(34)
C(9,II)	69(24)	41(22)	36(20)	50(33)	−4(35)	81(39)
C(8,II)	53(26)	148(42)	61(27)	119(56)	92(45)	18(55)
C(7,II)	72(31)	124(37)	65(28)	80(52)	151(51)	10(56)
C(6,II)	31(24)	89(33)	79(29)	10(47)	62(43)	−30(44)
C(α′,II)	82(29)	6(19)	87(29)	−20(37)	57(47)	45(33)
C(β′,II)	23(19)	43(22)	50(36)	−54(34)	44(34)	6(36)
C(β,II)	45(22)	40(22)	58(24)	26(36)	25(36)	14(35)
C(α,I)	92(30)	69(28)	32(21)	36(38)	−26(39)	97(48)
C(4,I)	61(26)	48(26)	96(33)	45(47)	−41(47)	49(47)
C(3,I)	47(25)	126(37)	28(22)	−101(47)	−46(37)	81(50)
C(2,I)	86(31)	112(37)	45(26)	6(51)	−35(44)	152(60)
C(1,I)	71(31)	125(41)	104(35)	−31(63)	65(52)	149(63)
C(9,I)	21(20)	120(36)	95(31)	36(52)	49(40)	68(44)
C(8,I)	93(33)	41(26)	187(50)	93(60)	26(68)	137(50)
C(7,I)	59(30)	129(45)	141(46)	119(75)	94(62)	72(59)
C(6,I)	82(29)	17(21)	89(30)	1(41)	45(47)	12(40)
C(α′,I)	50(25)	54(28)	86(32)	27(49)	15(45)	11(42)
C(β′,I)	79(27)	39(22)	31(20)	32(35)	−60(37)	94(41)
C(β,I)	85(29)	60(27)	43(23)	11(40)	29(41)	60(45)

* Temperature factor in the form: $T = \exp - 2\pi^2[U_{11}(ha^*)^2 + \ldots + 2U_{12}(ha^*kb^*)]$.

C(γ), and the midpoints of each pair of mirror-image carbon atoms of the aromatic system. The rotation angle is defined as positive for a rotation which appears clockwise to an observer looking from the phosphorus atom of that ligand to the metal atom. Several corresponding angles in Table 5 are within *ca.* 1° of each other, the largest difference being 3½°. Corresponding rotation angles of Table 6 differ by a few degrees only, the largest difference being 11°.

