Metal Complexes of Sulphur Ligands. Part IV.[1] Reaction of Bis(dialkylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group VB Atoms

By **David F. Steele** and **T. Anthony Stephenson,*** Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of the complexes $[Pt(S_2PR_2)_2]$ (R = Me or Et) with tertiary phosphines gives four co-ordinate complexes $[Pt(S_2PR_2)_2PR_3']$ and $[Pt(S_2PR_2)(PR_3')_2]S_2PR_2$. Variable-temperature ^1H n.m.r. studies of the neutral complexes indicate rapid unidentate–bidentate exchange at ambient temperatures and a full line-shape analysis of this process for complexes of general type $[Pt(S\text{–}S)_2ER_3']$ [$(S\text{–}S)^- = {}^-S_2CNEt_2$, ${}^-S_2P(OEt)_2$, or ${}^-S_2PMe_2$; E = P or As] suggests a concerted mechanism in which both bond-breaking and bond-making steps are important. For the complex $[Pd(S_2PMe_2)_2]$, the ionic complexes are too unstable to be isolated in pure form because of facile rearrangement to the neutral complexes. However, addition of either $NaBPh_4$ or $NaPF_6$ to solutions containing the ionic species provides a general method of synthesising the complexes $[M(S_2PR_2)(PR_3')_2]X$ (M = Pt or Pd; R = Me or Ph; X = BPh_4^- or PF_6^-). For M = Pt and X = BPh_4, these complexes readily react with Ph_4AsY (Y = Cl, Br, or I) giving Ph_4AsBPh_4 and $[Pt(S_2PMe_2)(PR_3')_2]Y$. However, for the complexes $[Pd(S_2PR_2)(PPh_3)_2]BPh_4$ (R = Me or Ph) dissolution in CH_2Y_2–EtOH,CHY_3–EtOH (Y = Cl or Br), or in acetone containing added halide ion produces rapid rearrangement to give $[Pd(S_2PR_2)Y(PPh_3)]$. This rearrangement does not occur for X = PF_6^- and a tentative mechanism involving a labile π- or σ-bonded phenyl group is suggested. Finally, an empirical i.r. method for distinguishing unidentate, bidentate, and ionic modes of co-ordination of the dimethylphosphinodithioato-group to platinum and palladium is briefly discussed.

IN Parts II[2] and III[1] of this series it was shown that the reaction of the complexes $[M(S\text{–}S)_2]$ [M = Pt or Pd; $(S\text{–}S)^- = {}^-S_2PPh_2$, ${}^-S_2CNR_2$, ${}^-S_2COR$, or ${}^-S_2P(OEt)_2$] with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate adducts $[M(S\text{–}S)_2PR_3']$ and $[M(S\text{–}S)(PR_3')_2](S\text{–}S)$ with unidentate–bidentate and bidentate–ionic dithio-ligand co-ordination respectively. {Similar results were briefly reported by Tebbe and Muetterties[3] for the complex $[Pd(S_2PF_2)_2]$.} It has also been demonstrated that the ionic complexes readily reverted to $[M(S\text{–}S)_2PR_3']$ when dissolved in non-polar solvents *via* nucleophilic attack by $(S\text{–}S)^-$ on the metal.[1,2] Furthermore, variable-temperature ^1H n.m.r. studies on the platinum 1 : 1 adducts of the dithiocarbamato- and dithiophosphato-complexes indicated rapid interchange of the uni- and bi-dentate dithio-ligands at ambient temperature, whereas at lower temperatures, intramolecular rearrangement became sufficiently slow for the ' frozen-out ' n.m.r. spectrum to be observed.[1] Activation energies for these processes were estimated from the coalescence temperatures by a standard method (see table 2, ref. 1).

However no activation energies could be obtained for the $[M(S_2PPh_2)_2ER_3']$ complexes[2] since phenyl groups are not amenable to such ^1H n.m.r. temperature studies. Therefore, in order to rectify this deficiency, and also to investigate the effect on complex reactivity of varying the substituent R, we have carried out a study of the reactions of the complexes $[M(S_2PR_2)_2]$ (M = Pt or Pd; R = Me or Et) with ligands containing Group VB atoms and the results are reported below.

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[1] Part III, (Miss) J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[2] Part II, (Miss) J. M. C. Alison, T. A. Stephenson, and (in part) R. O. Gould, *J. Chem. Soc.* (*A*), 1971, 3690.

[3] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1970, **9**, 629.

RESULTS AND DISCUSSION

Complexes of Stoicheiometry $[M(S_2PR_2)_2ER_3']$.—Reaction of the complex $[Pt(S_2PMe_2)_2]$ * with tertiary phosphines (1 : 1 molar ratio) in benzene or chloroform gave immediate yellow solutions from which complexes of stoicheiometry $[Pt(S_2PMe_2)_2PR_3']$ were readily isolated by concentration and precipitation with pentane. These complexes are diamagnetic (sharp ^1H n.m.r. signals) and non-conducting in dichloromethane. For the complex $[Pd(S_2PMe_2)_2]$, an excess of tertiary phosphine was required in order to obtain the 1 : 1 adducts free of starting material. Similar conditions are necessary to isolate a pure sample of $[Pt(S_2PMe_2)_2AsPh_3]$. However, with PEt_3 and $AsEt_3$ (for M = Pt) the products are too soluble to be satisfactorily isolated and, although treatment with ammonia and pyridine indicated some reaction in solution, attempts to isolate a solid complex only resulted in recovery of the starting material. In contrast, the palladium complex does not react with arsenic- or nitrogen-donor ligands {*cf.* $[Pd(S_2PPh_2)_2]$}.[2]

