841. *Four-, Five-, and Six-covalent Palladium*(II) *Complexes with a Di*(*tertiary*) *Arsine.*

By C. M. HARRIS and R. S. NYHOLM.

The complexes formed by bivalent palladium with the chelate group *o*-phenylene-bis(dimethylarsine) (termed " as " below) have been investigated. The following compounds have been prepared and studied: PdX_2,2as where X = Cl, Br, I, CNS, NO_2, and ClO_4. Molecular conductivities together with conductometric titrations and spectrophotometric absorption studies lead to the conclusion that the colourless diperchlorate is undoubtedly the four-covalent salt, $[Pd\ as_2](ClO_4)_2$, whereas the other compounds, which are highly coloured, behave as five-covalent complex salts of the type $[Pd\ as_2X]X$ in non-aqueous ionising solvents such as nitrobenzene. The reaction, $[Pd\ as_2]^{++} + X^- \longrightarrow [Pd\ as_2X]^+$, where X = Cl, Br, or I, is shown to be quantitative in nitrobenzene. By this reaction the halogeno-perchlorates $[Pd\ as_2X]ClO_4$ (X = Cl, Br, and I) have been prepared from acetone solution. These are typical uni-univalent electrolytes in nitrobenzene. Evidence is presented to support a distorted octahedral structure for $Pdas_2I_2$ in the solid state.

THE stereochemistry of bivalent palladium is characterised by the square arrangement in all its four-covalent complexes. This arrangement has been shown by *X*-ray crystallography to occur, for example, in the salt-like complexes $K_2[PdCl_4]$[1] and $[Pd(NH_3)_4]Cl_2,H_2O$ [2]

---

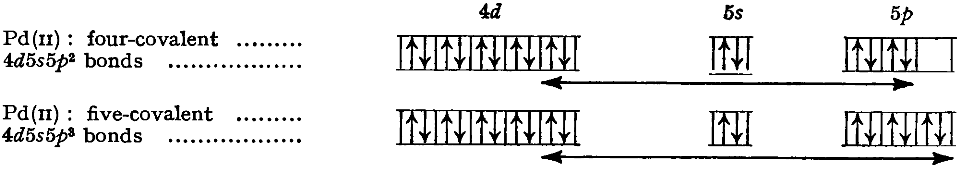
* The authors are grateful to the referees for drawing their attention to this work.

[1] Dickinson, *J. Amer. Chem., Soc.* 1922, **44**, 2404.

[2] Dickinson, *Z. Krist.* 1934, **88**, 281.

and in the non-electrolytes $[(NH_3)_2PdC_2O_4]^0$ and *trans*-$[(NH_3)_2PdI_2]^0$.[3] A similar arrangement has been observed in binuclear complexes in which the palladium atom is four-covalent, *e.g.*, $[PdCl_2,Et_3As]_2$.[4] The square arrangement in four-covalent palladium(II) complexes is considered by Pauling[5] to arise from the use of $4d5s5p^2$ hybrid bonds (see Fig. 1). This also explains the diamagnetism of all known palladium(II) complexes.

FIG. 1. *Electronic configuration of palladium complexes.*



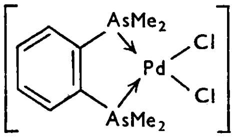
The co-ordination number six has been reported in a few unusual complexes whose structures have been little investigated. Thus, in the unstable trichelate diazoamino-complexes of palladium prepared by Dwyer,[6] and in di-(1 : 2 : 3-triaminopropane)palladium(II) iodide,[7] the palladium atom is presumably six-covalent if all donor atoms are linked to the metal atom. The structure of the black compound[8] of empirical formula $Pd(NH_3)_2Cl_3$ has recently been examined by Cohen and Davidson[9] who suggest that it is similar to that of the corresponding platinum compound $Pt(NH_3)_2Br_3$, the structure of which has been determined by *X*-ray crystallography.[10] The deeply coloured platinum compound contains equal numbers of square $Pt^{II}(NH_3)_2Br_2$ and octahedral $Pt^{IV}(NH_3)_2Br_4$ molecules. These are arranged in chains so that the Pt^{II} atoms form two additional weak bonds with bromide atoms of the Pt^{IV} molecules.

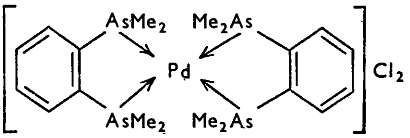
The isolation of five-covalent Pd(II) complexes does not appear to have been reported previously although evidence for the occurrence of five-covalent Pd(II) in aqueous solution has been put forward. Thus in spectrophotometric studies Sandaram and Sandell *[11] observed that an interaction between $[PdCl_4]^{2-}$ and Cl^- ions occurs in aqueous solution and they cautiously inferred that $[PdCl_5]^{3-}$ and $[PdCl_6]^{4-}$ ions were formed. It is interesting that Pauling[5] suggested that square co-ordinated Ni(II), Pd(II), and Pt(II) might conceivably form five-covalent complexes by utilising the single vacant 4*p*, 5*p*, or 6*p* orbital of the metal atom respectively. After some observations on the ditertiary arsine complexes of tervalent gold[12] and the behaviour of bivalent nickel with a tritertiary arsine,[13] the complexes of palladium(II) with the diarsine o-$C_6H_4(AsMe_2)_2$ (termed "as" in short formulæ below) have been reinvestigated with the above idea in mind. Some years ago Chatt and Mann,[14] who first studied this chelate group, prepared two complexes of palladium with the diarsine and assigned to them the structures (I) and (II), the former being a non-electrolyte. These workers noted that the compound (II), when recrystallised from water, yielded an almost colourless compound which rapidly changed to a deep yellow one, presumably owing to a loss of water of crystallisation. This change seemed interesting, particularly since palladium tetrammines are usually colourless, whereas chloropalladium(II) compounds (containing a Pd–Cl bond), as in (I), are often yellow. Further information was obtained on adding iodide ions to an aqueous solution of $PdCl_2,as_2$. An orange monohydrate, $PdI_2,2as,H_2O$, was precipitated at once; this was converted into

