Metal Complexes of Sulphur Ligands. Part 14.[1] Reaction of Palladium(II) and Platinum(II) Dithioacid Complexes with Tertiary Phosphinites, and the Crystal and Molecular Structure of Dimethylphosphinodithioato(diphenylphosphinito)(diphenylphosphinous acid)palladium(II)

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Prolonged reaction of $[Pd(S_2PMe_2)_2]$ with excess $PPh_2(OR)$ (R = Me or Et) in either methylene chloride or benzene gives the four-co-ordinate complex $[Pd(S_2PMe_2)(PPh_2O)\{PPh_2(OH)\}]$ (1a) shown by spectroscopic evidence and *X*-ray structural analysis to contain the symmetrically hydrogen-bonded $Ph_2POHOPPh_2$ ligand. Crystals of (1a) are monoclinic, space group $P2_1/m$, with $a = 6.86(1)$, $b = 22.12(2)$, $c = 9.69(1)$ Å, $\beta = 111.5(2)°$. The acidic hydrogen atom links two equivalent diphenylphosphinite groups with $O \cdots O$ 2.41 Å. Similar complexes $[M(S{-}S)(PPh_2O)\{PPh_2(OH)\}]$ (M = Pd, $S{-}S^- = [S_2PPh_2]^-$ or $[S_2CNEt_2]^-$; M = Pt, $S{-}S^- = [S_2PMe_2]^-$ or $[S_2CNEt_2]^-$) have been prepared by reaction of $[M(S{-}S)_2]$ with $PPh_2(OR)$ or, for M = Pd, by reaction of $[\{PdCl(PPh_2O)[PPh_2(OH)]\}_2]$ with the appropriate dithioacid anion (1 : 2 molar ratio). A careful study of the $[Pt(S_2CNEt_2)_2]{-}PPh_2(OMe)$ reaction has resulted in the isolation of the intermediates $[Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2]X$ (2; $X = [BPh_4]^-$ or Cl^-) and $[Pt(S_2CNEt_2)(PPh_2O)\{PPh_2(OMe)\}]$ (3) and a mechanism of formation of $[Pt(S_2CNEt_2)(PPh_2O)\{PPh_2(OH)\}]$ (1b) involving both nucleophilic attack on a P–OMe bond and subsequent hydrolysis of a P–OMe bond is proposed. In contrast, reaction of $[M(S_2COPr^i)_2]$ with $PPh_2(OEt)$ gives $[M(S_2CO)\{PPh_2(OEt)\}_2]$ (M = Pd or Pt), although $[Pd(S_2COPr^i)(PPh_2O)\{PPh_2(OH)\}]$ can be synthesised from $[\{PdCl(PPh_2O)[PPh_2(OH)]\}_2]$ and $K[S_2COPr^i]$ (1 : 2 molar ratio).

In some of the earlier papers in this series [2] the results of the reactions of various tertiary phosphines (L) with the square-planar $[M(S{-}S)_2]$ complexes {M = Pd or Pt; $S{-}S^- = [S_2PR_2]^-$, $[S_2CNR_2]^-$, $[S_2COR]^-$, or $[S_2P(OR)_2]^-$} have been reported. These studies clearly show that reaction occurs by stepwise cleavage of metal–sulphur bonds to generate the four-co-ordinate square-planar complexes $[M(S{-}S)_2L]$ and $[M(S{-}S)L_2][S{-}S]$ which exhibit unidentate–bidentate and bidentate–ionic modes of bonding of the dithioacid groups respectively. In addition, for these ionic $[S_2COR]^-$ and $[S_2P(OEt)_2]^-$ complexes, nucleophilic attack can also occur on a co-ordinated alkoxy-group to give $[M(S_2CO)L_2]$ and $[M\{S_2P(O)OEt\}L_2]$ respectively.

In this paper, we now report the results of reactions between various palladium(II) and platinum(II) dithioacid complexes and tertiary phosphinites $PPh_2(OR)$ (R = Me or Et) in which, on the basis of earlier work, both hydrolysis of the P–OR group [3] and/or nucleophilic attack on the P–OR group [4] might be expected to play a significant role.

RESULTS AND DISCUSSION

Addition of an excess of $PPh_2(OMe)$ to a methylene chloride solution of $[Pd(S_2PMe_2)_2]$ immediately gave a highly conducting solution which slowly decreased in conductivity when the solution was left to stand for 24 h. This decrease in conductivity was accompanied by a colour change from orange-yellow to pale yellow, and on addition of diethyl ether a pale yellow, non-conducting, crystalline precipitate (1a) was obtained. The ^1H n.m.r. spectrum of this product contained in addition to the phenyl multiplet, a sharp doublet at δ 1.97 p.p.m. [^2J(PH) 12.0 Hz] (relative intensity 10 : 3) assigned to the methyl protons of the $[S_2PMe_2]^-$ ligand but no signals between 3 and 4 p.p.m. which could be assigned to the methoxy-group of the phosphinite. The same complex was formed by using $PPh_2(OEt)$ or by carrying out the reactions in benzene which both eliminates the possible participation of chloride ion in these reactions {*cf.* the reaction of $[M(S_2CNR_2)(PR'_3)_2][S_2CNR_2]$ with CH_2Cl_2 which gave $[M(S_2CNR_2)(PR'_3)_2]Cl$ and $CH_2(S_2CNR_2)_2$ [5]} and suggests that either hydrolysis and/or nucleophilic attack on the P–OR group has occurred.

Complex (1a) analysed closely for $[Pd(S_2PMe_2)(PPh_2O)\{PPh_2(OH)\}]$ and is monomeric in chloroform at 37 °C. However, all attempts to observe the ^1H n.m.r. signal of the acid hydrogen on the co-ordinated diphenylphosphinous acid proved unsuccessful [*cf.* related studies on $[\{MX(PPh_2O)[PPh_2(OH)]\}_2]$ (M = Pt or Pd; X = Cl or Br) [6]] although Beaulieu *et al.*[3] found such a signal at δ 13.43 p.p.m. for $[PtH(PMePh_2)(PPh_2O)\{PPh_2(OH)\}]$.

The i.r. spectrum of (1a) shows several bands in the P–O stretching region (850—1 100 cm^{-1}).[7] However, the three strong bands at 850, 895, and 944 cm^{-1} are also observed for the starting material $[Pd(S_2PMe_2)_2]$ while that at 1 100 cm^{-1} corresponds to a band usually observed in phenylphosphine complexes [6] and can therefore be assigned to a ligand absorption. Thus, the remaining

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[1] Part 13, M. C. Cornock and T. A. Stephenson, *J.C.S. Dalton*, 1977, 683.

[2] For detailed references, see D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, 1973, 2124.