TABLE 1

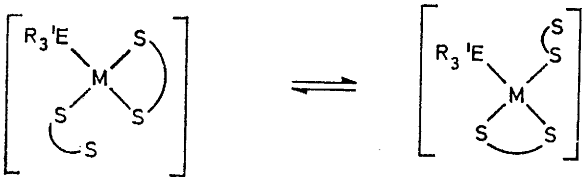
^1H N.m.r. data for various sulphur complexes [a]

Complex	Solvent	τ Value [b] CH$_3$(dithio-ligand) [c]	 CH$_3$(PR$_3'$) [d]	 Others [e]
$[Pt(S_2PMe_2)_2]$	CH_2Cl_2	7·99		
$[Pt(S_2PMe_2)_2PPh_3]$	CH_2Cl_2	8·09(4) [f] 7·98(2); 8·19(2) [g]		Ph 2·5(5)
$[Pt(S_2PMe_2)_2(PPh_2C_6F_5)]$	$CDCl_3$	7·91(6) 7·79(3); 8·03(3) [g]		Ph 2·2—2·5(5)
$[Pt(S_2PMe_2)_2(AsPh_3)]$	CH_2Cl_2	8·08(4) 7·99(2); 8·19(2) [g]		Ph 2·7(5)
$[Pt(S_2PMe_2)_2(PMePh_2)]$	CH_2Cl_2	7·98 [h] [3] [i]	7·63 [h]	Ph 2·6(2)
$[Pt(S_2PMe_2)_2(PMe_2Ph)]$	$CDCl_3$	7·95 [h] [18] [i]	8·04 [h]	Ph 2·6(5)
$[Pd(S_2PMe_2)_2(PPh_3)]$	CH_2Cl_2	8·06(4)		Ph 2·6(5)
$[Pd(S_2PMe_2)_2(PMePh_2)]$	$CDCl_3$	7·94 [h] [3] [i]	7·67 [h]	Ph 2·7(2)
$[Pd(S_2PMe_2)_2(PMe_2Ph)]$	$CDCl_3$	7·92 [h] [18] [i]	8·06 [h]	Ph 2·6(5)
$[Pt(S_2PMe_2)(PPh_3)_2]S_2PMe_2$	CH_2Cl_2	7·99 [j] [2] [i] 8·09 [k] 7·93(1); 8·14(1) [g]		Ph 2·7(5)
$[Pt(S_2PMe_2)(PPh_3)_2]PF_6$	CH_2Cl_2	7·95(1)		Ph 2·7(5)
$[Pt(S_2PMe_2)(PPh_3)_2]BPh_4$	$CDCl_3$	8·41(3)		Ph 2·7—3·3(25)
$[Pt(S_2PMc_2)(PMePh_2)_2]PF_6$	$CDCl_3$	7·99 [h] [3] [i]	8·14 [h,l]	Ph 2·6(5)
$[Pt(S_2PMe_2)(PMePh_2)_2]BPh_4$	$CDCl_3$	8·40 [h] [3] [i]	8·26 [h,l]	Ph 2·7—3·3(10)
$[Pt(S_2PMe_2)(AsPh_3)_2]PF_6$	$CDCl_3$	7·89(1)		Ph 2·7(5)
$[Pt(S_2PMe_2)(AsPh_3)_2]BPh_4$	$CDCl_3$	8·43(3)		Ph 2·8—3·3(25)
$[Pd(S_2PMe_2)(PPh_3)_2]PF_6$	$CDCl_3$	7·91(1)		Ph 2·6(5)
$[Pd(S_2PMe_2)(PPh_3)_2]BPh_4$	$CDCl_3$	8·41(3)		Ph 2·7—3·3(25)
$[Pd(S_2PMe_2)(Cl)PPh_3]$	$CDCl_3$	8·00(2)		Ph 2·6(5)

[a] At 301 K unless otherwise stated. [b] ±0·01. [c] All doublets with J_{PH} 13·0 Hz. [d] Triplet of doublets (platinum), J_{PtH} 38·0, J_{PH} 11·3 Hz; doublet (palladium) J_{PH} 11·0 Hz. [e] Phenyl resonance; complex multiplet. [f] Numbers in parentheses indicate normalised integrated intensities. [g] Measured at 223 K. [h] Resonances too close to integrate separately. [i] Two resonances of total intensity [ ]. [j] From the complex $[Pt(S_2PMe_2)(PPh_3)_2]S_2PMe_2$ with rapid bidentate–ionic exchange. [k] From the complex $[Pt(S_2PMe_2)_2PPh_3]$ with rapid unidentate–bidentate exchange. [l] Since $H_nPP'H_n'$ type spectrum, the coupling constant is $|J_{PH} + J_{PH}'| = 9{\cdot}5$ Hz.

Like the analogous complexes $[M(S\text{–}S)_2ER_3']$,[1] these 1 : 1 adducts apparently undergo a rapid intramolecular-rearrangement reaction, since, at ambient temperatures, all the complexes exhibited a single doublet for the dimethylphosphinodithioate methyl protons (with $J_{PH} \simeq$ 13·0 Hz), whereas, at lower temperatures, coalescence occurred, followed (in some instances) by the growth of two pairs of doublets of intensity ratio 1 : 1 (Table 1). This process is reversible and is in accordance with the facile unidentate–bidentate exchange process suggested earlier [1] [equation (1)].