TABLE 10

Atomic co-ordinates for (2), with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Pt	0·2512(0)	0·0165(1)	0·0382(1)
Br(2)	0·3543(1)	−0·2225(2)	−0·1196(2)
Br(1)	0·1380(1)	−0·1591(2)	0·0273(2)
Br(3)	0·0478(4)	0·3574(10)	0·3197(9)
P(I)	0·2673(2)	0·0457(4)	0·2248(4)
P(II)	0·3158(1)	0·2397(4)	0·0886(4)
P(III)	0·2325(2)	−0·0711(4)	−0·1690(4)
C(α,I)	0·3499(6)	0·1518(14)	0·3058(12)
C(4,I)	0·4167(7)	0·1229(28)	0·2490(18)
C(3,I)	0·4744(7)	0·2224(27)	0·3234(21)
C(2,I)	0·4577(6)	0·3218(18)	0·4600(18)
C(1,I)	0·3861(8)	0·3574(17)	0·5349(14)
C(9,I)	0·2299(7)	0·3705(16)	0·6210(15)
C(8,I)	0·1592(8)	0·3664(15)	0·6437(14)
C(7,I)	0·1216(7)	0·2675(21)	0·5283(14)
C(6,I)	0·1440(7)	0·1612(19)	0·4049(18)
C(α′,I)	0·2151(5)	0·1641(11)	0·3828(12)
C(β′,I)	0·2594(6)	0·2694(18)	0·4864(15)
C(β,I)	0·3360(8)	0·2602(19)	0·4412(20)
C(γ,I)	0·2558(7)	−0·1414(18)	0·1854(17)
C(δ,I)	0·2741(11)	−0·1419(23)	0·2991(23)
C(α,II)	0·3987(5)	0·2478(13)	0·0055(12)
C(4,II)	0·4571(6)	0·1986(24)	−0·0022(21)
C(3,II)	0·5215(6)	0·2295(19)	−0·0657(20)
C(2,II)	0·5217(7)	0·2920(24)	−0·1250(17)
C(1,II)	0·4611(9)	0·3381(22)	−0·1244(25)
C(9,II)	0·3200(6)	0·4441(16)	−0·0737(19)
C(8,II)	0·2518(8)	0·4777(17)	−0·0383(16)
C(7,II)	0·2013(7)	0·4337(18)	0·0235(14)
C(6,II)	0·2144(8)	0·3667(22)	0·0766(20)
C(α′,II)	0·2818(6)	0·3320(14)	−0·0432(14)
C(β′,II)	0·3309(7)	0·3633(13)	−0·0524(15)
C(β,II)	0·4006(6)	0·3120(14)	−0·0524(11)
C(γ,II)	0·3143(11)	0·3952(19)	0·2757(15)
C(δ,II)	0·3563(11)	0·5483(25)	0·2969(35)
C(α,III)	0·2986(6)	−0·0357(16)	−0·2608(16)
C(4,III)	0·3692(6)	−0·0715(19)	−0·3110(13)
C(3,III)	0·4177(9)	−0·0234(23)	−0·3920(21)
C(2,III)	0·3875(11)	0·0345(27)	−0·4270(24)
C(1,III)	0·3204(10)	0·0741(21)	−0·3939(21)
C(9,III)	0·1640(7)	0·1009(23)	−0·3000(17)
C(8,III)	0·0876(7)	0·1102(20)	−0·2434(18)
C(7,III)	0·0644(6)	0·0650(23)	−0·1787(21)
C(6,III)	0·0959(7)	0·0050(22)	−0·1345(18)
C(α′,III)	0·1699(6)	0·0062(19)	−0·1822(16)
C(β′,III)	0·1986(7)	0·0444(20)	−0·2660(18)
C(β,III)	0·2753(4)	0·0318(11)	−0·3063(10)
C(γ,III)	0·2118(11)	−0·2818(26)	−0·2862(28)
C(δ,III)	0·1941(12)	−0·3519(31)	−0·4249(31)
C(1)	0·0087(10)	0·4494(31)	0·1834(17)
C(2)	0·0478(12)	0·5136(20)	0·2835(25)
C(3)	0·0847(11)	0·6517(23)	0·3854(33)
C(4)	0·0839(11)	0·7460(36)	0·3390(51)
C(5)	0·0560(11)	0·7303(36)	0·2623(30)
C(6)	0·0247(15)	0·5751(69)	0·1686(38)

The agreement in Table 5 shows that the three metal–phosphorus bond directions vary very little and the rotation angles of Table 6 indicate almost the same disposition of the ligands in all three compounds.

The geometrical aspect of the interaction of ligands (II) and (III) is summarised in Table 7. This gives (i) an inclination angle, defined as the angle between the normals to the best planes for ligands (II) and (III) taken through all carbon atoms of the aromatic system; (ii) the ' mean separation ' of the planes: in this case most of the atoms in L(II) and L(III) may be considered as overlapping so the distance to the mean plane of the other ligand was calculated for each atom and the mean taken as the ' mean separation '; (iii) the angle of twist defined as an angle between lines AB(II) and AB(III) where AB is the intersection of the plane of symmetry of the ligand with a plane of projection [1] [*i.e.* L(II) is projected on to the least-squares plane of L(III)]. This angle is a measure of the degree of geometrical overlapping of the ligands.

