Metal Complexes of Sulphur Ligands. Part 12.[1] Synthesis, Characterisation, and Reactions of Palladium(II) and Platinum(II) Complexes of Type $[MX(PR'_3)(S{-}S)]$ (X = halide, $S{-}S^- = [S_2PR_2]^-$, $[S_2CNR_2]^-$, or $[S_2COR]^-$)

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Reaction of $[Pd(PR'_3)(S_2PPh_2)_2]$ ($PR'_3 = PPh_3$ or PMe_2Ph) with excess of AgX in acetone (X = Cl, Br, I, or SCN) leads to facile replacement of the unidentate $[S_2PPh_2]^-$ group by X^- to give $[PdX(PR'_3)(S_2PPh_2)]$. Similar reactions with $[Pt(PR'_3)(S{-}S)_2]$ ($S{-}S^- = [S_2PPh_2]^-$ or $[S_2CNEt_2]^-$) are not very efficient and a better general method of synthesising $[MX(PR'_3)(S{-}S)]$ complexes (M = Pd or Pt; X = Cl, Br, or I; $S{-}S^- = [S_2PMe_2]^-$, $[S_2CNEt_2]^-$, $[S_2CNPr^i_2]^-$, or $[S_2COEt]^-$) is by reaction of equimolar amounts of $[\{MX_2(PR'_3)\}_2]$ and alkali-metal dithioacid salts. The complexes $[MX(PR'_3)(S{-}S)]$ have been characterised by elemental analyses and molecular-weight, ^1H n.m.r., and i.r. measurements and some of their reactions have been investigated.

IN previous papers in this series[2] the results of the reactions of various tertiary phosphines, arsines, and stibines (L) with the square-planar $[M(S{-}S)_2]$ complexes {M = Pd or Pt; $S{-}S^- = [S_2PR_2]^-$, $[S_2COR]^-$, $[S_2CNR_2]^-$, or $[S_2P(OR)_2]^-$} have been reported. In particular, a study of the various rearrangement reactions exhibited by the products $[M(S{-}S)_2L]$ and $[M(S{-}S)L_2]Y$ (Y = $[BPh_4]^-$, Cl^-, or $[PF_6]^-$) has been described. One reaction was the conversion of $[Pd(PPh_3)_2(S_2PR_2)][BPh_4]$ (R = Me or Ph) into $[PdX(PPh_3)(S_2PR_2)]$ when dissolved in either CH_2X_2 or CHX_2 (X = Cl or Br).[2] Unfortunately, this particular rearrangement was confined to complexes containing a combination of Pd, PPh_3, $[S_2PR_2]^-$, and $[BPh_4]^-$ and thus does not provide a general method of synthesising the series $[MX(PR'_3)(S{-}S)]$ (X = halide).

Although $[NiX(PR'_3)(S{-}S)]$ {$S{-}S^- = [S_2CNR_2]^-$ (refs. 3—5) or $[S_2COR]^-$ (ref. 6)} complexes have recently been reported, $[PdX(PPh_3)(S_2PR_2)]$ represented the first palladium complex of this type. In this paper, we report the full results[7] of our attempts to find a general synthetic route to palladium(II) and platinum(II) complexes of this type, and also some reactions of these complexes.

RESULTS AND DISCUSSION

In contrast to the method of preparation of $[NiX(PR'_3)(S_2CNR_2)]$,[3-5] reaction of $PdCl_2$ (or $K_2[PtCl_4]$), PR'_3, and $Na[S_2CNR_2]\cdot3H_2O$ (or $Na[S_2PR_2]\cdot2H_2O$) gave only $[M(S{-}S)_2]$. However, reactions of $[Pd(PR'_3)(S_2PR_2)_2]$ with excess of AgX (X = Cl, Br, I, or SCN) in acetone readily gave high yields of the required $[PdX(PR'_3)(S_2PR_2)]$ by replacement of the unidentate $[S_2PR_2]^-$ group by X^- under mild conditions. Unfortunately, this method cannot be used to prepare the analogous $[PdX(PR'_3)(S_2CNR_2)]$ because of the inability to isolate the corresponding $[Pd(PR'_3)(S_2CNR_2)_2]$ complexes. Furthermore, the corresponding exchange reactions with $[Pt(PR'_3)(S{-}S)_2]$ ($S{-}S^- = [S_2PR_2]^-$ or $[S_2CNR_2]^-$) were very inefficient and produced only low yields of the required products $[PtX(PR'_3)(S{-}S)]$ (especially for $S{-}S^- = [S_2CNR_2]^-$) even on prolonged refluxing. Presumably, this is a reflection of the high lability of Pd–S

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[1] Part 11, M. C. Cornock, R. O. Gould, C. L. Jones, J. D. Owen, D. F. Steele, and T. A. Stephenson, preceding paper.