Although the activation energy at a coalescence temperature of 263 K has already been quoted in table 2 (ref. 1) for the complex $[Pt(S_2PMe_2)_2PPh_3]$, a full line-shape analysis has now been performed on the complexes $[Pt(S_2PMe_2)_2ER_3']$ (ER_3' = PPh_3, $PPh_2C_6F_5$, or $AsPh_3$) as well as $[Pt(S_2CNEt_2)_2PPh_3]$ and $[Pt\{S_2P(OEt)_2\}_2PPh_3]$ in order to obtain more accurate activation energies, and also the enthalpies and entropies of activation for these rearrangement processes. These data are given in Table 2. For the complexes $[Pt(S_2PMe_2)_2PR_3']$ (PR_3' = $PMePh_2$ or PMe_2Ph) and all the palladium 1 : 1 adducts, the rate of rearrangement was too rapid to obtain any kinetic parameters (single doublet even at 200 K). This



(1)

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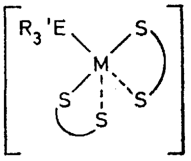
* Whilst this work was in progress, complete characterisation of the complexes $[M(S_2PR_2)_2]$ (M = Ni, Pd, or Pt; R = Me, Ph, F, CF_3, or OEt) was reported (R. G. Cavell, W. Byers, E. D. Day, and P. M. Watkins, *Inorg. Chem.*, 1972, **11**, 1598), although no reactions of the complexes were discussed.

latter observation is in accordance with the increased lability of palladium substitution reactions compared to those of platinum.[4]

A comparison of Table 2 with the activation energies derived from coalescence-temperature measurements (table 2, ref. 1) shows reasonable agreement. For all the 1 : 1 complexes studied, the rate of rearrangement was concentration independent, indicating a wholly intramolecular process, and for the complex $[Pt\{S_2P(OEt)_2\}_2PPh_3]$, activation parameters obtained in CH_2Cl_2 and CH_2Cl_2–CS_2 (1 : 1) were very similar, indicating the absence of a solvent-assisted bond-rupture mechanism. However, examination of the data for $(S–S)^- = {}^-S_2PMe_2$ reveals that the rate of rearrangement *is* dependent on the ligand ER_3'. The relative rates are in the order $PMe_2Ph \sim PMePh_2 \gg PPh_2C_6F_5 \sim PPh_3 > AsPh_3$, clearly indicating that cleavage of the metal–sulphur bond *trans* to ER_3' is an important factor in the rate-determining step. However, another important observation is that, although for $ER_3' = PPh_3$ free energies of activation for complexes with different dithio-ligands are quite similar (54—57 kJ mol^{-1}), the enthalpies of activation for the $^-S_2CNEt_2$ and $^-S_2P(OEt_2)_2$ complexes (29 and 33 kJ mol^{-1} respectively) are much lower than that for the $^-S_2PMe_2$ complex (54 kJ mol^{-1}). This is compensated for by the more unfavourable entropy terms in the first two complexes, although the large error limits incurred in determining $\Delta S^‡$ mean that such small differences must be treated with some caution. Since other studies indicate that the order of ligand-field strengths for these dithio-ligands is $^-S_2CNEt_2 > {}^-S_2P(OEt)_2 > {}^-S_2PR_2$,[5] then the lower enthalpy values for the stronger nucleophiles suggest that the bond-making process is also involved in the rate-determining step. A concerted mechanism involving a transition state such as (I) is also favoured by the small negative entropy values (a dissociative mechanism would give rise to a positive entropy term)[6] and the tendency for platinum(II) substitution reactions to occur by associative mechanisms.[4]



(I)

TABLE 2

Activation parameters obtained by line-shape analysis for some $[Pt(S–S)_2ER_3']$ complexes

Complex	Solvent	k_{rate} (298) s^{-1}	E_a kJ mol^{-1}	$\Delta H^‡_{298}$ kJ mol^{-1}	$\Delta S^‡_{298}$ J K^{-1} mol^{-1}	$\Delta G^‡_{298}$ kJ mol^{-1}
$[Pt(S_2PMe_2)_2AsPh_3]$	CH_2Cl_2	114	57·8 ± 1	55·3 ± 1	−19 ± 4	61·1 ± 2
$[Pt(S_2PMe_2)_2PPh_3]$	CH_2Cl_2	1 098	56·9 ± 1	54·5 ± 1	−4 ± 3	55·7 ± 2
$[Pt(S_2PMe_2)_2PPh_2C_6F_5]$	CH_2Cl_2	1 518	46·0 ± 3	43·5 ± 3	−38 ± 11	54·9 ± 7
$[Pt\{S_2P(OEt)_2\}_2PPh_3]$	CH_2Cl_2	620	31·7 ± 3	29·2 ± 3	−94 ± 10	57·1 ± 3
	CH_2Cl_2–CS_2 (50 : 50 v/v)	1 209	34·0 ± 3	31·3 ± 3	−81 ± 30	55·4 ± 9
$[Pt(S_2CNEt_2)_2PPh_3]$	CH_2Cl_2	2 068	35·1 ± 3	32·6 ± 3	−72 ± 36	54·1 ± 14

For completion, the complexes $[Pt(S_2PEt_2)_2]$ and $[Pt(S_2PEt_2)_2PPh_3]$ were also prepared. The ^1H n.m.r. spectra of both complexes consist of a doublet of quartets (CH_2) and a doublet of triplets (CH_3) (see Experimental section), indicating rapid unidentate–bidentate exchange in the latter complex at room temperature which is still fast even at 203 K.

