# **969.** *Some Complexes of Palladium*(II) *and Platinum*(II) *with Mixed Phosphorus–Nitrogen Ligands*

By H. P. Fritz, I. R. Gordon, K. E. Schwarzhans, and L. M. Venanzi

The preparation of the ligands $o$-$Me_2N\cdot C_6H_4\cdot PPh_2$, $(o\text{-}Me_2N\cdot C_6H_4)_2PPh$, and $(o\text{-}Me_2N\cdot C_6H_4)_3P$, and their complexes $[MX_2(\text{ligand})]$ (M = Pd or Pt; X = Cl, Br, or I), are described. It is shown that only the phosphorus and one of the nitrogen atoms of the terdentate and quadridentate ligands are bonded to the metal ions which exhibit their usual square-planar co-ordination.

Recent investigations showed that tris-($o$-diphenylphosphinophenyl)phospine, QP (Ia), and the corresponding arsine, QAS (Ib), react with palladium(II) and platinum(II) to give compounds of the type $[MX(Q)]^+$ (M = Pd or Pt; X = co-ordinating anion; Q = QP or QAS) with trigonal bipyramidal co-ordination.[1] The preferential formation of trigonal bipyramidal complexes by the quadridentate ligands QP and QAS must be strongly influenced by their steric requirements, but it is possible that the resulting structures may be caused by the electronic nature of the donor atoms, phosphorus or arsenic, which are strongly polarisable and able to act as $\pi$-acceptors.[1]

|  | $(o\text{-}R_2L\cdot C_6H_4)_3L'$<br>(I) |  | $(o\text{-}R_2L\cdot C_6H_4)_2L'Ph$<br>(II) |  | $(o\text{-}R_2N\cdot C_6H_4)LR'_2$<br>(III) |
|---|---|---|---|---|---|
| (QP) | a: R = Ph, L = P, L′ = P | (TP) |  |  | a: R = Me, L = P, R′ = Et |
| (QAS) | b: R = Ph, L = As, L′ = As | (TAS) |  |  | b: R = Me, L = As, R′ = Me |
| (PTN) | c: R = Me, L = N, L′ = P | (PDN) |  | (PN) | c: R = Me, L = P, R′ = Ph |

In order to study the effect of the electronic nature of the donor atoms on the geometry of the complexes, tris-($o$-dimethylaminophenyl)phosphine, PTN (Ic), bis-($o$-dimethylaminophenyl)phenylphosphine, PDN (IIc), and $o$-dimethylaminophenyldiphenylphosphine, PN (IIIc), were prepared and their palladium(II) and platinum(II) complexes investigated.

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[1] L. M. Venanzi, *Angew. Chem.*, 1964, **76**, 621; *Angew. Chem. Internat. Edn.*, 1964, **3**, 453.

The new ligands were prepared by reaction of *o*-dimethylaminophenyl-lithium with the appropriate phosphorus halide. They are white crystalline solids, stable in air and soluble in organic solvents. The complexes were prepared by addition of ethanolic solutions of the tetrahalogeno-complexes to ethanolic solutions of the ligands. It was observed that recrystallisation of the bromo- and iodo-complexes from solvent mixtures containing dichloromethane gave impure products. Their infrared spectra in the cæsium bromide region showed a band at about 330 cm.$^{-1}$ (a M–Cl stretching mode) which increased in intensity with repeated recrystallisation, indicating that anion-exchange was occurring. This was quenched by addition of the appropriate sodium halide to the solvent mixture.