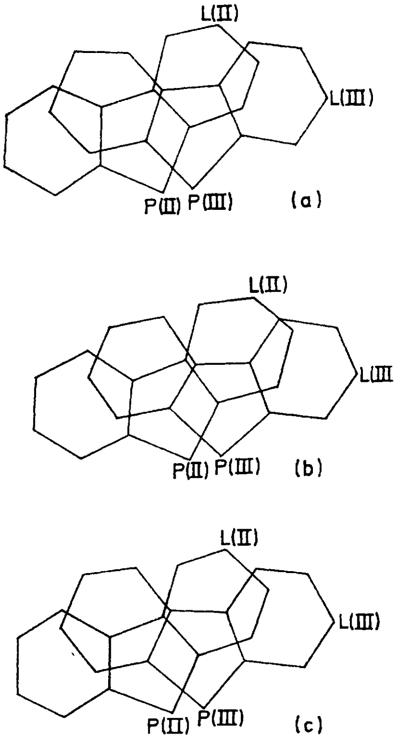

FIGURE 5 Projections of the ligand L(II) on the mean plane through the ligand L(III) for: (a) (1), (b) (2), and (c) (3)

Table 7 shows that (*a*) the planes of (II) and (III) are always nearly parallel (inclination angles ideally zero are in the range 1—6°); (*b*) the mean separation, *ca.* 3·4 Å as in other members of the series, is within the range for aromatic molecular complex interaction; and (*c*) the geometrical overlap is almost identical in the three compounds (angles of twist the same). This can also be seen in Figure 5 where for each of the three compounds L(II) is projected on the plane of L(III).

Apical Bond Length Variation.—In view of the close similarity in the main valency and conformational angles of the three compounds, the corresponding bond lengths might also be expected to differ very little.

TABLE 11

Anisotropic temperature factors (Å^2 × 10^3) for (2), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Pt	31(0)	34(0)	37(0)	35(1)	−11(1)	07(1)
Br(2)	57(1)	64(1)	56(1)	62(2)	4(2)	43(2)
Br(1)	45(1)	70(1)	65(1)	77(2)	−23(2)	−10(1)
Br(3)	250(7)	195(9)	286(10)	305(16)	132(13)	137(13)
P(I)	35(1)	39(2)	45(2)	39(3)	−8(3)	16(3)
P(III)	36(1)	35(2)	35(2)	34(3)	−15(3)	6(2)
P(II)	34(1)	31(2)	43(2)	36(3)	2(3)	9(2)
C(γ,I)	45(7)	48(8)	46(8)	43(13)	−37(12)	−35(12)
C(δ,I)	105(16)	54(12)	77(19)	52(24)	−75(27)	43(24)
C(γ,III)	109(11)	55(14)	119(20)	51(28)	−31(22)	19(19)
C(δ,III)	75(13)	79(16)	149(29)	81(35)	64(29)	87(24)
C(γ,II)	162(18)	40(9)	17(8)	49(15)	−20(18)	−9(20)
C(δ,II)	111(15)	67(15)	244(39)	258(47)	53(38)	8(23)
C(1)	77(12)	111(18)	6(7)	−38(17)	2(13)	6(23)
C(2)	145(19)	48(12)	132(24)	164(33)	122(35)	75(26)
C(3)	99(15)	51(12)	216(35)	179(37)	83(36)	57(22)
C(4)	53(13)	91(22)	326(52)	220(64)	107(42)	4(27)
C(5)	70(14)	181(33)	150(27)	292(58)	135(31)	175(39)
