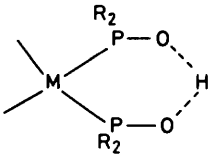
Metal Complexes of Sulphur Ligands. Part 22.[1] Reaction of Platinum(II) and Palladium(II) *NN*-Dialkyldithiocarbamates with Diphenylphosphine Chalcogenides

David M. Anderson, E. A. V. Ebsworth, T. Anthony Stephenson,* and Malcolm D. Walkinshaw
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reaction of $[Pt(S_2CNR_2)_2]$ (R = Et or Pr^i) with either $Ph_2P(O)H$ or prehydrolysed Ph_2PCl in alcohols give high yields of $[Pt(S_2CNR_2)\{(Ph_2PO)_2H\}]$ (1). In contrast, reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(S)H$ in alcohols give a variety of products, depending on the amount of sulphide used, the amount of water present in the reaction mixture, and the duration of reaction. Thus with an excess of $Ph_2P(S)H$ in dry methanol, $[NR_2H_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ (2) are formed and the structure of (2a) (R = Et) has been verified by *X*-ray analysis. The crystals are orthorhombic, space group $P2_12_12_1$ with a = 21.098(18), b = 11.679(8), c = 14.816(18) Å. Prolonged reaction in dry methanol gives $[Pt(S_2CNR_2)\{Ph_2P(OMe)\}(Ph_2PS)]$ (5) whereas with 1 : 1 mol ratios of Pt : $Ph_2P(S)H$, small amounts of the binuclear $[\{Pt(S_2CNEt_2)(Ph_2PS)\}_2]$ (6a) are formed. These are obtained in much higher yield by reaction of compound (2) with HCl gas in dry $CHCl_3$ and the structure of (6b) (R = Pr^i) confirmed by *X*-ray analysis. The crystals are monoclinic, space group $P2_1/c$ with a = 12.192(7), b = 9.272(6), c = 24.958(15) Å, and β = 116.232(28)°. Small amounts of the secondary phosphine complexes $[Pt(S_2CNR_2)(Ph_2PH)(Ph_2PS)]$ (4) are also formed in all these reactions and these can be synthesised in high yield by direct reaction of compound (2) with Ph_2PH. Finally, in wet methanol, the neutral complexes $[Pt(S_2CNR_2)(Ph_2POHSPPh_2)]$ (3) are formed together with some of compound (2). The corresponding reaction of $[Pd(S_2CNEt_2)_2]$ with an excess of $Ph_2P(S)H$ in dry methanol gives $[NEt_2H_2][Pd(S_2CNEt_2)(Ph_2PS)_2]$ and $[\{Pd(S_2CNEt_2)(Ph_2PS)\}_2]$ whereas the reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(Se)H$ gives only $[Pt(S_2CNR_2)(Ph_2PH)(Ph_2PSe)]$ in high yield. All these compounds have been characterised by a variety of physicochemical methods and a reaction scheme to account for the formation of compounds (2)—(6) from reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(S)H$ is suggested.

A variety of transition metal complexes containing the six membered ring (1) have been isolated in recent years. They were produced either by addition of phosphinous acids or their salts to suitable metal complexes or by solvolysis of



(1)

(R = Ph, OMe, or OEt)

co-ordinated P–X bonds (X = halogen, alkoxy, *etc.*).[2] Replacement of the proton in (1) by Lewis acids or transition metal ions is also well established.[2]

In contrast, no evidence has been found for the thio analogues of (1), although a number of compounds containing the R_2PS^- or $R_2P(S)H$ ligands, either *S*-bonded,[3] *P*-bonded,[3,4] or *S*/*P*-bonded (bridge [4b,5] or 'side-on' [6]) have been recently reported (see Discussion section).

Therefore, in an attempt to remedy this deficiency, the reactions of $[M(S_2CNR_2)_2]$ (M = Pt, R = Et or Pr^i; M = Pd, R = Et) with diphenylphosphine sulphide have been examined and the full results [7] of these studies are reported in this paper. For comparison, the reactions of $Ph_2P(E)H$ (E = O or Se) with $[Pt(S_2CNR_2)_2]$ are also described.

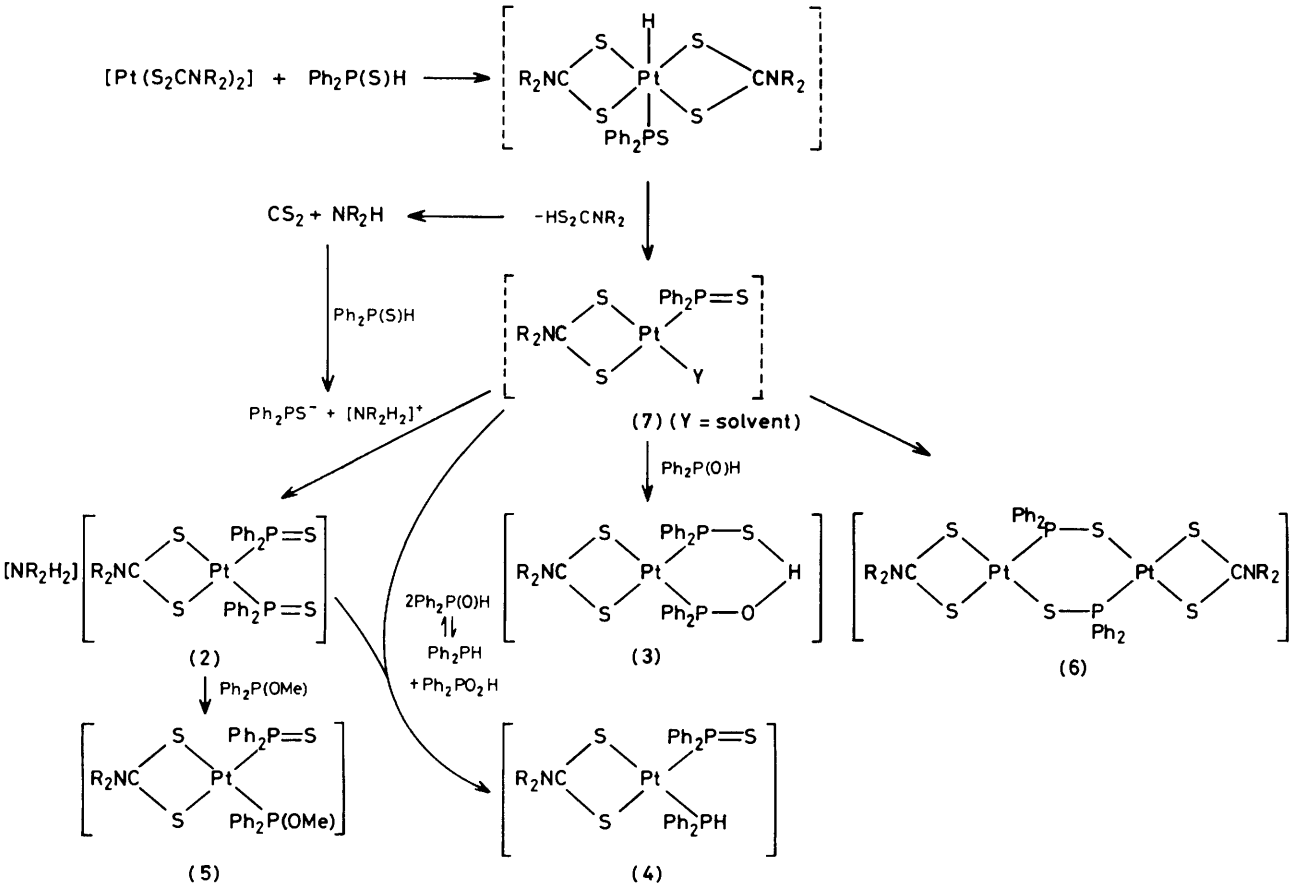
Results and Discussion

The reaction of $[Pt(S_2CNR_2)_2]$ (R = Et or Pr^i) with $Ph_2P(S)H$ in alcohols under reflux gives a variety of products (see Scheme) depending on the amount of sulphide used, the amount of water present in the reaction mixture, and the duration of the reaction. This is to be contrasted with the reaction of $[Pt(S_2CNR_2)_2]$ with either $Ph_2P(O)H$ or prehydrolysed Ph_2PCl under various conditions, where the only products isolated are the well known $[Pt(S_2CNR_2)\{(Ph_2PO)_2H\}]$, previously synthesised by reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(OMe)$ in wet solvents.[8]

Thus, when $[Pt(S_2CNR_2)_2]$ (R = Et or Pr^i) are refluxed with an excess of $Ph_2P(S)H$ in degassed, *dry* AnalaR methanol for 12 h, small amounts of the white crystalline solids $[NR_2H_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ (2a; R = Et and 2b; R = Pr^i) are precipitated. Concentration of the filtrate and addition of an excess of diethyl ether gives more of the products (*ca.* 50% total yield). Evidence for this formulation is based on elemental analyses, conductivity measurements in methanol, variable-temperature ^1H,† $^{31}P\{^1H\}$,† $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ n.m.r. studies. In addition an *X*-ray structural analysis was carried out on $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (2a). Details of the solution of the crystal structure are given in the Experimental section, final atomic parameters are given in Table 1, selected bond lengths and angles in Table 2, and a view of the molecule in Figure 1. The Figure

* *Supplementary data available* (No. SUP 23400; 39 pp.): observed and calculated structure factors, thermal parameters for (2a) and (6b); Table 1 (^1H n.m.r.), Table 2 (^{31}P n.m.r.), Table 5 ($^{31}P\{^1H\}$ n.m.r.) for all complexes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† These data are deposited (Tables 1 and 2) in Supplementary Publication No. SUP 23400.



