Metal Complexes of Sulphur Ligands. Part III.[1] Reaction of Platinum(II) *NN*-Dialkyldithiocarbamates, *O*-Ethyl Dithiocarbonate (Xanthate), and *OO'*-Diethyl Dithiophosphate with Tertiary Phosphines

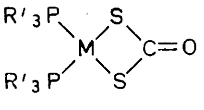
By (Miss) **J. M. C. Alison** and **T. A. Stephenson,*** Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Evidence is presented to show that the reaction of all $M(S-S)_2$ compounds [M = Pt, Pd; $(S-S)^- = {}^-S_2CNR_2$ (R = Me, Et), ${}^-S_2COR$ (R = Et, $PhCH_2$), ${}^-S_2P(OEt)_2$, and ${}^-S_2PR_2$ (R = Me, Et, Ph)] with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate compounds of formulae $[M(S-S)_2PR'_3]$ and $[M(S-S)(PR'_3)_2](S-S)$ with unidentate/bidentate (III) and ionic/bidentate (IV) co-ordintion respectively. All the ionic compounds readily revert to the $[M(S-S)_2PR'_3]$ complexes in the presence of non-polar solvents *via* nucleophilic attack by $(S-S)^-$ on the metal. In addition, for $(S-S)^- = {}^-S_2COR$, ${}^-S_2P(OEt)_2$, nucleophilic attack can also occur on a co-ordinated alkoxy group to give the novel compounds $[(R'_3P)_2MS_2CO]$ (I) and $[(R'_3P)_2MS_2P(O)OEt]$ (II) respectively.

For $[M(S-S)(PR'_3)_2](S-S)$ compounds containing ${}^-S_2CNR_2$, the presence of excess PR'_3 catalyses the reaction between dithiocarbamate ion and dichloromethane, giving $CH_2(S_2CNR_2)_2$ and $[M(S_2CNR_2)(PR'_3)_2]Cl,H_2O$. These conclusions are based on extensive physico-chemical studies and, in particular, the use of variable temperature ^1H n.m.r. spectroscopy.

RECENTLY, it was reported [2-4] that the reaction of tertiary phosphines with $M(S-S)_2$ (1 : 1 molar ratio) [M = Pt, Pd; $(S-S)^- = {}^-S_2CNEt_2$, ${}^-S_2COR$, ${}^-S_2P(OEt)_2$, and ${}^-S_2CR$] gave the complexes $[M(S-S)_2PR'_3]$ which were formulated as five-co-ordinate compounds on the basis of ^1H n.m.r. data. A brief mention was also made of the precipitation from solution of what may be six-co-ordinate species when an excess of methyldiphenylphosphine was added to platinum(II) compounds of ring-substituted dithiobenzoates [3] but no further details were given. It was also stated [2] that 'diethyldithiocarbamate complexes of palladium(II) and platinum(II) react only slowly (hours) with excess methyldiphenylphosphine to produce what appears to be phosphine co-ordinated substitution products' but a footnote added that 'these reactions have not been characterised completely to date'. When excess tertiary phosphine was added to these xanthate and dithiophosphate adducts, further reaction occurred to give the novel complexes $[(R'_3P)_2MS_2CO]$ (I) and $[(R'_3P)_2PdS_2P(O)OEt]$ (II) respectively,[4] for which no convincing mechanism of formation was suggested.

Other studies, however, on tertiary phosphine complexes of $M(S_2PR_2)_2$ (M = Pd, Pt; R = Ph,[1] Et,[5] Me [5]) and $Pd(S_2PF_2)_2$ [6] have suggested that the 1 : 1 and 1 : 2 adducts formed possess four-co-ordinate square planar structures of type (III) and (IV) respectively and these structural assignments have been confirmed by *X*-ray analyses on $[Pd(S_2PPh_2)_2PPh_3]$ [7] and $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$.[8]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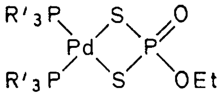
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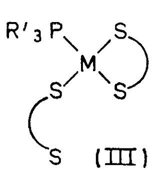
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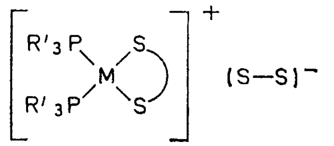
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In view of these latter results, it was therefore of some interest to re-examine and extend some of the work reported in publications 2—4; the results of this investigation are presented in this paper.

RESULTS AND DISCUSSION

Complexes of Stoicheiometry $[Pt(S_2CNR_2)_2PR'_3]$.—Reaction of $Pt(S_2CNEt_2)_2$ with either PPh_3 or $PMePh_2$ (1 : 1

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

[2] J. P. Fackler, jun., W. C. Seidel, and J. A. Fetchin, *J. Amer. Chem. Soc.*, 1968, **90**, 2707.

[3] J. P. Fackler, jun., J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, 1969, **91**, 1217.

[4] J. P. Fackler, jun., and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.

[5] Part IV, D. F. Steele and T. A. Stephenson, to be published.

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

[7] Miss J. M. C. Alison and R. O. Gould, to be published.

[8] C. A. Beevers and A. Fraser, to be published.

molar ratio) in carbon disulphide gives deep lemon-yellow solutions immediately from which crystalline yellow solids of stoicheiometry $[Pt(S_2CNEt_2)_2PR'_3]$ can be readily isolated. These are non-conducting, diamagnetic, and quite stable both in solid and solution state. For $PR'_3 = PMePh_2$, the ^1H n.m.r. at 301 K is identical to that reported earlier by Fackler *et al.*[2] (Table 1). In a further note,[3] these authors state that 'the p.m.r. behaviour of methyldiphenylphosphinebis(*NN*-diethyldithiocarbamato)platinum(II) is essentially

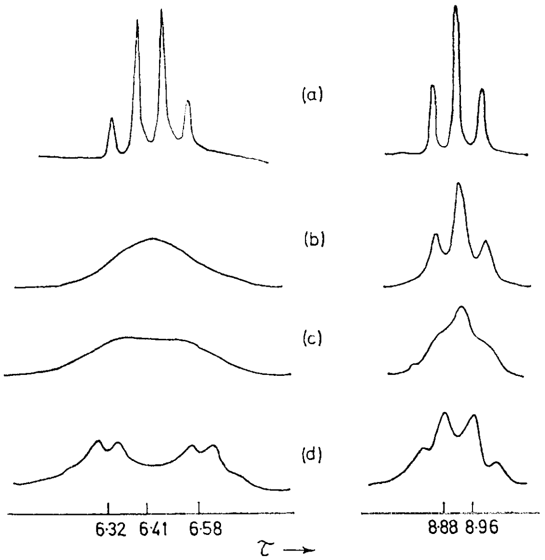


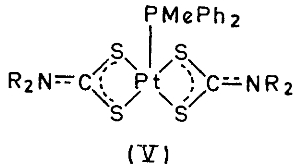
FIGURE 1 Variable temperature ^1H n.m.r. spectrum of $[Pt(S_2CNEt_2)_2PPh_3]$ in $CDCl_3$–CS_2 (for CH_2 quartet and CH_3 triplet) at (a) 301 K, (b) 243 K, (c) 233 K, and (d) 203 K

independent of temperature from room temperature to −70 °C in CS_2'. However, we find that the room-temperature n.m.r. spectrum in $CDCl_3$ or CS_2 is deceptively simple, since on cooling, the CH_2 quartet at τ 6·26 starts to broaden at *ca.* 253 K, coalesces at *ca.* 240 K, and, at 213 K, exhibits a limiting spectrum of two broadened signals (with some unresolved fine structure) centred at τ 6·37 and 6·17 (separation 20 Hz). Likewise, the single CH_3 triplet resonance (τ 8·80) starts to broaden at *ca.* 230 K and, at 213 K consists of an overlapping doublet of triplets centred at τ 8·82 and 8·76 (separation 6 Hz) * (Table 1).

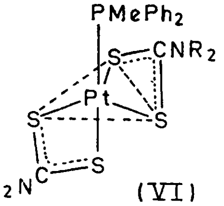
Similarly, $[Pt(S_2CNEt_2)_2PPh_3]$ (Figure 1) exhibits a single CH_2 quartet (τ 6·41) and CH_3 triplet (τ 8·89) at 301 K; at 203 K it has two broadened quartets at τ 6·58 and 6·32 (separation 26 Hz) and an overlapping doublet of triplets at τ 8·96 and 8·88 (separation 8 Hz). A study of the reaction between $Pt(S_2CNMe_2)_2$ and $PMePh_2$ (1 : 1 molar ratios) was also made. Although a pure, solid product could not be isolated by this method, solution studies were consistent with the results discussed above, *i.e.* a single methyl resonance at room temperature, broadening and splitting into two equivalent resonances at lower temperature (Table 1).