C(6)	90(20)	330(70)	106(28)	294(79)	76(35)	123(63)
C(α,I)	42(6)	33(6)	14(6)	12(10)	14(9)	25(9)
C(4,I)	48(8)	136(20)	55(12)	144(28)	33(14)	71(20)
C(3,I)	33(7)	107(16)	65(13)	105(25)	55(14)	51(16)
C(2,I)	30(6)	56(10)	55(12)	54(18)	−00(13)	12(12)
C(1,I)	69(10)	39(7)	20(7)	4(12)	21(13)	49(13)
C(9,I)	50(6)	38(7)	32(8)	39(12)	31(10)	9(10)
C(8,I)	71(9)	33(7)	23(8)	9(12)	18(13)	32(13)
C(7,I)	55(8)	76(10)	17(7)	34(13)	72(11)	89(15)
C(6,I)	53(8)	55(9)	59(12)	70(18)	47(15)	49(14)
C(α′,I)	34(5)	14(5)	34(7)	4(10)	12(10)	35(8)
C(β′,I)	39(6)	59(9)	45(9)	80(16)	42(11)	24(12)
C(β,I)	61(7)	62(10)	87(14)	126(22)	26(15)	48(14)
C(α,III)	30(5)	51(8)	64(11)	69(16)	41(12)	52(11)
C(4,III)	42(7)	91(11)	33(9)	116(18)	95(12)	45(13)
C(3,III)	66(9)	62(11)	49(13)	41(21)	53(17)	44(16)
C(2,III)	99(13)	75(15)	63(16)	86(28)	−6(22)	19(22)
C(1,III)	98(11)	55(9)	56(11)	87(18)	−32(17)	−24(17)
C(9,III)	47(7)	102(14)	50(10)	129(21)	61(12)	61(16)
C(8,III)	63(8)	74(10)	74(12)	135(21)	89(15)	92(15)
C(7,III)	22(6)	96(16)	107(19)	106(30)	11(17)	67(17)
C(6,III)	38(7)	92(14)	64(12)	119(24)	27(14)	42(15)
C(α′,III)	30(5)	78(10)	53(9)	104(18)	6(11)	20(11)
C(β′,III)	42(7)	64(9)	54(13)	31(18)	−5(15)	58(13)
C(β,III)	28(12)	20(12)	17(16)	−13(23)	−3(22)	−4(19)
C(α,II)	35(5)	26(5)	24(6)	8(9)	17(9)	33(8)
C(4,II)	25(6)	99(14)	97(16)	145(28)	18(15)	36(13)
C(3,II)	29(6)	62(10)	92(16)	109(23)	21(15)	8(12)
C(2,II)	36(7)	87(13)	47(11)	70(20)	30(13)	54(15)
C(1,II)	61(10)	53(11)	99(19)	55(25)	−47(22)	1(16)
C(9,II)	38(6)	33(7)	73(12)	41(16)	15(13)	20(10)
C(8,II)	74(11)	49(12)	36(11)	19(19)	−7(17)	53(19)
C(7,II)	54(7)	64(10)	33(9)	62(17)	18(12)	65(14)
C(6,II)	68(10)	63(12)	65(13)	94(23)	−4(17)	−7(17)
C(α′,II)	37(5)	35(7)	40(9)	43(13)	9(10)	23(9)
C(β′,II)	55(7)	20(5)	34(8)	5(10)	−1(11)	24(10)
C(β,II)	51(10)	35(6)	14(6)	34(11)	51(9)	48(11)