Scheme. Possible mechanism for formation of compounds in the $[Pt(S_2CNR_2)_2]$–$Ph_2P(S)H$ reaction (R = Et, compounds a; R = Pr^i, compounds b)

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses for $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (2a)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.462 40(10)	0.057 40(10)	0.489 30(10)	C(33)	0.279 0(11)	0.151 2(24)	0.295 1(18)
S(1)	0.530 5(5)	−0.104 0(7)	0.493 1(10)	C(34)	0.229 9(11)	0.225 7(24)	0.318 4(18)
P(2)	0.415 0(4)	0.230 3(7)	0.486 1(9)	C(35)	0.236 8(11)	0.299 2(24)	0.392 0(18)
P(1)	0.384 8(5)	−0.042 3(9)	0.561 5(8)	C(36)	0.292 8(11)	0.298 2(24)	0.442 2(18)
S(2)	0.558 7(5)	0.119 1(9)	0.423 1(8)	C(41)	0.303 5(11)	0.014 3(24)	0.572 0(23)
S(4)	0.410 0(6)	−0.082 7(9)	0.686 9(8)	C(42)	0.259 1(11)	−0.005 5(24)	0.503 9(23)
S(3)	0.397 9(6)	0.304 4(9)	0.602 4(8)	C(43)	0.198 6(11)	0.042 0(24)	0.510 2(23)
C(11)	0.376 2(10)	−0.178 8(16)	0.501 1(17)	C(44)	0.182 5(11)	0.109 3(24)	0.584 5(23)
C(12)	0.382 2(10)	−0.181 9(16)	0.407 4(17)	C(45)	0.226 9(11)	0.129 0(24)	0.652 6(23)
C(13)	0.377 0(10)	−0.285 8(16)	0.361 6(17)	C(46)	0.287 4(11)	0.081 6(24)	0.646 3(23)
C(14)	0.365 9(10)	−0.386 6(16)	0.409 5(17)	C(1)	0.584 9(19)	−0.015 7(21)	0.441 6(26)
C(15)	0.359 9(10)	−0.383 5(16)	0.503 2(17)	N(1)	0.647 5(15)	−0.044 2(30)	0.429 2(22)
C(16)	0.365 0(10)	−0.279 6(16)	0.549 0(17)	C(2)	0.698 0(26)	0.037 0(50)	0.399 0(40)
C(21)	0.461 4(13)	0.330 5(20)	0.416 9(18)	N(2)	0.491 5(15)	0.141 6(28)	0.722 6(22)
C(22)	0.493 8(13)	0.420 8(20)	0.457 8(18)	C(7)	0.559 5(17)	0.146 1(38)	0.690 0(29)
C(23)	0.526 5(13)	0.500 1(20)	0.404 9(18)	C(8)	0.485 8(30)	0.144 0(53)	0.823 2(29)
C(24)	0.526 8(13)	0.489 1(20)	0.311 2(18)	C(6)	0.592 8(23)	0.036 0(44)	0.718 9(33)
C(25)	0.494 3(13)	0.398 8(20)	0.270 3(18)	C(9)	0.420 1(31)	0.156 7(56)	0.848 0(44)
C(26)	0.461 7(13)	0.319 5(20)	0.323 1(18)	C(4)	0.671 8(26)	−0.162 9(37)	0.448 3(37)
C(31)	0.341 8(11)	0.223 7(24)	0.418 8(18)	C(5)	0.711 0(32)	0.015 7(61)	0.298 5(42)
C(32)	0.334 9(11)	0.150 2(24)	0.345 3(18)	C(3)	0.696 2(34)	−0.171 5(65)	0.545 2(42)

Table 2. Interatomic distances (Å) and angles (°) for compound (2a) with estimated standard deviations in parentheses

(*a*) Distances

Pt–S(1)	2.372(9)
Pt–S(2)	2.368(11)
Pt–P(1)	2.277(11)
Pt–P(2)	2.253(9)
S(1)–C(1)	1.72(3)
S(2)–C(1)	1.69(2)
P(1)–S(4)	1.99(1)
P(2)–S(3)	1.96(1)
P(1)–C(11)	1.83(2)
P(1)–C(41)	1.84(2)
P(2)–C(31)	1.84(2)
P(2)–C(21)	1.83(2)
C(1)–N(1)	1.37(5)
N(1)–C(2)	1.49(6) *
N(1)–C(4)	1.50(5) *
C(3)–C(4)	1.53(8) *
C(2)–C(5)	1.52(8) *
N(2)–C(8)	1.49(5) *
N(2)–C(7)	1.51(4) *
C(8)–C(9)	1.44(8)
C(7)–C(6)	1.52(6)

(*b*) Angles

S(1)–Pt–S(2)	74.4(4)
S(1)–Pt–P(1)	91.0(4)
S(2)–Pt–P(2)	95.7(4)
P(1)–Pt–P(2)	98.6(4)
Pt–S(1)–C(1)	85.2(1.1)
Pt–S(2)–C(1)	86.1(1.4)
S(1)–C(1)–S(2)	114.3(2.2)
C(1)–N(1)–C(2)	124.8(3.2)
C(1)–N(1)–C(3)	121.7(3.3)
N(1)–C(2)–C(5)	108.4(4.6)
N(1)–C(4)–C(3)	110.6(4.3)
Pt–P(1)–S(4)	111.6(6)
Pt–P(2)–S(3)	117.3(9)
Pt–P(1)–C(11)	106.6(9)
Pt–P(1)–C(41)	121.7(1.1)
Pt–P(2)–C(21)	110.3(9)
Pt–P(2)–C(31)	110.3(1.0)

* Bonds restrained to be near their expected values using the DFIX facility in SHELX which for example allows a C–C bond to be restrained to 1.54 Å with a standard deviation of 0.04.

shows the platinum atom to be co-ordinated in the expected square planar fashion by two sulphur and two phosphorus atoms. Each $[NEt_2H_2]^+$ cation lies close to one $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ anion making contacts N(2)···Pt 3.65, N(2)···S(4) 3.18, and N(2)···S(3) 3.27 Å. All atoms on other neighbouring anions are more than 4 Å from N(2). The P(1), P(2), S(3), S(4) plane is tilted 70° from the co-ordination plane and the sulphur atoms S(3) and S(4) are 4.7 Å apart (*cf.* $[Pd(S_2PMe_2)\{(Ph_2PO)_2H\}]$ where the PPOO plane is tilted 26.1° from the metal co-ordination plane and the O···H···O distance is 2.41 Å [8]).

Evidence for the retention in solution of strong ion pair interaction between the $[NR_2H_2]^+$ and $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ ions comes from the very low conductance values found in solvents such as dichloromethane and acetone. However, in methanol much higher conductance values are obtained and, furthermore, replacement of the $[NR_2H_2]^+$ cation with $[P(CH_2Ph)Ph_3]^+$ gives complexes which are well behaved 1 : 1 electrolytes in all these solvents. Retention of Pt–P(S)Ph_2 linkages in solution is confirmed by the large Pt–P

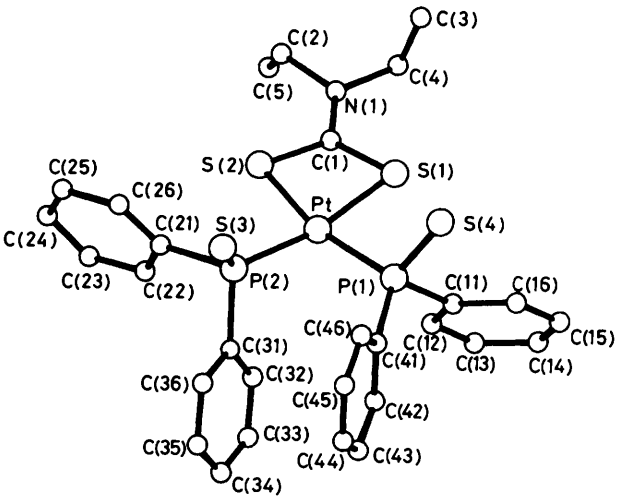
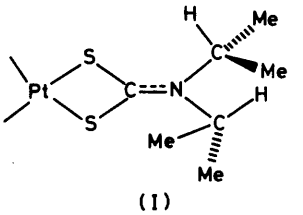


Figure 1. Molecular structure of $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (2a)

coupling constants (*ca.* 3 500 Hz, Table 2 of SUP 23400) typical of directly bound phosphorus atoms.