Complexes of Stoicheiometry $[M(S_2PMe_2)(ER_3')_2]X$.—Reaction of the complex $[Pt(S_2PMe_2)_2]$ with an excess of PR_3' ($PR_3' = PPh_3$ or $PMePh_2$) in methanol followed by light petroleum addition gave the pale yellow complexes $[Pt(S_2PMe_2)(PR_3')_2]S_2PMe_2$. The stability of these complexes with respect to rearrangement to $[Pt(S_2PMe_2)_2PR_3']$, by means of nucleophilic attack by $^-S_2PMe_2$ on the platinum–phosphorus bond, depends on the PR_3' group. For $PR_3' = PPh_3$, even recrystallisation from a polar solvent such as acetone gave only the 1 : 1 adduct, whereas for $PR_3' = PMePh_2$, the complex could be recrystallised from chloroform or even benzene without any rearrangement. This clearly indicates the lower nucleophilicity of $^-S_2PMe_2$ compared to $^-S_2CNR_2$ (*cf.* ref. 1). For the PPh_3 complex, variable-temperature ^1H n.m.r. studies (in CH_2Cl_2) showed the same phenomenon as observed earlier[1] for $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$, *i.e.* stabilisation of the ionic species at lower temperature (Table 1). However, in this instance, the complexity of the spectrum prevented attempts to estimate the equilibrium constant for this process from the ^1H n.m.r. data.

Reaction of the complex $[Pd(S_2PMe_2)_2]$ with an excess of PR_3' in methanol also gave some ionic products (conductivity evidence) but, on attempted isolation, these rapidly reverted to the 1 : 1 complexes. This is to be compared with the successful isolation of the pure ionic $^-S_2PPh_2$ palladium complexes[2] (except for PPh_3 and $PEtPh_2$), a fact which may reflect the stronger nucleophilicity of $^-S_2PMe_2$ compared to $^-S_2PPh_2$. For $PR_3' = PPh_3$, reaction either in very concentrated methanol solution or with a large excess of phosphine led to precipitation of the complex $[Pd(PPh_3)_4]$, a reaction not observed with $[Pd(S_2PMe_2)_2]$ and $PMePh_2$ or with $[Pt(S_2PMe_2)_2]$ and any phosphine.

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[4] See F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, London, 1972, p. 665.

[5] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 1968, **7**, 2625; A. Muller, V. V. Krishna Rao, and G. Klinksiek, *Chem. Ber.*, 1971, **104**, 1892; A. T. Casey, D. J. Mackey, and R. L. Martin, *Austral. J. Chem.*, 1971, **24**, 1587.

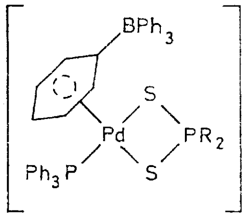
[6] See A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, 1970, **92**, 7061.

However, when the reaction of the complexes $[M(S_2PMe_2)_2]$ and an excess of PR_3' (*ca.* 1 : 3 mole ratio) in dilute methanol solution was followed by immediate addition of either sodium tetraphenylborate or hexafluorophosphate, precipitation of the ionic complexes $[M(S_2PMe_2)(PR_3)_2]X$ ($X = BPh_4^-$ or PF_6^-) occurred. A similar reaction between the complex $[Pd(S_2PPh_2)_2]$ and PPh_3 also resulted in formation of the previously unisolable $[Pd(S_2PPh_2)(PPh_3)_2]^+$ cation [2] as its BPh_4^- (or PF_6^-) salt. An interesting characteristic of the ^1H n.m.r. spectra of the BPh_4^- salts is that the resonances of both the $^-S_2PMe_2$ and PR_3' protons were shifted τ *ca.* 0·2—0·4 upfield with respect to the corresponding PF_6^- salts (Table 1). We suggest that this is a consequence of a ring-current effect in the BPh_4^- complexes which produces additional shielding of these methyl protons {*cf.* the $[Pt(S_2CNR_2)(PR_3')_2]X$ ($X = BPh_4^-$ or PF_6^-) series}.[1] Reaction of the platinum triphenylphosphine tetraphenylborate complexes with Ph_4AsY (Y = Cl, Br, or I) in chloroform led to immediate precipitation of the very insoluble Ph_4AsBPh_4 and the isolation of $[Pt(S_2PMe_2)(PPh_3)_2]Y$ from the filtrate. These complexes are quite stable in solution, exhibiting no tendency to rearrange to neutral 1 : 1 adducts.

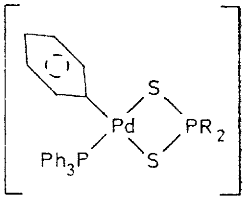
The corresponding complexes $[Pd(S_2PR_2)(PPh_3)_2]BPh_4$ (R = Me or Ph) behave in a different manner. Dissolution in chlorinated solvents such as CH_2Cl_2 or $CHCl_3$ (containing ethanol stabiliser) produced a rapid decrease in the conductivity of the solutions which turned orange-yellow and, after concentration and pentane addition, gave the neutral complexes $[Pd(S_2PR_2)(Cl)PPh_3]$. The corresponding bromo-complexes were obtained if the BPh_4^- salts were dissolved in $CHBr_3$ or CH_2Br_2 containing *ca.* 2% ethanol. In the absence of ethanol, the BPh_4^- salt was recovered unchanged, whereas addition of a few drops of alcoholic potassium hydroxide solution enhanced the rate of formation of the neutral complex. It would thus appear that the function of ethanol in this and similar rearrangement reactions [1] is to provide traces of base in order to facilitate formation of halide ion from the solvent. Rearrangement of the BPh_4^- complex also occurs in acetone solution containing added halide ion.