In agreement with this the differences for the basal bonds average only 0·01 Å but there is a striking difference of ten times that amount in the Pt–Br apical bond lengths. The bond is weak and there is a possible internal electronic reason for a difference. This may be the effect of change of R from Me to Et on the donating power of the phosphorus atom. This would be in the right sense, requiring Pt–Br(2) greater for R = Et than for R = Me.[3] There is, however, some difference in the environments of the molecules in the Me and Et compounds. This is in contrast to the pair (1) and (2), both with R = Et, which have nearly identical structural constants. The difference is readily seen in diagrams where whole molecules are projected on a particular plane through a neighbouring molecule. Another expression of it is that corresponding distances between the lines of the two parallel apical bonds in the structures differ by 0·5 Å. The variation in apical bond length may also be influenced by these differences.

The difference in apical bond length between (1) and (2) is 0·2 Å, twice as much as the difference between Me and Et compounds of Pt, (2) and (3). In this case the structural constants are very similar and the corresponding intermolecular distances will be nearly the same except for a few where the apical bond length difference is directly involved. For these few, the difference in intermolecular distance will not exceed 0·2 Å. The difference in apical bond lengths in the two compounds must be due almost entirely to the chemical difference between the metal atoms.

EXPERIMENTAL

Crystal Preparation.—The micro-crystalline green form of (1) was dissolved in chlorobenzene and recrystallised in a capillary tube. One green crystal 0·3 × 0·5 × 0·5 mm was obtained.

Yellow crystals of (2) and of (3) were obtained by evaporation of their solutions in bromobenzene.