[3] See W. B. Beaulieu, T. B. Rauchfuss, and D. M. Roundhill, *Inorg. Chem.*, 1975, **14**, 1732 and refs. therein.

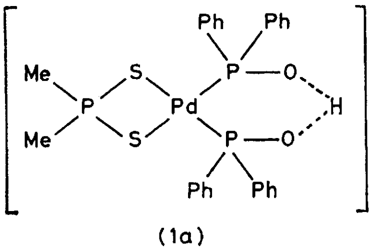
[4] See W. C. Trogler, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, 1975, **14**, 2748 and refs. therein.

[5] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[6] K. R. Dixon and A. D. Rattray, *Canad. J. Chem.*, 1971, **49**, 3997.

[7] J. Chatt and B. Heaton, *J. Chem. Soc. (A)*, 1968, 2745.

peak at 1 010 cm^{-1} is assigned to a ν(PO) stretching mode. The peak at 582 cm^{-1} is consistent with bidentate co-ordination of the $[S_2PMe_2]^-$ group.[2] The absence of ν(OH) in the normal region of the i.r. spectrum (*ca.* 3 200 cm^{-1}) is consistent with a symmetrical hydrogen-bonded system of the type first postulated by Dixon and Rattray [6] in $[\{MX(PPh_2O)[PPh_2(OH)]\}_2]$, *etc.*, and later confirmed by an *X*-ray structural analysis on the related $[\{Pd(SCN)(PPh_2O)[PPh_2(OH)]\}_2]$.[8]



(1a)

Further evidence for the validity of this statement is based on the ^{31}P n.m.r. spectrum (proton decoupled) of (1a) which shows the expected AX_2 pattern with resonances centred at δ 84.29 ($[S_2PMe_2]^-$) and 83.20 p.p.m. ($Ph_2POHOPPh_2$) respectively, and the fact that reaction of $[\{PdCl(PPh_2O)[PPh_2(OH)]\}_2]$ [6] with $Na[S_2PMe_2]\cdot 2H_2O$ (1 : 2 molar ratio) in methylene chloride gave (1a) in high yield. However, unequivocal proof of the solid-state structure of (1a) is given by the results of an *X*-ray structural analysis which is reported in detail below. Analogous complexes $[M(S\text{–}S)(PPh_2O)\{PPh_2(OH)\}]$ (M = Pd, $S\text{–}S^- = [S_2PPh_2]^-$ or $[S_2CNEt_2]^-$; M = Pt, $S\text{–}S^- = [S_2PMe_2]^-$, or $[S_2CNEt_2]^-$) were prepared by prolonged reaction of $[M(S\text{–}S)_2]$ with excess of $PPh_2(OR)$ in methylene chloride and fully characterised by elemental analyses, and i.r., ^1H, and ^{31}P n.m.r. spectroscopy (see Experimental section). The palladium complexes were also synthesised by reaction of $[\{PdCl(PPh_2O)[PPh_2(OH)]\}_2]$ with either $[NH_4][S_2PPh_2]$ or $Na[S_2CNEt_2]\cdot 3H_2O$ (1 : 2 molar ratio).

Crystal Data for (1a).—$C_{26}H_{27}O_2P_3PdS_2$, $M = 634$, pale yellow monoclinic needles, $a = 6.86(1)$, $b = 22.12(2)$, $c = 9.69(1)$ Å, $\beta = 111.5(2)°$, $U = 1\,368$ Å^3, $D_m = 1.50$, $Z = 2$, $D_c = 1.54$ g cm^{-3}. Space group = $P2_1/m$ (No. 13), Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) = 88.7 cm^{-1}.

Structure Determination.—Data for layers 0—4*kl* were collected on multifilm packs by the equi-inclination Weissenberg method. Intensities were evaluated by the Photoscan Service of the Atlas Computing Laboratory, and 1 228 independent reflections were measured above background. The crystal was a needle elongated along [100] with a length of 0.8 mm and a cross-section of 0.2 mm^2. Cylindrical absorption corrections [9] were applied to the data.

The data were put on a common scale statistically, and the position of the Pd atom was found from a Patterson summation; all the other non-hydrogen atoms were located in two subsequent difference-Fourier syntheses, and the space group was confirmed as $P2_1/m$ rather than the non-centric $P2_1$. The phenyl rings were constrained to be planar with all C–C distances 1.40 Å and all C–C–C angles 120°, and the model was refined isotropically with separate layer-scale factors and unit weights. For the last few cycles, only a single overall scale factor was refined, the palladium, phosphorus, and sulphur atoms being given anisotropic temperature factors, and a weighting scheme ($w = 30/|F_o|$ for $|F_o| > 30$ and otherwise $w = 1$) was applied. In the last cycle no shifts were greater than 0.1 times the estimated standard deviation, and the final *R* was 0.077. Hydrogen atoms could not be reliably located.

Final atomic parameters are given in Table 1, and the principal interatomic distances and angles in Table 2.

TABLE 1

Fractional co-ordinates and thermal parameters (all × 10^4) for (1a). For the phenyl rings [atoms C(1)—C(6) and C(7)—C(12)] the estimated standard deviation of the ring centres is 0.006 Å

	x	y	z	U
Pd	1 436(3)	2 500	822.7(1.2)	*
S	697(8)	1 776.5(1.3)	2 415(4)	*
P(1)	2 190(7)	1 765.9(1.4)	−532(3)	*
P(2)	−224(10)	2 500	3 255	*
O	3 766(18)	3 046(4)	−1 254(10)	379(22)
C(1)	3 271	1 090	496	302(27)
C(2)	1 989	675	848	400(33)
C(3)	2 860	1 535	1 659	402(33)
C(4)	5 014	47	2 117	493(39)
C(5)	6 298	462	1 766	459(37)
C(6)	5 426	984	956	363(31)
C(7)	−72	1 488	−2 047	271(27)
C(8)	240	1 114	−3 111	457(36)
C(9)	−1 476	917	−4 340	538(42)
C(10)	−3 505	1 098	−4 504	555(43)
C(11)	−3 817	1 472	−3 440	566(44)
C(12)	−2 100	1 667	−2 211	420(34)
C(13)	999(43)	2 500	5 242(24)	456(50)
C(14)	−3 076(55)	2 500	2 748(30)	661(72)

* Anisotropic thermal parameters (× 10^4):

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	278(13)	160(5)	200(5)	0	114(5)	0
S	570(40)	237(16)	387(17)	31(15)	308(20)	36(11)
P(1)	327(36)	239(17)	289(16)	14(14)	184(17)	1(11)
P(2)	421(49)	287(22)	242(21)	0	190(24)	0

The structure-factor table is deposited as Supplementary Publication No. SUP 22021 (4 pp., 1 microfiche).*

Description of the Structure.—The structure of (1a) is monomeric with crystallographic $m(C_s)$ symmetry. The co-ordination of palladium is very nearly square planar, and is illustrated in Figure 1. The Pd atom is less than 0.04 Å from the plane determined by P(1), S, P(1′), and S′, and the co-ordination distances and angles are normal for complexes of Pd^{II} with sulphur- and phosphorus-containing ligands. Figure 2 shows the projection of the complex into its symmetry plane. The dithiophosphinate ligand possesses a molecular plane of symmetry perpendicular to this, but inclined at an angle of 12.9°

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

[8] D. V. Naik, G. J. Palenik, S. Jacobson, and A. J. Carty, *J. Amer. Chem. Soc.*, 1974, **96**, 2286.

