Palladium(II), Platinum(II), and Rhodium(III) Complexes of *o*-phenylenebis(diphenylarsine) and (*o*-Diphenylarsinophenyl)diphenylphosphine

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Thirty five complexes of *o*-phenylenebis(diphenylarsine) (pdpa) and (*o*-diphenylarsinophenyl)diphenylphosphine (padpp) including types $[M(L)X_2]$, $[ML_2][ClO_4]_2$, $[M(L)_2X_2]$ (M = Pd or Pt; L = pdpa or padpp; X = Cl, Br, I, or CNS), and $[Pd(pdpa)_2X]ClO_4$ have been prepared. The planar thiocyanates are formulated [Pd(pdpa)(NCS)(SCN)] and [Pt(padpp)(NCS)(SCN)]. In dichloromethane the $[Pt(pdpa)(SCN)_2]$ complex partly isomerises to [Pt(pdpa)(NCS)(SCN)]. The five-co-ordinate $[PdL_2(NCS)]CNS$ (L = pdpa or padpp) species also isomerise in solution. The diperchlorates are planar, whilst in solution the $[M(L)_2X_2]$ complexes are predominantly five-co-ordinate. On heating, the $[M(L)_2X_2]$ (X = Cl, Br, or I) complexes dissociate in the solid state into $[M(L)X_2]$ and free L. The tendency to five-co-ordination is Pd > Pt and pdpa > padpp. Rhodium(III) halides form adducts $[Rh(pdpa)_2X_2]X$ (X = Cl, Br, or I), $[Rh(padpp)_2X_2]X$ (X = Cl or Br), and $[\{Rh(padpp)I_3\}_2]$.

PALLADIUM(II) and platinum(II) form complexes of stoicheiometry MLX_2 and ML_2X_2 with a range of bidentate Group 5B donor ligands, L (M = Pd or Pt; X = Cl, Br, I, or CNS).[1,2,]† The former are planar, but the structures of the latter depend on the nature of L, X, and the physical state. *o*-Phenylenebis(dimethylarsine) (pdma) complexes have been studied in detail. In the presence of counter-ions of poor co-ordinating ability (*e.g.* ClO_4^-) planar $[M(pdma)_2]^{2+}$ cations are formed. Corresponding halide complexes are formulated as $[M(pdma)_2X]X$ in solution and from these $[M(pdma)_2X]ClO_4$ are readily obtained.[3,4] In the solid state, *X*-ray studies have shown that $[Pt(pdma)_2]Cl_2$ contains planar $[Pt(pdma)_2]^{2+}$ cations,[5] and $[M(pdma)_2I_2]$ (M = Pd or Pt) have been described as tetragonally distorted octahedral complexes, although here too the M–I distances are large.[6]

Here we report results of our studies on palladium(II) and platinum(II) complexes of *o*-phenylenebis(diphenylarsine) (pdpa) and (*o*-diphenylarsinophenyl)diphenylphosphine (padpp). Some rhodium(III) complexes are also reported. We embarked on this study for two reasons. First, because of our interest in five-co-ordination.[7] It has been noted [8] as an empirical rule that the ease of formation of five-co-ordinate complexes occurs in the order $Ni^{II} > Pd^{II} > Pt^{II}$. This has been discussed in terms of the electronegativities of the three metals,[4] *s*–*p* separation energies,[9] and crystal-field stabilisation energies.[10] Rigid 'tripod' ligands seem to be able to overcome the tendency of Pd^{II} and Pt^{II} to adopt four-co-ordinate structures and produce trigonal-bipyramidal species,[11-14] but apart from these special cases five-co-ordination for Pd^{II} and Pt^{II} is rare. Westland studied the association of planar Pd^{II} and Pt^{II} complexes with halide ions and concluded that for a given metal ion the tendency to promote five-co-ordination was greater for $Ph_2AsCH_2CH_2AsPh_2$ complexes than for those containing $Ph_2PCH_2CH_2PPh_2$.[15] Thus the use of the ligands pdpa and padpp in complexes of Pd^{II} and Pt^{II} allowed us, at once, to examine in more detail the role of both metal ion and donor atom in the promotion of five-co-ordination. Our second purpose was to examine the mode of thiocyanate bonding in the $[ML(CNS)_2]$ complexes.