However, the presence of BPh_4^- ion also appears essential for facile rearrangement to occur since, when the complex $[Pd(S_2PR_2)(PPh_3)_2]PF_6$ was dissolved in halogenated solvents or in acetone with an excess of halide present, the ionic species was recovered unchanged. The rearrangement is also confined to the PPh_3 complexes, since we found no evidence of rearrangement for $[Pd(S_2PMe_2)(PMePh_2)_2]BPh_4$ when dissolved in chloroform. For the ionic platinum phosphine complexes, irrespective of the nature of the counter-anion, no rearrangement occurred, even after heating under reflux in chloroform–ethanol for 3 days. The arsine complex $[Pt(S_2PMe_2)(AsPh_3)_2]BPh_4$ did, however, react with halogenated solvents (as indicated by a decrease in conductivity), but no pure product could be isolated. This difference in behaviour between the platinum and palladium complexes is readily explicable in terms of the greater lability of palladium(II) complexes [4] coupled with the lower stability of these ionic palladium(II) species, as established in earlier studies.[1,2] Earlier work [2] has also revealed that the ionic platinum triphenylarsine complex is only stabilised by the presence of a large anion.

The role of the BPh_4^- ion and the reason why only this ion promotes the rearrangement reaction is not really understood. However, evidence exists in the literature both for formation of π-bonded BPh_4^- complexes by displacement of tertiary phosphines or phosphites [7] and for formation of metal–phenyl σ-bonds *via* fission of a boron–carbon bond.[8] Therefore it is not unreasonable to postulate that a similar process might occur here, giving a labile π- or σ-bonded phenyl intermediate such as (IIa) or (IIb) followed by displacement by a stronger nucleophile such as halide ion. At present, insufficient evidence is available to distinguish between these two possibilities.



(IIa)



(IIb)

I.r. Studies.—In earlier work with diphenylphosphinodithioates,[2] an empirical correlation was established between the mode of co-ordination of the dithio-group and the presence of certain i.r. bands. Thus, bidentate co-ordination was characterised by bands at 603, 570 cm^{-1}, unidentate 645, 540 cm^{-1}, and ionic at 650, 560 cm^{-1}.

TABLE 3

Characteristic bands (650—550 cm^{-1}) for determining the mode of co-ordination of the dimethylphosphinodithioato-group to palladium(II) and platinum(II) ions

Complex	Unidentate	Bidentate	Ionic
$[Pt(S_2PMe_2)_2]$		572s	
$[Pt(S_2PMe_2)_2PPh_3]$	598s	576w	
$[Pt(S_2PMe_2)_2AsPh_3]$	600s	572w	
$[Pd(S_2PMe_2)_2PMePh_2]$	600s	580w	
$[Pd(S_2PMe_2)_2PMe_2Ph]$	599s	582w	
$[Pd(S_2PMe_2)_2]$		575s	
$[Pt(S_2PMe_2)(PPh_3)_2]S_2PMe_2$		573w	610s
$[Pt(S_2PMe_2)(PMePh_2)_2]S_2PMe_2$		572w	610s
$[Pt(S_2PMe_2)(PPh_3)_2]BPh_4$ [a]		575w	
$[Pt(S_2PMe_2)(PPh_3)_2]PF_6$ [b]		572w,sh	
$[Pd(S_2PMe_2)(PMePh_2)_2]PF_6$ [b]		579w	
$[Pd(S_2PMe_2)(PPh_3)_2]BPh_4$ [a]		579w	
$[Pt(S_2PMe_2)(PPh_3)_2]Cl$		570w	
$[Pd(S_2PMe_2)Cl(PPh_3)]$		576m	

[a] Ionic region masked by BPh_4^- vibrations at 605s, 612m, and 625w cm^{-1}. [b] PF_6^- Vibrations at 612vw and 560vs cm^{-1}.

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[7] R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, 1970, **9**, 2339; L. M. Haines, *ibid.*, 1971, **10**, 1685; J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

[8] H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **91**, 596; H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 1226; R. J. Haines and A. L. du Preez, *J.C.S. Dalton*, 1972, 944.

These diagnostic band positions were then used to infer the types of bonding in other $^{-}S_2PPh_2$ complexes. Similarly for the $^{-}S_2PMe_2$ complexes, careful examination of the region 650—550 cm^{-1} also reveals that certain bands appear diagnostic of the different types of co-ordination (Table 3). For the reason discussed earlier,[2] *i.e.* extensive coupling of vibrations in these low-symmetry complexes, no attempt has been made to assign these bands to any specific mode of vibration, although they probably contain an appreciable contribution from PS_2^- stretching frequencies. There appears to be only one characteristic band in this region and comparison of the direction of shift of this band on change in co-ordination mode with those found earlier for $^{-}S_2PPh_2$ complexes [2] suggests that this is the higher-energy band. A band at 505 cm^{-1} in the complex $[Pt(S_2PMe_2)_2]$ can be assigned to the lower-energy band (corresponding to the 570 cm^{-1} band in $^{-}S_2PPh_2$ complexes). Unfortunately in all the adducts reported here, any change in the position of this latter band was masked by strong ligand vibrations.