[9] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1967, vol. 2, p. 291.

to the co-ordination plane. One result of this is that C(14) is only 3.56 Å from the Pd atom at $(1 + x,y,z)$.

The diphenylphosphinite ligands are symmetry related; this requires the hydrogen atom to lie symmetrically between the two oxygen atoms. The plane defined by P(1), P(1′), O, O′ is tilted 26.1° with respect to the co-ordination plane. This may also be expressed as a rotation of each ligand about the Pd–P bond of 27.3° from the position in which the symmetry planes of the diphenylphosphinite groups would coincide with the co-ordination plane. The ligands themselves are only slightly distorted from *m* symmetry; the planes of the two phenyl rings are inclined at 63 and 59° respectively to the Pd(1),P(1),O(1) plane, and at 85° to one another. A smaller rotation of the ligands would make the O(1) ··· O(1′) distance even shorter; a greater one would bring the rings C(7)—C(12) and C(7′)—C(12′) closer together. As it is, the separation of C(12) and C(12′) is 3.68 Å, and the hydrogen atoms bonded to these will be *ca.* 2.5 Å apart.

TABLE 2

Interatomic distances (Å) and angles (°) in (1a). Primed atoms are related to unprimed ones by the operation $x, \frac{1}{2}-y, z$. Estimated standard deviations are given only when atoms in the phenyl rings are not involved. Intermolecular contacts less than 3.5 Å are listed

Pd–S	2.403(4)	S–Pd–S′	83.5(2)
Pd–P(1)	2.264(4)	S–Pd–P(1)	92.4(1)
S–P(2)	2.000(6)	S–Pd–P(1′)	175.6(3)
P(1)–O	1.545(14)	P(1)–Pd–P(1′)	91.6(2)
P(1)–C(1)	1.800	Pd–S–P(2)	84.3(2)
P(1)–C(7)	1.807	Pd–P(1)–O	114.6(4)
P(2)–C(13)	1.796(22)	Pd–P(1)–C(1)	114.2
P(2)–C(14)	1.834(37)	Pd–P(1)–C(7)	113.8
O ··· O′	2.414(20)	O–P(1)–C(1)	105.1
O ··· C(11) $[1 + x,y,z]$	3.32	O–P(1)–C(7)	105.0
O ··· C(12) $[1 + x,y,z]$	3.38	C(1)–P(1)–C(7)	102.9
O ··· C(13) $[x,y,z - 1]$	3.45	S–P(2)–C(13)	110.1(6)
		S–P(2)–C(14)	110.9(5)
		C(13)–P(2)–C(14)	108.7(14)
		S–P(2)–S′	106.3(4)
		P(1)–C(1)–C(2)	120.8
		P(1)–C(1)–C(6)	119.2
		P(1)–C(7)–C(8)	118.9
		P(1)–C(7)–C(12)	121.2

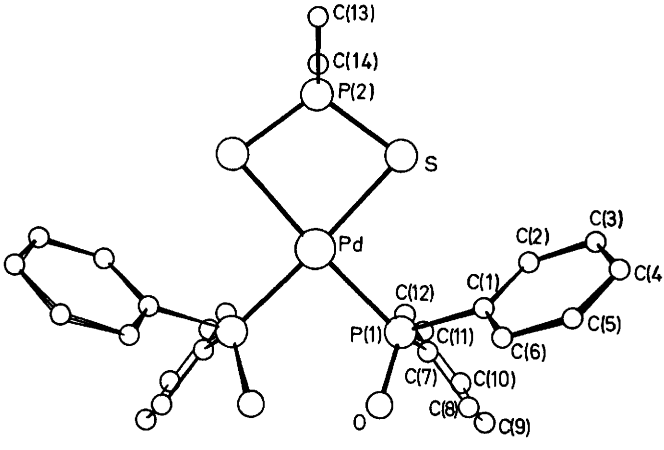

FIGURE 1 Projection of (1a) on to the co-ordination plane

Thus, the interaction of the diphenylphosphinite and diphenylphosphinous acid groups in (1a) is very similar to that in $[\{Pd(SCN)(PPh_2O)[PPh_2(OH)]\}_2]$ where an O ··· O distance of 2.421 Å and two independent P–O bonds of 1.549 and 1.536 Å were reported.[8] This supports the suggestion of Naik *et al.*[8] and other workers[3] that such interactions are normal for complexes of Pt^{II} and Pd^{II} containing diphenylphosphinite and diphenylphosphinous acid ligands in *cis* orientation to each other.

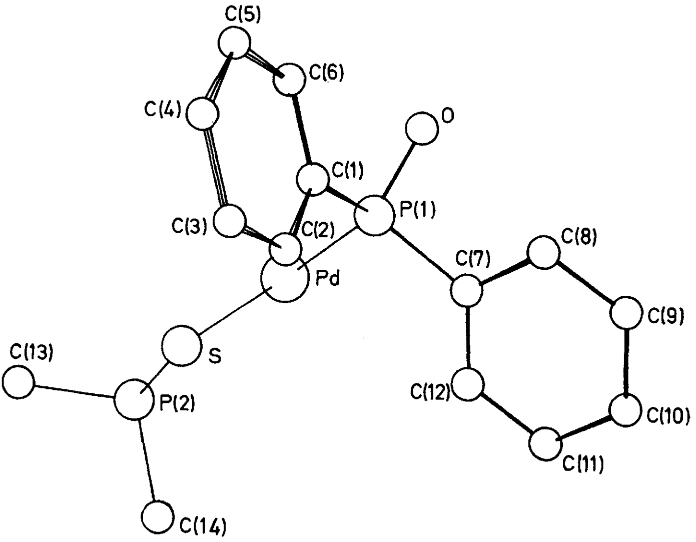

FIGURE 2 Projection of (1a) on to the symmetry plane

In an attempt to determine the detailed mechanism of formation of these complexes the nature of the products formed during the reaction of $[M(S_2CNEt_2)_2]$ with $PPh_2(OMe)$ were carefully examined. Thus, reaction of $[M(S_2CNEt_2)_2]$ with excess of $PPh_2(OMe)$ in methanol followed either immediately (Pt) or within 30 min (Pd) by addition of $Na[BPh_4]$ gave a precipitate of $[M(S_2CNEt_2)\{PPh_2(OMe)\}_2][BPh_4]$ (2). Complexes (2) were characterised by elemental analyses, conductivity measurements in methylene chloride which are indicative of 1 : 1 electrolytes, ^1H n.m.r. spectra which show the presence of a ' pseudo-triplet ' * for the methoxy-groups with $|^3J(PH) + {}^5J(PH)|$ 12.0 Hz † and magnetically equivalent ethyl groups, and ^{31}P n.m.r. spectra which for M = Pt shows the expected 1 : 4 : 1 triplet [J(PtP) 3 749.0 Hz] indicative of magnetically equivalent phosphorus-bonded $PPh_2(OMe)$ groups. These results clearly show that, as in the case of tertiary