[2] See D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, 1973, 2124, and refs. therein.

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

[4] J. A. McCleverty and N. J. Morrison, *J.C.S. Dalton*, 1976, 541.

[5] J. P. Fackler, jun., personal communication.

[6] C. Blejean and J. L. Chenot, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3166.

[7] Preliminary communication: M. C. Cornock and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 381.

compared to Pt–S bonds and the fact that dithiocarbamates form stronger bonds to platinum than phosphinodithioates.[2]

However, an excellent general method of synthesising a wide range of these complexes is by careful reaction of the well known halide-bridged dimers $[\{MX_2(PR'_3)\}_2]$ ($M = Pd$, $X = Cl$, Br, or I, $PR'_3 = PMe_2Ph$; $M = Pt$, $X = Cl$, $PR'_3 = PMe_2Ph$ or $PMePh_2$) with various alkali-metal dithioacid salts ($[S_2PMe_2]^-$, $[S_2CNEt_2]^-$, $[S_2CNPr^i_2]^-$, or $[S_2COEt]^-$) in 1 : 2 molar ratio in acetone (Pd) or acetone–dichloromethane (Pt).* All these complexes were characterised by elemental analyses (Table 1) and i.r. and ^1H n.m.r. spectroscopy (Table 2), and in several instances the monomeric nature of the products was established by mass spectroscopy and/or osmometric molecular-weight measurements in chloroform or acetone (Table 1).

TABLE 1

Analytical data for some palladium(II) and platinum(II) dithioacid complexes

Complex	Found (%) C	H	N	*M*	Calc. (%) C	H	N	*M*
$[Pd(PPh_3)(SCN)(S_2PPh_2)]$	55.3	3.7	2.0	711[a]	55.2	3.7	2.1	675
$[PdCl(PPh_3)(S_2PPh_2)]$	54.5	4.0			55.2	3.8		
$[PdBr(PPh_3)(S_2PPh_2)]$	51.9	3.9		722[a]	51.6	3.6		697
$[PdI(PPh_3)(S_2PPh_2)]$	50.0	3.7			48.4	3.4		
$[PdI(PMe_2Ph)(S_2PPh_2)]$	39.2	3.3			38.7	3.1		
$[PdCl(PMe_2Ph)(S_2PMe_2)]$	29.7	4.2			29.7	4.2		
$[PdBr(PMe_2Ph)(S_2PMe_2)]$	26.7	3.8			26.7	3.8		
$[PdI(PMe_2Ph)(S_2PMe_2)]$	24.3	3.5		496 ± 1[b]	24.2	3.4		496
$[PdCl(PMe_2Ph)(S_2CNEt_2)]$[c]	36.4	5.0	3.3	445,[d] 428 ± 1[b]	36.5	4.9	3.3	427
$[PdBr(PMe_2Ph)(S_2CNEt_2)]$	33.2	4.3	2.9	533,[d] 473 ± 1[b]	33.1	4.4	3.0	472
$[PdI(PMe_2Ph)(S_2CNEt_2)]$[e]	30.3	4.1	2.7	521 ± 1[b]	30.2	4.1	2.7	520
$[PdCl(PMe_2Ph)(S_2CNPr^i_2)]$	39.3	5.5	2.9		39.5	5.5	3.1	
$[Pd(PMe_2Ph)(PPh_3)(S_2CNEt_2)][BPh_4]$	67.8	6.0	1.3		67.8	5.9	1.4	
$[Pd(NC_5H_5)(PMe_2Ph)(S_2CNEt_2)][BPh_4]$	63.6	5.8	3.2		63.8	5.8	3.5	
$[PdCl(PMe_2Ph)(S_2COEt)]$	33.0	4.0			33.0	4.0		
$[PtCl(PMePh_2)(S_2CNEt_2)]$[f]	37.2	4.1	2.3	703[d]	37.4	4.0	2.4	578
$[PtCl(PMe_2Ph)(S_2CNEt_2)]$	29.4	4.0	2.9	611,[d] 516 ± 1[b]	30.2	4.1	2.7	516
$[PtBr(PPh_3)(S_2PPh_2)]$	47.7	3.2			45.8	3.2		
$[Pt(PPh_3)(SCN)(S_2PPh_2)]$	49.7	3.4	1.4		48.7	3.3	1.8	
$[Pt(PMePh_2)(S_2CNEt_2)(S_2PMe_2)]$	36.0	4.5	2.2		35.9	4.3	2.1	
$[Pt(AsPh_3)(PPh_3)(S_2PMe_2)][BPh_4]$	60.0	4.5			61.6	4.6		