TABLE 4

Analytical data for some platinum(II) and palladium(II) dithio-complexes

Complex	M.p.(t/°C)	Found (%)			Calc. (%)			Λ[a]
		C	H	Others	C	H	Others	
$[Pt(S_2PMe_2)_2PPh_3]$	211—214	37·0	3·7		37·4	3·8		
$[Pt(S_2PMe_2)_2PMePh_2]$	94	31·5	3·9		31·6	3·9		0·60
$[Pt(S_2PMe_2)_2PMe_2Ph]$	190	24·3	3·9	590 [b]	24·8	4·0	583 [c]	
$[Pt(S_2PMe_2)_2PPh_2C_6F_5]$	156—157	32·9	2·7	748 [b]	33·1	2·8	797 [c]	0·48
$[Pt(S_2PMe_2)_2AsPh_3]$	144—147	34·9	3·6	529 [b]	35·2	3·6	751 [c]	
$[Pd(S_2PMe_2)_2PPh_3]$	175 (decomp.)	42·8	4·4	507 [b]	42·9	4·4	618 [c]	
$[Pd(S_2PMe_2)_2PMePh_2]$	135	37·0	4·2		36·3	4·5		
$[Pd(S_2PMe_2)_2PMe_2Ph]$	196	29·4	4·6	550 [b]	29·2	4·7	494 [c]	
$[Pt(S_2PEt_2)_2PPh_3]$	175—177	40·9	4·7	761 [b]	40·9	4·6	735 [c]	
$[Pt(S_2PMe_2)(PPh_3)_2]S_2PMe_2$ [d]	156—158	48·1	4·2		49·6	4·3		48·7
$[Pt(S_2PMe_2)(PMePh_2)_2]S_2PMe_2$	200—203	42·7	3·9		42·6	3·6		22·3
$[Pt(S_2PMe_2)(PPh_3)_2]PF_6$	264—267	46·1	3·7		46·1	3·6		56·9
$[Pt(S_2PMe_2)(PPh_3)_2]BPh_4$	225—227	63·4	4·8		63·9	4·8		48·2
$[Pt(S_2PMe_2)(PPh_3)_2]Cl$	162—165	51·9	4·0	Cl, 4·6	51·8	4·1	Cl, 4·0	62·8
$[Pt(S_2PMe_2)(PPh_3)_2]Br$	199—201	51·6	4·2		49·4	3·9		47·5
$[Pt(S_2PMe_2)(PPh_3)_2]I$	242	46·3	3·8	I, 12·7	47·0	3·7	I, 13·0	
$[Pt(S_2PMe_2)(PMePh_2)_2]PF_6$	258	38·1	3·6		38·8	3·7		54·8
$[Pt(S_2PMe_2)(PMePh_2)_2]BPh_4$	98	57·9	4·6		60·0	5·1		43·0
$[Pt(S_2PMe_2)(AsPh_3)_2]BPh_4$	108—112	58·9	5·0		59·4	4·5		34·2
$[Pt(S_2PMe_2)(AsPh_3)_2]PF_6$	199—202	42·1	3·3		42·4	3·8		50·4
$[Pd(S_2PMe_2)(PPh_3)_2]BPh_4$	182 (decomp.)	69·6	6·0		69·2	5·2		32·2 [e]
$[Pd(S_2PMe_2)(PPh_3)_2]PF_6$	211 (decomp.)	50·6	3·9		50·7	4·0		57·9
$[Pd(S_2PMe_2)(PMePh_2)_2]PF_6$	202—204 (decomp.)	42·9	4·1		43·2	4·2		52·6
$[Pd(S_2PPh_2)(PPh_3)_2]BPh_4$	89	68·4	5·3		69·2	5·3		
$[Pd(S_2PPh_2)(PPh_3)_2]PF_6$	235 (decomp.)	55·4	3·7		56·3	3·9		57·4
$[Pd(S_2PMe_2)(PMe_2Ph)_2]BPh_4$	165	65·9	5·5		65·7	5·5		38·5
$[Pd(S_2PMe_2)Cl(PPh_3)]$	191	45·8	4·0	Cl, 6·5 539 [b]	45·4	4·0	Cl, 6·7 529 [c]	
$[Pd(S_2PMe_2)Br(PPh_3)]$	215—218 (decomp.)	42·2	3·7	Br, 14·0	41·9	4·0	Br, 14·3	
$[Pd(S_2PPh_2)Cl(PPh_3)]$	226—228 (decomp.)	54·5	4·0	Cl, 5·4	55·2	3·8	Cl, 5·6	

[a] In Ω^{-1} cm^2 mol^{-1}; measured in CH_2Cl_2 (10^{-3}M) at 298 K. [b] Experimental molecular weight (acetone). [c] Calc. molecular weight. [d] Contaminated with a small amount of the complex $[Pt(S_2PMe_2)_2PPh_3]$. [e] Immediate reading; after 45 min, $\Lambda = 3{\cdot}2\ \Omega^{-1}$ cm^2 mol^{-1}.

EXPERIMENTAL

Microanalyses were carried out by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were measured in dry acetone at 37 °C on a Perkin-Elmer–Hitachi osmometer calibrated with benzil. Analytical data for all the new complexes are given in Table 4. I.r. spectra were recorded in the region 4 000—200 cm^{-1} on a Perkin-Elmer 225 grating spectrometer using Nujol mulls on caesium iodide plates. ^{1}H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Mass spectra were obtained on an AEI MS9 mass spectrometer and conductivity measurements on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Köfler hot-stage microscope and are uncorrected.

Materials.—Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine (B.D.H.); triphenylarsine (Ralph Emanuel). Triphenylphosphine and triphenylarsine were recrystallised from ethanol before use. Methyldiphenylphosphine was made by the Grignard method from chlorodiphenylphosphine. Sodium dimethyl- and diethyl-phosphinodithioates were made by standard methods.[9] Triethylarsine and pentafluorophenyl(diphenyl)phosphine were kindly supplied by Dr. D. I. Nichols. Operations involving free tertiary phosphines (other than PPh_3) were carried out under an atmosphere of nitrogen.