Data Collection.—Intensity data for all three structures were collected on a Hilger and Watts four-circle diffractometer with Mo radiation for (1) and Cu radiation for (2) and (3). Balanced filters, zirconium and ytterbium in the Bragg angle range 0—10° or cobalt and nickel in the Bragg angle range 0—30° were used for Mo and Cu radiation respectively. The limiting Bragg angles for (1), (2), and (3) were 20 ($\sin\theta/\lambda = 0{\cdot}49$), 70 ($\sin\theta/\lambda = 0{\cdot}60$), and 62° ($\sin\theta/\lambda = 0{\cdot}56$). Values for the merging R, $\Sigma(F_i - F_{\text{mean}})/\Sigma F_{\text{mean}}$ were 0·087, 0·054, and 0·051. The numbers of independent reflections involved were: compound (1) 1930 ($I > 2\sigma$), (2) 5817 ($I > 3\sigma$), and (3) 3320 ($I > 3\sigma$). Absorption corrections were carried out[4] on the data for (2) and (3).

Structure Determinations.—The structures were solved by Patterson and Fourier methods. Positions of the six heavy atoms were found in each case from the Patterson vectors. They were used to phase the Fourier synthesis for the complete structures. Ploto plot[5] was used in each case to check for any solvent molecules previously undetected. Structure (1) was refined anisotropically by using Killean[6] absolute weights till R converged to 0·095. Structures (2) and (3) were anisotropically refined to R 0·097 and 0·092 with relative weights calculated from $1/w = [1 + (F_0 - P_2)/P_1]^2$, [$P_1 = 52{\cdot}3$, $P_2 = 13{\cdot}8$ for structure (2) and $P_1 = 38{\cdot}7$, $P_2 = 13{\cdot}8$ for structure (3)]. The sums of squares of ratios were reduced to 28·2, 18·3, and 48·6 respectively. The root-mean-squares (shift-to-σ) were less than 0·02, 0·01, and 0·03.

TABLE 12

Atomic co-ordinates for (3), with estimated standard deviations in parentheses

	x/a	y/b	z/c
Pt	−0·0228(1)	−0·0148(1)	0·2445(0)
Br(2)	0·1191(2)	−0·0876(2)	0·1415(1)
Br(1)	−0·0043(4)	−0·1863(4)	0·3580(2)
P(I)	−0·2234(14)	−0·1735(14)	0·2274(9)
C(α,I)	−0·3204(20)	−0·1538(16)	0·1462(11)
C(4,I)	−0·2738(20)	−0·1219(17)	0·0738(10)
C(3,I)	−0·3651(21)	−0·1184(18)	0·0205(11)
C(2,I)	−0·5083(19)	−0·1482(16)	0·0358(11)
C(1,I)	−0·5530(17)	−0·1755(15)	0·1069(11)
C(9,I)	−0·6224(19)	−0·2377(16)	0·2713(11)
C(8,I)	−0·6347(21)	−0·2655(17)	0·3461(11)
C(7,I)	−0·5239(16)	−0·2702(14)	0·3885(9)
C(6,I)	−0·3768(19)	−0·2136(16)	0·2831(10)
C(α′,I)	−0·3864(14)	−0·2411(13)	0·3571(8)
C(β′,I)	−0·4907(12)	−0·2099(13)	0·2398(9)
C(β,I)	−0·4600(18)	−0·1798(16)	0·1630(10)
C(γ,I)	−0·1976(14)	−0·3275(14)	0·2369(2)
P(II)	−0·0746(17)	0·1581(14)	0·1786(9)
C(α,II)	0·0131(24)	0·2545(18)	0·0959(10)
C(4,II)	0·0257(24)	0·2227(18)	0·0325(10)
C(3,II)	0·0962(23)	0·3182(21)	−0·0309(11)
C(2,II)	0·1598(22)	0·4460(20)	−0·0280(12)
C(1,II)	0·1495(20)	0·4817(18)	0·0357(11)
C(9,II)	0·0858(18)	0·5236(16)	0·1791(11)
C(8,II)	0·0485(20)	0·5238(18)	0·2458(12)
C(7,II)	−0·0230(19)	0·4094(18)	0·2994(11)
C(6,II)	−0·0634(20)	0·2906(17)	0·2843(10)
C(α′,II)	−0·0250(16)	0·2916(14)	0·2158(9)
C(β′,II)	0·0498(15)	0·4058(14)	0·1633(9)
C(β,II)	0·0739(17)	0·3869(15)	0·0945(9)
C(γ,II)	−0·2598(19)	0·1310(18)	0·1614(13)
P(III)	0·1948(15)	0·1105(14)	0·2695(9)
C(α,III)	0·2997(18)	0·2545(17)	0·2051(10)
C(4,III)	0·3436(20)	0·2679(19)	0·1369(19)
C(3,III)	0·4363(21)	0·3853(20)	0·0954(13)
C(2,III)	0·4796(19)	0·4940(17)	0·1235(11)
C(1,III)	0·4318(20)	0·4807(20)	0·1925(12)
C(9,III)	0·3141(26)	0·4063(24)	0·3519(13)
C(8,III)	0·2620(24)	0·3590(24)	0·4194(12)
C(7,III)	0·1746(20)	0·2308(19)	0·4485(10)
C(6,III)	0·1516(17)	0·1454(16)	0·4044(9)
C(α′,III)	0·2087(16)	0·1923(15)	0·3363(10)
C(β′,III)	0·2906(16)	0·3260(15)	0·3075(10)
C(β,III)	0·3431(15)	0·3593(16)	0·2331(11)
C(γ,III)	0·3160(14)	0·0243(14)	0·2941(12)
Br(3)	0·6314(4)	0·0290(3)	0·4224(2)
C(1)	0·6880(25)	0·2003(21)	0·4369(12)
C(2)	0·7969(22)	0·2344(22)	0·4798(11)
C(3)	0·8402(26)	0·3595(24)	0·4851(25)
C(4)	0·7671(27)	0·4402(21)	0·4468(11)
C(5)	0·6670(24)	0·4141(25)	0·4099(13)
C(6)	0·6151(27)	0·2784(25)	0·3974(14)