EXPERIMENTAL

Preparation of the Ligands.—o-*Phenylenebis*(*diphenylarsine*) (*pdpa*). A solution of lithium diphenylarsenide in tetrahydrofuran (thf), prepared [16] from lithium (4·0 g), triphenylarsine (47·0 g), and dry thf (400 cm^3), was added dropwise under a dinitrogen atmosphere to a stirred solution of (*o*-bromophenyl)diphenylarsine [17] (35·0 g, 0·09 mol) in thf (200 cm^3). When addition was complete the resulting solution was heated under reflux for 1 h, cooled, and hydrolysed by cautious addition of deoxygenated aqueous ammonium chloride solution. The organic layer was dried over anhydrous sodium sulphate overnight. The solvent was rotatory evaporated to leave a brown oil which, on addition of ice-cold methanol, precipitated the crude ligand. Recrystallisation from n-butanol afforded white crystals (26 g, *ca.* 54%) (Found: C, 67·7; H, 4·8. Calc. for $C_{30}H_{24}As_2$: C, 67·5; H, 4·5%), m.p. 199 °C (lit.,[18] 200 °C).

(o-*Diphenylarsinophenyl*)*diphenylphosphine* (*padpp*). This was prepared by the method of Nicpon and Meek,[19] though we found it could also be satisfactorily prepared

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† In this study CNS is used to describe co-ordinated thiocyanate when the mode of attachment to the metal is not specified. The complexes $M(L)_2X_2$ (M = Pd or Pt) are shown without square brackets as their structure in the solid state is not known with certainty.

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from lithium diphenylphosphide and (*o*-bromophenyl)-diphenylarsine in an analogous preparation to that described above (Found: C, 73·1; H, 4·8. Calc. for $\mathrm{C_{30}H_{24}AsP}$: C, 73·5; H, 5·0%), m.p. 189 °C (lit.,[19] 190—192 °C).

Preparation of the Complexes.—Specific details are given for the palladium(II)–pdpa complexes; those of padpp and platinum(II) complexes of padpp and pdpa were isolated by analogous routes (except for $\mathrm{PtL_2Cl_2}$ which are better prepared as described below).

Dichloro[o-*phenylenebis*(*diphenylarsine*)]*platinum*(II). A dichloromethane solution (10 cm^3) of pdpa (0·54 g, 1·00 mmol) was added to a stirred ethanolic solution (25 cm^3) of disodium tetrachloropalladate(II) (0·30 g, 1·00 mmol), and a yellow solid was immediately precipitated. The solid was filtered, dissolved in the minimum quantity of boiling *NN*-dimethylformamide (dmf), cooled, and induced to crystallise by the addition of diethyl ether. Recrystallisation from dichloromethane–ethanol yielded *crystals* in 67% yield. The *complexes* $\mathrm{[Pd(pdpa)X_2]}$ (X = Br, I, *or* NCS) were prepared similarly in the presence of excess of NaX. The thiocyanate complex crystallised with some difficulty and was better obtained by precipitation with diethyl ether from a dichloromethane solution.

Bis[o-*phenylenebis*(*diphenylarsine*)]*palladium*(II) *diperchlorate*. To a solution of the complex $\mathrm{[Pd(pdpa)Cl_2]}$ (1·00 g), prepared as below, in acetone (30 cm^3) was added a mixture of perchloric acid (20 cm^3, 73%) and water (200 cm^3). Immediate precipitation of a yellow *powder* occurred. This was filtered, rinsed well with diethyl ether, and recrystallised from dichloromethane–ethanol, yield *ca.* 90%.