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* A ' pseudo-triplet ' pattern consists of a sharp doublet with a broad hump situated between the doublet and signifies a relatively large J(PP) compared to the $[J(PH) + J(PH)']$ value {*cf.* *cis*-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$.[10]}

† *cf.* *cis*-$[MCl_2\{PPh_2(OMe)\}_2]$ (M = Pd or Pt) with $[^3J(PH) + {}^5J(PH)]$ 12.5 Hz.[11]

[10] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 739.

[11] See D. A. Couch, S. D. Robinson, and J. N. Wingfield, *J.C.S. Dalton*, 1974, 1309.

phosphines,[2,5] the initial rapid increase in conductivity on mixing $[M(S-S)_2]$ and $PPh_2(OR)$ is due to the formation of $[M(S-S)\{PPh_2(OR)\}_2][S-S]$ presumably by stepwise cleavage of metal–sulphur bonds.

However, rather surprisingly, treatment of a methylene chloride solution of (2; M = Pt) with $Na[S_2CNEt_2]\cdot3H_2O$ in acetone led after 3 d only to the recovery of starting materials. Hence, because of the strong possibility that the presence of the large anion was inhibiting further reaction of the cation, (2) was treated with an equimolar amount of $[AsPh_4]Cl\cdot HCl$ which precipitated the very insoluble $[AsPh_4][BPh_4]$ and left a methylene chloride solution containing $[Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2]Cl$. This solution was divided into three parts which were treated as described below.

One portion of this solution was treated with an equimolar amount of $Na[S_2CNEt_2]\cdot3H_2O$ which gave an immediate precipitate of sodium chloride. The conductivity of the filtered solution was then monitored over a period of 3 d and found to decrease steadily. At the end of this period, evaporation of the solvent and addition of diethyl ether gave a non-conducting microcrystalline pale yellow solid (3). The ^1H n.m.r. spectrum of (3) consisted of a doublet at δ 3.87 $[PPh_2(OMe)]$, two closely spaced quartets at 3.52 and 3.56, a triplet at 1.23 p.p.m. ($[S_2CNEt_2]^-$), and a multiplet in the aromatic region. The ^{31}P n.m.r spectrum (proton decoupled) in $CDCl_3$ at 223 K consisted of two doublets at δ 38.89 and 94.14 p.p.m. (relative intensity *ca.* 1 : 1) with $J(PP)$ 28.0 Hz, indicative of a *cis* arrangement of different phosphorus-containing ligands bound to Pt^{II}.[12] Each of the doublets exhibited platinum satellites with $J(PtP)$ 3 264.8 and 4 212.3 Hz respectively, confirming directly bonded phosphorus atoms in each ligand. The i.r. spectrum showed a strong $\nu(PO)$ stretch at 1 050 cm^{-1} with $\nu(CN)$ at 1 530 cm^{-1} indicative of bidentate $[S_2CNEt_2]^-$ co-ordination.[13] All this spectroscopic information together with the analytical data is consistent with the formulation of (3) as $[Pt(S_2CNEt_2)(PPh_2O)\{PPh_2(OMe)\}]$. By analogy with the complex $[Ni(\eta-C_5H_5)\{P(OEt)_3\}\{PO(OEt)_2\}]$ which shows two doublets centred at δ 147.5 $[P(OEt)_3]$ and 85.8 p.p.m. $[PO(OEt)_2]$,[14] and the position of the $PPh_2(OMe)$ resonance for $[Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2][BPh_4]$ (94.20 p.p.m.), the resonance at 94.14 p.p.m. is assigned to $PPh_2(OMe)$ and that at 38.89 p.p.m. to $[PPh_2O]^-$.

Complex (3) was also isolated by reaction of $[Pt(S_2CNEt_2)_2]$ and excess of $PPh_2(OMe)$ in methylene chloride for only 10 min, followed by precipitation by addition of diethyl ether–pentane. Thus, these experiments clearly demonstrate that ionic $[Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2][S_2CNEt_2]$ readily rearranges to (3) by nucleophilic attack of $[S_2CNEt_2]^-$ on a co-ordinated $PPh_2(OMe)$ group. Related studies of nucleophilic attack on co-ordinated alkoxyphosphorus ligands are well documented.[4,12,15]

Another portion of the $[Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2]Cl$ solution was treated with an equimolar amount of $Na[S_2CNEt_2]\cdot3H_2O$ together with a few drops of $PPh_2(OMe)$ and, after filtering off the sodium chloride precipitate, the solution was left to stand for 2 d. Removal of solvent from the non-conducting solution then gave a very pale yellow microcrystalline solid readily identified as $[Pt(S_2CNEt_2)(PPh_2O)\{PPh_2(OH)\}]$ (1b). This complex was also formed if a methylene chloride solution of $[Pt(S_2CNEt_2)(PPh_2O)\{PPh_2(OMe)\}]$ (3) was treated with a small amount of $PPh_2(OMe)$ for a prolonged period, whereas in the absence of free $PPh_2(OMe)$ only (3) was recovered from solution.

Thus, these studies indicate that (3) is slowly converted into (1b), probably by displacement of the co-ordinated $PPh_2(OMe)$ group by free $PPh_2(OH)$ and subsequent formation of the stable six-membered $Pt\overline{PPh_2OHOP}Ph_2$ ring structure. Evidence for the generation of some $PPh_2(OH)$ under these conditions comes from ^1H n.m.r. studies on $PPh_2(OMe)$–$CDCl_3$ solutions which show the appearance of methanol and the concomitant disappearance of methoxy-resonances on prolonged standing. Conductivity studies on $PPh_2(OMe)$–CH_2Cl_2 solutions indicate that $PPh_2(OH)$ and not $[PPh_2O]^-$ is formed under these conditions. Furthermore, these observations are consistent with earlier studies which indicate that tertiary phosphinites undergo more ready hydrolysis when not co-ordinated to a transition metal.[16] Similar displacement reactions of co-ordinated $PPh_2(OR)$ by free $PPh_2(OH)$ are also proposed [3,17] to explain the formation of $[Pt(PPh_2O)_2\{PPh_2(OH)\}_2]$ from $[Pt\{PPh_2(OBu^n)\}_4]$ and free $PPh_2(OBu^n)$ when left in ethanol for 4 d.