All these observations are analogous to those observed for the variable-temperature ^1H n.m.r. spectra exhibited by $[Pt\{S_2P(OEt)_2\}_2PMePh_2]$[3], $[Pt(S_2PMe_2)_2PR'_3]$ ($PR'_3 = PPh_3$, $PMePh_2$, *etc.*)[5] and the variable-temperature ^{19}F n.m.r. spectrum of $[Pd(S_2PF_2)_2P(MeC_6H_4)_3]$.[6] In all cases, the temperature dependence is completely reversible, indicating that no gross chemical change has occurred. Furthermore, the close similarity of the activation energies for the temperature-dependent reaction manifested by these 1 : 1 adducts of $^-S_2P(OEt)_2$, $^-S_2PMe_2$, and $^-S_2CNR_2$ (estimated from the coalescence temperature by standard methods)[9] (Table 2) is indicative of a common mechanism to produce averaging of the protons attached to the dithioacid ligands. This strongly suggests that for $(S\text{–}S)^- = {}^-S_2CNR_2$, the observed temperature dependence is *not* due to restricted rotation about the C–N bond as found, for example, in dithiocarbamate esters[10] (Table 2). A full line-shape analysis for all compounds of type $[M(S\text{–}S)_2(ER'_3)]$ (E = P, As, Sb) is at present in progress to ascertain accurate rate data and will be published later.

The observation of magnetically inequivalent alkyl groups at low temperature for $[Pt(S_2CNR_2)_2PR'_3]$ is inconsistent with the square pyramidal structure (V)

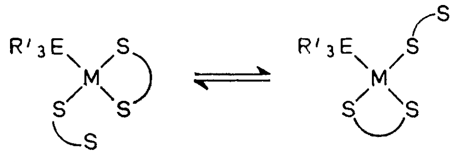


(V)



(VI)

postulated earlier for the low-temperature form,[3] since the alkyl groups in (V) will be magnetically equivalent, even allowing for restricted rotation about the C–N bond. Although the low-temperature spectrum is not incompatible with the five-co-ordinate trigonal-bipyramidal structure (VI), we suggest that a better explanation for the temperature-dependent n.m.r. spectra of *all* the compounds of formula $[M(S\text{–}S)_2(ER'_3)]$ is the presence of an equilibrium of type (1) between two n.m.r. *equivalent* four-co-ordinate complexes. At higher temperatures, rapid interchange of bidentate and unidentate



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dithio-ligands produces an averaging of the magnetic nuclei attached to the dithio-ligands whereas at lower temperatures, intramolecular rearrangement becomes

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* The discrepancy between this behaviour and that reported in ref. 3 may be due to the smaller limiting separation observable on a 60 MHz instrument (3·6 Hz for the CH_3 resonance) in addition to the failure to observe the temperature dependence of the CH_2 quartet in the earlier study.

[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, in 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 223.

[10] C. E. Holloway and M. H. Gitlitz, *Canad. J. Chem.*, 1967, **45**, 2659.

TABLE 1

^1H N.m.r. data for various sulphur compounds

			τ Value [a]					
Compound	Solvent	T/K	Dithio-ligand		$CH_3(PR'_3)$ [b]	Others [c]	J_{PH} [d]	J_{PtH} [e]
			CH_3 [f]	CH_2 [g]				
$Ph_3(PhCH_2)PS_2CNEt_2$	$CDCl_3$	301	8·86(3) [h]	5·86 (2)		Ph, 2·0—3·0(10) CH_2, 4·58(1) (d) J_{CH_2-P} 14·0 [d]		
$Pt(S_2CNEt_2)_2$	$CDCl_3$	301	8·70(3)	6·40(2)				
$Pt(S_2CNEt_2)_2PPh_3$	$CDCl_3$–CS_2	301	8·89(12)	6·41(8)		Ph, 2·2—2·8(15)		
		203	8·96(6); 8·88(4)	6·58(4); 6·32(4)				
$Pt(S_2CNEt_2)_2(PMePh_2)$	$CDCl_3$	301	8·80(12)	6·26(8)			10·0	38·0
					7·72(3)	Ph, 2·2—2·6(10)		
		213	8·82(6); 8·76(6)	6·37(4); 6·17(4)				
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	$CDCl_3$	301	8·80(6)	6·26[4] [i] 6·09	8·16(3) (s) (br)			
						Ph, 2·4—2·6(10)		
		213	8·80(6)	6·37(2); 5·77(2)	8·09(3)		9·0 [j]	34·0
$Pt(S_2CNMe_2)_2(PMePh_2)$	$CDCl_3$–CS_2	301	6·64(12) (s)				10·7	35·0
					7·69(3)	Ph, 2·6(10)		
		193	6·81(6) (s); 6·46(6) (s)					
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	$CDCl_3$	301	6·71 (s) [6] [i] 6·53 (s)		8·30(3) (s)			
						Ph, 2·6(10)		
		213	6·65(3) (s); 6·39(3) (s)		8·10(3)		9·5 [j]	35·0
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl,H_2O$	$CDCl_3$	301	8·78(3)	6·40(2)		Ph, 2·6(15) H_2O, 7·8(1) [k]		
$[Pt(S_2CNEt_2)(PPh_3)_2]PF_6$	$CDCl_3$	301	8·75(3)	6·42(2)		Ph, 2·6(15)		
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	$CDCl_3$	301	8·94(3)	6·68(2)		Ph, 2·5—3·2(25)		
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$	$CDCl_3$	301	8·73(3)	6·36(2)	8·06(3)	Ph, 2·6(10) H_2O, 7·20(1) [k]	10·0 [j]	34·0
		253	8·73(3)	6·36(2)	8·06(3)	H_2O, 7·00(1) [k]		
$[Pt(S_2CNEt_2)(PMePh_2)_2]PF_6$	$CDCl_3$	301	8·72(3)	6·38(2)	8·06(3)	Ph, 2·5(10)	10·0 [j]	35·0
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	$CDCl_3$	301	8·84(3)	6·56(2)	8·30(3)	Ph, 2·5—3·2(20)	10·0 [j]	35·0
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	$CDCl_3$	301	8·62(3)	6·22(2)	8·20(6)	Ph, 2·6(5), H_2O, 8·10(1) [k]	10·0 [j]	35·0
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]BPh_4$	$CDCl_3$	301	8·74(3)	6·40(2)	8·60(6)	Ph, 2·5—3·2(15)	10·0 [j]	34·0
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl,H_2O$	$CDCl_3$	301	6·70(3) (s)			Ph, 2·6—2·7(15) H_2O, 7·9(1) [k]		
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	$CDCl_3$	301	7·40(3) (s)			Ph, 2·6—3·2(25)		
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$	$CDCl_3$	301	6·73(3) (s)		8·10(3)	H_2O, 7·50(1) [k] Ph, 2·6(10)	10·0 [j]	36·0
		243	6·73(3) (s)		8·10(3)	H_2O, 7·10(1) [k]		
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	$CDCl_3$	301	7·25(3) (s)		8·35(3)	Ph, 2·6—3·2(25)	10·0 [j]	35·0
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	$CDCl_3$	301	6·55(3) (s)		8·10(6)	Ph, 2·5(5); H_2O, 7·70(2) [k]	10·0 [j]	35·0
$[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	$CDCl_3$	301	6·60(3) (s)		8·35(6) (s)	Ph, 2·6(5); H_2O, 7·80(2) [k]		
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	$CDCl_3$	301	7·05(3) (s)		8·65(6)	Ph, 2·6—3·2(15)	10·0 [j]	37·0
$CH_2(S_2CNEt_2)_2$	$CDCl_3$	301	8·83(6)	6·28(2); 5·96(2)		CH_2, 4·60(1) (s)		
		313	8·83(6)	6·12(4) (s)				
$CH_2(S_2CNMe_2)_2$	$CDCl_3$	301	6·66(3) (s); 6·45(3) (s)			CH_2, 4·64(1) (s)		
		313	6·57(6) (s)					
$[Pt_2\{S_2P(OEt)_2\}_2PPh_3]$	$CDCl_3$	301	8·70(12)	5·90(8) [l]		Ph, 2·6(15)		
		213	8·74(6); 8·66(6)	5·90(8) [l]				
$[Pt\{S_2(OEt_2\}_2AsPh_3]$ [m]	$CDCl_3$	301	8·69(12)	6·00(8) [l]		Ph [n]		
		223	8·71(6); 8·62(6) -	6·00(8) [l]				
$[Pt\{S_2P(OEt)_2(PPh_3)\}_2]BPh_4$	$CDCl_3$	301	8·66(3)	5·88(2) [o]		Ph, 2·5—3·2(25)		
$Pt(S_2P(O)OEt)(PPh_3)_2$	$CDCl_3$	301	8·80(3)	6·05(2) [o]		Ph, 2·5—2·8(30)		
$Pt(S_2COEt)_2PPh_3$	$CDCl_3$	301	8·62(6)	5·46(4)		Ph, 2·5(15)		
	CS_2	183	8·62(6) (s) (br)	5·46(4) (s) (br)				
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	$CDCl_3$	301	8·66(3)	5·58(2)		Ph, 2·5—3·2(50)		