Dichlorobis[o-*phenylenebis*(*diphenylarsine*)]*palladium*(II). Disodium tetrachloropalladate(II) (0·20 g, 0·68 mmol) in ethanol (15 cm^3) was stirred with pdpa (0·78 g, 0·145 mol) in dichloromethane (20 cm^3). After 1 h the solution was rotatory evaporated to dryness and the resulting red *oil* was extracted with dichloromethane. Addition of a small quantity of ethanol to this solution induced fairly rapid crystallisation, yield *ca.* 75%. The *complexes* $\mathrm{Pd(pdpa)_2X_2}$ (X = Cl, Br, *or* NCS) were obtained similarly using an excess of NaX in the original mixture of $\mathrm{Na_2[PdCl_4]}$ and pdpa. $\mathrm{[Rh(pdpa)X_2]X}$ (X = Cl, Br, *or* I) were obtained analogously from pdpa, $\mathrm{RhCl_3}$, and excess of NaX.

Chlorobis[o-*phenylenebis*(*diphenylarsine*)]*palladium*(II) *perchlorate–dichloromethane* (1/1). A solution of the complex $\mathrm{Pd(pdpa)_2Cl_2}$ (0·62 g, 0·50 mmol) in the minimum amount of dichloromethane was treated dropwise with lithium perchlorate (0·05 g, 0·50 mmol) in ethanol (5 cm^3). The solution was rotatory evaporated to a volume of *ca.* 10 cm^3 when precipitation occurred. The *precipitate* was recrystallised from dichloromethane–ethanol, yield *ca.* 60%. The *complexes* $\mathrm{[Pd(pdpa)_2X]ClO_4,CH_2Cl_2}$ (X = Br *or* I) were obtained similarly.

$\mathrm{Pt(L)_2Cl_2}$ (L = pdpa *or* padpp). A solution of dipotassium tetrachloroplatinate(II) (0·40 g, 1·0 mmol) in water (15 cm^3) was heated under reflux with the ligand (2·0 mmol) in dmf (15 cm^3) for 0·5 h. The yellow solution was concentrated to small volume, cooled, and diethyl ether added. The resulting *precipitate* was crystallised from dichloromethane–ethanol, yield *ca.* 75%.

Physical measurements were obtained as previously described.[20] The Ramsay method [21] was used to calculate ν(C≡N) integrated absorptions.

RESULTS AND DISCUSSION

$\mathrm{[M(L)X_2]}$ *Complexes.*—Palladium(II)–padpp complexes have been described by Nicpon and Meek.[19] The other $\mathrm{[M(L)X_2]}$ (M = Pd, L = pdpa; M = Pt, L = pdpa or padpp; X = Cl, Br, I, or NCS) (Table) complexes were prepared by reaction of the ligand with the appropriate $\mathrm{[MX_4]^{2-}}$ ion. The products are only very slightly soluble in polar solvents, EtOH or $\mathrm{MeNO_2}$, but dissolve readily in 1,2-dichloroethane in which they are non-electrolytes. Their electronic spectra in dichloromethane and the solid state (Table) were similar and are characteristic of planar $\mathrm{[M(L)X_2]}$ complexes. A comparison of the energies of the lowest *d–d* band in corresponding complexes of pdpa and padpp showed that the expected spectrochemical order is observed, donor set AsP > $\mathrm{As_2}$. Where ligand absorptions did not interfere, the i.r. spectra exhibited two ν(M–X) frequencies as expected for the (necessarily) *cis*-configuration.*