When the methylene chloride solution of $[Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2]Cl$ was treated with only a few drops of $PPh_2(OMe)$ and left for several days (1b) was again isolated, whereas in the absence of $PPh_2(OMe)$ some of (3) was produced. However, the rate of decrease in conductivity in both these solutions was much slower compared to those containing $[S_2CNEt_2]^-$ ion which is simply a reflection of the greater nucleophilicity of $[S_2CNEt_2]^-$ compared to Cl^- ion.

A summary of the reactions involved in the formation of $[M(S_2CNEt_2)(PPh_2O)\{PPh_2(OH)\}]$ is given in the Scheme and, to our knowledge, this represents only the second example of a system where *both* nucleophilic attack on a P–OR bond *and* subsequent hydrolysis of a P–OR bond play an essential role in determining the product composition (see ref. 18 for the other example). It is expected that a similar mechanism would explain the formation of $[M(S_2PR_2)(PPh_2O)\{PPh_2(OH)\}]$ from $[M(S_2PR_2)_2]$ and excess of $PPh_2(OR)$ but attempts to confirm this have not been completely successful. For

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[12] See J. Grosse and R. Schmutzler, *J.C.S. Dalton*, 1976, 405 and refs. therein.

[13] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 1152 and refs. therein.

[14] V. Harder and H. Werner, *Helv. Chim. Acta*, 1973, **56**, 1620.

[15] J. Grosse and R. Schmutzler, *J.C.S. Dalton*, 1976, 412.

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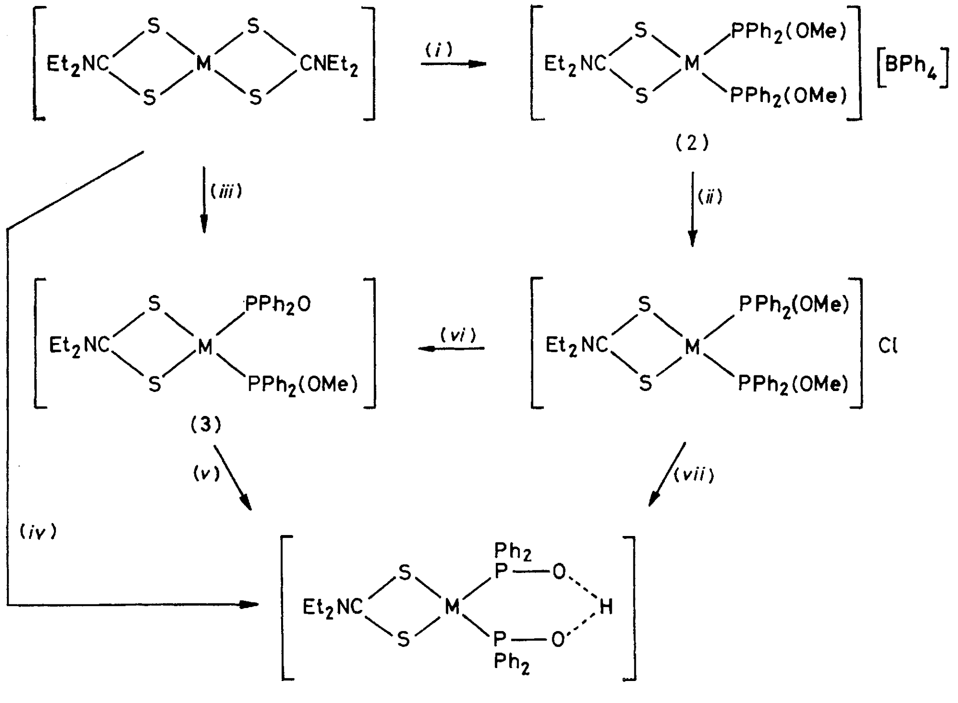
example, reaction of $[\mathrm{Pd(S_2PPh_2)_2}]$ and $\mathrm{PPh_2(OMe)}$ in methanol followed by addition of $\mathrm{Na[BPh_4]}$ gave a pale yellow precipitate but this rapidly turned brown {*cf.* the analogous $[\mathrm{Pd(S_2PPh_2)(PPh_3)_2][BPh_4]}$ [2] which also rapidly decomposed in the solid state}. However, treatment of $[\mathrm{Pd(S_2PPh_2)_2}]$ with $\mathrm{PPh_2(OMe)}$ in methylene chloride followed by solvent removal after *ca.* 10 min and addition of diethyl ether gave a pale yellow non-conducting solid whose ^{1}H n.m.r. spectrum was consistent with the formulation $[\mathrm{Pd(S_2PPh_2)(PPh_2O)\{PPh_2(OMe)\}}]$ {δ 3.80 (d, 3) [^3J(PH) 12.0 Hz], $\mathrm{PPh_2(OMe)}$; 7.00—8.00 p.p.m., (30), Ph} and, therefore, it is highly likely that the mechanism shown in the Scheme also applies to $[\mathrm{S_2PR_2}]^-$ complexes.



(1b)

SCHEME Proposed mechanism for conversion of $[\mathrm{M(S_2CNEt_2)_2}]$ into $[\mathrm{M(S_2CNEt_2)(PPh_2O)\{PPh_2(OH)\}}]$. (*i*) $\mathrm{PPh_2(OMe)}$, $\mathrm{Na[BPh_4]}$, MeOH; (*ii*) $[\mathrm{AsPh_4]Cl{\cdot}HCl}$; (*iii*) $\mathrm{PPh_2(OMe),CH_2Cl_2}$ (10 min reaction time); (*iv*) $\mathrm{PPh_2(OMe)}$, $\mathrm{CH_2Cl_2}$ (24 h); (*v*) $\mathrm{PPh_2(OH)}$; (*vi*) $[\mathrm{S_2CNEt_2}]^-$ (or $\mathrm{Cl^-}$); (*vii*) $[\mathrm{S_2CNEt_2}]^-$ (or $\mathrm{Cl^-}$), $\mathrm{PPh_2(OMe)}$