[3] Mann, Crowfoot, Gattiker, and Wooster, *J.*, 1935, 1642.
[4] Mann and Wells, *J.*, 1938, 702; Wells, *Proc. Roy. Soc.*, 1938, *B*, **167**, 169.
[5] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 2nd Edn., 1948, pp. 98—103.
[6] Dwyer, *J. Amer. Chem. Soc.*, 1941, **63**, 78.
[7] Mann, *J.*, 1929, 656.
[8] Drew, Pinkard, Preston, and Wardlaw, *J.*, 1932, 1895.
[9] Cohen and Davidson, *J. Amer. Chem. Soc.*, 1951, **73**, 1955.
[10] Brosset, *Arkiv Kemi, Min., Geol.*, 1948, **25**, No. 19.
[11] Sunderam and Sandell, *J. Amer. Chem. Soc.*, 1955, **77**, 855.
[12] Harris and Nyholm, unpublished work; Harris, Ph.D. Thesis, 1955, New South Wales; Harris, Nyholm, and Stephenson, *Rec. Trav. chim.*, 1956, **75**, 687.
[13] Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.
[14] Chatt and Mann, *J.*, 1939, 1622.

the deep red anhydrous compound by refluxing it with acetone. This red iodide, PdI_2,as_2, gave a reddish solution in nitrobenzene. The molecular conductivities of the bis(diarsine)-palladium(II) chloride and iodide and later the orange bromide indicated that those compounds function as uni-univalent electrolytes in nitrobenzene solution (see Table 1); for comparison, Table 2 lists the molecular conductivities of a considerable number of compounds in this solvent. These figures, together with the observed marked difference in colour between $[Pd\ as_2][ClO_4]_2$, the cation of which is colourless, and the compound $Pd\ as_2I_2$ which is red both in the solid state and in nitrobenzene solution, suggested that part of the halogen is covalently bound to the palladium atom even in nitrobenzene. The perchlorate, $Pd(ClO_4)_2,as_2$, was then prepared by treating an aqueous solution of the chloride with perchloric acid. This compound, which is colourless, is undoubtedly the four-covalent palladium(II) complex $[Pd\ as_2](ClO_4)_2$; its molecular conductivity is approximately double those of the halides (Table 1).

(I)





(II)

TABLE 1. *Molecular conductivities of palladium–diarsine complexes in nitrobenzene at 25°.*

Compound	Colour	Molar concn. (×10⁴)	Mol. conductivity (mho)	Compound	Colour	Molar concn. (×10⁴)	Mol. conductivity (mho)
$[Pd\ as_2](ClO_4)_2$	Colourless	4·1	46·2	$[Pd\ as_2I]I$	Red	5·5	26·9
$[Pd\ as_2Cl]Cl$ ...	Deep yellow	5·7	25·7	$[Pd\ as_2I]ClO_4$	Red	5·6	27·9
$[Pd\ as_2Cl]ClO_4$...	Deep yellow	5·3	29·0	$[Pd\ as_2NO_2]NO_2$	Orange	2·3	25·5
$[Pd\ as_2Br]Br$ ...	Orange	5·1	25·1	$[Pd\ as_2CNS]CNS$	Yellow	2·8	30·0
$[Pd\ as_2Br]ClO_4$	Orange	5·4	25·4				

TABLE 2. *Summary of the molecular conductivities of various complexes in nitrobenzene solution.*

Compound	Molar concn. (× 10⁴)	Temp.	Mol. conductivity
$[Cu\ as_2]X$ [a] ($X = ClO_4$, Br, I, $CuCl_2$, $CuBr_2$)	9·2 —1·75	25°	23·3—29·4
$[Au\ as_2]X$ [b] ($X = ClO_4$, Br, I, picrate, AuI_2, CuI_2)	8·2 —2·5	20	22·1—27·4
$[Cu(phen)_2]X$ [b] ($X = ClO_4$, I, CNS)	10—2·5	20	25·0—29·4
$[Cu(dipy)_2]ClO_4$ [b]	10	20	27·7
$[Cu(AsPh_2Me)_4]ClO_4$ [c]	39	25	24·4
$[phen\ H][AuX_4]$ [b] (X = Cl, Br)	10—12·3	25	29·7—33·0
$[Au(phen)X_2]ClO_4$ [b] (X = Cl, Br)	10—2·5	25	33·0—33·1
$[Au(dipy)Cl_2]ClO_4$ [b]	8·0	25	33·7
$[Au(py)_2Br_2]ClO_4$ [b]	5·0	25	30·5
$[Au(phen)X_2][AuX_4]$ [b] (X = Cl, Br)	5·7—7·0	25	27·1—27·7
$[dipy, Au, Et_2][AuEt_2Br_2]$ [d]	28 —2	25	24·6—26·7
$[Fe(dipy)_3]I_2$ [b]	2·5	20	57·8
$[Cu(phen)_2](ClO_4)_2$ [b]	5·0	25	43·1
$[Cu(AsPh_2MeO)_4](ClO_4)_2$ [e]	36·3	25	38·6
$[Co(triarsine)_2](ClO_4)_2$ [f]	12	25	44·9