Since the complexes described here were isolated from boiling dmf (>100 °C), they should be in the thermodynamically stable form.[22] No evidence for isomerisation was obtained after recrystallisation from dichloromethane. The padpp complex contained both *N*- and *S*-bonded thiocyanate groups, [Pd(padpp)(NCS)(SCN)],[22] and our pdpa complex was similar. In the solid state (Nujol mull), i.r.* absorptions at 2 100sh and 2 060br cm^{-1} were assigned to ν(CN) of *S*- and *N*-bonded thiocyanates, respectively.[23] For the $\mathrm{[Pd(pdpa)X_2]}$ complexes, the lowest-energy visible absorption moved to lower energy in the order Cl > CNS > Br > I, whereas two *N*-bonded groups would produce NCS > Cl > Br > I and two *S*-bonded groups Cl > Br > SCN > I.[22] Integrated-intensity measurements * confirmed that one thiocyanate group is *S*-bonded [$\bar{\nu}_{\frac{1}{2}}$ (band width at half height) = 14 cm^{-1}, *A* (intensity of band) = 2·7 × 10^4 cm^{-2} mol^{-1}] and one is *N*-bonded ($\bar{\nu}_{\frac{1}{2}}$ = 43 cm^{-1}, *A* = 10·5 × 10^4 cm^{-2} mol^{-1}).[24] In having *S*- and *N*-coordination in both the solid state and dichloromethane solution, the complex [Pd(pdpa)(NCS)(SCN)] differs from $\mathrm{[Pd(dpae)(SCN)_2]}$ [dpae = 1,2-bis(diphenylarsino)-ethane] [22] which contains two *S*CN groups in the solid state, but partially isomerises to the *N*-bonded isomer in solution. *cis*-1,2-Bis(diphenylphosphino)-ethylene (dppen) and *cis*-1,2-difluoro-1,2-bis(diphenylphosphino)ethylene (fdppen) give rise to $\mathrm{[Pd(dppen)(SCN)_2]}$ [25] and [Pd(fdppen)(NCS)(SCN)] [26] complexes, respectively. Therefore, subtle changes in the phosphine

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or arsine ligand can alter the mode of CNS co-ordination, and explanations in terms of, for example, antisymbiosis[27,28] are inadequate. The platinum complex [Pt(padpp)(NCS)(SCN)] was similar to its Pd analogue,[22] whereas $[Pt(pdpa)(SCN)_2]$ in the solid state contains two Pt–SCN linkages, but in dichloromethane solution a weak absorption at 2 090 cm^{-1} showed some *N*-bonded isomer was present (*cf.* ref. 22).