The complexes of the type $[MX_2(\text{ligand})]$ (see Table 1) are stable, crystalline solids, readily soluble in organic solvents. They are diamagnetic and non-electrolytes in nitromethane solution. These solutions do not react with iodomethane, and it might be inferred that all the donor atoms of the multidentate ligand are bonded to the central metal atom. As will be apparent later, only the phosphorus atom and one of the nitrogen atoms are bonded to the metal atom, and therefore the iodomethane test is not diagnostic for unco-ordinated dimethylanilino-groups. Presumably this is due to a deactivation of

TABLE 1

Colours, decomposition points, conductivities, and analyses (%) of palladium(II) and platinum(II) complexes with the ligands PTN (Ic), PDN (IIc), and PN (IIIc)

| No. | Formula | Colour | Decomp. pt. | $\Lambda_M$ (mho) * |
|---|---|---|---|---|
| 1 | $[PdCl_2(PN)]$ | Chrome yellow | 287—288° | 0·3 |
| 2 | $[PdBr_2(PN)]$ | Yellow-orange | 284—285 | 2 |
| 3 | $[PdI_2(PN)]$ | Deep red | 268—269 | 4 |
| 4 | $[PdCl_2(PDN)]$ | Chrome yellow | 274—275 | 1 |
| 5 | $[PdBr_2(PDN)]$ | Yellow-orange | 263—264 | 6 |
| 6 | $[PdI_2(PDN)]$ | Deep red | 255—256 | 8·6 |
| 7 | $[PdCl_2(PTN)]$ | Yellow | 229—230 | 5·1 |
| 8 | $[PdBr_2(PTN)]$ | Orange | 225—226 | 6·8 |
| 9 | $[PdI_2(PTN)]$ | Deep red | 219—220 | 9·3 |
| 10 | $[PtCl_2(PN)]$ | Cream-white | 295—296 | 1·3 |
| 11 | $[PtBr_2(PN)]$ | Pale yellow | 285—286 | 5 |
| 12 | $[PtI_2(PN)]$ | Chrome yellow | 279—280 | 7 |
| 13 | $[PtCl_2(PDN)]$ | Cream-white | 274—275 | 0·2 |
| 14 | $[PtBr_2(PDN)]$ | Pale yellow | 273—274 | 3·2 |
| 15 | $[PtI_2(PDN)]$ | Chrome yellow | 264—265 | 3 |
| 16 | $[PtCl_2(PTN)]$ | Pale yellow | 238—239 | 8 |
| 17 | $[PtBr(PTN)]$ | Pale yellow | 232—233 | 8·3 |
| 18 | $[PtI_2(PTN)]$ | Yellow | 216—217 | 5·6 |

| | Carbon | | Hydrogen | | Nitrogen | | Phosphorus | | Platinum | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. |
| 1 | 49·8 | 49·7 | 4·0 | 4·2 | 3·1 | 2·9 | 6·5 | 6·4 | | |
| 2 | 42·1 | 42·0 | 3·6 | 3·5 | 2·5 | 2·5 | 5·4 | 5·4 | | |
| 3 | 35·9 | 36·1 | 3·1 | 3·0 | 2·4 | 2·1 | 4·7 | 4·7 | | |
| 4 | 50·4 | 50·2 | 4·5 | 4·8 | 5·0 | 5·3 | 6·0 | 5·9 | | |
| 5 | 43·6 | 43·0 | 4·1 | 4·1 | 4·8 | 4·6 | 5·2 | 5·0 | | |
| 6 | 37·2 | 37·3 | 3·5 | 3·6 | 3·7 | 4·0 | 4·5 | 4·4 | | |
| 7 | 50·9 | 50·6 | 5·4 | 5·3 | 7·3 | 7·4 | 5·3 | 5·4 | | |
| 8 | 43·7 | 43·8 | 4·8 | 4·6 | 6·3 | 6·4 | 4·8 | 4·7 | | |
| 9 | 38·5 | 38·3 | 4·0 | 4·0 | 5·9 | 5·6 | 4·1 | 4·1 | | |
| 10 | 42·2 | 42·0 | 3·5 | 3·5 | 2·6 | 2·5 | 5·4 | 5·4 | 34·2 | 34·2 |
| 11 | 36·6 | 36·4 | 2·9 | 3·1 | 2·2 | 2·1 | 4·7 | 4·7 | 29·6 | 29·6 |
| 12 | 31·9 | 31·8 | 2·9 | 2·7 | 1·6 | 1·9 | 4·2 | 4·1 | 26·0 | 25·9 |
| 13 | 43·1 | 43·0 | 4·1 | 4·1 | 4·6 | 4·6 | 5·1 | 5·0 | 32·0 | 31·8 |
| 14 | 37·4 | 37·6 | 3·6 | 3·6 | 3·7 | 4·0 | 4·5 | 4·4 | 27·9 | 27·8 |
| 15 | 33·0 | 33·1 | 3·1 | 3·2 | 3·5 | 3·5 | 3·9 | 3·9 | 24·6 | 24·5 |
| 16 | 43·9 | 43·8 | 4·7 | 4·6 | 6·3 | 6·4 | 4·8 | 4·7 | 29·5 | 29·7 |
| 17 | 38·5 | 38·6 | 4·1 | 4·1 | 5·7 | 5·6 | 4·2 | 4·2 | 26·0 | 26·2 |
| 18 | 34·4 | 34·3 | 3·7 | 3·6 | 4·8 | 5·0 | 3·6 | 3·7 | 23·3 | 23·2 |