[a] Kabesh and Nyholm, *J.*, 1951, 38. [b] Harris, " Researches on the Co-ordination Compounds of the Group IB Elements and Related Compounds," Ph.D. Thesis, New South Wales, 1955. [c] Nyholm, *J.*, 1952, 1257. [d] Foss and Gibson, *J.*, 1949, 3063. [e] Nyholm, *J.*, 1951, 1767. [f] Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.

Thus, it seemed likely that the halide compounds PdX_2,as_2 (X = Cl, Br, or I) could well be five-covalent complexes of the type $[Pd\ as_2X]X$ in nitrobenzene solution.

In keeping with this was the fact that addition of halide ions to a nitrobenzene or acetone solution of the colourless perchlorate, [Pd as_2]$(ClO_4)_2$, resulted in an immediate colour change ranging from yellow for chloride ions to reddish-brown in the case of iodide ions. This was confirmed by titrating conductometrically the di-(*o*-phenylenebisdimethylarsine)-palladium(II) ion, in the form of the perchlorate, with halide ions (Cl^-, Br^-, and I^-) in nitrobenzene solution. A sharp end-point was obtained in each case (see Figs. 2—4) after the addition of one g.-ion of halide per g.-ion of the colourless four-covalent di-

$$[\mathrm{Pd\ as_2}]^{++} + \mathrm{X}^- \longrightarrow [\mathrm{Pd\ as_2X}]^+$$

(*o*-phenylenebisdimethylarsine)palladium(II) ion, with the formation of the coloured halogenodi-(*o*-phenylenebisdimethylarsine)palladium(II) ion. By using this reaction we succeeded in isolating the coloured crystalline perchlorates, [Pd as_2X]ClO_4 [X = Cl (yellow), Br (orange) and I (deep red)], from acetone solution. The molecular conductivities of these perchlorates (see Table 1) were similar to those of the halides and in keeping with those of other uni-univalent electrolytes in nitrobenzene solution.

Conductometric titrations of [Pd as_2]$(ClO_4)_2$ (100 *ml. of* 5 × 10^{-4}M-*solution*) *with halide ions in nitrobenzene at* 25°.

FIG. 2. FIG. 3. FIG. 4.

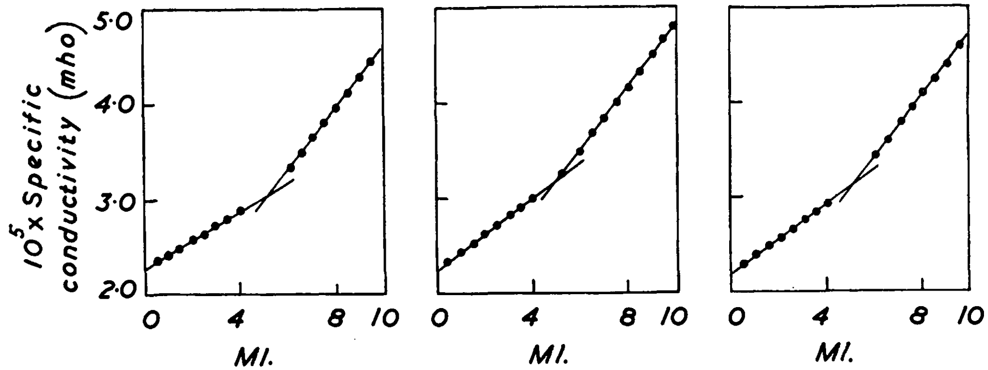


FIG. 2 : *Titration with* 10^{-2}M-$AsPh_3MeCl$. FIG. 3 : *Titration with* 10^{-2}M-NEt_4Br. FIG. 4 : *Titration with* 10^{-2}M-1-*methylquinolinium iodide.* (*Conductivities corrected for dilution.*)

The monoiododi-(*o*-phenylenebisdimethylarsine)palladium(II) ion is suitably coloured for spectrophotometric measurements in nitrobenzene solution and has an absorption maximum in this solvent at 4300 Å (Fig. 5). The colourless di-(*o*-phenylenebisdimethylarsine)palladium(II) ion does not absorb at this wavelength and, by applying the methods of continuous variation to mixtures of the [Pd as_2]$^{++}$ ion and iodide ions in nitrobenzene, the curve in Fig. 6 was obtained. This shows that [Pd as_2]$^{++}$ ions and iodide ions react together giving a maximum optical density at a wavelength of 4300 Å, when these ions are in a 1 : 1 ratio. This confirms the results of the conductometric titrations.