Some physical and spectral properties of the complexes

Complex	Colour	$10^3\bar{\nu}_{max.}$[a]/cm^{-1} ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)	$10^3\bar{\nu}_{max.}$[b]/cm^{-1}	$\Lambda/\Omega^{-1}\ cm^2\ mol^{-1}$
$[Pd(pdpa)Cl_2]$	Pale yellow	37·2 (21 930), 27·2 (3 648)	27·0	<1 [c]
$[Pd(pdpa)Br_2]$	Yellow	34·2 (23 740), 28·1 (sh), 25·4 (4 652)	26·2	<1 [c]
$[Pd(pdpa)I_2]$	Orange	34·7 (25 190), 32·0 (26 940), 22·5 (6 300)	22·7 , 20·0 (sh)	<1 [c]
[Pd(pdpa)(NCS)(SCN)]	Yellow	32·0 (20 200), 27·0 (6 650)	27·6	3 [c]
$[Pt(pdpa)Cl_2]$	White	37·8 (12 200), 33·8 (sh) (*ca.* 2 950)		<1 [c]
$[Pt(pdpa)Br_2]$	White	36·5 (6 690), 31·5 (3 740)		<1 [c]
$[Pt(pdpa)I_2]$	Yellow	34·0 (13 280), 26·9 (7 640)	26·7	<1 [c]
$[Pt(pdpa)(SCN)_2]$	Yellow-green	38·5 (sh), 29·8 (1 900)		*ca.* 1 [c]
$[Pt(padpp)Cl_2]$	White	37·4 (13 030), 31·2 (1 550)		<1 [c]
$[Pt(padpp)Br_2]$	White	36·3 (14 450), 30·7 (2 740)		<1 [c]
$[Pt(padpp)I_2]$	Yellow	33·8 (15 060), 27·5 (4 090)	27·0	<1 [c]
[Pt(padpp)(NCS)(SCN)]	White	30·5 (sh) (*ca.* 2 000)		*ca.* 1 [c]
$Pd(pdpa)_2Cl_2$	Red	27·5 (6 570), 20·7 (sh) (*ca.* 330)	26·4, 19·6	48
$Pd(pdpa)_2Br_2$	Red	25·4 (5 190), 20·2 (sh) (*ca.* 290)	27·2, 19·3	51
$Pd(pdpa)_2I_2$	Purple-brown	23·0 (3 890), *ca.* 19·4 (sh) (*ca.* 1 020)	24·8, 20·0, 17·5 (sh)	41
$Pd(pdpa)_2(CNS)_2$	Red	24·3 (1 740)	23·7, 19·4	104
$[Pd(pdpa)_2][ClO_4]_2$	Yellow	29·1 (29 200)		172
$[Pd(pdpa)_2Cl]ClO_4,CH_2Cl_2$	Orange-yellow	28·6 (9 950), *ca.* 21·0 (sh) (220)	26·8, *ca.* 20·6	76
$[Pd(pdpa)_2Br]ClO_4,CH_2Cl_2$	Brown	29·7 (20 890), 26·0 (sh), 20·2 (sh) (420)	26·4 (sh), 20·0 (sh)	75
$[Pd(pdpa)_2I]ClO_4,2CH_2Cl_2$	Brown	29·5 (24 020), 22·6 (4 430), 19·0 (sh) (1 800)	23·8, 18·7 (sh)	69
$Pd(padpp)_2Cl_2,CH_2Cl_2$	Red	28·5 (20 760), *ca.* 22·2 (sh) (430)	26·8, 20·6	75
$Pd(padpp)_2Br_2,CH_2Cl_2$	Red	30·5 (39 800), 27·0 (sh), 21·2 (490)	26·0, 19·5	74
$Pd(padpp)_2I_2,CH_2Cl_2$	Purple	39·7 (34 400), 25·0 (sh), 20·8 (850)	24·2, 20·3, *ca.* 17·8	74
$Pt(padpp)_2(CNS)_2$	Red	29·7 (42 000), *ca.* 22·0 (sh)	24·1 (sh), 19·6	152
$[Pd(padpp)_2][ClO_4]_2,2CH_2Cl_2$	White	29·4 (*ca.* 42 000)		188
$Pt(pdpa)_2Cl_2$	Yellow	*ca.* 25·0 (sh) (290)	23·2	74
$Pt(pdpa)_2Br_2,CH_2Cl_2$	Orange	31·3 (12 460), 23·8 (sh) (390)	22·8	73
$Pt(pdpa)_2I_2,CH_2Cl_2$	Brown	29·9 (16 760), *ca.* 27·0 (sh), 22·2 (1 300)	24·1, 20·2	71
$Pt(pdpa)_2(CNS)_2$	Pale yellow	*ca.* 29·1 (sh) (4 810), *ca.* 23·0 (sh) (110)	26·7 (sh)	151
$Pt(padpp)_2Cl_2,CH_2Cl_2$	Yellow	31·0 (25 190), 24·3 (sh) (480)	23·2	128
$Pt(padpp)_2Br_2,2CH_2Cl_2$	Orange	25·2 (sh) (340)	23·8	125
$Pt(padpp)_2I_2,CH_2Cl_2$	Red-orange	30·0 (17 800), 24·6 (1 137), 22·3 (sh) (600)	25·3, 21·0	115
$Pt(padpp)_2(CNS)_2,CH_2Cl_2$	White	29·6 (7 690), 23·5 (sh)		182
$[Rh(pdpa)_2Cl_2]Cl,CH_2Cl_2$	Yellow	30·0 (42 020), 22·8 (440)	26·8 (sh), 23·3	60
$[Rh(pdpa)_2Br_2]Br$	Orange	29·8 (*ca.* 30 000), *ca.* 21·3 (420)	24·8 (sh), 22·0	57
$[Rh(pdpa)_2I_2]I$	Dark brown	24·8 (4 650), *ca.* 22·6 (sh)	21·8	14 [c]
$[Rh(padpp)_2Cl_2]Cl$	Yellow	30·2 (36 660), 23·4 (480)	*ca.* 27·0 (sh), 23·8	62
$[Rh(padpp)_2Br_2]Br$	Yellow	30·1 (28 230), 22·2 (244)	*ca.* 27·0 (sh), 22·3	59
$[\{Rh(padpp)I_3\}_2]$	Brown	34·0 (55 160), *ca.* 22·0 (sh) (7 960)	27·0, *ca.* 24·4 (sh), *ca.* 19·1 (sh)	2 [c]
$[Rh(padpp)_2I_2]$	Dark brown	22·0 (sh) (*ca.* 3 700)	27·0, 23·5, *ca.* 18·0 (sh)	8

[a] In dichloromethane. [b] Solid reflectance. [c] *ca.* 10^{-3}M Solution in 1,2-dichloroethane; all other conductivities measured in *ca.* 10^{-3}M-nitromethane.