* For $10^{-3}$M-solutions in nitrobenzene at 20°.

the nitrogen atoms by co-ordination, the effect being transmitted through the aromatic system.[2] In this context it is interesting to note that *o*-dimethylaminophenyldiethylphosphine (IIIa) gives only a monomethiodide.[3]

The co-ordination numbers and stereochemistries of the complexes were unambiguously established by the physical measurements desribed below.

*Infrared Measurements.*—Two regions of the spectrum proved to be particularly informative: (a) 2750—2800 cm.$^{-1}$; (b) 340—270 cm.$^{-1}$.

Absorption in region (a) is characteristic of *N*-methylanilines. This band disappears either on co-ordination or on quaternarisation.[4] The free ligands and all the complexes of the terdentate ligand PDN and of the quadridentate ligand PTN show this diagnostic band, which is absent in the complexes of the bidentate ligand PN.

In region (b) the chloro-complexes show two characteristic bands at about 330 and 285 cm.$^{-1}$ analogous to those found[5] in complexes *cis*-[$PtCl_2L_2$], which have been assigned to symmetric and antisymmetric stretching modes of the $PtCl_2$-group.

*Visible and Ultraviolet Spectra.*—These were recorded for dichloromethane solutions and for solids. The solution spectra (Table 2) of the complexes of any one metal halide with the three ligands are practically identical. Slight differences are observed in the solid reflection spectra of such sets of compounds. The solid reflection spectra, however, are fully analogous to the solution spectra. The ratio of the frequencies of the lowest-energy band in the palladium and platinum iodide complexes is 1 : 1·22, in agreement with the general order of increase in crystal-field splitting between the second and third transition series of 1 : 1·21.[6]

*Proton Magnetic Resonance Spectra.*—The results are given in Table 3. As can be seen, the proton resonance signals from the *N*-methyl group in the free ligands show chemical shifts of 154—161 c./sec. with respect to the tetramethylsilane standard, while the signals due to co-ordinated *N*-methyl groups are shifted further to lower fields, *e.g.*, in [$PtX_2$(PN)] (X = Br or I) the shifts due to co-ordination are 73·5 and 75·5 c./sec., respectively. The co-ordinatively bound nitrogen is depleted of electrons, and thus the shielding of the methyl protons is reduced. Similar, but smaller, shifts are observed for the protons on the aromatic rings.

*Platinum complexes.* The methyl protons in the complexes of the terdentate ligand PDN and of the quadridentate ligand PTN give rise to signals in the range 55—75 c./sec. towards lower fields, and in the range 14—19 c./sec. towards higher fields, than the free ligand. The former singals are clearly due to methyl protons attached to bound nitrogen atoms, and the latter are attributed to methyl protons attached to free nitrogen atoms.