s(singlet); d(doublet); br(broad).

[a] ±0·01. [b] Triplet of doublets unless otherwise stated. [c] Phenyl resonance; complex multiplet. [d] ±0·2 Hz. [e] ±0·5 Hz. [f] Triplet unless otherwise stated ($J_{CH_2CH_3}$ 7·0 Hz). [g] Quartet unless otherwise stated ($J_{CH_2CH_3}$ 7·0 Hz). [h] Numbers in parentheses indicate normalised integrated intensities. [i] Two resonances of total intensity [ ] [j] Since $H_nPP'H_n'$ type spectrum, coupling constant is $|J_{PH} + J_{PH'}|$. [k] τ Value is concentration dependent. [l] Complex multiplet. [m] $Pt\{S_2P(OEt)_2\}_2$ + excess $AsPh_3$ *in situ*. [n] Not recorded since an excess of $AsPh_3$ present. [o] Overlapping doublet of quartets with $J_{CH_2CH_3}$ 7·0 Hz; J_{CH_2-P} 9·4 Hz.

sufficiently slow for the ' frozen-out ' n.m.r. spectrum to be observed.*

It should be noted that for $(S-S)^- = {}^-S_2CNR_2$, the limiting low-temperature spectra are not *completely* consistent with those expected for the frozen-out structure (VII). Even assuming that rotation about the Pt–S and C–N bonds of the unidentate dithio-group is sufficiently rapid to average R^1 and R^2, R^3 and R^4 are magnetically inequivalent and three resonances of intensity ratio 1 : 1 : 2 are theoretically expected, whereas only two resonances are observed.

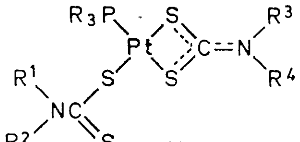
TABLE 2

Free-energy of activation and coalescence temperature (T_c/K) obtained from ^1H n.m.r. spectra for various sulphur compounds

Compound	T_c/K [a]	$\Delta G^*_{T_c}$ [b]
$Pt\{S_2P(OEt)_2\}_2PPh_3$	238 [c]	52·3
$Pt(S_2PMe_2)_2PPh_3$	263	55·5
$Pt(S_2CNEt_2)_2PPh_3$	243 [d]	50·8
	233 [c]	51·2
$Pt(S_2CNEt_2)_2PMePh_2$	238 [d]	50·2
	228 [c]	49·6
$Pt(S_2CNMe_2)_2PMePh_2$	213	43·8
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	253 [d]	51·2
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	223	46·5
$CH_2(S_2CNEt_2)_2$	233	65·7 [e]
$CH_2(S_2CNMe_2)_2$	243	64·4 [f]

[a] ±1 K. [b] ±1·0 kJ mol^{-1}. [c] Measured on CH_3 triplets. [d] Measured on CH_2 quartets. [e] *Cf.* $EtSCSNEt_2$[10] $\Delta G^*_{298\,K}$ 63·8 kJ mol^{-1}. [f] *Cf.* $MeSCSNMe_2$[10] $\Delta G^*_{298\,K}$ 61·8 kJ mol^{-1}.

However, the atoms (S and P) inducing the magnetic inequivalence in R^3 and R^4 are well removed (six bonds) from these groups, so that the separation between the R^3 and R^4 resonances may well be too small to be resolved, particularly at 213 K where machine line-broadening is also appreciable. A similar inconsistency is found for the square-planar compounds $[Ni(S_2CNR_2)Cl(PR'_3)]$[12] (VIII) (*one* R resonance at 213 K)[13] and even in compounds such as $Me_2NCOS(SiH_3)$ where the magnetic inequivalence is produced by atoms (S and O), four bonds removed from the methyl protons, the separation at 301 K of the two methyl groups is only 12 Hz.[14]



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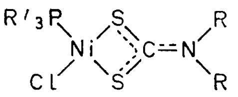

(VIII)

Although we are unable to rule out unequivocally the presence of a five-co-ordinate trigonal bipyramidal structure to explain the low-temperature ^1H n.m.r. data, there is a substantial amount of evidence which supports the interpretation given in equation (1). This is as follows. (i) There is a very close similarity of chemical shifts and coupling constants (for the methyl phosphine ^1H n.m.r. resonance at 301 K) for *all* the dithio-compounds $[Pt(S-S)_2(PMePh_2)]$,[1,2,5] which is indicative of a similar structure and the *X*-ray analysis of $[Pd(S_2PPh_2)_2PPh_3]$[7] (isomorphous with the corresponding platinum complex) shows this to be of type (III).†‡ Furthermore, for $[Pt(S_2CNEt_2)_2PMePh_2]$, the position of the low-field CH_2 quartet (τ 6·17) is intermediate between those found for ionic [τ 5·86 in $Ph_3(PhCH_2)PS_2CNEt_2$] and bidentate [τ 6·40 in $Pt(S_2CNEt_2)_2$] diethyldithiocarbamate groups, suggesting that it probably arises from a unidentate group.

(ii) For the $^-S_2PPh_2$ compounds reported earlier,[1] both room- and low-temperature isomeric forms of $[M(S_2PPh_2)_2PPh_3]$ (M = Pt, Pd) can be isolated. However, the characteristic i.r. bands of ' bidentate ' and ' unidentate ' dithiophosphinate co-ordination[1] remain unchanged which suggests that a structure of type (III) persists at all temperatures.

(iii) Reaction of either $Pt(S-S)_2$ or $[Pt(S-S)_2PR'_3]$ with an excess of tertiary phosphine gives ionic species containing the $[Pt(S-S)(PR'_3)_2]^+$ cation (see later) which is indicative of stepwise cleavage of metal–sulphur bonds by tertiary phosphine.

Therefore, all this evidence suggests (to us) that a structure of type (III) is more feasible than a five-co-ordinate formulation; however, as in all interpretations, utilising ' sporting ' methods, a degree of uncertainty naturally remains.

Platinum(II) NN-*Dialkyldithiocarbamates with an Excess of Tertiary Phosphine*.—If a suspension of $Pt(S_2CNEt_2)_2$ in acetone is treated with an excess of $PMePh_2$, a pale yellow solution is formed from which pale yellow crystals are rapidly deposited. This compound has an analysis consistent with the formula $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$; the ionic formulation is confirmed by the presence of additional i.r. bands corresponding to those found in $NaS_2CNEt_2,3H_2O$ (but not in co-ordinated dithiocarbamate groups) and the ready synthesis of $[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$. As noted earlier[1] for the ionic PR'_3 complexes of $Pt(S_2PPh_2)_2$, this complex also readily dissociates to $[Pt(S_2CNEt_2)_2(PMePh_2)]$ in the presence of nonpolar solvents. In this instance, the increased nucleophilicity of $^-S_2CNEt_2$ compared to $^-S_2PPh_2$[15] enhances this tendency. Thus, although the

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* A similar conclusion has recently been reached by Powell and Chan[11a] for these compounds on the basis of detailed variable-temperature ^1H n.m.r. studies on the related complexes [π-allyl $Pd(PMe_2Ph)$ (X–Y)] (X–Y = $^-S_2CNMe_2$, $^-S_2COMe$). In addition Davis *et al.*[11b] invoke a similar mechanism for interconversion processes in molybdenum dialkyldithiocarbamates.