$M(L)_2X_2$ *Complexes.*—Reaction of pdpa and padpp with $Na_2[MX_4]$ (M = Pd or Pt; X = Cl, Br, I, or CNS) in a 2 : 1 molar ratio in $EtOH–CH_2Cl_2$ produced $M(L)_2X_2$ complexes which were often obtained as dichloromethane adducts (Table) (see ref. 29 for examples of the frequent occurrence of adducts with halogenocarbons).

On addition of an acetone solution of the complexes $M(L)_2Cl_2$ (M = Pd, L = pdpa; M = Pt, L = pdpa or padpp) to a large excess of warm dilute aqueous perchloric acid, immediate precipitation of yellow or white solids occurred, $[ML_2][ClO_4]_2$. The corresponding reaction with $Pd(padpp)_2Cl_2$ resulted in precipitation of a salmon pink solid which, after drying *in vacuo* for 12 h, showed strong i.r. absorptions assignable to water molecules (3 350 and 1 630 cm^{-1}). Recrystallisation from dichloromethane converted this into $[Pd(padpp)_2][ClO_4]_2,2CH_2Cl_2$. In nitromethane solutions the diperchlorates are 1 : 2 electrolytes (Λ 170—185 $\Omega^{-1}\ cm^2\ mol^{-1}$), and a plot of $\Lambda_0 - \Lambda_e$ (Λ_0 = conductance at infinite dilution, and Λ_e = conductance at equivalent concentration) against $c^{1/2}$ for $[Pd(pdpa)_2][ClO_4]_2$ gave a gradient of 550, consistent with a 1 : 2 electrolyte formulation.[30] The i.r. spectra of all four complexes showed very strong absorptions at *ca.* 1 080 cm^{-1} and a sharp band at *ca.* 620 cm^{-1}, indicative of ionic perchlorate groups,[31] and the electronic spectra exhibited an intense absorption > 29 000 cm^{-1}, consistent with the presence of planar $[ML_2]^{2+}$ cations.

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The $Pd(padpp)_2X_2,CH_2Cl_2$ complexes are deeply coloured crystalline solids, only slightly soluble in polar solvents. In 10^{-3}M-nitromethane they are 1 : 1 electrolytes (Λ 73—75 Ω^{-1} cm^2 mol^{-1}),* but with increasing dilution dissociation of the second halide occurred as evidenced by curved plots of $\Lambda_0 - \Lambda_e$ against $c^{1/2}$. The electronic spectra of the complexes in dichloromethane consisted of relatively weak absorptions or shoulders at 22 000—20 000 cm^{-1} and a more intense band (or bands) at higher energy, characteristic of five-co-ordinate palladium(II).[13] In the solid state the lowest-energy absorption occurred at 21 000—18 000 cm^{-1}, and this bathochromic shift is compatible with a tetragonal structure perhaps involving weak association of a further halide ion. The Nujol mull i.r. spectra of the three complexes were virtually identical and no ν(Pd–X) vibrations were detected.