However, different behaviour with temperature is found when the R group is changed from Et to Pr^i. Thus for R = Et, the ^1H n.m.r. spectrum of the $[NEt_2H_2]^+$ salt in $CDCl_3$ from 301 to 220 K consists of two methyl triplets of equal intensity at δ 1.05 ($Et_2NCS_2^-$) and 1.52 p.p.m. ($[NEt_2H_2]^+$) and a single methylene quartet at δ 3.43 p.p.m. (attributed to accidental overlap of the $Et_2NCS_2^-$ and $[NEt_2H_2]^+$ resonances). Likewise, the $[NPr^i_2H_2]^+$ salt in $CDCl_3$ at 301 K shows two methyl doublets at δ 1.26 ($Pr^i_2NCS_2^-$) and 1.62 ($[NPr^i_2H_2]^+$) and two broad methine resonances at 4.38 ($Pr^i_2NCS_2^-$) and 4.12 p.p.m. ($[NPr^i_2H_2]^+$).* On lowering the temperature, the peaks from the $Pr^i_2NCS_2^-$ group broaden and then separate into further resonances at δ 1.08, 1.42 (CH_3) and 3.78, 4.90 p.p.m. (CH) whereas those from the $[NPr^i_2H_2]^+$ cation remain unaffected. Similar behaviour is observed in the $^{13}C-\{^1H\}$ n.m.r. spectra of these $[NR_2H_2]^+$ salts (see Experimental section).

The reason for this temperature dependent behaviour of the isopropyl but not the ethyl complexes can be attributed to hindered rotation about the N–C bonds at lower temperatures which leads to the 'freezing-out' of the preferred conformer (I), and thus produces magnetically inequivalent

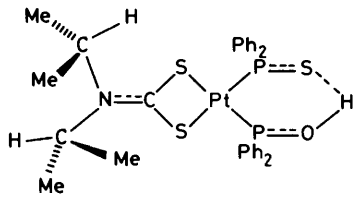


(I)

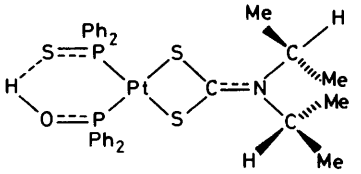
methyl and methine n.m.r. signals. Similar results have been found for $[Pt(S_2CNPr^i_2)_2]$ itself [9] and for the other di-isopropyldithiocarbamate compounds described in this paper (see Table 1 of SUP 23400).

If however, $[Pt(S_2CNR_2)_2]$ (R = Et or Pr^i) and an excess of

* These assignments are confirmed by homonuclear decoupling experiments and by comparison with the spectra of the $[P(CH_2Ph)Ph_3]^+$ salts (see Table 1 of SUP 23400).



(IIa)



(IIb)

$Ph_2P(S)H$ are refluxed in degassed technical-grade methanol for 12 h, removal of the white precipitates $[NR_2H_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ and concentration of the yellow filtrates gives small yields (*ca.* 20%) of amorphous, pale yellow solids (3). These are non-conducting in methanol and their room temperature ^{31}P-$\{^1H\}$ n.m.r. spectra (Table 2 of SUP 23400) clearly reveal that they contain two *directly* bonded, magnetically inequivalent, phosphorus-containing ligands. The size of $^2J_{PP}$ (*ca.* 28 Hz) suggests these phosphorus atoms are *cis* to each other and their chemical shift positions of *ca.* δ 31 and 64 p.p.m. indicate the presence of thiophosphorus and oxyphosphorus groups respectively. Furthermore, like $[Pt(S_2CNR_2)\{(Ph_2PO)_2H\}]$, the ^1H n.m.r. spectrum of (3b) (R = Pr^i) contains, in addition to the isopropyl groups, a weak broad resonance at δ 12.06 p.p.m. which disappears on addition of D_2O.

On cooling below 240 K, the ^{31}P-$\{^1H\}$ n.m.r. spectrum of (3b) (Table 2 of SUP 23400) shows *two* sets of magnetically inequivalent phosphorus-containing ligands arising from the two conformers (IIa) and (IIb) respectively.

Therefore on the basis of this spectroscopic evidence, together with analytical data, these compounds are formulated as the mixed chalcogenides $[Pt(S_2CNR_2)(Ph_2POHSPPh_2)]$. Although these compounds are not sufficiently soluble for osmometric molecular weight studies, mass spectroscopic measurements, which show the parent ion peaks $[Pt(S_2CNR_2)(Ph_2POHSPPh_2)]^+$, support their formulation as mononuclear complexes.

In the absence of *X*-ray structural analysis, it is very difficult to determine unequivocally whether the hydrogen is co-ordinated either to the oxygen and/or the sulphur atom. Support for the suggestion that it is co-ordinated more strongly to the oxygen atom comes from the observation that addition of NEt_3 to a $CDCl_3$ solution of (3b) leads to the *in situ* generation of $[NEt_3H][Pt(S_2CNPr^i_2)(Ph_2PS)(Ph_2PO)]$ and the ^{31}P-$\{^1H\}$ n.m.r. spectrum of this anion shows very little change from (3b) in the chemical shift of the thiophosphorus group (from δ 31.2 to 33.5 p.p.m.) whereas that of the oxyphosphorus group shifts from δ 65.4 to 50.8 p.p.m. However, it must also be noted that whereas $^1J_{PtP}$ of the oxyphosphorus group only changes from 3 774 to 3 847 Hz on deprotonation of (3b), that of the thiophosphorus group changes from 3 172.0 to 3 449.7 Hz and this would suggest that some interaction of the sulphur atom with the proton also occurs.

Further support for interaction of the proton with both the oxygen and sulphur atoms comes from examination of the i.r. spectra of these compounds. Thus, in (3b), there is a weak broad band centred at 2 190 cm^{-1} which disappears on deprotonation. By comparison with the value expected for a pure ν(PO–H) stretch (*ca.* 3 200 cm^{-1}) and that found for symmetrically hydrogen-bonded $R_2PO{-}H{-}OPR_2$ units (*ca.* 1 200—1 600 cm^{-1}),[2] this band can be tentatively assigned to a $\nu(Ph_2PO{-}H \cdots SPPh_2)$ stretching vibration.

Addition of CsCl to the above solution precipitates $Cs[Pt(S_2CNPr^i_2)(Ph_2PS)(Ph_2PO)]\cdot 2H_2O$ but unfortunately it is too insoluble for n.m.r. studies. Treatment of this salt, however with DCl in $CHCl_3$ gives *in situ* the neutral complex $[Pt(S_2CNPr^i_2)(Ph_2PODSPPh_2)]$. Unfortunately n.m.r. measurements are inconclusive in establishing the position of the deuterium but the i.r. spectrum (Nujol mull) reveals a new band at *ca.* 1 530 cm^{-1} [partially masked by ν(CN) (dithiocarbamate)] which can be tentatively assigned to a $\nu(Ph_2PO{-}D \cdots SPPh_2)$ stretching vibration.

In a more direct attempt to synthesise the $[Pt(S_2CNPr^i_2)(Ph_2PODSPPh_2)]$ complex, $[Pt(S_2CNPr^i_2)_2]$ was treated with an excess of $Ph_2P(S)H$ in degassed, dry methanol to which some D_2O was added. However, after refluxing for 24 h the small amount (20%) of white precipitate produced is not $[Pt(S_2CNPr^i_2)(Ph_2PODSPPh_2)]$ but the unusual secondary phosphine complex $[Pt(S_2CNPr^i_2)(Ph_2PS)(Ph_2PH)]$ (4b). It should be noted that *in situ* n.m.r. studies reveal that products such as (3b) and (2b) are still present in solution. Evidence for this formulation is based on high resolution ^1H and ^{31}P-$\{^1H\}$ n.m.r. studies (Tables 1 and 2 of SUP 23400), analytical, molecular weight (monomer in C_6H_6), and conductance data (non-conducting in methanol) and the observation that reaction of $[NPr^i_2H_2][Pt(S_2CNPr^i_2)(Ph_2PS)_2]$ with an excess of Ph_2PH in chloroform gives an almost quantitative yield of the same product.

The role of D_2O in producing this unusual product is not really understood. However, one possibility is that the D_2O–MeOH medium helps to precipitate out compound (4b), since *in situ* n.m.r. studies on the $[Pt(S_2CNR_2)_2]$–$Ph_2P(S)H$ reaction reveal that *small* amounts of (4) are present in solution, irrespective of the reaction conditions employed in these studies.