† As pointed out by a referee, we have assumed that the *essential* feature of the solid-state structure (*viz.* the unidentate–bidentate co-ordination) is retained in solution, but this assumption is strongly supported by both the characteristic chemical shifts of the two CH_2 quartets for the dithiocarbamate compounds and by the characteristic i.r. bands for the dithiophosphinate compounds.

‡ *Note added in proof:* An *X*-ray structural analysis of $[Pt(S_2CNEt_2)_2PMePh_2]$ by J. M. C. Alison and R. O. Gould is now sufficiently advanced to show unequivocally that the structure in the solid state is also of type III.

[11] (*a*) J. Powell and A. W. L. Chan, *J. Organometallic Chem.*, 1972, **35**, 203; (*b*) R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 994.

[12] P. L. Maxfield, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 693.

[13] J. A. McCleverty, personal communication.

[14] C. Glidewell and D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1970, 279.

[15] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 1968, **7**, 2625.

ionic complex is insoluble in benzene, a yellow solution slowly forms with time and $[\mathrm{Pt(S_2CNEt_2)_2(PMePh_2)}]$ is isolated. Even in diethyl ether, a suspension of the ionic complex turns deep yellow (24 h) and the neutral compound is recovered.

The ^{1}H n.m.r. spectrum of the ionic compound in $\mathrm{CDCl_3}$ is of some interest (Figure 2). At room temperature, a deep yellow solution is formed and although the integration of $^-\mathrm{S_2CNEt_2}$ to $\mathrm{PMePh_2}$ protons is correct for $[\mathrm{Pt(S_2CNEt_2)(PMePh_2)_2}]\mathrm{S_2CNEt_2}$, the equilibrium lies well to the right-hand side of equation (2). This is evident since the position of the $\mathrm{CH_2}$ quartet (τ 6·26)

$$[\mathrm{Pt(S_2CNR_2)(PMePh_2)_2}]\mathrm{S_2CNR_2} \rightleftharpoons [\mathrm{Pt(S_2CNR_2)_2PMePh_2}] + \mathrm{PMePh_2} \quad (2)$$

is identical to that found for $[\mathrm{Pt(S_2CNEt_2)_2PMePh_2}]$ at room temperature and since there is a further quartet of lower intensity centred at τ 6·09, which we attribute to the ionic complex. In addition, the methyl phosphine resonance is a broad singlet at τ 8·16 {*cf.* for $[\mathrm{Pt(S_2CNEt_2)_2PMePh_2}]$, a triplet of doublets centred at τ 7·72},[2] indicative of rapid exchange between free and bound phosphine.

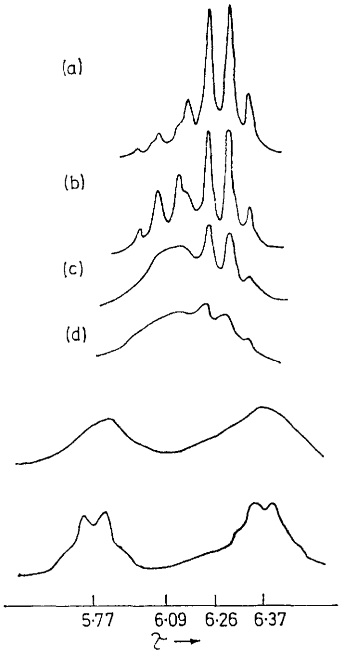

FIGURE 2 Variable-temperature ^{1}H n.m.r. spectrum of $[\mathrm{Pt(S_2CNEt_2)(PMePh_2)_2}]\mathrm{S_2CNEt_2}$ in $\mathrm{CDCl_3}$ ($\mathrm{CH_2}$ quartet) at (a) 301 K, (b) 283 K, (c) 263 K, (d) 256 K, (e) 223 K, and (f) 213 K

However, on cooling, the solution becomes progressively paler and the ^{1}H n.m.r. shows the growth of the quartet at τ 6·09, accompanied by a decrease in intensity of the quartet at τ 6·26. At 273 K, the two quartets are of comparable intensity but at 263 K, the low-field quartet starts to broaden, whilst the one at high-field remains sharp. At 253 K, a single broad resonance is observed and further lowering of temperature to 213 K produces two quartets at τ 6·37 (bidentate) and 5·77 (ionic) (separation 60 Hz). In addition, the methyl phosphine resonance sharpens such that at 213 K, a strong doublet, centred at τ 8·09 with weak ^{195}Pt satellites is observed {*cf.* $[\mathrm{Pt(S_2PPh_2)(PMePh_2)_2}]\mathrm{S_2PPh_2}$ [1] with a triplet of doublets at τ 7·99}. Raising of the temperature to 301 K shows the process is reversible, the pale yellow solution once more becoming deep yellow.

Thus, down to *ca.* 265 K, the ^{1}H n.m.r. changes signify a shift to the left-hand side of equation (2). A similar observation was made earlier [16] for $[\mathrm{Pd(S_2PPh_2)(PEt_3)_2}]\mathrm{S_2PPh_2}$ where the intensity of the 560 cm^{-1} i.r. band (characteristic of a 1 : 2 compound) increased with respect to the 540 cm^{-1} band (characteristic of a 1 : 1 compound) as the temperature was lowered. In this instance, an estimate of the equilibrium constant for (2) can be computed from the ^{1}H n.m.r. data. This gives $K_{300\,\mathrm{K}}$ 0·33 mol l^{-1}, ΔH 60 kJ mol^{-1}, ΔS 191 J K^{-1} mol^{-1}. Below 265 K, the ^{1}H n.m.r. changes are interpreted as a slowing down of the exchange between ionic and bidentate dithiocarbamate groups such that at 213 K, the spectrum corresponds to that expected for a 'frozen-out' ionic structure of type (IV) [{*cf.* $[\mathrm{Pd(S_2PF_2)(PPh_3)_2}]\mathrm{S_2PF_2}$[6]}. The absence at 213 K of a quartet at τ 6·17 shows that the equilibrium lies completely to the left-hand side of (2) at this temperature. From the coalescence temperature (*ca.* 250 K), an estimate of the activation energy for the interchange of ionic and bidentate groups can be obtained (Table 2).

Similarly, reaction of $\mathrm{Pt(S_2CNMe_2)_2}$ and an excess of $\mathrm{PMePh_2}$ in acetone gives a crystalline sample of $[\mathrm{Pt(S_2CNMe_2)(PMePh_2)_2}]\mathrm{S_2CNMe_2}$. Detailed ^{1}H n.m.r. studies in $\mathrm{CDCl_3}$ show the same phenomenon as above, namely, a methyl ($^-\mathrm{S_2CNMe_2}$) resonance (τ 6·71) at 301 K, corresponding to $[\mathrm{Pt(S_2CNMe_2)_2(PMePh_2)}]$ and when the temperature is lowered, the growth of a peak at τ 6·53 (1 : 2 complex), followed by broadening (*ca.* 220 K) and splitting into two equivalent resonances at τ 6·65 and 6·39 (213 K). Analysis of the higher-temperature region gives $K_{300\,\mathrm{K}}$ 0·22 mol l^{-1}, ΔH 69 kJ mol^{-1}, ΔS 218 JK^{-1} mol^{-1} and, from the coalescence temperature, an estimate of the activation energy for ionic–bidentate ligand exchange can be obtained (Table 2). All attempts to synthesise $[\mathrm{Pt(S_2CNEt_2)(PPh_3)_2}]\mathrm{S_2CNEt_2}$ have been unsuccessful, the only product isolated being $[\mathrm{Pt(S_2CNEt_2)_2PPh_3}]$ [*cf.* the $\mathrm{Pd(S_2PPh_2)_2}$–$\mathrm{PPh_3}$ system].[1,16]

If the reactions between $\mathrm{Pt(S_2CNEt_2)_2}$ and an excess of $\mathrm{PR'_3}$ are carried out in dichloromethane solution, the initial pale yellow solutions slowly decolourise during several hours, the qualitative rate of decolouration being $\mathrm{PMe_2Ph} \simeq \mathrm{PMePh_2} > \mathrm{PPh_3}$. This phenomenon is accompanied by a steady rise in conductivity, the value finally corresponding to that expected for a 1 : 1 electrolyte. Concentration of the solution and addition of diethyl ether gives white microcrystalline solids (A). The ^{1}H n.m.r. of these compounds are similar to those expected for $[\mathrm{Pt(S_2CNR_2)(PR'_3)_2}]\mathrm{S_2CNR_2}$ (with averaging of ionic and bidentate dithiocarbamate groups) (Table 1)