In nitromethane solution (10^{-3}M) the observed conductivity values of the complexes $Pd(pdpa)_2X_2$ were $\Lambda = 40$—50 Ω^{-1} cm^2 mol^{-1} and increased on addition of free ligand, showing that, like palladium(II) complexes of dpae,[22] they are partly dissociated into $[Pd(pdpa)X_2]$ and free ligand. That some five-co-ordinate $[Pd(pdpa)_2X]^+$ cations exist in solution was shown by the appearance of low-energy absorptions in the electronic spectra of the $Pd(pdpa)_2X_2$ complexes (Table). Moreover, when concentrated solutions of $Pd(pdpa)_2X_2$ in dichloromethane were treated with $LiClO_4$ (1 mol), five-co-ordinate $[Pd(pdpa)_2X]ClO_4,xCHCl_2$ complexes were isolated. These are 1 : 1 electrolytes in nitromethane and the conductances were unaffected by addition of free pdpa. Thus the complexes do not measurably undergo ligand dissociation in solution. Reaction (1) can possibly be viewed as displacement of

$$[Pd(pdpa)_2X]X \rightleftharpoons [Pd(pdpa)X_2] + pdpa \qquad (1)$$

pdpa by X$^-$, and this will not occur when the unco-ordinated halide (X$^-$) is replaced by the very weakly co-ordinating perchlorate ion (this may be an over-simplification of the factors involved). The electronic spectra of the $[Pd(pdpa)_2X]ClO_4,xCH_2Cl_2$ species in the solid state and in solution were extremely alike and thus five-co-ordinate cations of similar structure exist in both states.

The $Pt(L)_2X_2$ (L = pdpa or padpp) complexes were essentially similar to the $Pd(padpp)_2X_2$ complexes, the diarsine derivatives showing no evidence of dissociation to $[Pt(pdpa)X_2]$. The $Pt(pdpa)_2X_2$ complexes are 1 : 1 electrolytes in nitromethane, but $Pd(padpp)_2X_2$ had significantly higher conductivities, indicating that partial dissociation of the second halide occurred. A comparison of the conductivities of the $Pd(padpp)_2X_2$ and $Pt(L)_2X_2$ (L = pdpa or padpp) complexes showed that dissociation in solution increases in the order $Pd(padpp)_2X_2 \sim Pt(pdpa)_2X_2 < Pt(padpp)_2X_2$ or, conversely, that the stability of the five-co-ordinate $[ML_2X]^+$ species is Pd > Pt and pdpa > padpp. This result correlated well with Westland's conclusions on complexes of $Ph_2PCH_2CH_2PPh_2$ and $Ph_2AsCH_2CH_2AsPh_2$.[15]

The $M(L)_2X_2$ (X = halide) complexes became much paler on heating to 120—250 °C,† the colours of the products being reminiscent of the corresponding $[M(L)X_2]$, and suggesting that reaction (2) occurs;

$$M(L)_2X_2 \xrightarrow{\text{Heat}} [M(L)X_2] + L \qquad (2)$$

this does not reverse on cooling. In order to examine this effect, small samples (*ca.* 0·5 g) of the $M(L)_2X_2$ complexes were heated under a dinitrogen atmosphere at *ca.* 200 °C for 0·5 h, and i.r. mull and solid-reflectance spectra of the products recorded. The latter were identical with those of the corresponding $[M(L)X_2]$ complexes, whilst the far-i.r. spectra were a superimposition of those of $[M(L)X_2]$ and the free ligand. The reactions were reversed by dissolving the products in dichloromethane, when the $M(L)_2X_2$ species were obtained on evaporation. This thermal dissociation is restricted to the dihalides; the halogenoperchlorate and diperchlorate salts blackened on heating, whilst the thiocyanate complexes melted with decomposition.

In the solid state, both red $[PdL_2(NCS)]CNS$ (L = pdpa or padpp) complexes are five-co-ordinate and contain Pd–NCS linkages, as evidenced by broad ν(CN) bands at 2 085 (padpp complex) and 2 082 cm^{-1} (pdpa complex) and ν(CS) at 778 (padpp) and 775 cm^{-1} (pdpa) in the i.r. spectra (unco-ordinated CNS$^-$ groups in these complexes were indicated by bands at *ca.* 2 040—2 050 cm^{-1}), and the visible spectral bands at *ca.* 20 000 cm^{-1}. In dichloromethane the i.r. spectrum of the padpp complex exhibited ν(CN) at 2 055s,br and 2 120sh cm^{-1}, but there was no absorption at 2 085 cm^{-1}, indicating that on dissolution $[Pd(padpp)_2(NCS)]CNS$ isomerised to $[Pd(padpp)_2(SCN)]CNS$. However, the integrated-absorption value for the ν(CN) bands of the complex in solution was very low, and, in agreement with the conductance value in 10^{-3}M-nitromethane solution which approached that of a 1 : 2 electrolyte (Table), it is concluded that a small amount of $[Pd(padpp)_2(SCN)]CNS$, but mainly $[Pd(padpp)_2](CNS)$, is present in solution. In the solid state the pdpa complex appears to be five-co-ordinate and contain *N*-bonded thiocyanate. In dichloromethane solution ν(CN) bands occurred at 2 110, 2 070, and 2 050 cm^{-1}, indicating that both Pd–SCN and Pd–NCS linkages were present, but the nature and concentration of these various species could not be determined.