The complexes of PDN give two signals attributable to methyl groups attached to co-ordinated nitrogen. Furthermore, two $^{195}Pt$–N–C–$H$ couplings are observed. This splitting is probably caused by the complete asymmetry of the molecule, which results in the two methyl groups attached to a bound nitrogen atom having different environments. This molecular asymmetry may arise as follows: the free dimethylamino-group in the terdentate ligand PDN ($N_1$ in Figure 1) exerts a strong steric effect on the nearest methyl group on the bound nitrogen atom ($N_2$ in Figure 1), causing a distortion of the $C_{ring}$–N–$C_{Me}$ bond angle, as is clearly indicated by molecular models.

This splitting is not observed in complexes of the quadridentate ligand PTN since in this case both substituents on the bound nitrogen atom are equally influenced by free $Me_2N$ groups.

The proton signals in complexes [$PtI_2$(ligand)] (ligand = PN, PDN, or PTN) are split by the $^{195}Pt$ nuclear spin. This splitting provides further evidence for Pt–N co-ordination.

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[2] F. G. Mann and J. Watson, *J. Org. Chem.*, 1948, **13**, 502.

[3] F. G. Mann and H. R. Watson, *J.*, 1957, 3950.

[4] G. D. Meakins and R. D. Hill, *J.*, 1958, 760.

[5] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J.*, 1964, 734.

[6] C. J. Ballhausen, " Introduction to Ligand Field Theory," McGraw-Hill, New York, 1962.

TABLE 2

Visible and ultraviolet absorption spectra of complexes

| | Solution * | | Solid † | |
|---|---|---|---|---|
| Formula | $E_{max.}$ (cm.$^{-1}$) | $\varepsilon_{max.}$ (l. mole$^{-1}$ cm.$^{-1}$) | $E_{max.}$ (cm.$^{-1}$) | $D$ |
| [$PdCl_2$(PN)] | 36,200 | 7350 | *ca.* 36,000 | 0·9 |
| | 28,300 | 1220 | 27,800 | 0·785 |
| [$PdBr_2$(PN)] | 34,400 | 13,900 | | |
| | 28,200 | 2900 | 28,500 | sh |
| | | | 26,000 | 0·597 |
| [$PdI_2$(PN)] | 31,200 | 14,100 | 30,800 | 1·08 |
| | 26,000 | 2320 | 26,000 | 0·905 |
| | 21,700 | 3090 | 21,500 | 0·965 |
| [$PdCl_2$(PDN)] | 37,200 | 13,200 | | |
| | *ca.* 34,000 | sh | | |
| | 27,400 | 1930 | 27,400 | 0·955 |
| [$PdBr_2$(PDN)] | 35,200 | 13,000 (in $CHCl_3$) | 35,000 | |
| | 29,600 | sh | | |
| | 26,000 | 2460 | 26,000 | 0·69 |
| [$PdI_2$(PDN)] | 38,700 | sh | | |
| | 36,200 | sh | | |
| | 31,400 | 13,100 | 31,600 | 1·18 |
| | 25,900 | sh | 26,200 | sh |
| | 21,800 | 3260 | 22,000 | 1·0 |
| [$PdCl_2$(PTN)] | *ca.* 36,800 | sh (in $CHCl_3$) | | |
| | *ca.* 30,000 | sh | | |
| | 27,600 | 2320 | 26,900 | 0·572 |
| [$PdBr_2$(PTN)] | 35,200 | 13,900 | 30,600 | sh |
| | *ca.* 29,400 | sh | 27,200 | sh |
| | 26,500 | 2640 | 26,000 | 0·825 |
| [$PdI_2$(PTN)] | *ca.* 40,000 | sh | | |
| | *ca.* 36,000 | sh | *ca.* 37,000 | sh |
| | 31,200 | 12,700 | 31,300 | 0·865 |
| | 25,600 | 2730 | 25,500 | 0·69 |
| | 21,800 | 3260 | 21,500 | 0·77 |
| [$PtCl_2$(PN)] | 37,400 | 5400 | | |
| | 36,700 | sh | 33,200 | sh |
| | 30,800 | sh | 30,100 | 0·455 |
| [$PtBr_2$(PN)] | 37,000 | sh | | |
| | 36,200 | sh | | |
| | 32,000 | sh | 31,900 | sh |
| | *ca.* 28,600 | sh | 29,000 | sh |
| | *ca.* 25,000 | sh | 25,800 | sh |
| [$PtI_2$(PN)] | 37,600 | 17,800 | | |
| | 32,300 | sh | *ca.* 32,500 | sh |
| | 26,400 | 2020 | 26,500 | 0·97 |
| | *ca.* 22,600 | sh | *ca.* 23,000 | sh |
| [$PtCl_2$(PDN)] | 37,500 | sh | | |
| | 36,600 | sh | 36,600 | sh |
| | 33,500 | sh | 34,500 | sh |
| | 29,000 | sh | 29,000 | sh |
| [$PtBr_2$(PDN)] | 36,800 | sh | | |
| | 33,000 | sh | 32,200 | sh |
| | 28,100 | sh | 27,900 | sh |
| [$PtI_2$(PDN)] | 38,800 | sh | | |
| | 31,000 | sh | 30,300 | sh |
| | 26,800 | 2122 | 26,700 | 0·805 |
| [$PtCl_2$(PTN)] | *ca.* 43,000 | sh | | |
| | *ca.* 37,500 | sh | 32,200 | sh |
| | *ca.* 30,000 | sh | *ca.* 29,600 | sh |
| [$PtBr_2$(PTN)] | 42,000 | sh | 38,600 | sh |
| | 37,000 | sh | 32,500 | sh |
| | *ca.* 32,600 | sh | 29,000 | sh |
| [$PtI_2$(PTN)] | 42,600 | sh | | |
| | 39,000 | sh | | |
| | 31,500 | sh | 31,200 | sh |
| | 26,900 | 2700 | 26,700 | 0·838 |