The orange nitro-compound, $Pd(NO_2)_2$,2Diarsine, and the yellow thiocyanato-complex, $Pd(CNS)_2$,2Diarsine, were prepared from aqueous solutions of the chloride by double decomposition. They also function as uni-univalent electrolytes in nitrobenzene solution.

It is interesting that the yellow chloro-compound, $PdCl_2$,2Diarsine, dissolves readily in water to a colourless solution containing [Pd as_2]$^{++}$ ions which give a precipitate of the diperchlorate, [Pd as_2]$(ClO_4)_2$, on the addition of perchloric acid. This presumably arises from the removal of covalently bound chlorine because of hydration effects: [Pd as_2Cl]$^+$ $\rightleftharpoons$ [Pd as_2]$^{++}$ + Cl^-. The fact that this equilibrium occurs in dilute aqueous solution is reflected in the molecular conductivity of the chloride ($\Lambda_M = 180$ mho in 0·88 × 10^{-3}M-solution at 19°). The orange bromo-complex, Pd as_2Br_2, undergoes an analogous change in water, forming a colourless solution with a similar conductivity ($\Lambda_M =$ 168 mho in 10^{-3}M-solution at 21°). The red iodo-complex is almost insoluble in cold water and hence its conductivity could not be measured. It dissolves in boiling water, however, forming a pale orange solution owing to the presence of $[Pd\,as_2I]^+$ ions. The red perchlorate $[Pd\,as_2I]ClO_4$ is precipitated on dropwise addition of perchloric acid. If a large excess of perchloric acid is added all at once the mixed compound $[Pd\,as_2](ClO_4)_2$, $[Pd\,as_2I]ClO_4$, is precipitated as deep yellow needles. The fact that the iodine atom appears to be more difficult to remove from the five-covalent palladium atom in aqueous solution parallels the lower hydration energy of the iodide ion compared with that for chloride and bromide ions.

Some interesting questions are posed by the isolation of these apparently five-covalent complex ions. First, there is the nature of the binding; secondly, the probable stereochemistry; and finally the question as to why such compounds do not appear to have been isolated previously. Provided that suitable bonding orbitals are available, the main factors which seem to limit the co-ordination number of a metal atom are (i) steric effects and (ii) the resulting charge on the metal ion. The existence of six-covalent Pd(IV) complex ions [in which the Pd(IV) atom must be even smaller than Pd(II)] suggests that steric factors are not significant when using simple ligands. However, the second factor is apparently of greater importance. In the electroneutrality principle, Pauling [15] suggests that metal atoms tend to have charges of zero or at most between +1 and −1 unit. For metals a slight positive charge is more likely than a negative one. Hence ligands likely to leave the Pd(II) atom with a high negative charge are not favourable for increasing the co-ordination number. In order that the Pd(II) atom should not acquire too high a negative charge one could use ligands of high electronegativity (*e.g.*, Cl^-) which tend to form polar covalent bonds, most of the electron density due to the presence of the bonding σ electron pair being located on the ligand. This, for example, is presumably why fluoride ions form an $[FeF_6]^{3-}$ ion whereas the $[FeCl_4]^-$ ion is the more stable species with the chloride ion as ligand. Another means by which the metal atom could acquire a positive charge—or decrease its negative charge—would be for it to form double bonds to the ligand using *d* electron pairs of the metal atom. It will be noted that in this work we have made use of a ligand involving As(III), which, we believe, has a high capacity for double-bond formation. Also the fact that there is the maximum possible charge of +2 units on the $[Pd\,as_2]^{2+}$ cation is expected to facilitate the addition of the halide ion. Finally, in the case of the chloro-complex at least, the existence in nitrobenzene is presumably attributable partly to the lower solvation energy of nitrobenzene than of water;

FIG. 5. *Absorption spectrum of iododi-*(o-*phenylenebisdimethylarsine*)*palladium*(II) *iodide* (4·63 × 10^{-4}M *in nitrobenzene*).

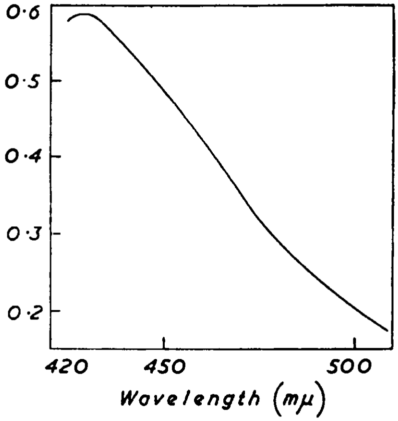
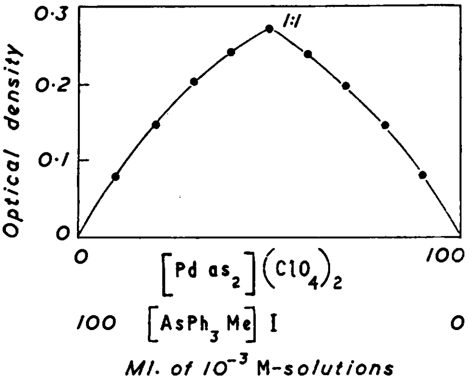


FIG. 6. *Continuous variation study of the reaction*, $[Pd\,as_2]^{++} + I^- \longrightarrow [Pd\,as_2I]^+$, *in nitrobenzene at* 430 mμ (0·5 *cm. cell*). (Optical density corrected for absorption by $AsPh_3MeI$.)