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[16] T. A. Stephenson and B. D. Faithful, *J. Chem. Soc.* (*A*), 1970, 1504.

except that integration of all these compounds shows that there are insufficient dithiocarbamate protons for this formulation. In fact, the ^{1}H n.m.r. spectra are consistent with the formulation $[Pt(S_2CNEt_2)(PR'_3)_2]X$ (where X is an anion *not* containing protons), except for the presence of an additional weak resonance in the region τ 6—8. The position of this resonance depends on solvent, solute concentration, and temperature; lowering the temperature or increasing the concentration or the solvent polarity shifts the peak to lower field, phenomena indicative of the presence of a hydrogen-bonded species. The dithiocarbamate ethyl resonance is temperature independent and has a chemical shift compatible with bidentate co-ordination. We suggest that the species arising from prolonged reaction of $Pt(S_2CNEt_2)_2$ and an excess of PR'_3 in dichloromethane are the compounds $[Pt(S_2CNEt_2)(PR'_3)_2]Cl{\cdot}H_2O$ (A); we have amassed considerable evidence to support this rather surprising conclusion.

The solid (A) reacts with $NaBPh_4$ or NH_4PF_6 in acetone–methanol solution to give the compounds $[Pt(S_2CNEt_2)(PR'_3)_2]Y$ ($Y = BPh_4^-$, PF_6^-) which have been fully characterised by ^{1}H n.m.r., analyses, and conductivity measurements (Tables **1**, **4**, and **3** respectively). An interesting feature of the ^{1}H n.m.r. of these compounds is the upfield shift (*ca.* 0·2 p.p.m.) of both $^-S_2CNEt_2$ and PR'_3 resonances in the BPh_4^-, compared to the PF_6^- and Cl^- compounds. Similar observations have been made for the $[Pt(S_2PMe_2)(PR'_3)_2]Y$ series [5] and we suggest that this is a consequence of a ring-current effect in the BPh_4^- complex which is, of course, absent in the other compounds. Evidence for a water molecule is based on the appearance of very weak OH stretches and bends in the mull i.r. spectra of compounds (A), the presence of oxygen (established by direct analysis and ESCA measurements *), and the similarity of the position of the hydrogen-bonded resonance to that recently reported for $[Co(CO)_2(PPh_3)_2(H_2O)Cl]$ (τ 7·4).[17] We suggest that the water molecule is hydrogen-bonded to the cation since addition of chloride ion produces no change in its resonance position. The presence of chloride ion is confirmed by direct analysis, ESCA * measurements, and the fact that after treating (A) with a chloride anion-exchange resin for several days, the ^{1}H n.m.r., i.r. spectra, and m.p. are unchanged.

The chloride ion can only arise, of course, from the dichloromethane used in this reaction. A careful examination of the ethereal filtrate results in the isolation of an organothio-compound, shown by elemental analysis, mass, and ^{1}H n.m.r. spectroscopy to be $CH_2(S_2CNEt_2)_2$ (B). This compound has been recently prepared in high yield by refluxing sodium diethyldithiocarbamate with anhydrous dichloromethane.[18] We find that, unless both solvent and sodium salt are scrupulously dried, only very small amounts of (B) can be isolated. However, a more convenient method of preparation is by shaking a mixture of $NaS_2CNEt_2 3H_2O$, CH_2Cl_2 (solvent grade), and any tertiary phosphine for 12 h. The reason why the addition of PR'_3 facilitates the formation of (B) is not at present clear. The ^{1}H n.m.r. spectrum of (B) is of interest in that at room temperature there are two CH_2 quartets. At a higher temperature these coalesce and the estimated free energy of activation for the barrier to free rotation about the C–N bond compares favourably with the value obtained earlier [10] for $EtSCSNEt_2$ (Table 2). Rather surprisingly, this temperature dependence of (B) was not noted in the original preparation.[18]

TABLE 3

Equivalent conductivities (298 K) in CH_2Cl_2 of some platinum dithio-compounds containing tertiary phosphines

Compound	Conc. (10^{-4}M)	Λ [a]
Ph_4AsCl,HCl	9·8	55·3
Bu_4NClO_4	10·1	22·7
	3·1	32·1
$Pt(S_2CNMe_2)_2$	9·2	3·0
$Pt(S_2CNEt_2)_2$	9·4	0·2
$Pt(S_2CNEt_2)_2PPh_3$	16·5	0·7
$Pt(S_2CNEt_2)_2PMePh_2$	17·3	4·3
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl,H_2O$	12·5	34·2
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	9·0	40·9
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$	11·2	36·6
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	2·4	50·1
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	14·7	38·6
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	8·8	43·8
$[Pt(S_2CNMe_2)(PEtPh_2)_2]BPh_4$	0·4	36·4
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl,H_2O$	6·9	57·5
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	2·5	51·6
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$	6·4	57·5
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	10·2	42·2
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	7·9	50·1
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]BPh_4$	5·9	42·7
$[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$	9·4	27·7
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	10·2	21·6
$Pt(S_2P\{OEt\}_2)_2$ + excess PPh_3	10·0	31·0

[a] In Ω^{-1} cm^2 mol^{-1}.

The mechanism of formation of (A) is most likely *via* prior formation of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$. Support for this hypothesis comes from a study of the behaviour of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ in CH_2Cl_2. The initial deep yellow solution, containing a mixture of 1 : 2, 1 : 1 compounds, and free $PMePh_2$, slowly decolourises, a change accompanied by a steady rise in conductivity (Table 5). Removal of the solvent and addition of diethyl ether gives a precipitate of $[Pt(S_2CNEt_2)(PMePh_2)_2]ClH_2O$ and the ethereal filtrate contains $CH_2(S_2CNEt_2)_2$. Similarly, in $CHCl_3$ (plus ethanol stabiliser) the solution also decolourises and (A) is formed. In this instance, the nature of the organic side-products has not been investigated. This is to be contrasted with the behaviour of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ in ethanol-free $CHCl_3$ and $CDCl_3$ (see earlier), where only nucleophilic attack of $^-S_2CNEt_2$ on the platinum ion occurs. At this juncture, it is not obvious (to us) why ethanol has such a profound effect on the course of the reaction.

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* We thank Dr. M. Barber and Mr. P. Swift of A.E.I. Scientific Apparatus Ltd. for these measurements.

[17] J. A. Bowden and R. Colton, *Austral. J. Chem.*, 1968, **21**, 891.

[18] P. R. Heckley, D. G. Holah, A. N. Hughes, and F. Leh, *Canad. J. Chem.*, 1970, **48**, 3827.

Finally, prolonged reaction of $Pt(S_2CNMe_2)_2$ and an excess of PR'_3 in CH_2Cl_2, followed by precipitation with diethyl ether gives a mixture of $[Pt(S_2CNMe_2)(PR'_3)_2]Cl,H_2O$ and $CH_2(S_2CNMe_2)_2$. The latter, which can be extracted with benzene, is best prepared by shaking a mixture of NaS_2CNMe_2, CH_2Cl_2, and a tertiary phosphine (PPh_3, $PMePh_2$, and PMe_2Ph were successfully used). Without the phosphine, the only product is tetramethylthiuram disulphide. Again, the room-temperature ^1H n.m.r. shows two CH_3 resonances, which coalesce at a higher temperature (Table 2). Similarly $Pd(S_2CNMe_2)_2$ and an excess of PMe_2Ph in CH_2Cl_2 give $[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl2H_2O$.