* Solution in dichloromethane unless otherwise specified. † Solid reflectance spectra, solid diluted with KCl to 10% mixture.

TABLE 3

Nuclear magnetic resonance spectra of palladium(II) and platinum(II) complexes

| Compound | Chemical shifts (c./sec.) * $H_{Ar}$ | $H_{co\text{-}ord.}$ | $H_{unco\text{-}ord.}$ | Coupling constants $J(^{195}Pt–N–C–H)$ (c./sec.) | Concn. (%) |
|---|---|---|---|---|---|
| (PN) | 435 | — | 154 | — | 5 |
| (PDN) | 422 | — | 159 | — | 15 |
| (PTN) | 422 | — | 160·5 | — | sat. |
| $[PdBr_2(PN)]$ | 459 | 217 | — | — | sat. |
| $[PdI_2(PN)]$ | 455 | 218·5 | — | — | 10 |
| $[PdBr_2(PDN)]$ | 446 | 179 | 179 | — | sat. |
| | 446 | 219·5 †<br>204·5 † | 146 † | — | sat. |
| $[PdI_2(PDN)]$ | 444 | 178 | 178 | — | 10 |
| | 444 | 220·5 †<br>207·5 † | 142 † | — | sat. |
| $[PdBr_2(PTN)]$ | 447 | 167 | 167 | — | 10 |
| | 447 | 167 † | 167 † | — | |
| $[PdI_2(PTN)]$ | 443 | 168 | 168 | — | sat. |
| | 443 | 168 † | 168 † | — | |
| $[PtBr_2(PN)]$ | 453 | 227·5 | — | 33·5 | sat. |
| $[PtI_2(PN)]$ | 460 | 229·5 | — | 34 | sat. |
| $[PtBr_2(PDN)]$ | 448 | 230<br>214·5 | 145·5 | 32<br>34 | sat. |
| $[PtI_2(PDN)]$ | 448 | 234·5<br>219 | 143 | 34<br>35 | sat. |
| $[PtI_2(PTN)]$ | 444 | 226 | 141 | 36 | 5 |

The values refer to the centre of the signal group: $H_{Ar}$ = aromatic proton signal; $H_{co\text{-}ord.}$ = proton signals of the co-ordinated $NMe_2$ group; $H_{unco\text{-}ord.}$ = proton signals of the free $NMe_2$ groups.