If $[Pt(S_2CNPr^i_2)_2]$ is refluxed with an excess of $Ph_2P(S)H$ in degassed, dry AnalaR methanol for a prolonged period (36 h), work-up gives a monomeric, neutral, pale yellow solid (45% yield) which on the basis of analytical data, together with ^1H and ^{31}P-$\{^1H\}$ n.m.r. studies (Tables 1 and 2 of SUP 23400) is formulated as $[Pt(S_2CNPr^i_2)(Ph_2PS)\{Ph_2P(OMe)\}]$ (5b). Thus, the ^1H n.m.r. spectrum of (5b) in $CDCl_3$ at 301 K shows a doublet characteristic of $Ph_2P(OMe)$ at δ 3.56 p.p.m. ($^3J_{PH}$ 13.0 Hz) and in the ^{31}P-$\{^1H\}$ n.m.r. spectrum, resonances at δ 92.7 $[Ph_2P(OMe)]$ (*cf.* $[Pt(S_2CNEt_2)(Ph_2PO)\{Ph_2P(OMe)\}]$, δ 94.1 p.p.m. $[P(OMe)]$[8]) and 28.2 p.p.m. (Ph_2PS) are observed.

Finally, in this very versatile $[Pt(S_2CNR_2)_2]$–$Ph_2P(S)H$ reaction, if $[Pt(S_2CNEt_2)_2]$ is refluxed in degassed dry ethanol with an *equimolar* amount of $Ph_2P(S)H$ for 6 h, work-up of the solution gives a very small yield (*ca.* 10%) of the binuclear complex $[\{Pt(S_2CNEt_2)(Ph_2PS)\}_2]$ (6a). The same compound and the corresponding isopropyl complex can be synthesised in much higher yield by treatment of $[NR_2H_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ (2) in degassed, dry $CHCl_3$ with HCl gas (either directly or dissolved in ethanol). Presumably addition of HCl to compound (2) leads to loss of $Ph_2P(S)H$, and then facile self-dimerisation of the reactive intermediate formed to give (6).

These binuclear complexes are characterised by elemental analyses, osmometric molecular weight measurements in benzene, ^1H (Table 1 of SUP 23400), ^{31}P-$\{^1H\}$ (Table 5 of SUP 23400), and ^{195}Pt-$\{^1H\}$ n.m.r. studies. In addition, an *X*-ray structural analysis was carried out on $[\{Pt(S_2CNPr^i_2)(Ph_2PS)\}_2]\cdot 2CDCl_3$ (6b). Details of the solution of the crystal structure are given in the Experimental section, final atomic parameters are given in Table 3, selected bond lengths and angles in Table 4, and a view of the molecule is in Figure 2. The molecule is a

Table 3. Fractional atomic co-ordinates with estimated standard deviations in parentheses for $[\{Pt(S_2CNPr^i_2)(Ph_2PS)\}_2]\cdot 2CDCl_3$ (6b)

Atom	*x*	*y*	*z*
Pt(1)	0.206 22(5)	−0.011 41(6)	0.058 80(3)
P(1)	0.052 8(3)	0.027 7(4)	0.082 4(2)
S(1)	−0.104 2(3)	−0.087 6(4)	0.035 6(2)
S(2)	0.379 8(4)	−0.057 5(5)	0.043 7(2)
S(3)	0.349 7(4)	−0.101 9(5)	0.148 1(2)
C(1)	0.547 5(14)	0.108 1(17)	0.880 7(7)
N(1)	0.430 0(12)	0.139 8(14)	0.853 4(6)
C(2)	0.630 3(17)	−0.187 3(20)	0.209 8(8)
C(3)	0.636 1(20)	−0.064 7(24)	0.251 9(10)
C(4)	0.580 7(22)	−0.327 8(26)	0.221 0(11)
C(5)	0.646 0(16)	−0.133 9(19)	0.113 6(8)
C(6)	0.687 0(22)	−0.283 1(27)	0.106 1(11)
C(7)	0.753 2(19)	−0.026 2(24)	0.145 6(10)
C(11)	0.012 6(10)	0.215 8(9)	0.079 6(5)
C(12)	0.100 4(10)	0.318 9(9)	0.085 2(5)
C(13)	0.073 0(10)	0.465 4(9)	0.083 8(5)
C(14)	−0.042 2(10)	0.508 7(9)	0.076 7(5)
C(15)	−0.130 0(10)	0.405 6(9)	0.071 0(5)
C(16)	−0.102 6(10)	0.259 2(9)	0.072 4(9)
C(21)	0.083 7(10)	−0.024 3(11)	0.157 8(4)
C(22)	0.072 0(10)	0.068 5(11)	0.199 0(4)
C(23)	0.088 9(10)	0.016 3(11)	0.254 6(4)
C(24)	0.117 4(10)	−0.128 7(11)	0.268 9(4)
C(25)	0.129 0(10)	−0.221 4(11)	0.227 7(4)
C(26)	0.112 2(10)	−0.169 3(11)	0.172 2(4)
Cl(1)	0.373 9(7)	0.025 0(11)	0.568 4(4)
Cl(2)	0.523 9(10)	0.215 0(10)	0.659 6(4)
Cl(3)	0.555 4(9)	0.188 7(11)	0.555 2(4)
C(8)	0.449 7(22)	0.186 3(27)	0.583 4(11)

Table 4. Interatomic distances (Å) and angles (°) for compound (6b) with estimated standard deviations in parentheses

(*a*) Distances

Pt(1)–P(1)	2.225(5)	N(1)–C(5)	1.488(30)
Pt(1)–S(1)	2.313(4)	C(5)–C(7)	1.556(27)
Pt(1)–S(2)	2.347(5)	C(5)–C(6)	1.510(33)
Pt(1)–S(3)	2.299(4)	C(2)–C(3)	1.528(32)
P(1)–S(1*)	2.048(5)	C(2)–C(4)	1.513(34)
P(1)–C(11)	1.804(10)	Pt(1)···Pt(1*)	4.571(7)
P(1)–C(21)	1.814(11)	S(1)···S(1*)	4.030(7)
S(2)–C(1)	1.757(16)	P(1)···P(1*)	3.763(5)
S(3)–C(1)	1.699(21)	C(8)–Cl(1)	1.710(26)
C(1)–N(1)	1.319(20)	C(8)–Cl(2)	1.728(25)
N(1)–C(2)	1.482(23)	C(8)–Cl(3)	1.720(34)

(*b*) Angles

P(1)–Pt(1)–S(1)	93.93(15)	S(2)–C(1)–S(3)	109.2(8)
P(1)–Pt(1)–S(3)	99.87(17)	S(3)–C(1)–N(1)	128.7(13)
S(2)–Pt(1)–S(1)	91.47(16)	S(2)–C(1)–N(1)	122.1(16)
S(2)–Pt(1)–S(3)	74.65(18)	C(2)–N(1)–C(1)	122.0(17)
Pt(1)–P(1)–S(1*)	116.56(23)	C(5)–N(1)–C(1)	120.4(14)
Pt(1)–S(1)–P(1*)	108.66(22)	C(3)–C(2)–C(4)	114.5(22)
C(11)–P(1)–C(21)	103.11(60)	C(6)–C(5)–C(7)	113.7(17)
Pt(1)–S(3)–C(1)	89.4(5)		
Pt(1)–S(2)–C(1)	86.5(7)		

* Denotes atom related by a centre of inversion.

dimer lying on a crystallographic inversion centre with a chair shaped six-membered Pt(1)–P(1)–S(1*)–Pt(1*)–P(1*)–S(1) ring. The platinum atom is co-ordinated in a square planar arrangement by two sulphur atoms of the dithiocarbamate group and one phosphorus atom and one sulphur atom in the six-membered ring. The maximum deviation from the best plane of Pt and these four atoms is 0.04 Å. This plane is

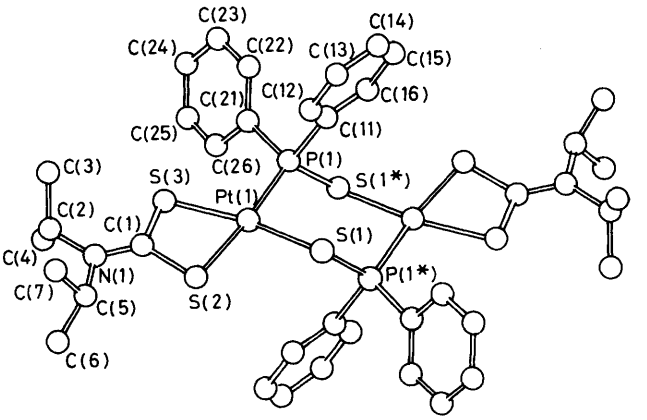


Figure 2. Molecular structure of $[\{Pt(S_2CNPr^i_2)(Ph_2PS)\}_2]\cdot 2CDCl_3$ (6b)

inclined by 54° from the plane defined by P(1), S(1*), P(1*), S(1) (*cf.* the chair-shaped $[\{Ni(\eta\text{-}C_5H_5)(Me_2PS)\}_2]$ molecule where the corresponding interplane angle is 56.1° [5e]). All bond lengths and angles are within the expected ranges (see Table 4). The shortest intermolecular contacts are Cl(1) · · · C(15) and S(2) · · · C(8) (both 3.6 Å).