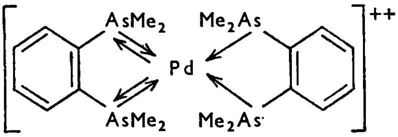


---

[15] Pauling, " Victor Henri Memorial Volume," Liège, 1948, p. 8; *J.*, 1948, 1461.

water would tend to break the Pd–Cl bond more readily because of the hydration energy of the chloride ion.

If it is assumed that the formation of this type of five-covalent complex involves the use of the empty $5p$ orbital by a pair of electrons from the ligand (*e.g.*, an iodide ion) we suggest that the conditions most likely to favour the addition of the negatively charged ligand is the *size of the positive charge* on the palladium. In the $[Pd(NH_3)_4]^{++}$ ion, the palladium receives a share of eight electrons, the distribution between the Pd and the N atoms being dependent on their electronegativities. If sharing were equal, the Pd(II) atom would have a formal charge of -2 units, but taking reasonable values for the electronegativities of palladium and nitrogen (1·5 and 3·0 respectively) we arrive at a figure of approximately $-0{\cdot}6$ unit of charge (see Pauling[16]). Double bonding involving the use of $4d_\varepsilon$ electron pairs of palladium to form a $d\pi$ bond to nitrogen in an ion such as $[Pd(NH_3)_4]^{++}$ is not feasible since the nitrogen has no vacant orbital. With these diarsine compounds, however, the arsenic atom has vacant d orbitals capable of forming such a π bond and for reasons discussed elsewhere (see Craig *et al.*[17]) such π bonding is expected. If the structure involved only *single* bonds between palladium and arsenic [four ordinary σ bonds of the type $As \longrightarrow Pd$; see (II)], then, reasonable values being assumed for the electronegativities of arsenic (2·0) and palladium (1·5), the charge on the palladium atom is expected to be about $-1{\cdot}6$ units of charge. Craig *et al.*[17] have shown that in a square complex a maximum of two strong π bonds (at right angles) is expected to occur. If this is assumed to take place [see (III)], the charge on the palladium atom will change to something of the order of $+0{\cdot}6$ unit. It must be emphasised that we place no absolute significance on these figures: they are calculated simply to establish the kind of charge distribution expected as the result of added π bonding. This change is in the sense required to favour union with an X^- ion to form a covalent bond. It follows from either the application of the simple Fajan rules or the Pauling neutrality principle.[15]



(III)

The effect of solvation calls for comment. In the reaction $[Pd\,as_2X]^+ + nH_2O \rightleftharpoons [Pd\,as_2]^{++} + X^-(H_2O)_n$, the two opposing tendencies in comparisons of the different anions (Cl^-, Br^-, I^-) are the Pd–X bond strength (to the fifth position) and the hydration energy of the X^- anion. The latter increases in the sequence $I^- < Br^- < Cl^-$ and hence, since the order of stability * in water is Pd–I > Pd–Br > Pd–Cl, it is concluded that the hydration energy increases more rapidly in the sequence $I^- < Br^- < Cl^-$ than does the bond energy Pd–I < Pd–Br < Pd–Cl.

Assuming that the square arrangement of the palladium and four arsenic atoms remains unaltered, then from a consideration of the position of the vacant p orbital one might expect a square pyramidal arrangement in the $[Pd\,as_2X]^+$ ion with the X^- group utilising the vacant $5p$ orbital normal to the plane containing the palladium and arsenic atoms. Kimball[18] predicted the trigonal bipyramid for the use of one s, three p, and one d orbital † as in gaseous PCl_5.[19] Daudel and Bucher[20] have however pointed out that a square pyramidal arrangement should result if, in the combination dsp^3, the d orbital has a lower energy (*e.g.*, has a lower principal quantum number) than the s and p orbitals. This also

* The term "stability," used here, refers to free energy (ΔG) of dissociation in water. It does not necessarily parallel bond energy.

† Kimball did not distinguish between the cases where the d orbitals were in the lower or upper energy levels, *i.e.* $(n - 1)dnsnp^3$ and $nsnp^3nd$.

[16] Ref. 5, p. 70.

[17] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332, and references contained therein.

[18] Kimball, *J. Chem. Phys.*, 1940, **8**, 194.

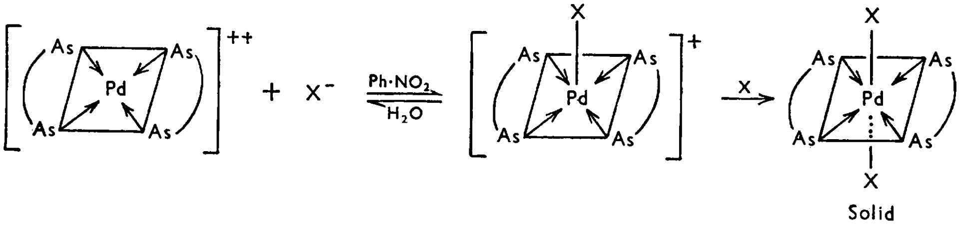
[19] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836; Rouault, *Compt. rend.*, 1938, **207**, 620.