* At 60 Mc./sec., from tetramethylsilane, in dichloromethane solution, at 305°K.

† As above, in deuterochloroform solution, at 220°K.

The $^{195}Pt$-N-C-$H$ coupling constants are of the order of about 34 c./sec., in good agreement with the value of 45 found in $[Pt\ en_2]^{2+}$.[7]

The approximate relative ratios of methyl protons are 1 : 1 : 2 in $[PtX_2(PDN)]$ and 1 : 2 in $[PtX_2(PTN)]$. In the former case this corresponds to one methyl group attached to the bound nitrogen, uninfluenced by the neighbouring groups (C1), one sterically hindered methyl group (C2) also attached to the bound nitrogen, and two methyl groups (C3 and C4) attached to the free nitrogen atom. In the last case the ratio arises from two methyl groups attached to the bound nitrogen and four methyl groups attached to the two free nitrogen atoms.

*Palladium complexes.* The spectra of the complexes with the bidentate ligand were analogous to those of the corresponding platinum compounds, except for the absence of metal–proton nuclear spin coupling.

The palladium complexes with the terdentate and quadridentate ligands, PDN and PTN, respectively, gave only one sharp signal due to methyl protons between 6·5 and 20 c./sec. to higher fields than that of the ligand (see Table 3), suggesting either a co-ordination number higher than that of the corresponding platinum complexes or rapid exchange of the particular nitrogen atom bonded to the metal ion. Low-temperature spectra showed the second alternative to be correct. At —30° the palladium complexes of the terdentate ligand PDN showed a flat proton resonance signal, about 100 c./sec. wide, due to methyl protons; at —53° the spectra were fully analogous to those of the corresponding platinum complexes, showing two signals arising from the methyl protons attached to a bound nitrogen atom and one signal due to methyl protons belonging to " free " nitrogen atoms (see Figure 2). The spectra of the complexes of the quadridentate ligand PTN at —55° showed only a broadening of the sharp signal observed at room temperature. The apparatus used did not allow the measurement of spectra below —55°.

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[7] D. B. Powell and N. Sheppard, *J.*, 1959, 791.

Phosphorus–proton spin splitting was not discernible in any of the complexes investigated.

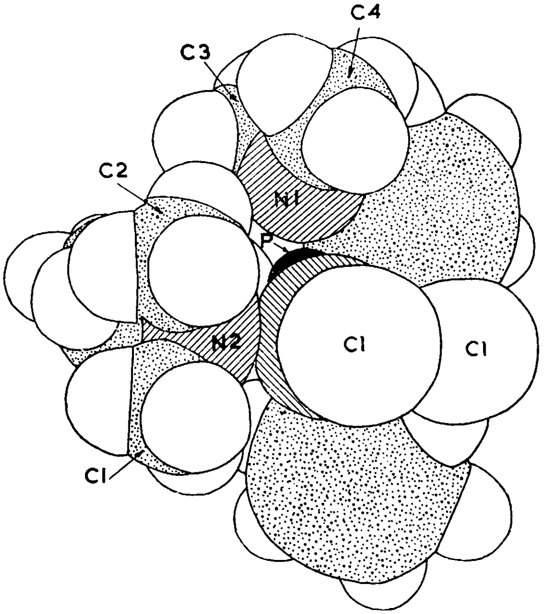

FIGURE 1. Model of the complex [$PdCl_2$(PDN)] [PDN = (*o*-$Me_2N{\cdot}C_6H_4)_2PPh$]