Good evidence for the retention of the binuclear unit in solution is provided by the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of compounds (6) in $CDCl_3$ at 301 K (Figure of ref. 7 and Table 5 of SUP 23400) which show the characteristic pattern expected for a binuclear platinum(II) phosphine complex (see ref. 10 for a detailed discussion). This is supported for R = Pr^i by an osmometric molecular weight determination in benzene.

When $[Pd(S_2CNEt_2)_2]$ is refluxed in degassed, dry AnalaR methanol with an excess of $Ph_2P(S)H$ for 2 h, an orange precipitate of $[\{Pd(S_2CNEt_2)(Ph_2PS)\}_2]$ is formed in high yield (60%) and work-up of the filtrate gives a small amount (20%) of $[NEt_2H_2][Pd(S_2CNEt_2)(Ph_2PS)_2]$. Both these compounds were fully characterised by the techniques described earlier.

In contrast to the variety of products found in reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(S)H$, only one type of compound has been isolated, to date, in the reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(Se)H$, namely $[Pt(S_2CNR_2)(Ph_2PSe)(Ph_2PH)]$ (R = Et or Pr^i). These compounds which are isolated in high yield (>80%) by heating $[Pt(S_2CNR_2)_2]$ in degassed, dry AnalaR methanol with an excess of $Ph_2P(Se)H$ for 8 h have been characterised, as for the analogous complex $[Pt(S_2CNR_2)(Ph_2PS)(Ph_2PH)]$ (4), on the basis of elemental analysis, osmometric molecular weight determinations in C_6H_6, ^1H (Table 1 of SUP 23400), and $^{31}P\text{-}\{^1H\}$ (Table 2 of SUP 23400) n.m.r. spectroscopy. The compound $[Pt(Se_2CNEt_2)(Ph_2PSe)(Ph_2PH)]$ is prepared under the same conditions by reaction of $[Pt(Se_2CNEt_2)_2]$ with $Ph_2P(Se)H$.

To conclude this paper, it is of interest to speculate briefly on how the reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(S)H$ gives such a wide variety of products. As shown in the Scheme, the first step is probably oxidative addition of $Ph_2P(S)H$ to $[Pt(S_2CNR_2)_2]$ to generate the unstable, six-co-ordinate platinum(IV) complex $[PtH(S_2CNR_2)_2(Ph_2PS)]$. Facile reductive elimination of HS_2CNR_2 (which readily decomposes to CS_2 and NR_2H [11]) would then produce the reactive intermediate $[Pt(S_2CNR_2)(Ph_2PS)(Y)]$ (7) (Y = solvent) † from

† *trans* Oxidative addition of $Ph_2P(S)H$ to give $[PtH(S_2CNR_2)_2(Ph_2PS)]$ and co-ordination of solvent in compound (7) have been assumed, but *cis* addition and absence of co-ordinated solvent will not invalidate the proposed reaction pathways. It is also possible that the Ph_2PS^- ligand is bonded ' side-on ' in (7) (*cf.* ref. 6).

which, depending on reaction conditions, the various observed products can be generated.

For example, for equimolar ratios of $[Pt(S_2CNR_2)_2]$ to $Ph_2P(S)H$, self-dimerisation of (7) to give $[\{Pt(S_2CNR_2)(Ph_2PS)\}_2]$ (6) is favoured whereas in wet solvents, hydrolysis of free $Ph_2P(S)H$ will produce some $Ph_2P(O)H$ which will react with (7) and/or the anion (2) to form $[Pt(S_2CNR_2)(Ph_2POHSPPh_2)]$ (3). Reaction of $Ph_2P(O)H$ with compound (2) in $CDCl_3$ for short periods will in fact give appreciable amounts of (3). In dry methanol, deprotonation of $Ph_2P(S)H$ by NR_2H (formed by decomposition of HS_2CNR_2) will give $[NR_2H_2]^+$ and Ph_2PS^-. The latter can then react with (7) to form the $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ anion (2) as its $[NR_2H_2]^+$ salt. Alternatively, formation of (2) could involve direct reaction of (7) with $Ph_2P(S)H$ to give $[Pt(S_2CNR_2)\{(Ph_2PS)_2H\}]$ (*cf.* $[Pt(S_2CNR_2)\{(Ph_2PO)_2H\}]$) followed by rapid deprotonation by NR_2H to give (2). The former pathway is more likely, however, since it can be shown that in dry methanol, $Ph_2P(S)H$ is readily deprotonated by NEt_2H. Furthermore, the conversion of $[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ to $[\{Pt(S_2CNR_2)(Ph_2PS)\}_2]$ on treatment with HCl demonstrates that protonation of co-ordinated Ph_2PS leads to facile dissociation of a $Ph_2P(S)H$ group. Prolonged reaction of $Ph_2P(S)H$ in dry methanol will produce some $Ph_2P(OMe)$ and this can then react with either the intermediate (7) or the anion (2) to give $[Pt(S_2CNR_2)(Ph_2PS)\{Ph_2P(OMe)\}]$ (5). The feasibility of the latter reaction is readily confirmed by the high yield formation of (5) from reaction of $[NR_2H_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ with $Ph_2P(OMe)$ (n.m.r. study).

The origin of the small amounts of $[Pt(S_2CNR_2)(Ph_2PS)(Ph_2PH)]$ (4) in all these reactions is much more speculative. Attempts to generate (4) by direct removal of sulphur and oxygen atoms from compounds (2) and (3) respectively have been unsuccessful. However, it can be demonstrated that reaction of the anion (2) with Ph_2PH under very mild conditions will give high yields of (4) and furthermore, it is well known [12] that $Ph_2P(O)H$ will disproportionate to give some Ph_2PH and Ph_2PO_2H and likewise, $Ph_2P(S)H$ might give Ph_2PH and Ph_2PS_2H. Therefore, it is suggested that the small amounts of (4) formed in these $[Pt(S_2CNR_2)_2]$–$Ph_2P(S)H$ reactions are due to the reaction of either the anion (2) and/or the intermediate (7) with traces of Ph_2PH produced by disproportionation of $Ph_2P(O)H$ or $Ph_2P(S)H$.

The observation of *high* yields of $[Pt(S_2CNR_2)(Ph_2PSe)(Ph_2PH)]$ from reaction of $[Pt(S_2CNR_2)_2]$ and $Ph_2P(Se)H$ could be explained by postulating initial formation of the anion $[Pt(S_2CNR_2)(Ph_2PSe)_2]^-$ followed by rapid loss of an atom of Se, perhaps by interaction with H_2O or MeOH. Alternatively, under these reaction conditions, $Ph_2P(Se)H$ might decompose extensively to Ph_2PH which could readily react with an intermediate such as $[Pt(S_2CNR_2)(Ph_2PSe)(Y)]$ and/or the anion above to give $[Pt(S_2CNR_2)(Ph_2PSe)(Ph_2PH)]$.

For the reaction of $[Pt(S_2CNR_2)_2]$ with $Ph_2P(O)H$, a similar scheme can be proposed except that reaction of the intermediate $[Pt(S_2CNR_2)(Ph_2PO)(Y)]$ with $Ph_2P(O)H$ produces only the very stable and methanol-insoluble $[Pt(S_2CNR_2)\{(Ph_2PO)_2H\}]$.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined in benzene on a Perkin-Elmer-Hitachi (model 115) osmometer calibrated with benzil. Infrared spectra were recorded in the region 4 000—200 cm^{-1} on Perkin-Elmer 457 and 557 grating spectrometers using Nujol mulls on caesium iodide plates or potassium bromide discs. Hydrogen-1 n.m.r. spectra were obtained on Varian Associates EM-360, HA-100, or Bruker WH-360 spectrometers. Phosphorus-31 n.m.r. spectra (proton noise decoupled) were obtained on a JEOL-FX60Q spectrometer operating in the pulse and Fourier transform mode at 22.24 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H_3PO_4. Carbon-13 n.m.r. spectra (proton noise decoupled) were obtained on a Varian CFT20 spectrometer operating at 20 MHz (^{13}C chemical shifts quoted in p.p.m. to high frequency of $SiMe_4$). Platinum-195 n.m.r. spectra were obtained on a Bruker WH-360 spectrometer and chemical shifts referenced to 77.068 725 MHz (which is equivalent to 21.4 MHz when external $SiMe_4$ at 100 MHz). Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge at 298 K. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Crystal Structure Determination of $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (2a).—*Crystal data.* $C_{33}H_{42}N_2P_2PtS_4$, $M = 850$, clear yellow orthorhombic plates, $a = 21.098(18)$, $b = 11.679(8)$, $c = 14.816(18)$ Å, $U = 3\,650.7$ Å^3, $Z = 4$, $D_c = 1.546$ g cm^{-3}, $F(000) = 1\,704$, space group $P2_12_12_1$ (no. 19), Mo-K_α radiation, $\lambda = 0.710\,69$ Å, and $\mu = 43.74$ cm^{-1}. Intensity data were measured using a Stoe Stadi-2 diffractometer. A crystal of dimensions $0.08 \times 0.2 \times 0.28$ mm (rotation axis) was used to record layers *hk*0 through *hk*15 with $2\theta_{max.} = 50°$ in the ω-scan mode. 1 480 Unique reflections had $I > 3\sigma(I)$ and an empirical absorption correction was applied.[13]