TABLE 4

Analytical data for some platinum(II) dithio-compounds

Compound	M.p. (°C)	Found (%) C	H	N	Others	Required (%) C	H	N	Others
$Pt(S_2CNEt_2)_2PPh_3$	150—152	44·9	4·6	4·0		44·6	4·6	3·7	
$Pt(S_2CNEt_2)_2PMePh_2$	163—165	40·2	4·7	4·4		39·9	4·8	4·1	
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	135—138	44·6	4·3	3·4		46·0	4·6	3·3	
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	132—133	48·5	5·2	3·5	S, 14·2	48·5	5·2	3·2	S, 14·4
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl,H_2O$	196—197	51·8	4·2	2·4		52·4	4·3	1·6	
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	223—226	65·7	4·9	1·3		65·3	4·8	1·2	
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$	120—124	45·3	4·3	2·3	Cl, 4·4	45·3	4·4	1·8	Cl, 4·6
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	198—203	61·5	5·0	1·5		61·5	5·0	1·4	
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	109—111	34·7	4·6	2·5	Cl, 5·7	35·4	4·6	2·2	Cl, 5·5
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	144—148	57·3	5·3	1·9		56·7	5·3	1·5	
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl,H_2O$	174—175	53·1	4·4	1·7		53·4	4·6	1·5	
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	94—97	66·2	5·1	1·4		65·8	5·1	1·2	
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$	210—212	47·6	4·5	1·6	Cl, 4·5 [a]	46·8	4·5	1·8	Cl, 4·5 [a]
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	169—171	62·4	5·2	1·3		62·2	5·3	1·3	
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	99—100	38·9	5·2	2·2	Cl, 5·3	37·5	5·1	2·1	Cl, 5·3
$Pt\{S_2P(OEt)_2\}_2PPh_3$	97—101	38·1	4·2			37·7	4·2		
$Pt(S_2P(O)OEt)(PPh_3)_2$	227—230	51·2	4·0			52·1	4·0		
$[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$	84—86	61·9	4·8			62·1	5·0		
$Pt(S_2COEt)_2PPh_3$	164—169	42·5	3·4			41·4	3·6		
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	86—90	65·4	5·0			65·2	4·8		

[a] Found, O, 1·1. Required, 2·0%.

^1H N.m.r. for all these compounds are given in Table 1, conductivities in Tables 3 and 5, and some analyses in Table 4.

TABLE 5

Variation of equivalent conductivity with time for some platinum(II) dithio-compounds

$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ ($7{\cdot}1{\cdot}10^{-4}$M) in CH_2Cl_2

Time (min)	0	1·0	3·0	5·0	15·0	30·0	∞ [a]
Λ [b]	10·4 [c]	13·5	22·3	27·1	36·9	41·8	50·1 [d]

$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ ($10{\cdot}7{\cdot}10^{-4}$M) in CH_2Cl_2

Time (min)	0	15·0	∞ [a]
Λ [b]	16·4 [c]	42·2 [d]	45·0

$Pt(S_2COEt)_2$($10{\cdot}10^{-4}$M) + excess PPh_3 in CH_2Cl_2

Time (min)	0	0·25	0·5	1·0	3·0	15·0
Λ [b]	15·7	13·7	13·2	12·5	9·2	7·0

$Pt(S_2COEt)_2$ ($30{\cdot}0{\cdot}10^{-4}$M) + excess PPh_3 in CH_3NO_2

Time (min)	0	3·0	6·0	10·0	26·0	35·0	60
Λ [b]	90	80	71	61	50	33	19

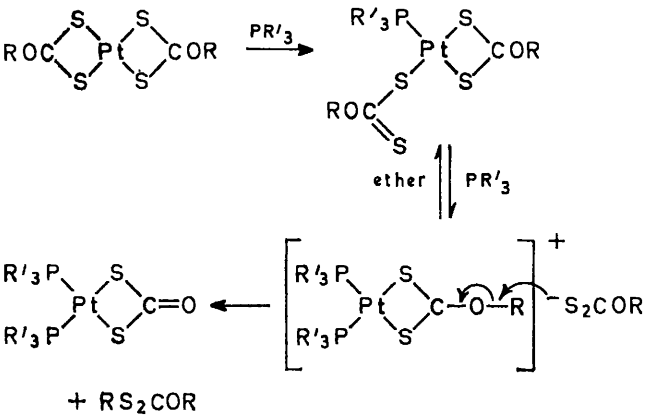
[a] 24 Hours. [b] In Ω^{-1} cm^2 mol^{-1}. [c] Yellow solution of $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$, $Pt(S_2CNR_2)_2(PMePh_2)$, and $PMePh_2$. [d] Decolourised solution containing $[Pt(S_2CNR)_2(PMePh_2)_2]Cl,H_2O$ and $CH_2(S_2CNR_2)_2$.

Xanthates and Dithiophosphates.—Reaction of $Pt(S_2P\{OEt\}_2)_2$ or $Pt(S_2COEt)_2$ with $PMePh_2$ (1 : 1 molar ratio) gives the compounds $[Pt(S–S)_2PMePh_2]$, originally formulated as five-co-ordinate species.[2,3] We suggest that these should be reformulated as four-co-ordinate compounds of type (III) on the basis of the detailed arguments given above for the related dithiocarbamate complexes. For comparison, we have made the triphenylphosphine and triphenylarsine analogues of these compounds and variable-temperature ^1H n.m.r. studies for $^-S_2P\{OEt\}_2$ parallel those reported earlier for the $PMePh_2$ derivative [3] (Tables 1 and 2). For $[Pt(S_2COEt)_2PPh_3]$ in CS_2, coalescence of the CH_3 triplet occurs at 188 K, but even at 173 K, the limiting spectrum has not been reached.

The reaction of either $M(S–S)_2$ or $[M(S–S)_2PR'_3]$ [M = Pt, Pd; $(S–S)^- = {}^-S_2COEt$, $^-S_2COCH_2Ph$, $^-S_2P(OEt)_2$] with an excess of PR'_3 is of considerable interest. Fackler and Seidel [4] have studied the former in some detail and have convincingly demonstrated that the final products are the novel compounds $[(R'_3P)_2MS_2CO]$ (I) and $[(R'_3P)_2PdS_2P(O)OEt]$ (II) respectively and that for the xanthate reaction, xanthate esters are also formed. At that time, neither the detailed mechanism nor the role played by tertiary phosphines in these rearrangement reactions were understood. In this final section, we would therefore like to present evidence which rationalises these rearrangement reactions within the context of the overall mechanistic framework developed in this paper and in earlier work [1,6] for the reaction of platnum and palladium dithioacid complexes with tertiary phosphines.

We suggest that the reaction of platinum (or palladium) xanthates with PR'_3 is as given by the Scheme below, namely stepwise cleavage of metal–sulphur bonds to give the ionic 1 : 2 complex, followed by nucleophilic attack of the xanthate anion on the alkoxy-group of the co-ordinated xanthate to give the neutral dithiocarbonate complex and a xanthate ester. A similar scheme involving the ionic intermediate $[M(S_2P\{OEt'\}_2)(PR'_3)_2]$-

$(S_2P\{OEt\}_2)$ would explain the formation of $[(R'_3P)_2MS_2P(O)(OEt)]$. This mechanism accounts for all the experimental observations made by Fackler and Seidel.[4] For example, the observation that platinum compounds undergo the rearrangement more readily than palladium and that carbon disulphide inhibits the reaction relative to chloroform is readily explicable in terms of the tendency of platinum to form the ionic 1 : 2 adducts more easily than palladium (*cf.* earlier S_2PPh_2 studies [1]) and the requirement of a fairly polar solvent to promote both the formation and stabilisation of the ionic intermediate. The fact that the ethyl group is eliminated less readily than the benzyl group is consistent with the greater stability of the benzylcarbonium ion generated in the transition state.



SCHEME Proposed mechanism for reaction of $[Pt(S_2COR)_2]$ [R = Et, $PhCH_2$) with an excess of PR'_3

However, it is also possible to give more *direct* experimental proof for such a reaction scheme. On reaction of $Pt(S_2COEt)_2$ and an excess of PPh_3 in CH_2Cl_2, immediate decolouration, accompanied by a rapid increase in conductivity occurs (with a maximum value corresponding to *ca.* two-thirds of that expected for a 1 : 1 electrolyte). This is followed by a steady decrease and the isolation of (I) (Table 5). In nitromethane, the maximum value corresponds closely to that expected for a 1 : 1 electrolyte but again the readings decrease steadily with time (Table 5) and attempts to isolate the ionic species have been unsuccessful. For example, addition of an excess of light petroleum (b.p. 40—60 °C) within 20 s of mixing, give a precipitate of $[Pt(S_2COEt)_2PPh_3]$ together with a small amount of $[(PPh_3)_2PtS_2CO]$. This clearly demonstrates that both nucleophilic attack of $^-S_2COEt$ on a platinum–phosphorus bond and on a co-ordinated alkoxy-group are ready reactions. Presumably, lowering the polarity of the solution by addition of light petroleum facilitates attack on the metal. Although the ionic intermediate with xanthate as counter anion is too labile to be isolated, addition of $NaBPh_4$ to an acetone–methanol solution of $Pt(S_2COEt)_2$ and an excess of PPh_3 (within 30 s of mixing) gives a precipitate of $[Pt(S_2COEt)(PPh_3)_2]BPh_4$, which has been fully characterised by ^1H n.m.r., analysis, and conductivity measurements (Tables 1, 3, and 4).