Detailed results of positional and temperature parameters are given in Tables 8—13. Final observed and calculated structure factors for all three compounds are

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Crystal Data.—For each compound the constants given first are those of a unit cell found convenient for data collection and structure determination. At the end of each section an alternative cell is given. For (1) and (2) this is the cell obtained by Delaunay reduction which leads to structurally comparable cells. For (3) the cell given is structurally comparable with those for (1) and (2) but does not obey the Delaunay convention of $b > a$. The matrix for transformation from one cell to the reduced form is given in each case.

TABLE 13

Anisotropic temperature factors for (3), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Pt	55(0)	49(0)	75(0)	−20(1)	15(1)	39(1)
Br(2)	73(1)	78(1)	102(1)	−46(2)	30(2)	59(2)
Br(1)	87(1)	71(1)	88(1)	−4(2)	−2(2)	48(2)
P(I)	61(2)	55(2)	76(3)	−20(4)	21(4)	50(4)
C(α,I)	43(7)	69(9)	83(10)	−59(15)	−21(13)	35(13)
C(4,I)	93(12)	65(10)	101(13)	−41(18)	49(21)	54(18)
C(3,I)	90(12)	71(10)	84(12)	−43(17)	−19(19)	52(18)
C(2,I)	101(13)	81(11)	92(14)	−45(20)	1(21)	62(20)
C(1,I)	77(11)	64(9)	113(14)	−40(18)	−2(20)	36(16)
C(9,I)	64(9)	61(8)	116(14)	−44(18)	39(18)	50(15)
C(8,I)	80(11)	64(9)	113(14)	−24(18)	34(20)	62(17)
C(7,I)	94(13)	80(11)	99(14)	−18(19)	78(22)	55(19)
C(6,I)	72(9)	56(8)	91(12)	−40(15)	19(16)	37(14)
C(α′,I)	86(12)	78(10)	84(12)	−40(17)	43(19)	59(18)
C(β′,I)	51(7)	48(7)	80(10)	−16(13)	18(13)	31(12)
C(β,I)	35(6)	66(8)	88(11)	−44(15)	−13(12)	42(11)
C(γ,I)	78(10)	63(9)	108(13)	−32(17)	33(18)	63(16)
P(II)	65(2)	53(2)	80(3)	−24(4)	14(4)	49(4)
C(α,III)	51(8)	60(8)	93(11)	−33(15)	17(15)	38(13)
C(4,III)	73(11)	83(11)	89(12)	−35(18)	21(18)	65(18)
C(3,III)	77(11)	76(11)	110(15)	−17(21)	41(21)	27(18)
C(2,III)	89(13)	88(13)	117(17)	4(23)	48(23)	60(21)
C(1,III)	75(11)	81(11)	114(15)	−26(20)	8(20)	64(18)
C(9,III)	88(12)	103(14)	115(16)	−103(25)	−22(22)	80(21)
C(8,III)	120(18)	108(17)	115(17)	−86(28)	−17(28)	93(29)
C(7,III)	104(16)	130(18)	105(15)	−96(17)	−10(24)	107(28)
C(6,III)	84(12)	91(12)	86(12)	−29(19)	22(19)	68(19)
C(α′,III)	65(9)	79(10)	88(11)	−76(18)	−6(16)	52(16)
C(β′,III)	59(9)	58(8)	111(13)	−67(17)	0(17)	43(14)
C(β,III)	63(9)	58(8)	115(13)	−58(17)	8(17)	53(14)
C(γ,III)	48(7)	73(10)	132(15)	−64(20)	−13(17)	64(14)
P(III)	67(2)	52(2)	82(3)	−26(4)	17(4)	51(4)
C(α,II)	79(10)	65(8)	77(10)	−17(14)	25(16)	76(16)
C(4,II)	139(18)	79(11)	85(12)	−21(19)	19(22)	110(24)
C(3,II)	116(16)	105(14)	90(13)	−28(22)	20(22)	120(25)
C(2,II)	107(14)	88(13)	98(14)	−4(22)	37(23)	95(23)
C(1,II)	79(12)	80(11)	102(14)	−8(19)	33(20)	56(18)
C(9,II)	66(10)	72(10)	113(14)	−48(18)	−9(18)	59(16)
C(8,II)	86(11)	76(12)	116(16)	−73(16)	2(21)	73(19)
C(7,II)	83(12)	85(12)	110(15)	−78(22)	9(21)	69(20)
C(6,II)	72(10)	76(11)	94(12)	−46(18)	−1(17)	57(17)
C(α′,II)	65(9)	59(8)	95(11)	−44(15)	3(16)	80(14)
C(β′,II)	58(8)	55(8)	101(12)	−37(15)	7(15)	55(13)
C(β,II)	79(10)	63(9)	81(10)	−25(15)	15(16)	73(16)
C(γ,II)	77(11)	74(11)	156(19)	−32(23)	−34(23)	102(19)
Br(3)	148(3)	96(2)	186(3)	−48(4)	−48(5)	78(3)
C(1)	115(16)	88(14)	105(15)	−10(23)	54(25)	54(25)
C(2)	83(13)	104(16)	100(14)	−31(23)	−21(21)	64(23)
C(3)	118(18)	116(17)	105(16)	−36(26)	53(26)	54(29)
C(4)	130(19)	89(14)	106(16)	−37(24)	117(28)	60(27)
C(5)	88(14)	121(18)	111(17)	8(27)	49(24)	100(27)
C(6)	118(18)	122(18)	139(21)	−22(31)	16(31)	126(31)