The MULTAN-77 system [14] was used to locate the Pt atom and its four square planar co-ordinated atoms. Subsequent full-matrix least-squares refinement and interpretation of difference-Fourier maps using SHELX [15] enabled all non-hydrogen atoms in the structure to be located. Positional and anisotropic vibrational parameters for the Pt, S, and P atoms were refined. For all other non-hydrogen atoms only the positional and isotropic vibrational parameters were varied. The phenyl rings were constrained to be planar with all C–C distances 1.395 Å. In the final cycles of full-matrix least-squares refinement a number of bond lengths between carbon and nitrogen atoms were restrained with a low weight to their expected values (Table 2). A unit weighting scheme was found to give satisfactory variances of $|F|$ analysed in ranges of $|F|$. In the last cycle of refinement no shifts were greater than 0.1 times the estimated standard deviation, and the final R was 0.064.

Crystal Structure Determination of $[\{Pt(S_2CNPr^i_2)(Ph_2PS)\}_2]\cdot 2CDCl_3$ (6b).—*Crystal data.* $C_{38}H_{48}N_2P_2Pt_2S_6\cdot 2CDCl_3$, $M = 1\,417$, clear yellow monoclinic plates, $a = 12.192(7)$, $b = 9.272(6)$, $c = 24.958(15)$ Å, $\beta = 116.232(28)°$, $U = 2\,531$ Å^3, $Z = 2$, $D_c = 1.81$ g cm^{-3}, $F(000) = 1\,400$, space group $P2_1/c$ (no. 14), Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 63.9$ cm^{-1}. After preliminary photography, intensity data were measured on a Stoe Stadi-2 diffractometer. A crystal of dimensions $0.28 \times 0.28 \times 0.15$ mm was used to record layers *h*0*l* through *h*10*l* with $2\theta_{max.} = 50°$. Of 4 453 unique reflections, 3 126 had $I > 2\sigma(I)$ based on counting statistics. An empirical absorption correction was applied.[13]

The position of the Pt atom was determined from a Patterson map. Subsequent difference-Fourier syntheses revealed all non-hydrogen atoms in the molecule. Structure refinement was carried out using SHELX.[15] The phenyl rings were constrained to be planar with all C–C distances 1.395 Å. In the final cycles of least-squares refinement Pt, P, S, and Cl were given anisotropic vibration parameters. No hydrogen atoms were included. A unit weighting scheme was found to give satisfactory variances of $|F|$ analysed in ranges of $\sin\theta$ and $|F|$. The final R factor was 0.064 based on 3 126 reflections.

Materials.—Potassium tetrachloroplatinate(II), palladium(II) chloride (Johnson-Matthey p.l.c.), $Na[S_2CNEt_2]\cdot H_2O$ (Ralph Emanuel) $Na[S_2CNPr^i_2]$,[16] $[M(S_2CNR_2)_2]$ (M = Pd or Pt),[17] and $[Pt(Se_2CNEt_2)_2]$ [18] were made as described elsewhere. Diphenylphosphine-sulphide and -selenide were prepared by reaction of diphenylphosphine with equimolar amounts of sulphur and selenium respectively.[19]

Reactions were carried out under nitrogen in degassed AnalaR methanol (freshly distilled from magnesium turnings), degassed dry chloroform, ethanol, or degassed technical grade methanol using standard Schlenk techniques for work-up and isolation. Volatile gases were handled on a Pyrex vacuum line using standard techniques.

Di-isopropylammonium NN-*Di-isopropyldithiocarbamatobis(diphenylthiophosphinito)platinate*(II) (2b).—The complex $[Pt(S_2CNPr^i_2)_2]$ (0.95 g, 1.70 mmol) was refluxed in degassed, dried AnalaR methanol (50 cm^3) with an excess of diphenylphosphine sulphide (1.40 g, 6.40 mmol). After 12 h, the white product was filtered off, the yellow filtrate concentrated to *ca.* one quarter of its original volume, and diethyl ether (20 cm^3) added to precipitate the bulk of the product as a white microcrystalline solid. The products were combined, recrystallised from chloroform–diethyl ether (*ca.* 1 : 1 v/v), washed with more diethyl ether and dried *in vacuo*, m.p. 156—159 °C (yield 0.82 g; 51%) (Found: C, 49.3; H, 5.5; N, 3.0. Calc. for $C_{37}H_{50}N_2P_2PtS_4$: C, 49.0; H, 5.5; N, 3.1%). Mull i.r. spectrum: ν(NH) 2 670; δ(NH) 1 586; ν(CN) (dithiocarbamate) 1 495; ν(PS) 620, 600, 580 cm^{-1}. Λ(2.2×10^{-3} mol dm^{-3} in MeOH) 36.2 S cm^2 mol^{-1}, Λ[1×10^{-2} mol dm^{-3} in $(CH_3)_2CO$] 7.6 S cm^2 mol^{-1}. $^{13}C-\{^1H\}$ n.m.r. in $CDCl_3$ at 301 K: δ 19.5(s) [$^-S_2CN(CHMe_2)_2$]; 20.0(s) [$NH_2(CHMe_2)_2^+$]; 47.5(s) [$NH_2(CHMe_2)_2^+$]; 50.5(s) [$^-S_2CN(CHMe_2)_2$] 126.3—139.7(m) (Ph_2PS^-); 205.2(br) p.p.m. [$^-S_2CN(CHMe_2)_2$] (no PtC coupling observed). $^{13}C-\{^1H\}$ n.m.r. in $CDCl_3$ at 214 K: δ 18.7(s), 19.5(s) [*ca.* 1 : 3 intensity, suggesting two $^-S_2CN(CHMe_2)_2$ with $^+NH_2(CHMe_2)_2$ superimposed on higher frequency resonance]; 46.9(s) [$NH_2(CHMe_2)_2^+$]; 49.7(s), 50.9(s) [equal intensity, $^-S_2CN(CHMe_2)_2$]; 125.0—138.0(m) (Ph_2PS^-); 203.0 p.p.m. (1 : 4 : 1 triplet, $^2J_{PtC}$ *ca.* 73 Hz) [$^-S_2CN(CHMe_2)_2$].

Diethylammonium NN-*Diethyldithiocarbamatobis(diphenylthiophosphinito)platinate*(II) (2a).—This complex was prepared as for (2b) from $[Pt(S_2CNEt_2)_2]$ and $Ph_2P(S)H$; m.p. 164—166 °C (yield 30—40%) (Found: C, 46.7; H, 4.9; N, 3.1. Calc. for $C_{33}H_{42}N_2P_2PtS_4$: C, 46.6; H, 4.9; N, 3.3%). Mull i.r. spectrum: ν(NH) 2 660; δ(NH) 1 588; ν(CN) (dithiocarbamate) 1 510; ν(PS) 623, 600, 580 cm^{-1}; Λ(2.4×10^{-3} mol dm^{-3} in MeOH) 50.0 S cm^2 mol^{-1}. $^{13}C-\{^1H\}$ n.m.r. in $CDCl_3$ at 301 K: δ 10.5(s) [$^-S_2CN(CH_2Me)_2$]; 12.1(s) [$NH_2(CH_2Me)_3^+$]; 39.5(s) [$NH_2(CH_2Me)_2^+$]; 43.5(s) [$^-S_2CN(CH_2Me)_2$]; 125.1—139.4(m) (Ph_2PS^-); 205.4 p.p.m. (1 : 4 : 1 triplet; $^2J_{PtC}$ 78.5 Hz) [$^-S_2CN(CH_2CH_3)_2$]. $^{195}Pt-\{^1H\}$ n.m.r. in $CDCl_3$ at 301 K: δ 116.7(t) p.p.m. ($^1J_{PtP}$ 3 428 Hz).