Similarly, reaction of $Pt\{S_2P(OEt)_2\}_2$ with an excess of PPh_3 in CH_2Cl_2 produces rapid decolouration and the conductivity of the final solution corresponds to that of a 1 : 1 electrolyte (Table 3). Although in this instance, the conductivity readings are quite steady with time, all attempts to isolate the ionic species either by rapid removal of solvent or precipitation with diethyl ether have given only the rearranged product $[(PPh_3)_2PtS_2P(O)OEt)]$ together, in the latter case, with some $[Pt(S_2P\{OEt\}_2)_2PPh_3]$. However, it is possible to isolate and characterise $[Pt(S_2P\{OEt\}_2)(PPh_3)_2]BPh_4$ (Tables 1, 3, and 4) by addition of an excess of $NaBPh_4$ to an acetone–methanol mixture of the same reactants. It should be noted that for xanthate and dithiophosphate, there is no evidence here, or elsewhere,[18] for side-reactions with chlorinated solvents.

Conclusion.—Reaction of platinum (and palladium) dithioacid compounds with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate adducts of type (III) and (IV). For $(S\text{-}S)^- = {}^-S_2PR_2$ (R = Me, Et, Ph, and probably F), the ionic 1 : 2 compounds readily revert to the 1 : 1 compounds in nonpolar solvents by means of nucleophilic attack by $^-S_2PR_2$ on the metal. Similar processes occur for $^-S_2P(OEt)_2$, ^-S_2COR, and $^-S_2CNR_2$ but, in addition, competing nucleophilic attacks on a co-ordinated alkoxy-group occur with the first two anions and on chlorinated solvents (catalysed by free PR'_3) for the latter anion.

Although we have not investigated the dithiocarboxylate adducts reported earlier [2,3] the very recent brief mention of ' essentially planar PtS_3P co-ordination for $[Pt(S_2CC_6H_4\text{-}iPr)_2PPh_3]$ with the dangling sulphur atom 3·58 Å from the platinum(II) ion ' [19] [*cf.* in $Pd(S_2PPh_2)_2PPh_3]$ >3·5 Å away] [7] suggests these compounds also conform to the general pattern.

EXPERIMENTAL

Microanalyses were by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Analytical data for many of the new compounds are given in Table 4. I.r. spectra were recorded in the region 4000—200 cm^{-1} on a Perkin-Elmer 225 Grating Spectrometer, using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. ^1H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Mass spectra were measured on an A.E.I. MS9 mass spectrometer and conductivity measurements on a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Materials.—Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine, sodium diethyldithiocarbamate (B.D.H.); sodium dimethyldithiocarbamate (Ralph Emanuel). The other tertiary phosphines were prepared by standard literature methods.

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[19] D. R. Swift, Ph.D. Thesis, Case Western Reserve University 1970, cited in J. P. Fackler, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 1009.

NN-Dialkyldithiocarbamate Complexes.—*Bis*(NN-*dimethyldithiocarbamate*)*platinum*(II). Potassium tetrachloroplatinate(II) in a minimum volume of hot water was mixed with an ethanolic solution of an excess of sodium *NN*-dimethyldithiocarbamate and shaken for 24 h. The yellow product was washed with water and ethanol and air-dried, m.p. 305—308° (Found: C, 16·8; H, 2·9; N, 6·3. Calc. for $C_6H_{12}N_2PtS_4$: C, 16·6; H, 2·8; N, 6·4%). *Bis*(NN-*diethyldithiocarbamate*)*platinum*(II) [20] (m.p. 245—250 °C) was prepared in the same way using K_2PtCl_4 and NaS_2CNEt_2-$3H_2O$.

Bis(NN-*dimethyldithiocarbamate*)*palladium* (II).[20] Palladium(II) acetate [21] was dissolved in benzene–dichloromethane and shaken for several hours with an ethanolic solution containing an excess of $NaS_2CNMe_2,2H_2O$. The yellow precipitate was filtered off, washed with water and ethanol, and air-dried (Found: C, 20·3; H, 3·3; N, 7·5. Calc. for $C_6H_{12}N_2PdS_4$: C, 20·8; H, 3·5; N, 8·1%).

Bis(NN-*diethyldithiocarbamato*)*triphenylphosphineplatinum*(II). Bis(*NN*-diethyldithiocarbamato)platinum(II) was suspended in carbon disulphide and treated with triphenylphosphine ($<1:1$ molar ratio). An orange-yellow solution was immediately formed, together with unchanged Pt-$(S_2CNEt_2)_2$; the later was removed by filtration. Partial removal of the solvent followed by cooling (200 K) gave the yellow crystalline *product*; this was washed with diethyl ether and dried *in vacuo*. *Bis*(NN-*diethyldithiocarbamato*)*methyldiphenylphosphine platinum*(II) was prepared in the same way, using a deficiency of $PMePh_2$ under nitrogen. Preparation of the PMe_2Ph compound was complicated by the side-reaction between the phosphine and CS_2.[22] These products are soluble in chloroform, dichloromethane, carbon disulphide, and benzene; and insoluble in ethanol, acetone, and dimethyl sulphoxide.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)-*platinum*(II) NN-*Diethyldithiocarbamate*. $Pt(S_2CNEt_2)_2$ (0·90 mmol) in acetone (5 ml) was treated with an excess of methyldiphenylphosphine (1·0 ml, 4·0 mmol) to give an immediate yellow solution from which yellow crystals of the *product* rapidly separated. These were washed with light petroleum (b.p. 40—60°) and dried *in vacuo* (40 °C). (NN-*Dimethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)*platinum*(II) NN-*dimethyldithiocarbamate* was made by the same method. These compounds are very unstable, readily rearranging to form $[Pt(S_2CNR_2)_2(PMePh_2)]$ and free $PMePh_2$ on prolonged exposure to benzene, diethyl ether, or acetone. Attempts to make the corresponding triphenylphosphine and dimethylphenylphosphine ionic species were unsuccessful. The former gave only $[Pt(S_2CNEt_2)_2PPh_3]$ and the latter an intractable oil.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)-*platinum*(II) *chloride monohydrate*. Method (A). $Pt(S_2CNEt_2)_2$ in dichloromethane (dried over $MgSO_4$) was treated with a three-fold excess of $PMePh_2$ under nitrogen. The initial yellow solution slowly became colourless (*ca.* 1—2 h) and concentration *in vacuo* followed by addition of an excess of diethyl ether gave a white microcrystalline precipitate of the *product*. This was washed with diethyl ether and dried *in vacuo* (40 °C).

Method (B). The same compound was also made by prolonged exposure of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ to dichloromethane. The initial deep yellow solution slowly became colourless (*ca.* 2 h) and concentration of the solution followed by addition of an excess of diethyl ether gave the *product*. In addition, solvent removal from the ethereal filtrates in methods (A) or (B) gave an oil which, on trituration with light petroleum (b.p. 60—80°), gave a white crystalline *solid* characterised as *methylene bis*(NN-*diethyldithiocarbamate*), m.p. 70—71 °C [Found: C, 42·6; H, 7·2; N, 9·0. Calc. for $C_{11}H_{22}N_2S_4$: C, 42·6; H, 7·1; N, 9·0%]. Another method of preparation is to shake a mixture of $NaS_2CNEt_23H_2O$, dichloromethane (not scrupulously dried), and a tertiary phosphine (PPh_3, $PMePh_2$, or PMe_2Ph) for 24 h. Solvent removal and trituration of the resulting oil with light petroleum (b.p. 60—80°) gave the *product* characterised by m.p. and mass [18] and ^1H n.m.r. spectroscopy. The same compound was also formed (but in lower yield) when the reaction was carried out in the absence of PR'_3. Complexes $[Pt(S_2CNEt_2)(PR'_3)_2]Cl,H_2O$ ($PR'_3 = PPh_3$, $PMePh_2$) were also made by the procedure outlined in method (A), together with some $CH_2(S_2CNEt_2)_2$.