Finally, it was of some interest to examine the reaction between palladium(II) and platinum(II) alkyl dithiocarbonates and $\mathrm{PPh_2(OR)}$ because of the presence of two types of alkoxy-group which might undergo nucleophilic attack. Thus, reaction of $[\mathrm{Pd(S_2COPr^i)_2}]$ in methylene chloride with excess of $\mathrm{PPh_2(OEt)}$ gave an immediate red conducting solution which slowly turned yellow accompanied by a steady decrease in conductivity. Treatment of the latter with diethyl ether–light petroleum (b.p. 60—80 °C) gave a non-conducting yellow solid analysing for $[\mathrm{Pd(S_2CO)\{PPh_2(OEt)\}_2}]$. The i.r. spectrum contained bands at 1 690s, 1 618s, and 1 586w cm^{-1} characteristic of ν(CO) in dithiocarbonato-complexes,[19] but no bands between 1 200 and 1 300 cm^{-1} attributable to $[\mathrm{S_2COPr^i}]^-$ groups. The ^{1}H n.m.r. spectrum consisted of a triplet at δ 1.06 ($\mathrm{CH_3}$) and a complicated multiplet at 3.79 p.p.m. ($\mathrm{CH_2}$) similar to that reported for *cis*-$[\mathrm{PdCl_2\{PPh_2(OEt)\}_2}]$.[11,*] The ^{31}P n.m.r. spectrum (proton decoupled) contained a single resonance at 116.62 p.p.m. An analogous complex was formed by reaction of $[\mathrm{Pt(S_2COPr^i)_2}]$ with $\mathrm{PPh_2(OEt)}$.

Thus, this evidence clearly indicates that nucleophilic attack of the $[\mathrm{S_2COPr^i}]^-$ ion occurred specifically on the co-ordinated $[\mathrm{S_2COPr^i}]^-$ propoxy-group in the $[\mathrm{M(S_2COPr^i)\{PPh_2(OEt)\}_2][S_2COPr^i]}$ intermediate and no evidence has been found for further reactions of the $[\mathrm{M(S_2CO)\{PPh_2(OEt)\}_2}]$ products, *e.g.* displacement of $\mathrm{PPh_2(OEt)}$ by free $\mathrm{PPh_2(OH)}$. However, $[\mathrm{Pd(S_2COPr^i)(PPh_2O)\{PPh_2(OH)\}}]$ can be readily synthesised by reaction of $[\mathrm{\{PdCl(PPh_2O)[PPh_2(OH)]\}_2}]$ with $\mathrm{K[S_2COPr^i]}$ (1 : 2 molar ratio).

EXPERIMENTAL

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on a

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* The multiplet appears to consist of a 1 : 3 : 3 : 1 quartet of 'pseudo-triplets' with ^3J(HH) 7.0 Hz and $|^3J(\mathrm{PH}) + {^5J}(\mathrm{PH})|$ 6.5 Hz, whereas for *cis*-$[\mathrm{PdCl_2\{PPh_2(OEt)\}_2}]$ a quartet of overlapping virtual-coupling doublets is observed with $^3J(\mathrm{HH}) = |^3J(\mathrm{PH}) + {^5J}(\mathrm{PH})|$ 7.0 Hz.

[19] See M. C. Cornock, R. O. Gould, C. L. Jones, J. D. Owen, D. F. Steele, and T. A. Stephenson, *J.C.S. Dalton*, **1977**, 496, and refs. therein.

Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge. Hydrogen-1 n.m.r. spectra were obtained on Varian Associates HA-100 and EM360 spectrometers, ^{31}P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4). Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson, Matthey Ltd), $Na[S_2CNEt_2]\cdot 3H_2O$, $Na[BPh_4]$, and $[AsPh_4]Cl\cdot HCl$ (B.D.H.), and $PPh_2(OMe)$ and $PPh_2(OEt)$ (Maybridge Chemical Company) were obtained as indicated. The compounds $Na[S_2PMe_2]\cdot 2H_2O$,[20] $[NH_4][S_2PPh_2]$,[20] $K[S_2COPr^i]$,[21] $[M(S_2CNEt_2)_2]$,[22] $[M(S_2PR_2)_2]$ (R = Me [2] or Ph [23]), and $[M(S_2COPr^i)_2]$ (M = Pd or Pt) [24] were synthesised as described earlier. Solvents were used as purchased.

Infrared bands diagnostic of $[S_2PPh_2]^-$,[23] $[S_2PMe_2]^-$,[2] and $[S_2CNEt_2]$ [13] bidentate co-ordination are listed for each complex and, unless otherwise stated, ^{1}H n.m.r. spectra were recorded in $CDCl_3$ at 301 K and ^{31}P n.m.r. spectra (proton decoupled) in $CDCl_3$ at 303 K. Relative intensities are given in parentheses and s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and pt = pseudo triplet.

Palladium Complexes.—Dimethylphosphinodithioato(diphenylphosphinito)(diphenylphosphinous acid)palladium(II).* *Method* (*A*). An excess of $PPh_2(OR)$ (R = Me or Et) was added to a methylene chloride solution of $[Pd(S_2PMe_2)_2]$ and the solution was left to stand for 24 h. The resulting pale yellow solution was then reduced in volume and diethyl ether was added to give an off-white microcrystalline *precipitate*. The product was filtered off, washed with diethyl ether, and dried in air, m.p. 225—227 °C (decomp.), $\nu(PS_2)$ at 582 cm^{-1}, $\nu(PO)$ at 1 010 cm^{-1} [Found: C, 49.1; H, 4.3; P, 14.3; Pd, 16.1; S, 10.3%; *M* (in $CHCl_3$) 550. Calc. for $C_{26}H_{27}O_2P_3PdS_2$: C, 49.2; H, 4.3; P, 14.7; Pd, 16.7; S, 10.1%; *M* 634]. N.m.r. spectra: ^{1}H, 1.97 (d,6) [$^{2}J(PH)$ 12.0 Hz] ($[S_2PMe_2]^-$) and 7.20—7.90 p.p.m. (m, 20) (Ph); ^{31}P, 83.20 (d,2) ($Ph_2\mathit{P}OHO\mathit{P}Ph_2$) and 84.29 p.p.m. (t,1) ($S_2\mathit{P}Me_2$) [$^{3}J(PP)$ 7.4 Hz].