^{1}H *N.m.r. Variable-temperature Studies.*—The variable-temperature unit on the HA 100 spectrometer was used with methanol as a calibrant. Spectra were run at 5 K intervals in the range 313—200 K. Spectra were simulated using a computer program based on that of Nakagawa.[10] The exchange process was considered for the purpose of computation as consisting of n two-site exchanges, where n is the multiplicity of the resonance being monitored. The single-

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[9] W. Kuchen, W. Strolenberg, and J. Metten, *Chem. Ber.*, 1963, **96**, 1733; R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.*, 1971, **10**, 2710.

[10] T. Nakagawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 1006.

line simulated spectra were then superimposed with suitable weighting for intensities and the results plotted out on the line printer; *e.g.*, a doublet was considered as two two-site exchanges of intensity ratio 1 : 1.

Experimental spectra were fitted to the computed spectra by finding the best fit between the ratio of maximum to minimum heights in the multiplet and the life-times so obtained were used to construct Arrhenius plots in which straight lines were fitted by the least-squares method. Broadening of the lines due to effects other than exchange (*e.g.* increased viscosity and lower solubility at lower temperatures) had to be taken into account, otherwise values of the life-times particularly at lower temperatures were artificially enhanced. This was accomplished by measuring the natural linewidth at both the high- and low-temperature limits and then using these different values in the regions near these limits. A similar technique has been used elsewhere.[11] Final activation parameters, obtained by the usual methods, are shown in Table 2 along with assessed error limits.

Bis(dimethylphosphinodithioato)platinum(II).— Potassium tetrachloroplatinate(II) (5·00 g, 12·0 mmol) in a minimum volume of hot water was shaken with an excess of sodium dimethylphosphinodithioate dihydrate (4·40 g, 24·0 mmol) for several minutes. The immediate yellow-orange precipitate which formed was filtered off, washed with water, methanol, and diethyl ether and recrystallised from chloroform (Yield 4·25 g, 80%) (Found: C, 10·7; H, 2·6. Calc. for $C_4H_{12}P_2PtS_4$: C, 10·8; H, 2·7%). The same complex was prepared independently by Cavell *et al.*[12] and the electronic, i.r., and mass spectra are thoroughly discussed in their paper.

Bis(dimethylphosphinodithioato)(triphenylphosphine)platinum(II).—The complex $[Pt(S_2PMe_2)_2]$ was suspended in benzene or chloroform and treated with a 1 : 1 mole ratio of triphenylphosphine. On warming gently, a yellow solution was formed which was filtered, concentrated, and the product precipitated by addition of pentane. The yellow *complex* was recrystallised from chloroform–pentane. In a similar manner, *bis(dimethylphosphinodithioato)(methyldiphenylphosphine)platinum*(II), *bis(dimethylphosphinodithioato)(dimethylphenylphosphine)platinum*(II), and *bis(dimethylphosphinodithioato)[pentafluorophenyl(diphenyl)phosphine]-platinum*(II) were prepared.

Bis(dimethylphosphinodithioato)(triphenylarsine)platinum(II).—A suspension of $[Pt(S_2PMe_2)_2]$ in benzene or chloroform was treated with an excess of triphenylarsine. On concentration and addition of pentane, the complex was precipitated as a yellow powder which was filtered off, washed with light petroleum, and air-dried. The products with triethylarsine and triethylphosphine were too soluble to isolate and with pyridine and ammonia only starting material was isolated on removal of the solvent.

Bis(diethylphosphinodithioato)platinum(II) was prepared as for the complex $[Pt(S_2PMe_2)_2]$ using K_2PtCl_4 and $NaS_2PEt_2,2H_2O$ (Found: C, 19·4; H, 4·1. Calc. for $C_8H_{20}P_2PtS_4$: C, 19·3; H, 4·0%). ^1H N.m.r. spectrum: τ 8·00 (CH_2, doublet of quartets, $J_{CH_2CH_3}$ 7·0 Hz; J_{P-CH_2} 9·0 Hz) an 8·64 (CH_3, doublet of triplets, J_{P-CH_3} 21·0 Hz). I.r. spectrum (650—500 cm^{-1}): 580w,sh, 570s, and 500m cm^{-1}.

Bis(diethylphosphinodithioato)(triphenylphosphine)platinum(II) was prepared as for the complex $[Pt(S_2PMe_2)_2PPh_3]$. ^1H N.m.r. spectrum (301 K): τ 2·60 (phenyl multiplet); 8·06 (CH_2, J_{P-CH_3} 11·0 Hz); and 8·82 (CH_3, $J_{CH_2-CH_3}$ 7·0 Hz, J_{P-CH_3} 21·0 Hz). On cooling, some broadening of the $-CH_2$ and $-CH_3$ resonances at 203 K occurred indicating still rapid unidentate–bidentate exchange at this temperature. I.r. spectrum (650—550 cm^{-1}): 590s and 572w,sh cm^{-1}.

Bis(dimethylphosphinodithioato)palladium(II).— *Method* (*A*). Palladium(II) acetate[13] was dissolved in benzene–acetone and heated under reflux for 2 h with a slight excess of sodium dimethylphosphinodithioate dihydrate in methanol. On cooling, the dark red-brown crystalline *powder* was filtered off and washed with water, methanol, and diethyl ether (Found: C, 13·9; H, 3·4. Calc. for $C_4H_{12}P_2PdS_4$: C, 13·5; H, 3·4%).