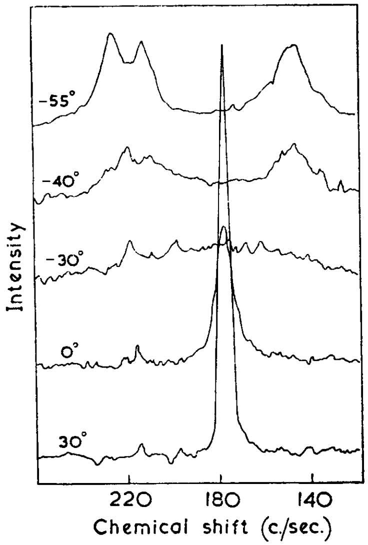

FIGURE 2. Temperature dependence of the proton magnetic resonance of [$PdI_2$(PDN)] in deuterochloroform [PDN = (*o*-$Me_2N{\cdot}C_6H_4)_2PPh$]

## DISCUSSION

The results of the above measurements show that all the complexes are four-co-ordinate with square planar structure, all the ligands being bound to the central metal atom by one phosphorus and one nitrogen atom.

The complexes of the bidentate ligand PN are similar to those prepared by Mann and his co-workers who used ligands such as *o*-dimethylaminophenyldiethylphosphine (IIIa) [3] and *o*-dimethylaminophenyldimethylarsine (IIIb).[8] These ligands showed a strong tendency to form uncharged complexes of the type [$MX_2$(ligand)], although charged species of the type [M(ligand)$_2$]$^{2+}$ could be isolated. All attempts to prepare cationic complexes with the ligand PN were unsuccessful. Molecular models show that the presence of phenyl substituents in this ligand prevents the formation of square planar complexes of the latter type. This parallels the behaviour observed in palladium and platinum complexes of *NNN'N'*-tetramethleyethylenediamine, which gives only complexes of the type [$MX_2$(ligand)].[9]

The observation that the terdentate and quadridentate ligands, PDN and PTN, respectively, act only as bidentate ligands contrasts with the behaviour of the terdentate ligands TP (IIa) and TAS (IIb), and that of the quadridentate ligands QP (Ia) and QAS (Ib). It is interesting to note that the two terdentate ligands above give square planar complexes of the type [MX(ligand)]$^+$, and even five-co-ordinate complexes of the type [$MX_2$(ligand)].[10] As mentioned earlier, the quadridentate ligands QP and QAS give five-co-ordinate complexes with trigonal bipyramidal structure.[1] This difference is probably due to the deactivation of the dimethylamino nitrogen donors, which are known to be weak, by electron-withdrawal by co-ordination of the two bound donor atoms, transmitted through aromatic systems. This effect will be operative also in the phosphorus and arsenic ligands, TP, TAS, QP, and

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[8] F. G. Mann and F. H. C. Stewart, *J.*, 1955, 1269.
[9] F. G. Mann and H. R. Watson, *J.*, 1958, 2772.
[10] J. G. Hartley, L. M. Venanzi, and D. C. Goodall, *J.*, 1963, 3930.

QAS, but it is obviously not sufficient to lower the co-ordinating ability of some of the donor atoms to the extent of rendering them inactive.

As the quadridentate nitrogen–phosphorus ligand PTN is in fact only bidentate in these complexes, it is not possible to deduce whether the preferential formation of trigonal bipyramidal complexes by QP and QAS is due mainly to steric or to electronic causes.

## Experimental

*Preparation of the Ligands.*—*o*-Bromodimethylaniline was prepared by the method of Gilman and Banner.[11] The product, after fractionation, contained small amounts of primary and secondary amines; these were removed by treatment with acetic anhydride. The preparation of n-butyl-lithium and its subsequent reactions were carried out in an atmosphere of argon.