The following complexes were prepared similarly using $[Pd(S_2PPh_2)_2]$ and $[Pd(S_2CNEt_2)_2]$ respectively. *Diphenylphosphinito(diphenylphosphinodithioato)(diphenylphosphinous acid)palladium*(II), m.p. 184—185 °C, $\nu(PS_2)$ at 620 and 570 cm^{-1}, $\nu(PO)$ at 1 009 cm^{-1} (Found: C, 56.8; H, 4.3. Calc. for $C_{36}H_{31}O_2P_3PdS_2$: C, 57.0; H, 4.1%). N.m.r. spectra: ^{1}H, 7.20—7.80 p.p.m. (m) (Ph); ^{31}P, 78.66 (t,1) ($[S_2\mathit{P}Ph_2]^-$) and 83.46 p.p.m. (d,2) ($Ph_2\mathit{P}OHO\mathit{P}Ph_2$) [$^{3}J(PP)$ 6.7 Hz]. NN-*Diethyldithiocarbamato(diphenylphosphinito)(diphenylphosphinous acid)palladium*(II), m.p. 218—220 °C, $\nu(CN)$ at 1 514 cm^{-1}, $\nu(PO)$ at 1 017 cm^{-1} (Found: C, 52.7; H, 4.7; N, 2.1. Calc. for $C_{29}H_{31}NO_2P_2PdS_2$: C, 53.0; H, 4.7; N, 2.1%). N.m.r. spectra: ^{1}H, 1.20 (t,6), 3.67 (q,4) ($[S_2CN\mathit{Et}_2]^-$) [$^{3}J(HH)$ 7.0 Hz], and 7.20—7.90 (m, 20) (Ph); ^{31}P, 84.50 p.p.m. (s).

Method (*B*). $[Pd(S_2PMe_2)(PPh_2O)\{PPh_2(OH)\}]$. The salt $Na[S_2PMe_2]\cdot 2H_2O$ (0.036 g) in acetone was added to a methylene chloride solution of $[\{PdCl(PPh_2O)[PPh_2(OH)]\}_2]$ (0.13 g) (2 : 1 molar ratio) and the resulting pale yellow solution was shaken for 30 min. After filtering through Celite to remove sodium chloride, addition of diethyl ether gave an off-white *precipitate* which was filtered off and washed with water, methanol, and diethyl ether. The complex $[Pd(S_2COPr^i)(PPh_2O)\{PPh_2(OH)\}]$, m.p. 184—186 °C (decomp.), $\nu(PO)$ at 1 020 cm^{-1} (Found: C, 51.5; H, 4.5. Calc. for $C_{28}H_{28}O_3P_2PdS_2$: C, 52.1; H, 4.3%) was similarly prepared using $K[S_2COPr^i]$ (1 : 2 molar ratio) as were $[Pd(S_2PPh_2)(PPh_2O)\{PPh_2(OH)\}]$ and $[Pd(S_2CNEt_2)(PPh_2O)\{PPh_2(OH)\}]$ from $[NH_4][S_2PPh_2]$ and $Na[S_2CNEt_2]\cdot 3H_2O$ respectively.

(NN-*Diethyldithiocarbamato*)*bis*(*methyl diphenylphosphinite*)*palladium*(II) *tetraphenylborate*. An excess of $PPh_2(OMe)$ was added to a suspension of $[Pd(S_2CNEt_2)_2]$ in methanol. The resulting yellow-orange solution was shaken for *ca*. 30 min and then filtered into a methanolic solution of $Na[BPh_4]$ to give a sticky yellow precipitate. Addition of diethyl ether and trituration of the solution gave a pale yellow microcrystalline *solid* which was filtered off and washed with diethyl ether, m.p. 150—152 °C, $\nu(CN)$ at 1 532 cm^{-1}, $\nu(PO)$ at 1 030 cm^{-1}, Λ (1×10^{-3} mol dm^{-3} in CH_2Cl_2) 40.0 S cm^2 mol^{-1} (Found: C, 65.9; H, 5.6; N, 1.6. Calc. for $C_{55}H_{56}BNO_2P_2PdS_2$: C, 65.7; H, 5.6; N, 1.4%). Hydrogen-1 n.m.r. spectrum: 1.07 (t,6), 3.46(q) ($[S_2CNEt_2]^-$) [$^{3}J(HH)$ 7.0], 3.27 (pt,10) † [$PPh_2(OMe)$] [$|^{3}J(PH) + {}^{5}J(PH)|$ 12.0 Hz], and 6.80—7.90 p.p.m. (m,40) (Ph).

(*Dithiocarbonato*)*bis*(*ethyl diphenylphosphinite*)*palladium*(II). An excess of $PPh_2(OEt)$ was added to $[Pd(S_2COPr^i)_2]$ in methylene chloride giving a red solution. The solution was then left for 24 h during which time the solution became yellow. Removal of some solvent *in vacuo* and addition of diethyl ether–light petroleum (b.p. 60—80 °C) gave a yellow *solid* which was filtered off and washed with diethyl ether, $\nu(CO)([S_2CO]^{2-})$ at 1 690s, 1 618s, and 1 586w cm^{-1} (Found: C, 52.7; H, 4.6. Calc. for $C_{29}H_{30}O_3P_2PdS_2$: C, 52.9; H, 4.6%). N.m.r. spectra: ^{1}H, 1.06 (t,6), 3.79 (m,qpt,4) [$PPh_2(O\mathit{Et})$] [$^{3}J(HH)$ 7.0, $|^{3}J(PH) + {}^{5}J(PH)|$ 6.5 Hz], and 7.20—7.80 p.p.m. (m,20) (Ph); ^{31}P, 116.62 p.p.m. (s).

Platinum Complexes.—Dimethylphosphinodithioato(diphenylphosphinito)(diphenylphosphinous acid)platinum(II). An excess of $PPh_2(OMe)$ was added to a methylene chloride solution of $[Pt(S_2PMe_2)_2]$ and the solution was left to stand for 48 h. The resulting very pale yellow solution was then reduced in volume and diethyl ether was added to give a white *precipitate*. The product was filtered off, washed with diethyl ether, and dried in air, m.p. 248—250 °C (decomp.), $\nu(PS_2)$ at 580 cm^{-1}, $\nu(PO)$ at 1 020 cm^{-1} (Found: C, 43.4; H, 3.9; P, 12.8; S, 9.2. Calc. for $C_{26}H_{27}O_2P_3PtS_2$: C, 43.1; H, 3.7; P, 12.9; S, 8.8%). Phosphorus-31 n.m.r. spectra: 59.11 (t.d,2) ($Ph_2\mathit{P}OHO\mathit{P}Ph_2$) [$^{1}J(PtP)$ 3 690.6, $^{3}J(PP)$ 9.2H_z] and 88.38 p.p.m. (t.t,1) ($[S_2\mathit{P}Me_2]^-$) [$^{2}J(PtP)$ 178.8 Hz].

The following complex was prepared similarly from

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* Following the suggestion in ref. 3, we have used the term diphenylphosphinite to describe *P*-bonded $[PPh_2O]^-$ rather than the previously used diphenylphosphinate.

† 10 is the total relative intensity of the methylene quartet and methoxy pseudo-triplet because the resonances are too close to integrate separately.

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[24] G. W. Watt and B. J. McCormick, *J. Inorg. Nuclear Chem.*, 1965, **27**, 898.