Benzyltriphenylphosphonium NN-*Diethyldithiocarbamatobis(diphenylthiophosphinito)platinate*(II).—The compound $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.115 g, 0.135 mmol) was refluxed in AnalaR methanol (30 cm^3) with a three-fold excess of $[P(CH_2Ph)Ph_3]Cl$ (0.16 g; 0.40 mmol) for 3 h. The solution was filtered hot and degassed water (20 cm^3) was added to give a sticky pale yellow solid. This was washed several times with methanol, then dissolved in CH_2Cl_2 (1 cm^3) and reprecipitated by addition of methanol (20 cm^3) to give an off-white *solid* (0.035 g, 23%) (Found: C, 57.1; H, 4.6; N, 1.2. Calc. for $C_{54}H_{52}NP_3PtS_4$: C, 57.4; H, 4.6; N, 1.2%). Mull i.r. spectrum: ν(CN) 1 510; ν(PS) 620, 600, 585 cm^{-1}. Λ(3.5×10^{-3} mol dm^{-3} in CH_3OH) 92.5 S cm^2 mol^{-1}.

Caesium NN-*Di-isopropyldithiocarbamatobis(diphenylthiophosphinito)platinate*(II).—The compound $[NPr^i_2H_2][Pt(S_2CNPr^i_2)(Ph_2PS)_2]$ (0.23 g, 0.27 mmol) was refluxed in AnalaR methanol (20 cm^3) with an excess of CsCl (0.20 g; 1.20 mmol) for 1 h. Addition of degassed water (20 cm^3) to the cooled solution then precipitated the product as a sticky white solid. After washing with methanol, this was dissolved in a minimum amount of $CHCl_3$, and triturated with more methanol to give the product as a white microcrystalline *solid*, m.p. 248—251 °C (decomp.) (0.17 g, 66%) (Found: C, 38.8; H, 3.6; N, 1.3. Calc. for $C_{31}H_{34}CsNP_2PtS_4$: C, 39.7; H, 3.6; N, 1.5%). This compound was too insoluble for solution studies. Mull i.r. spectrum: ν(CN) 1 500; ν(PS) 620, 600, 585 cm^{-1}.

NN-*Di-isopropyldithiocarbamato[(diphenylthiophosphinito)-diphenylphosphinous acid]platinum*(II) (3b).—The complex $[Pt(S_2CNPr^i_2)_2]$ (0.55 g, 1.00 mmol) was refluxed in degassed technical-grade methanol (30 cm^3) with $Ph_2P(S)H$ (0.76 g, 3.00 mmol) for 12 h. After filtering off the white solid, $[NPr^i_2H_2][Pt(S_2CNPr^i_2)(Ph_2PS)_2]$ (0.27 g, 30%), the yellow solution was concentrated and then triturated with diethyl ether to give an amorphous pale yellow *solid*. This was washed with more diethyl ether and dried *in vacuo*, m.p. 175—178 °C (0.16 g, 20%) (Found: C, 47.1; H, 4.5; N, 1.7. Calc. for $C_{31}H_{35}NOP_2PtS_3$: C, 47.1; H, 4.5; N, 1.8%). Mull i.r. spectrum: ν(PO–H) 2 190; ν(CN) 1 500; ν(P–OH) 905; ν(PS) 620, 600, 585 cm^{-1}.

NN-*Diethyldithiocarbamato[(diphenylthiophosphinito)-diphenylphosphinous acid]platinum*(II) (3a).—The complex $[Pt(S_2CNEt_2)_2]$ (0.71 g, 1.50 mmol) was refluxed in degassed technical grade methanol (30 cm^3) with $Ph_2P(S)H$ (0.87 g, 4.00 mmol) for 12 h. Careful trituration of the solution with diethyl ether–light petroleum (b.p. 40—60 °C) (1 : 1 v/v) then gave a precipitate of $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.45 g, 35%). Removal of solvent from the filtrate, dissolution in chloroform, and addition of diethyl ether gave the product as an amorphous pale yellow *solid*.

The same compound was prepared by direct reaction of $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ with $Ph_2P(O)H$ (1 : 1 mol ratio) in $CDCl_3$. After heating to 60 °C for 5 min and then leaving for 30 min, the $^{31}P-\{^1H\}$ n.m.r. spectrum showed that considerable amounts of (3a) had been generated together with free $Ph_2P(S)H$.

Caesium NN-*Di-isopropyldithiocarbamato(diphenylphosphinito)(diphenylthiophosphinito)platinate*(II) *Dihydrate.*—The complex $[Pt(S_2CNPr^i_2)(Ph_2POHSPPh_2)]$ (0.25 g; 0.31 mmol) was refluxed in technical-grade methanol (20 cm^3) and NEt_3 (1 cm^3) for 1 h. An aqueous solution of excess CsCl was then added to the cooled solution and a small amount of sticky yellow solid was filtered off. The solution was then concentrated to precipitate the white *product*, m.p. 271—275 °C (0.16 g, 55%) (Found: C, 39.2; H, 4.0; N, 1.5. Calc. for $C_{31}H_{38}CsNO_3P_2PtS_3$: C, 38.8; H, 4.0; N, 1.5%). Mull i.r. spectrum: ν(CN) 1 500; ν(PO) 1 050; ν(PS) 620, 600, 585 cm^{-1}.

NN-*Di-isopropyldithiocarbamato(diphenylphosphine)-(diphenylthiophosphinito)platinum*(II) (4b).—*Method* A. The complex $[NPr^i_2H_2][Pt(S_2CNPr^i_2)(Ph_2PS)_2]$ (0.07 g, 0.15 mmol) was dissolved in a minimum amount of degassed chloroform (5.0 cm^3) and treated with an excess of Ph_2PH (0.10 cm^3) in degassed benzene (1.0 cm^3). After stirring for 2 h at ambient

temperature, the product had precipitated as a white microcrystalline solid which was washed with diethyl ether and dried *in vacuo*, m.p. 190—192 °C (0.09 g, 80%) [Found: C, 48.1; H, 4.5; N, 2.0%; *M* (C_6H_6, osmometrically) 730. Calc. for $C_{31}H_{35}NP_2PtS_3$: C, 48.1; H, 4.5; N, 1.8%; *M* 774]. Mull i.r. spectrum: ν(CN) 1 505; ν(PS) 620, 600, 585 cm^{-1} [ν(PH) (KBr disc) 2 350 cm^{-1}].

Method B. The compound $[Pt(S_2CNPr^i_2)_2]$ (0.52 g, 1.00 mmol) was refluxed with an excess of $Ph_2P(S)H$ (0.70 g, 3.20 m mol) in dry degassed methanol (50 cm^3) to which D_2O (1 cm^3) had been added. After 24 h, a small amount of the white *product* was filtered off (0.17 g, 22%). The pale yellow filtrate was examined by ^{31}P-{^1H} n.m.r. spectroscopy and shown to consist of a mixture of $[Pt(S_2CNPr^i_2)\{(Ph_2PO)_2H\}]$, $[Pt(S_2CNPr^i_2)(Ph_2POHSPPh_2)]$, $[Pt(S_2CNPr^i_2)(Ph_2PS)(Ph_2PH)]$, and unreacted $Ph_2P(S)H$.

In fact, small amounts of $[Pt(S_2CNPr^i_2)(Ph_2PS)(Ph_2PH)]$ have been observed (by ^{31}P-{^1H} n.m.r. spectroscopy) in virtually every reaction between $[Pt(S_2CNPr^i_2)_2]$ and $Ph_2P(S)H$.

NN-*Di-isopropyldithiocarbamato*(*diphenylthiophosphinito*)-(*methyl diphenylphosphinite*)*platinum*(II) (5b).—The compound $[Pt(S_2CNPr^i_2)_2]$ (0.55 g, 1.00 mmol) was refluxed in degassed, dried AnalaR methanol (30 cm^3) with diphenylphosphine sulphide (0.76 g, 3.50 mmol) for a *prolonged* period (36 h). The cloudy pale yellow solution was then filtered and, on cooling, a pale yellow solid was precipitated. This was redissolved by refluxing [in methanol (20 cm^3)] for 30 min and then refiltered. After cooling and triturating with diethyl ether, the product was obtained as a creamy white microcrystalline *solid* which was washed with ethanol and diethyl ether and dried *in vacuo*, m.p. 187—189 °C (0.36 g, 45%) [Found: C, 47.8; H, 4.6; N, 1.8%; *M* (C_6H_6, osmometrically) 795. Calc. for $C_{32}H_{37}NOP_2PtS_3$: C, 47.8; H, 4.6; N, 1.7%; *M* 804]. Mull i.r. spectrum: ν(CN) 1 505; ν(P–OC) 1 040; ν(PS) 630, 600, 585 cm^{-1}. The same compound was readily formed in high yield (n.m.r. studies) by direct reaction of $[NPr^i_2H_2][Pt(S_2CNPr^i_2)(Ph_2PS)_2]$ with $Ph_2P(OMe)$ in $CDCl_3$ at ambient temperature.