*Tris-*(o-*dimethylaminophenyl*)*phosphine*, PTN (Ic). n-Butyl-lithium (170 ml. of a 1·47M-solution) was cooled to $-20°$ and 2-bromo-*NN*-dimethylaniline (50 g.) in ether (100 ml.) was added during 1 hr., with stirring. The mixture was allowed to warm to room temperature, left for 1 hr., then cooled again to $-40°$ and phosphorus trichloride (53 ml.) in ether (50 ml.) added dropwise over 1·5 hr. The mixture was then allowed to warm up to room temperature and left for 1 hr., cooled in ice–water, and acidified with 1N-hydrochloric acid. The aqueous layer was neutralised with concentrated sodium hydroxide solution and the product extracted with ether. The ethereal layer was dried, the solvent evaporated at the pump, and the residual *solid* recrystallised twice from ethanol. Yield 30%, m. p. 109° (Found: C, 73·5; H, 7·5; N, 10·7; P, 7·9. $C_{24}H_{30}N_3P$ requires C, 73·6; H, 7·7; N, 10·7; P, 7·9%).

*Bis-*(o-*dimethylaminophenyl*)*phenylphosphine*, PDN (IIc). This was prepared, as described above, from n-butyl-lithium (65 ml. of a 1·54M-solution), 2-bromo-*NN*-dimethylaniline (20 g.) in ether (50 ml.), and phenyldichlorophosphine (6·8 ml.) in ether (50 ml.). The *product* was recrystallised from 80% ethanol. Yield 45%, m. p. 84·5° (Found: C, 75·6; H, 7·1; N, 8·0; P, 8·9. $C_{22}H_{25}N_2P$ requires C, 75·8; H, 7·2; N, 8·0; P, 8·9%).

o-*Dimethylaminophenyldiphenylphosphine*, PN (IIIc). This was prepared, as described above, from n-butyl-lithium (165 ml. of a 1·52M-solution), 2-bromo-*NN*-dimethylaniline (50 g.) in ether (50 ml.), and diphenylchlorophosphine (44 ml.) in ether (50 ml.). The *product* was recrystallised from ethanol. Yield 55%, m. p. 113—114° (Found: C, 78·4; H, 6·8; N, 4·6; P, 10·2. $C_{20}H_{20}NP$ requires C, 78·7; H, 6·6; N, 4·6; P, 10·15%).

*Preparation of the Complexes.*—The *chloro-complexes* were prepared by adding one equivalent of sodium tetrachloro-metallate, in ethanol, to a hot ethanolic solution of the ligand, heating the solution for a few minutes, and filtering while still hot. The products, which separated on cooling, were recrystallised from n-butanol (platinum compounds) or from ethanol (palladium compounds). The *bromo-* and *iodo-complexes* were prepared by reaction of the chloro-complex with the appropriate sodium halide and were recrystallised from n-butanol (platinum complexes) or from ethanol (palladium complexes) to which the appropriate sodium halide had been added.

*Analyses.*—Platinum and phosphorus were determined spectrophotometrically.[12] Ashing of the samples for metal analysis was done with nitric and perchloric acids and for the phosphorus analyses with perchloric acid and *ca.* 10 mg. of vanadium pentoxide.

*Physical Measurements.*—Conductivity, and magnetic measurements, and visible, ultraviolet, and infrared spectra were done as described elsewhere.[10] The observed metal–chlorine stretching vibrations (in $cm.^{-1}$) were: [$PdCl_2$(PN)] 340br,vs, 290br,vs; ($PtCl_2$(PN)] 337—329br,vs, 298vs, 273s; [$PdCl_2$(PDN)] 330br,s, 281 br,vs; [$PtCl_2$(PDN)] 337br,s, 293br,s; [$PdCl_2$(PTN)] 331br,vs, 281br,vs; [$PtCl_2$(PTN)] 340br,vs, 279br,vs.

Proton magnetic resonance spectra were obtained with a Varian A-60 analytical spectrometer with variable-temperature unit. Chemical shifts are given relative to internal tetramethylsilane, positive to the low-field side.

The authors thank the D.S.I.R. for a studentship to I. R. G.

(I. R. G. and L. M. V.) Inorganic Chemistry Laboratory, University of Oxford.
(H. P. F. and K. E. S.) Institut für Anorganische Chemie,
University of Munich.

[*Received, February* 18*th*, 1965.]

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