$[\mathrm{Pt(S_2CNEt_2)_2}]$ and $\mathrm{PPh_2(OMe)}$. NN-*Diethyldithiocarbamato(diphenylphosphinito)(diphenylphosphinous acid)platinum*(II), m.p. 242—244 °C, ν(CN) at 1 530 $\mathrm{cm^{-1}}$, ν(PO) at 1 020 $\mathrm{cm^{-1}}$ [Found: C, 46.9; H, 4.4; N, 1.9%; *M* (in $\mathrm{CHCl_3}$) 758. Calc. for $\mathrm{C_{29}H_{31}NO_2P_2PtS_2}$: C, 46.7; H, 4.2; N, 1.9%; *M* 766]. Hydrogen-1 n.m.r. spectrum: 1.20 (t,6), 3.53 (q,4) ($[\mathrm{S_2CNEt_2}]^-$) [^3J(HH) 7.0 Hz], and 7.20—7.90 p.p.m. (m,20) (Ph). It was also obtained by addition of $\mathrm{PPh_2(OMe)}$ to a methylene chloride solution of ‘ $[\mathrm{Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2]Cl}$ ’ and leaving for several days, by reaction of the same solution with $\mathrm{Na[S_2CNEt_2]\cdot 3H_2O}$ and $\mathrm{PPh_2(OMe)}$ (formed more rapidly), or by reaction of a methylene chloride solution of $[\mathrm{Pt(S_2CNEt_2)(PPh_2O)\{PPh_2(OMe)\}}]$ with $\mathrm{PPh_2(OMe)}$ for 24 h.

(NN-*Diethyldithiocarbamato)bis(methyldiphenylphosphinite)platinum*(II) *tetraphenylborate*. An excess of $\mathrm{PPh_2(OMe)}$ was added to a suspension of $[\mathrm{Pt(S_2CNEt_2)_2}]$ in methanol to give a colourless solution. This was then added to a methanolic solution of $\mathrm{Na[BPh_4]}$ to give a sticky white *precipitate* which on trituration with diethyl ether gave a white microcrystalline *solid*, m.p. 156—158 °C, ν(CN) at 1 532 $\mathrm{cm^{-1}}$, ν(PO) at 1 030 $\mathrm{cm^{-1}}$, Λ (1×10^{-3} mol $\mathrm{dm^{-3}}$ in $\mathrm{CH_2Cl_2}$) 42.0 S $\mathrm{cm^2}$ $\mathrm{mol^{-1}}$ (Found: C, 60.6; H, 5.1; N, 1.3. Calc. for $\mathrm{C_{55}H_{56}BNO_2P_2PdS_2}$: C, 60.3; H, 5.1; N, 1.3%). N.m.r. spectra: ^{1}H, 1.10 (t,6), 3.33 (q) ($[\mathrm{S_2CN}Et_2]^-$) [^3J(HH) 7.0 Hz], 3.27 (pt,10) * $[\mathrm{PPh_2(O}Me)]$ [$|^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})|$ 12.0 Hz], and 6.80—7.90 p.p.m. (m, 40) (Ph); ^{31}P, 94.20 p.p.m. (t) [^1J(PtP) 3 749.0 Hz].

NN-*Diethyldithiocarbamato(diphenylphosphinito)(methyl diphenylphosphinite)platinum*(II). An excess of $\mathrm{PPh_2(OMe)}$ was added to a methylene chloride solution of $[\mathrm{Pt(S_2CNEt_2)_2}]$. Partial removal of solvent after 10 min and addition of diethyl ether–pentane gave a very pale yellow *solid* which was filtered off, washed with diethyl ether and pentane, and dried in air, m.p. 205—207 °C, ν(CN) at 1 530 $\mathrm{cm^{-1}}$, ν(PO) at 1 050 $\mathrm{cm^{-1}}$ (Found: C, 47.5; H, 4.4; N, 1.9. Calc. for $\mathrm{C_{30}H_{33}NO_2P_2PtS_2}$: C, 47.4; H, 4.3; N, 1.8%). N.m.r. spectra: ^{1}H, 1.23 (t,6), 3.52 (q), 3.56 (q,4) ($[\mathrm{S_2CNEt_2}]^-$) [^3J(HH) 7.0 Hz], 3.87 (d,3) $[\mathrm{PPh_2(OMe)}]$ [^3J(PH) 12.0 Hz], and 7.00—7.90 p.p.m. (m,20) (Ph); ^{31}P (in $\mathrm{CDCl_3}$ at 223 K), 38.89 (t.d,1) * ($[\mathrm{PPh_2O}]^-$) [^1J(PtP) 3 264.8, ^2J(PP) 27.7 Hz] and 94.14 p.p.m. (t.d,1) $[\mathrm{PPh_2(OMe)}]$ [^1J(PtP) 4 212.3, ^2J(PP) 28.0 Hz].

This complex was also synthesised by reaction of $\mathrm{Na[S_2CNEt_2]\cdot 3H_2O}$ (0.05 g) with a methylene chloride solution of ‘ $[\mathrm{Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2]Cl}$ ’ (0.17 g) (made *in situ* by reaction of $[\mathrm{Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2][BPh_4]}$ with $\mathrm{[AsPh_4]Cl\cdot HCl}$). The mixture was left for 3 d and then slow evaporation of the solvent gave the product as a microcrystalline pale yellow *solid*. If the solution of ‘ $[\mathrm{Pt(S_2CNEt_2)\{PPh_2(OMe)\}_2]Cl}$ ’ was left for several days some of this product could be identified on solvent removal.

(Dithiocarbonato)bis(ethyl diphenylphosphinite)platinum(II). This complex was prepared as for the corresponding palladium complex starting from $[\mathrm{Pt(S_2COPr^i)_2}]$ and $\mathrm{PPh_2(OEt)}$, m.p. 190—192 °C, ν(CO)($[\mathrm{S_2CO}]^{2-}$) at 1 690s, 1 618s, and 1 586w $\mathrm{cm^{-1}}$ (Found: C, 46.6; H, 4.0. Calc. for $\mathrm{C_{29}H_{30}O_3P_2PtS_2}$: C, 46.6; H, 4.0%).

All the standard crystallographic calculations were made at the Edinburgh Regional Computing Centre using the ‘ *X*-Ray ’74 ’ system.[25]

We thank Johnson, Matthey Ltd. for loans of potassium tetrachloroplatinate(II) and palladium(II) chloride, the S.R.C. for support (to M. C. C. and C. L. J.), Dr. A. S. F. Boyd for obtaining the ^{31}P n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.

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* At 303 K, the $[\mathrm{PPh_2O}]^-$ resonance appeared broader (and weaker) than the $\mathrm{PPh_2(OMe)}$ resonance which is possibly a reflection of the different ^{31}P relaxation times in these groups.

[25] ‘ *X*-Ray ’ Program System, Computer Science Center, University of Maryland, Technical Report TR 192, version of January 1974.