[20] Daudel and Bucher, *J. Chim. phys.*, 1945, **42**, 6.

follows from the group theory approach.[21] Jensen and Nygaard [22] have concluded from electric-dipole measurements that the square pyramidal arrangement does indeed occur in $NiBr_3,2Et_3P$ in which they believe that $3d4s4p^3$ bonds are present. The pentacarbonyl, $Fe(CO)_5$, on the other hand, has been shown by Ewens and Lister [23] to possess a trigonal bipyramidal arrangement even though the expected hybridisation involves $3d4s4p^3$ orbitals.

Although the compounds PdX_2,2Diarsine (where X = Cl, Br, I, NO_2, and SCN) function as uni-univalent electrolytes $[Pd\,as_2X]^+X^-$ in nitrobenzene solution they apparently do not possess this structure in the solid state. Single crystals of the iodide have been examined by *X*-ray crystallography by Mr. N. C. Stephenson and shown to consist of discrete molecules of $Pd\,as_2I_2$ with elongated Pd–I bonds in the *trans*-octahedral positions. This compound is isomorphous with the corresponding bivalent platinum and nickel compounds and their structures will be discussed in detail in a forthcoming paper.[24] This type of octahedral complex may be considered to arise from the use of four square $4d5s5p^2$ bonds and two longer $5p5d$ bonds (in the case of palladium) normal to the plane.*

The nature of these palladium–diarsine complexes is at present best explained by the equilibria in the annexed sketch, involving four-, five-, and six-covalent palladium(II). It remains to be seen from crystal-structure determinations whether the apparently five-covalent ion, $[Pd\,as_2X]^+$, persists in the solid state. The structure of compounds of the type $[M\,as_2X]ClO_4$ (where M = Pd^{II}, Pt^{II}, and Ni^{II} and X = halogen) is now being studied in collaboration with Mr. Stephenson.



It is interesting that the rapid exchange of ligand with $[Ni(CN)_4]^{2-}$, $[Pt(CN)_4]^{2-}$, and $[PtX_4]^{2-}$, as shown by exchange and kinetic studies, has been thought to involve a five co-ordinated transition state employing the outer "*p*" orbital of the metal.[25]

EXPERIMENTAL

Di-(o-*phenylenebisdimethylarsine*)*palladium*(II) *Perchlorate*.—A solution of the chloride was prepared by heating together an alcoholic solution (16 ml.) of *o*-phenylenebisdimethylarsine (2·67 g.) with potassium tetrachloropalladate (1·55 g.) in alcohol (30 ml.) and water (16 ml.). The filtered solution was diluted with water (110 ml.), boiled, and treated dropwise with perchloric acid (73%). The colourless crystals which were immediately deposited were filtered from the hot solution and washed with hot water followed by cold acetone. This yielded 3·6 g. of vacuum-dried material [Found: C, 27·6; H, 4·0; Cl (as ClO_4^-), 8·2; Pd, 12·1. $C_{20}H_{32}O_8Cl_2As_4Pd$ requires C, 27·4; H, 3·7; Cl, 8·1; Pd, 12·15%]. The *compound* was sparingly soluble in hot acetone and nitrobenzene. In the latter solvent it functions as a bi-univalent electrolyte (see Table 1).

---

* Alternatively the shape can be interpreted by using ligand (crystal) field theory. A filled non-bonding dz^2 orbital is normal to the plane of the four square $4d5s5p^2$ bonds and this is expected to cause repulsion of the ligands along the *z* axis, *i.e.*, in the remaining two positions of the (distorted) octahedron. This is in accord with the fact that the two Pd–I bonds are longer than one would expect for a normal covalent bond.

[21] Craig, personal communication.

[22] Jensen and Nygaard *Acta Chem. Scand.*, 1949, **3**, 474.

[23] Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681.

[24] Harris, Nyholm, and Stephenson, unpublished researches; see also *Nature*, 1956, **177**, 1127.

[25] Adamson, Welker, and Wright, *J. Amer. Chem. Soc.*, 1951, **73**, 4786; Taube, *Chem. Rev.*, 1952, **50**, 69.

Dichloro-di-(o-*phenylenebisdimethylarsine*)*palladium*(II).—An aqueous solution (5·0 ml.) of potassium tetrachloropalladate(II) (0·50 g.) was treated with alcohol (10 ml.), followed by an alcoholic solution (5·0 ml.) of *o*-phenylenebisdimethylarsine (0·89 g.), refluxed for about 10 min., filtered, and evaporated to dryness on a water-bath. A solution of the yellow residue in water (10 ml.) was evaporated to a small bulk and cooled in ice-water. The white crystals deposited were filtered off and washed with a small amount of ice-cold water followed by acetone. The acetone converted the white crystals (presumably a hydrate) into a yellow compound which was dried in a vacuum (P_2O_5) (yield 0·18 g.) (Found: C, 32·4; H, 4·2; Cl, 9·7. $C_{20}H_{32}Cl_2As_4Pd$ requires C, 32·0; H, 4·3; Cl, 9·5%). This *compound* is very soluble in cold water, sparingly soluble in nitrobenzene, and insoluble in acetone. Addition of perchloric acid to the filtrate gave 0·73 g. of di-(*o*-phenylenebisdimethylarsine)palladium(II) perchlorate.