The platinum(II) derivatives are square planar in the solid state, $[PdL_2][CNS]_2$; the reflectance spectra were almost identical with those of $[PtL_2][ClO_4]_2$, and i.r. absorptions were assignable to ionic thiocyanate [ν(CN) at *ca.* 2 055 cm^{-1}]. The salt $[Pt(padpp)_2][CNS]_2$ dissolved in dichloromethane with no isomerisation, but the solution i.r. spectrum of $[Pt(pdpa)_2][CNS]_2$ contained

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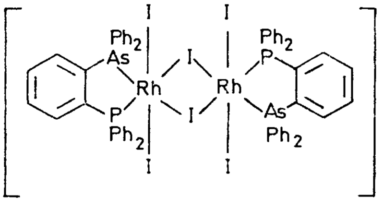
* 1M = 1 mol dm^{-3}.

† Accurate observation of the temperature at which one coloured species changed into another was difficult, and the values quoted in the Supplementary Publication are only approximate.

a new weak sharp absorption at 2 105 cm^{-1} suggesting the presence of some [Pt(pdpa)$_2$(SCN)]$^+$, and a weak shoulder at *ca.* 23 000 cm^{-1} in the visible spectrum also suggests a five-co-ordinate moiety.

Rhodium(III) *Complexes.*—Rhodium trihalides reacted with pdpa or padpp in a 1 : 2 molar ratio to form [Rh(L)$_2$X$_2$]X (L = pdpa, X = Cl, Br, or I; L = padpp, X = Cl or Br) as yellow or brown microcrystalline materials. The chloro- and bromo-complexes had Λ values in the range 57—62 Ω^{-1} cm^2 mol^{-1} in 10^{-3}M-nitromethane solutions which, although a little low for assignments as 1 : 1 electrolytes, may be due to the bulkiness of the [Rh(L)$_2$X$_2$]$^+$ cations. Electronic spectra of the salts [Rh(L)$_2$X$_2$]X (X = Cl or Br) were essentially similar in solution and in the solid state, consisting of a weak band or shoulder at 21 000—24 000 cm^{-1}, and an intense shoulder at 30 000 cm^{-1}. The strong ligand absorptions in the far-i.r. region were sufficient to prevent identification of ν(Rh–X), and hence it was not possible to distinguish between the *cis*-(C_{2v}) or *trans*-structures (D_{4h}) for the octahedral cations.

Repeated attempts to prepare the salt [Rh(padpp)$_2$I$_2$]I failed; instead a brown powder was obtained, elemental analyses (C, H, and I) of which corresponded to the formula ' Rh(padpp)$_2$I$_2$.' No indication of Rh–H bonds was observable in i.r. spectra of this complex and it is diamagnetic, ruling out Rh^{II}. A possible formulation is [Rh(padpp)(*o*-C$_6$H$_4$PPhC$_6$H$_4$AsPh$_2$)I$_2$].[32] When the RhI$_3$: padpp ratio was increased a brown complex was obtained, which is a non-electrolyte in 1,2-dichloroethane and has a molecular weight of 1 884 in 10^{-3}M-chloroform solution, consistent with the formulation [{Rh(padpp)I$_3$}$_2$] (*M*, 1 948) and probably structure (A).



(A)

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[32] M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266; W. J. Keim, *J. Organometallic Chem.*, 1968, **14**, 179.