(1) *Dibromotris-*(5*-ethyl-*5H*-dibenzophosphole*)*palladium-*(II). $(C_{14}H_{13}P)_3PdBr_2,C_6H_5Cl$, $M = 1015·5$, Triclinic, $a = 11·52 \pm 0·02$, $b = 19·96 \pm 0·03$, $c = 10·59 \pm 0·02$ Å, $\alpha = 89·68 \pm 0·02$, $\beta = 107·65 \pm 0·02$, $\gamma = 106·18 \pm 0·02°$, $U = 2220$ Å^3, $D_m = 1·52$ (by flotation), $Z = 2$, $D_c = 1·52$, $F(000) = 1020$. Space group, $P\bar{1}$. Mo-K_α radiation, $\lambda = 0·7107$ Å, μ(Mo-K_α) = 25·18 cm^{-1}; $t_{op.} = 0·79$ mm; terminal R 0·095; green crystal 0·30 × 0·51 × 0·52 mm. Reduced cell constants (Delaunay): $a = 19·96 \pm 0·03$, $b = 20·07 \pm 0·03$, $c = 10·59 \pm 0·02$ Å, $\alpha = 99·69 \pm 0·02°$, $\beta = 90·32 \pm 0·02°$, $\gamma = 146·56 \pm 0·03°$; transformation matrix (1,1,0/−1,0,0/0,0,1).

(2) *Dibromotris-*(5*-ethyl-*5H*-dibenzophosphole*)*platinum-*(II). $(C_{14}H_{13}P)_3PtBr_2,C_6H_5Br$, $M = 1148·70$, Triclinic, $a = 19·92 \pm 0·02$, $b = 11·48 \pm 0·02$, $c = 13·12 \pm 0·02$ Å, $\alpha = 129·55 \pm 0·02$, $\beta = 76·21 \pm 0·02$, $\gamma = 105·95 \pm 0·02°$, $U = 2216·3$ Å^3, $D_m = 1·73$, $Z = 2$, $D_c = 1·72$, $F(000) = 1120$. Space group $P\bar{1}$. Cu-K_α radiation, $\lambda = 1·5418$ Å, μ(Cu-K_α) = 108·47 cm^{-1}; $t_{op.} = 0·18$ mm; terminal R 0·092; yellow crystal 0·25 × 0·27 × 0·70 mm. Reduced cell

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constants (Delaunay): $a = 19{\cdot}92 \pm 0{\cdot}02$, $b = 20{\cdot}07 \pm 0{\cdot}02$, $c = 10{\cdot}58 \pm 0{\cdot}02$ Å, $\alpha = 99{\cdot}57 \pm 0{\cdot}02$, $\beta = 90{\cdot}02 \pm 0{\cdot}02$, $\gamma = 146{\cdot}62 \pm 0{\cdot}03°$; transformation matrix $(-1,0,0/-1,-1,0/1,1,1)$.

(3) *Dibromotris-*(5-*methyl-*5H-*dibenzophosphole*)*platinum-*(II). $(C_{13}H_{11}P)_3PtBr_2,C_6H_5Br$, $M = 1106{\cdot}6$, Triclinic, $a = 10{\cdot}26 \pm 0{\cdot}02$, $b = 11{\cdot}61 \pm 0{\cdot}02$, $c = 10{\cdot}46 \pm 0{\cdot}03$ Å, $\alpha = 72{\cdot}41 \pm 0{\cdot}02$, $\beta = 94{\cdot}12 \pm 0{\cdot}02$, $\gamma = 110{\cdot}58 \pm 0{\cdot}02°$, $U = 2067$ Å^3, $D_m = 1{\cdot}78$, $Z = 2$, $D_c = 1{\cdot}78$, $F(000) = 1072$. Space group $P\bar{1}$. Cu-K_α radiation, $\mu(\text{Cu-}K_\alpha) = 116{\cdot}29$ cm^{-1}; $t_{\text{op.}} = 0{\cdot}17$ mm; terminal R 0·097; yellow crystal $0{\cdot}18 \times 0{\cdot}30 \times 0{\cdot}40$ mm. Reduced cell constants: $a = 19{\cdot}46 \pm 0{\cdot}03$, $b = 19{\cdot}42 \pm 0{\cdot}03$, $c = 10{\cdot}26 \pm 0{\cdot}02$ Å, $\alpha = 97{\cdot}93 \pm 0{\cdot}02$, $\beta = 94{\cdot}12 \pm 0{\cdot}02$, $\gamma = 145{\cdot}20 \pm 0{\cdot}02°$; transformation matrix $(-1,0,0/0,0,1/1,1,0)$.

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