This compound was more conveniently obtained by adding a solution of di-(*o*-phenylenebisdimethylarsine)palladium(II) perchlorate in boiling acetone to an acetone solution of excess of lithium chloride, and the yellow crystals deposited were washed with boiling acetone (Found: C, 31·8, 31·95; H, 4·3, 4·6; Cl, 9·6%). The compound functions as a uni-univalent electrolyte in nitrobenzene solution (see Table 1) but approaches the value of a bi-univalent electrolyte in aqueous solution (Λ_M = 180 mho in 0·88 × 10^{-3}M-solution at 19°).

Chlorodi-(o-*phenylenebisdimethylarsine*)*palladium*(II) *Perchlorate.*—A solution of di-(*o*-phenylenebisdimethylarsine)palladium(II) perchlorate (0·44 g.) in boiling acetone (400 ml.) was treated with an acetone solution (10 ml.) of lithium chloride (0·21 g./100 ml.). The resulting golden solution was evaporated to 100 ml. and kept at the b. p. for some time, deep yellow crystals being deposited. The *compound* was washed with hot acetone (yield of vacuum-dried material 0·09 g.) (Found: C, 29·05; H, 3·9; Cl, 8·7. $C_{20}H_{32}O_4Cl_2As_4Pd$ requires C, 29·5; H, 4·0; Cl, 8·7%). The compound was very sparingly soluble in nitrobenzene in which it functions as a uni-univalent electrolyte (see Table 1).

Dibromodi-(o-*phenylenebisdimethylarsine*)*palladium*(II).—A boiling acetone solution (400 ml.) of di-(*o*-phenylenebisdimethylarsine)palladium(II) perchlorate (0·41 g.) was added to a boiling acetone solution (100 ml.) of lithium bromide (3·0 g.). The orange-yellow solution was heated for some minutes. The orange crystals deposited were filtered off from the colourless solution and washed well with hot acetone (yield of vacuum-dried material, 0·37 g.) (Found: C, 28·7; H, 4·0; Br, 19·05. $C_{20}H_{32}Br_2As_4Pd$ requires C, 28·6; H, 3·85; Br, 19·1%). This *compound* is soluble in cold water to a colourless solution. Its conductivity is midway between that of a uni-univalent and a bi-univalent electrolyte in water (Λ_M = 168 mho in 10^{-3}M-solution 21°), although in nitrobenzene it functions as a uni-univalent electrolyte (Table 1).

Bromodi-(o-*phenylenebisdimethylarsine*)*palladium*(II) *Perchlorate.*—A boiling acetone solution (400 ml.) of di-(*o*-phenylenebisdimethylarsine)palladium(II) perchlorate (0·40 g.) was treated with an acetone solution (20·0 ml.) of lithium bromide (0·20 g./100 ml.) and evaporated to 150 ml., orange crystals being deposited. The solution was cooled and the *compound* filtered off and washed with cold acetone (yield, 0·15 g. of vacuum-dried material) (Found: C, 28·1; H, 3·9; Br, 9·6. $C_{20}H_{32}O_4ClBrAs_4Pd$ requires C, 28·0; H, 3·8; Br, 9·3%).

Di-iododi-(o-*phenylenebisdimethylarsine*)*palladium*(II).—A solution of *o*-phenylenebisdimethylarsine (1·14 g.) in alcohol (6 ml.) was added to potassium tetrachloropalladate(II) (0·66 g.) in water (10) ml.) and alcohol (20 ml.). The mixture was boiled for some minutes, diluted with water (100 ml.), and filtered at the b. p. into a solution of sodium iodide (3·0 g.) in hot water (30 ml.). The orange crystals deposited were filtered off and washed with cold water, then with absolute alcohol in which they were somewhat soluble to an orange-yellow solution. They appeared to be slowly becoming red (dehydration). On transference to acetone (50 ml.) and refluxing they were immediately converted into deep red (anhydrous) crystals. The red crystals were washed with cold acetone and dried under vacuum (yield 1·6 g.) (Found: C, 25·5, 25·5; H, 3·2, 3·4; I, 27·0; Pd, 11·3. $C_{20}H_{32}I_2As_4Pd$ requires C, 25·75; H, 3·5; I, 27·2; Pd, 11·4%). The *compound* is sparingly soluble in nitrobenzene in which it functions as a uni-univalent electrolyte (Table 1). It is insoluble in cold water but sparingly soluble at the b. p.

This compound was also isolated as an orange monohydrate by dissolving the anhydrous compound (0·25 g.) in boiling water (250 ml.) and adding the yellow solution with stirring, to a hot solution (30 ml.) of sodium iodide (2·0 g.). The orange needles were filtered off and washed with cold water, followed by dry ether, and dried at 120° (yield, 0·23 g. of orange crystals) (Found: I, 26·6. $C_{20}H_{34}OI_2As_4Pd$ requires I, 26·7%). Refluxing this *monohydrate* with acetone converted it into the red anhydrous compound.