Method (*B*). Palladium(II) chloride was suspended in acetone and heated under reflux for 3 h with an excess of $NaS_2PMe_2,2H_2O$. The resulting orange-red solution was filtered hot and, on cooling, deposited the orange-red crystalline *product* which was purified as before.

Although the products formed by these methods are different in colour they had the same i.r. and mass spectra and behaved in the same way with tertiary phosphines. Spectral parameters are reported elsewhere.[12]

Bis(dimethylphosphinodithioato)(triphenylphosphine)palladium(II).—A suspension of the complex $[Pd(S_2PMe_2)_2]$ in benzene was treated with an *excess* of triphenylphosphine (*ca.* 1 : 2 mole ratio). On warming gently, a dark red solution was obtained which, on addition of pentane, precipitated the orange-yellow *product* which was recrystallised from chloroform. A similar method was used to make the complexes $[Pd(S_2PMe_2)_2PMePh_2]$ and $[Pd(S_2PMe_2)_2PMe_2Ph]$.

(Dimethylphosphinodithioato)bis(triphenylphosphine)platinum(II) *Dimethylphosphinodithioate*.—A suspension of the complex $[Pt(S_2PMe_2)_2]$ in a small amount of methanol was treated with triphenylphosphine (1 : 4 mole ratio). The mixture was boiled for 2 min, filtered, and then an excess of diethyl ether was added. The resulting yellow-buff precipitate was filtered off, washed with light petroleum, and dried *in vacuo* (40 °C). *(Dimethylphosphinodithioato)bis(methyldiphenylphosphine)platinum*(II) *dimethylphosphinodithioate* was prepared in a similar manner. The ionic triphenylphosphine complex readily reverted to $[Pt(S_2PMe_2)_2PPh_3]$ on attempted recrystallisation; in contrast, the ionic methyldiphenylphosphine complex was unchanged, even on recrystallisation from such non-polar solvents as benzene or chloroform. Attempts to prepare pure samples of the corresponding palladium complexes proved unsuccessful; only mixtures of 1 : 1 and 1 : 2 adducts were formed which rapidly reverted to the pure 1 : 1 complexes even in acetone.

(Dimethylphosphinodithioato)bis(triphenylphosphine)platinum(II) *Tetraphenylborate*.—A suspension of the complex $[Pt(S_2PMe_2)_2]$ in methanol was gently warmed with excess of triphenylphosphine (*ca.* 1 : 3 mole ratio), then filtered, and a concentrated methanolic solution of sodium tetraphenylborate added, giving an immediate pale yellow precipitate. Recrystallisation from acetone gave the crystalline *product*. The same method was used to prepare all the complexes $[M(S_2PMe_2)(PR_3)_2]X$ ($X = BPh_4^-$, or PF_6^-; M = Pt or Pd) listed in Table 4, and also $[Pt(S_2PMe_2)(AsPh_3)_2]BPh_4$ and $[Pd(S_2PPh_2)(PPh_3)_2]BPh_4$. However, for M = Pd and $PR_3 = PPh_3$, reaction in very concentrated methanolic

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[11] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1967, **6**, 1512.

[12] R. G. Cavell, W. Byers, E. D. Day, and P. M. Watkins, *Inorg. Chem.*, 1972, **11**, 1598.

[13] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

solution using a large excess of triphenylphosphine gave instead a yellow crystalline precipitate of *tetrakis(triphenylphosphine)palladium*(0), m.p. 103—105 °C (lit.,[14] 100—105 °C) (Found: C, 74·7; H, 5·1. Calc. for $C_{72}H_{60}P_4Pd$: C, 75·1; H, 5·2%).

(Dimethylphosphinodithioato)bis(triphenylphosphine)-platinum(II) *Chloride*.—The complex $[Pt(S_2PMe_2)(PPh_3)_2]$-BPh_4 (0·20 g) was dissolved in chloroform (10 cm^3) and treated with Ph_4AsCl,HCl (0·07 g) (1 : 1 mole ratio) in chloroform (5 cm^3). The mixture was stirred for 10 min, the precipitate of Ph_4AsBPh_4 filtered off, the solution concentrated, and diethyl ether–pentane added to precipitate the *complex* as a white powder, which was recrystallised from chloroform–pentane. The complexes $[Pt(S_2PMe_2)(PPh_3)_2]Y$ ($Y = Br^-$ or I^-) were made in similar manner.

Chloro(dimethylphosphinodithioato)triphenylphosphine-palladium(II).—The complex $[Pd(S_2PMe_2)(PPh_3)_2]BPh_4$ was dissolved in chloroform (containing ethanol stabiliser), warmed briefly, and then set aside (*ca.* 5—10 min) until the conductivity of the solution was very low (*ca.* 0·6 $\mu\Omega^{-1}$). Precipitation with pentane then gave the orange-yellow *product*, which was recrystallised from benzene–pentane. The same complex was obtained much more slowly from dichloromethane solution.

Bromo(dimethylphosphinodithioato)triphenylphosphinepalladium(II) was prepared in analogous fashion using $CHBr_3$ or CH_2Br_2 plus ethanol (*ca.* 2%) as solvent, the reaction taking *ca.* 30 min for completion. The complex $[Pd(S_2PPh_2)(Cl)PPh_3]$ was similarly prepared from $[Pd(S_2PPh_2)(PPh_3)_2]BPh_4$ and chloroform.

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[3/539 *Received*, 13*th March*, 1973]

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[14] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1961, 1186.