(NN-*Dimethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)*platinum*(II) *chloride monohydrate*. Method A. The method used was exactly as for the preparation of $[Pt(S_2CNEt_2)(PMePh_2)_2]ClH_2O$, using a suspension of $Pt(S_2CNMe_2)_2$ in dichloromethane and a three-fold excess of $PMePh_2$. Precipitation with either diethyl ether or light petroleum (b.p. 60—80 °C) gave a mixture of $[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$ and $CH_2(S_2CNMe_2)_2$. The latter was removed by careful washing with benzene, and the remaining crystalline *product* was washed with diethyl ether and dried *in vacuo* (40 °C). From the benzene washings, *methylenebis*(NN-*dimethyldithiocarbamate*) was isolated (m.p. 93—96°) [Found: C, 33·7; H, 5·3; N, 10·9. $C_7H_{14}N_2S_4$ requires C, 33·1; H, 5·1; N, 11·0%]. The compound was also made by shaking a mixture of NaS_2CNMe_2, CH_2Cl_2, and tertiary phosphine (PPh_3, $PMePh_2$, or PMe_2Ph); mass spectrum: 254 $[CH_2(S_2CNMe_2)_2{}^+]$, 166 $[Me_2NCS_2CH_2S^+]$, and 88 $[Me_2NCS^+]$ (*cf.* ref. 18).

In the absence of tertiary phosphine, only tetramethylthiuram disulphide (Found: C, 31·3; H, 5·2; N, 11·9. Calc. for $C_6H_{12}N_2S_4$: C, 30·0; H, 5·0; N, 11·7%) and NaS_2CNMe_2 were detected.

Method (B). From $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ dissolved in CH_2Cl_2, the deep yellow solution slowly becoming colourless. Precipitation with diethyl ether and extraction of $CH_2(S_2CNMe_2)_2$ with benzene gave the white *product*.

$[Pt(S_2CNMe_2)(PR'_3)_2]Cl,H_2O$ ($PR'_3 = PPh_3$, PMe_2Ph, $PEtPh_2$) and $[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$ were also made by the procedure outlined in method (A), together with some $CH_2(S_2CNMe_2)_2$.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)*platinum*(II) *tetraphenylborate*. $[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$ was dissolved in methanol and treated with a concentrated acetone solution of $NaBPh_4$. The white precipitate of the *product* was washed with water and light petroleum (b.p. 60—80 °C) and dried *in vacuo* (40 °C). The same compound was also obtained by reaction between $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ and $NaBPh_4$ in ethanol.

Similarly, the complexes $[Pt(S_2CNR_2)(PR'_3)_2]BPh_4$ (R = Me, Et; $PR'_3 = PPh_3$, PMe_2Ph, $PEtPh_2$) were prepared from $[Pt(S_2CNR_2)(PR'_3)_2]Cl,H_2O$ and an excess of $NaBPh_4$.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)-*platinum*(II) *hexafluorophosphate*. $[Pt(S_2CNEt_2)(PMePh_2)_2]$-

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[20] C. K. Jorgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571.

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

[22] See L. Maier in *Progr. Inorg. Chem.*, 1963, **5**, 129.

Cl,H_2O in acetone–methanol was added to an aqueous solution of ammonium hexafluorophosphate to give a white colloidal precipitate. Partial removal of solvent *in vacuo* gave a white *powder* which was washed with water and light petroleum (b.p. 60—80°) and dried *in vacuo* (40 °C). [Pt(S_2CNMe_2)($PMePh_2$)$_2$]PF_6 and [Pt(S_2CNEt_2)(PPh_3)$_2$]PF_6 were also prepared by this method.

OO′-*Diethyl Dithiophosphate Complexes*.—*Bis*(OO′-*diethyl dithiophosphate*)*platinum*(II) was prepared as described earlier (m.p. 124 °C) [20] (Found: C, 17·2; H, 3·5. Calc. for $C_8H_{20}O_4P_2PtS_4$: C, 17·0; H, 3·6%).

Bis(OO′-*diethyl dithiophosphate*)(*triphenylphosphine*)*platinum*(II). Pt[$S_2P(OEt)_2$]$_2$ was shaken with triphenylphosphine (1 : 1 molar ratio) in dichloromethane to give a lemon-yellow solution. Slow evaporation of the solvent in the presence of an excess of light petroleum (b.p. 40—60°) gave yellow crystals of the *product*. [Pt{$S_2P(OEt)_2$}$_2$-$AsPh_3$] was prepared *in situ* by reaction of Pt{$S_2P(OEt)_2$}$_2$ and an excess of $AsPh_3$ in $CDCl_3$.

O-*Ethyl dithiophosphatobis*(*triphenylphosphine*)*platinum*(II). Pt{$S_2P(OEt)_2$}$_2$ and PPh_3 (*ca.* 1 : 3 molar ratios) were refluxed in $CHCl_3$ for *ca.* 3 h during which time the initial yellow solution slowly became colourless. Removal of solvent and addition of diethyl ether gave a white *product*. Reaction of Pt{$S_2P(OEt)_2$}$_2$ and an excess of PPh_3 in CH_2Cl_2 rapidly gave a colourless conducting solution, presumably containing the ionic [Pt{$S_2P(OEt)_2$}(PPh_3)$_2$]$S_2P(OEt)_2$, but removal of solvent by a stream of nitrogen and washing with light petroleum (b.p. 40—60 °C) was sufficient to cause rearrangement to [(PPh_3)$_2$Pt(S_2P(O)OEt)].

(OO′-*Diethyl dithiophosphate*)*bis*(*triphenylphosphine*)*platinum*(II) *tetraphenylborate*. [Pt{$S_2P(OEt)_2$}$_2$] in methanol was treated with an excess of triphenylphosphine in a minimum volume of acetone, followed by addition of an aqueous solution of $NaBPh_4$. The white *precipitate* was well washed with water and diethyl ether and dried *in vacuo* (40 °C).

O-*Ethyl Dithiocarbonate Complexes*.—Bis(O-*ethyl dithiocarbonato*)*triphenylphosphineplatinum*(II). Pt(S_2COEt)$_2$ [23] and PPh_3 (1 : 1 molar ratio) were shaken in a minimum volume of $CHCl_3$ to give a lemon-yellow solution. Trituration with an excess of light petroleum (b.p. 40—60 °C) gave a pale yellow crystalline precipitate which was washed with diethyl ether and dried *in vacuo* (40 °C). The same product (contaminated with a small amount of [Pt(S_2CO)-(PPh_3)$_2$]) was also obtained by reaction of Pt(S_2COEt)$_2$ with an excess of PPh_3 in CH_2Cl_2 followed by immediate addition of an excess of light petroleum (b.p. 40—60 °C).

(*Dithiocarbonate*)*bis*(*triphenylphosphine*)*platinum*(II)–*chloroform*. Pt(S_2COEt)$_2$ was shaken with an excess of PPh_3 in dichloromethane to give a colourless conducting solution. Partial removal of solvent and addition of light petroleum (b.p. 60—80 °C) gave a white *product*, which was non-conducting when redissolved in CH_2Cl_2 (m.p. 256 °C) [Found: C, 49·2; H, 3·3. Calc. for $C_{38}H_{31}$-$Cl_3OP_2PtS_2$: C, 49·1; H, 3·3%].

O-*Ethyl dithiocarbonatobis*(*triphenylphosphine*)*platinum*(II) *tetraphenylborate*. Pt(S_2COEt)$_2$ in acetone–methanol was treated with an excess of PPh_3 in a minimum volume of acetone, followed immediately by addition of an aqueous solution of $NaBPh_4$. The resulting white *precipitate* was well washed with water and diethyl ether and dried *in vacuo* (40 °C).

We thank Johnson–Matthey Ltd. for loans of potassium tetrachloroplatinate(II) and palladium(II) chloride, the S.R.C. for an award (to J. M. C. A.), Professor J. I. G. Cadogan, Dr. R. O. Gould, and Dr. D. Leaver for helpful discussions, and Mrs. M. Groves and Mr. J. Miller for obtaining the variable-temperature ^1H n.m.r. spectra.

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