Iododi-(o-*phenylenebisdimethylarsine*)*palladium*(II) *Perchlorate.*—A boiling acetone solution (400 ml.) of di-(*o*-phenylenebisdimethylarsine)palladium(II) perchlorate (0·48 g.) was treated with an acetone solution (10·0 ml.) of sodium iodide (0·75 g./100 ml.), then evaporated to 100 ml., and the deep red crystals were filtered off and washed with boiling acetone (yield of vacuum-dried material, 0·14 g.) (Found : C, 26·35; H, 3·5; I, 14·0; Cl, 4·3. $C_{20}H_{32}O_4ClIAs_4Pd$ requires C, 26·5; H, 3·6; I, 14·0; Cl, 3·9%). This *compound* was sparingly soluble in nitrobenzene in which it functions as a uni-univalent electrolyte (see Table 1). It possessed $\chi_g = -0{\cdot}22 \times 10^{-6}$ and is hence diamagnetic.

This salt was also obtained from Pd as_2I_2 as follows. A boiling aqueous solution (250 ml.) of the di-iodo-complex (0·20 g.), on dropwise addition of 72% perchloric acid (1·0 ml.), gave an immediate precipitate of the perchlorate. The compound was washed with hot water and cold acetone (yield of vacuum-dried material, 0·16 g.) (Found : C, 26·4; H, 3·5; I, 13·8; Cl, 4·3%).

The Mixed Compound Pd as_2IClO_4,Pd $as_2(ClO_4)_2$.—The iodide, Pd as_2I_2 (0·20 g.), was dissolved in boiling water (200 ml.) and treated rapidly with 72% perchloric acid (5·0 ml.). The yellow *perchlorate* deposited was filtered off, washed with cold water and cold absolute alcohol, and dried overnight in a vacuum (P_2O_5) (yield 0·16 g.) (Found : C, 26·6; H, 3·7; I, 7·0; Pd, 12·1. $C_{32}H_{40}O_{12}Cl_3IAs_4Pd$ requires C, 26·95; H, 3·6; I, 7·1; Pd, 12·0%). If the compound is washed with boiling water or cold acetone it is converted into the red compound [Pd as_2I]ClO_4.

Dinitrodi-(o-*phenylenebisdimethylarsine*)*palladium*(II).—A solution of the chloride was prepared by heating *o*-phenylenebisdimethylarsine (0·57 g.) with potassium tetrachloropalladate(II) (0·33 g.) in alcohol (8·0 ml.) and water (3·0 ml.). The filtered solution was diluted with water (25 ml.) and treated with sodium nitrite solution (6·0 g. in 10 ml.). On cooling to room temperature, a yellow crystalline *compound* was slowly deposited. This was filtered off, washed with small quantities of cold water, and then with large quantities of acetone. A further crop of crystals was obtained from the filtrate by adding more sodium nitrite (5·0 g.). When washed with acetone the crystals changed from light yellow to orange, presumably owing to loss of water of crystallisation (yield of vacuum-dried material, 0·23 g.) (Found : C, 31·2; H, 4·0; N, 3·7. $C_{20}H_{32}O_4N_2As_4Pd$ requires C, 31·2; H, 4·2; N, 3·6%). The compound was sparingly soluble in warm nitrobenzene in which it functions as a uni-univalent electrolyte (see Table 1). This compound is soluble in water to a colourless solution.

Dithiocyanatodi-(o-*phenylenebisdimethylarsine*)*palladium*(II).—A boiling solution of the chloride prepared as described in the previous paragraph was treated dropwise with an aqueous solution (15 ml.) of ammonium thiocyanate (2·0 g.). After a few minutes' heating the yellow precipitate was filtered off and washed with cold water followed by acetone (yield of vacuum-dried material, 0·67 g.) (Found : C, 33·2; H, 3·95; N, 3·4; Pd, 13·3. $C_{22}H_{32}N_2S_2As_4Pd$ requires C, 33·2; H, 4·1; N, 3·5; Pd, 13·4%). The *compound* is practically insoluble in water and sparingly soluble in warm nitrobenzene in which it functions as a uni-univalent electrolyte (Table 1).

Analyses.—Palladium. This could not be estimated by ignition to the metal owing to the presence of arsenic which tends to alloy with the palladium. The compound was decomposed by fuming with 36N-sulphuric acid (3 ml.) and drops of perchloric acid. After cooling and dilution with water the palladium was precipitated by dimethylglyoxime in the normal manner and the precipitate ignited to metallic palladium. The ignited metal was allowed to cool to room temperature in an atmosphere of methanol (filter-paper moistened with methanol held over mouth of crucible) to prevent the formation of palladium oxide.

Halogen (*excluding perchlorate*). Since the compound [Pd as_2]$(ClO_4)_2$ is soluble in hot dilute nitric acid the halogen (excluding chlorine from perchlorate) was determined gravimetrically as silver halide.

Other elements. Carbon and hydrogen were determined microanalytically by Dr. E. Challen. The chlorine in the form of perchlorate was determined by Dr. Zimmermann of the Australian Microanalytical Service, Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

The authors thank Messrs. Garrett, Davidson, and Matthey (of Sydney) for the palladium used.

School of Applied Chemistry, N.S.W. University of Technology,
Broadway, Sydney, New South Wales.
William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

[*Received, May* 9*th*, 1956.]