NN-*Diethyldithiocarbamato*[*hydrogen bis*(*diphenylphosphinito*)]*platinum*(II).—*Method* A. The compound $[Pt(S_2CNEt_2)_2]$ (0.14 g, 0.30 mmol) was suspended in methanol (30 cm^3) and shaken for 6 h with a three-fold excess of $Ph_2P(O)H$ (0.20 g, 1.0 mmol). The product was precipitated as a white *solid*, washed with ethanol and diethyl ether, and recrystallised from chloroform–diethyl ether (*ca.* 1 : 1 v/v), m.p. 242—244 °C (0.13 g, 60%) (Found: C, 46.7; H, 4.2; N, 1.8. Calc. for $C_{29}H_{31}NO_2P_2PtS_2$: C, 46.7; H, 4.2; N, 1.9%). Mull i.r. spectrum: ν(CN) 1 530; ν(PO) 1 020 cm^{-1}.

Method B. The compound $[Pt(S_2CNEt_2)_2]$ (0.14 g, 0.30 mmol) was shaken with an excess of Ph_2PCl (0.50 cm^3) in technical-grade methanol (30 cm^3) until all the yellow starting material had been replaced by the white microcrystalline *product* (0.18 g, 85%).

The complex $[Pt(S_2CNPr^i_2)\{(Ph_2PO)_2H\}]$ was similarly prepared from $[Pt(S_2CN^iPr_2)_2]$ and $Ph_2P(O)H$ or Ph_2PCl in aqueous methanol, m.p. 289—292 °C (Found: C, 46.5; H, 4.4; N, 1.6. Calc. for $C_{31}H_{35}NO_2P_2PtS_2$: C, 48.1; H, 4.5; N, 1.8%). Mull i.r. spectrum: ν(CN) 1 510; ν(PO) 1 020 cm^{-1}.

Bis[(NN-*diethyldithiocarbamato*)(μ-*diphenylthiophosphinito*)*platinum*(II)] (6a).—*Method* A. The complex $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (0.38 g, 0.45 mmol) was dissolved in degassed, dry chloroform (5 cm^3) and treated with an excess of concentrated dry ethanolic HCl (0.50 cm^3) and stirred at ambient temperature for 24 h. Further ethanol (5 cm^3) was then added to complete the precipitation of the pale yellow *product* which was washed with ethanol, cold diethyl ether–light petroleum (b.p. 40—60 °C) (1 : 1 v/v) and dried *in vacuo*, m.p. 237 °C (decomp.) (0.21 g, 84%) (Found: C, 36.2; H, 3.7; N, 2.6. Calc. for $C_{34}H_{20}N_2P_2Pt_2S_6$: C, 36.4; H, 3.6; N, 2.5%). Mull i.r. spectrum: ν(CN) 1 516, ν(PS) 610, 600, 580 cm^{-1}. The same compound could be made by reaction of $[NEt_2H_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ with an excess of gaseous HCl in $CHCl_3$. After leaving for 1 h at ambient temperature, the bright yellow solution was treated with diethyl ether–light petroleum (b.p. 40—60 °C) (1 : 1 v/v) to give the yellow product (quantitative yield).

Method B. The complex $[Pt(S_2CNEt_2)_2]$ (0.29 g, 0.60 mmol) was refluxed in degassed dry ethanol (30 cm^3) for 6 h with an equimolar amount of $Ph_2P(S)H$ (0.13 g, 0.60 mmol). The bright yellow solution was evaporated to dryness and the residue shaken with diethyl ether. After concentration of the diethyl ether solution and leaving for 24 h, a small amount of yellow crystalline *product* was obtained (0.034 g, 10%). ^{195}Pt-{^1H} n.m.r. spectrum in $CDCl_3$ at 301 K: δ(Pt) 368.4 p.p.m.; $^1J_{PtP}$ 3 652.3, $^2J_{PtP}$, 80.6 Hz, $^3J_{PtPt}$, could not be measured.

Bis[(NN-*di-isopropyldithiocarbamato*)(μ-*diphenylthiophosphinito*)*platinum*(II)] (6b).—The compound $[NPr^i_2H_2][Pt(S_2CNPr^i)_2(Ph_2PS)_2]$ (0.50 g, 0.50 mmol) was treated with an excess of concentrated dry, ethanolic HCl (0.50 cm^3) in degassed, dry $CHCl_3$ (5 cm^3) at ambient temperature for 12 h. Addition of ethanol then precipitated the pale yellow solid which was washed with ethanol and dried *in vacuo*, m.p. 283 °C (decomp.) (0.21 g, 68%) [Found: C, 39.0; H, 4.2; N, 2.2%; *M* (C_6H_6 osmometrically) 1 305. Calc. for $C_{38}H_{48}N_2P_2Pt_2S_6$: C, 38.8; H, 4.1; N, 2.4%; *M* 1 176]. Mull i.r. spectrum: ν(CN) 1 500; ν(PS) 610, 600, 580 cm^{-1}.

Recrystallisation from $CDCl_3$ gave crystals containing two $CDCl_3$ of solvation which were suitable for *X*-ray analysis.

NN-*Diethyldithiocarbamato*(*diphenylphosphine*)(*diphenylselenophosphinito*)*platinum*(II).—The compound $[Pt(S_2CNEt_2)_2]$ (0.31 g, 0.64 mmol) was refluxed in degassed dried AnalaR methanol (30 cm^3) with diphenylphosphine selenide (0.50 g, 1.90 mmol) for 8 h. The microcrystalline pale yellow precipitate was filtered off, washed with methanol and diethyl ether, and dried *in vacuo*, m.p. 198—200 °C (decomp.) (0.44 g, 84%) [Found: C, 43.2; H, 3.9; N, 1.8%; *M* (C_6H_6, osmometrically) 632. Calc. for $C_{29}H_{31}NP_2PtS_2Se$: C, 43.0; H, 3.8; N, 1.7%; *M* 791]. Mull i.r. spectrum: ν(CN) 1 500; ν(PSe) 520 cm^{-1}.

NN-*Di-isopropyldithiocarbamato*(*diphenylphosphine*)-(*diphenylselenophosphinito*)*platinum*(II).—The compound $[Pt(S_2CNPr^i_2)_2]$ (0.58 g, 1.10 mmol) and $Ph_2P(Se)H$ (1.14 g, 4.30 mmol) were refluxed as above to give the microcrystalline pale yellow *product*, m.p. 216—217 °C (0.76 g, 86%) [Found: C, 44.6; H, 4.3; N, 1.6%; *M* (C_6H_6 osmometrically) 796. Calc. for $C_{31}H_{35}NP_2PtS_2Se$: C, 44.4; H, 4.2; N, 1.7%; *M* 820]. Mull i.r. spectrum: ν(CN) 1 500; ν(PSe) 520 cm^{-1}. Similarly, reaction of $[Pt(Se_2CNEt_2)_2]$ (0.15 g, 0.22 mmol) and $Ph_2P(Se)H$ (0.19 g; 0.73 mmol) in methanol gave the yellow solid *NN*-diethyldiselenocarbamato(diphenylphosphine)(diphenylselenophosphinito)platinum(II), m.p. 209—211 °C (0.15 g, 32%). Mull i.r. spectrum: ν(CN) 1 510br; ν(PSe) 520 cm^{-1}.

Bis[(NN-*diethyldithiocarbamato*)(μ-*diphenylthiophosphinito*)*palladium*(II)].—The compound $[Pd(S_2CNEt_2)_2]$ (0.60 g, 1.50 mmol) was refluxed in degassed, dry AnalaR methanol (30 cm^3) with an excess of $Ph_2P(S)H$ (0.98 g, 4.50 mmol) for 2 h. The deep orange microcrystalline *solid* was filtered off

and washed with diethyl ether and dried *in vacuo*, m.p. 193—195 °C (0.42 g, 60%) [Found: C, 43.3; H, 4.3; N, 2.9%; *M*(C_6H_6,osmometrically) 932. Calc. for $C_{34}H_{40}N_2P_2Pd_2S_6$: C, 43.3; H, 4.3; N, 3.0%; *M* 942]. Mull i.r. spectrum: ν(CN) 1 510; ν(PS) 585 cm^{-1}.

Treatment of the yellow filtrate with diethyl ether (50 cm^3) and subsequent cooling for 6 h gave the yellow crystalline solid diethylammonium *NN*-diethyldithiocarbamato(bis(diphenylthiophosphinito)palladate(II) which was washed with cold diethyl ether and dried *in vacuo*, m.p. 130—132 °C (0.21 g, 18%) (Found: C, 51.2; H, 5.5; N, 3.4. Calc. for $C_{24}H_{42}N_2P_2PdS_4$: C, 52.7; H, 5.4; N, 3.6%). Mull i.r. spectrum: ν(NH) 2 645; δ(NH) 1 590; ν(CN) (dithiocarbamate) 1 510; ν(PS) 620, 600, 585 cm^{-1}.

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