[a] Molecular weight measured osmometrically at 37 °C in acetone. [b] From parent-ion peak (^{106}Pd or ^{195}Pt isotope) in mass spectrum. [c] Cl, 8.2 (Calc.: 8.3%). [d] Measured osmometrically at 37 °C in chloroform. [e] I, 24.8 (Calc.: 24.5%). [f] Cl, 6.0 (Calc.: 6.1%).

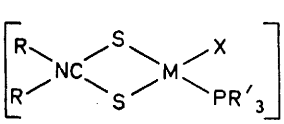
TABLE 2

Hydrogen-1 n.m.r. data in $CDCl_3$ at 301 K for some palladium(II) and platinum(II) dithioacid complexes

	δ[a]/p.p.m.			
	Dithio-ligand			
Complex	CH_3[b]	CH_2[b]	Me of phosphine[c]	Ph
$[PdCl(PMe_2Ph)(S_2PMe_2)]$	2.00 (d)[d]		1.77 (d)	7.32—7.80 (m)
$[PdCl(PMe_2Ph)(S_2CNEt_2)]$	1.24 (t), 1.22 (t)	3.72 (q), 3.62 (q)	1.80 (d)	7.38—7.90 (m)
$[PdCl(PMe_2Ph)(S_2CNPr^i_2)]$	1.45 (d), 1.33 (d)	4.60 (m)[e]	1.75 (d)	7.32—7.90 (m)
$[PdI(PMe_2Ph)(S_2CNEt_2)]$	1.25 (t), 1.22 (t)	3.70 (q), 3.59 (q)	1.95 (d)	7.35—7.80 (m)
$[PdCl(PMe_2Ph)(S_2COEt)]$	1.45 (t)	4.60 (q)	1.88 (d)	7.32—7.80 (m)
$[Pd(PMe_2Ph)(PPh_3)(S_2CNEt_2)][BPh_4]$	1.20 (t)	3.63 (q), 3.50 (q)	1.17 (d)	6.70—7.70 (m)
$[Pd(NC_5H_5)(PMe_2Ph)(S_2CNEt_2)][BPh_4]$	1.27 (t)	3.70 (q), 3.58 (q)	1.46 (d)	6.70—7.80 (m)[f]
$[PtCl(PMePh_2)(S_2CNEt_2)]$	1.26 (t), 1.19 (t)	3.64 (q), 3.47 (q)	2.16 (t of d)[g]	7.32—7.82 (m)
$[PtCl(PMe_2Ph)(S_2CNEt_2)]$	1.28 (t), 1.25 (t)	3.66 (q), 3.55 (q)	1.83 (t of d)[h]	7.32—7.86 (m)
$[Pt(PMePh_2)(S_2CNEt_2)(S_2PMe_2)]$	1.29 (t), 1.21 (t), 1.99 (d of t)[d,i]	3.68 (q), 3.50 (q)	2.29 (t of d)[j]	7.32—7.80 (m)

[a] ±0.01; d = doublet, t = triplet, q = quartet, m = multiplet. [b] $^2J(CH_3CH_2)$ 7.0 Hz. [c] $^2J(PH)$ 11.0 Hz. [d] $^2J(PH)$ 13.0 Hz. [e] Methine resonance. [f] Pyridine resonances at 8.56 (d) p.p.m. Others masked by phenyl resonances. [g] $^3J(PtH)$ 34.0 Hz. [h] $^3J(PtH)$ 35.5 Hz. [i] $^4J(PtH)$ 5.0 Hz. [j] $^3J(PtH)$ 36.0 Hz.

The i.r. spectra of these complexes show bands characteristic of bidentate dithioacid co-ordination (see Experimental section). However, full confirmation of structure (1) was obtained from the ^1H n.m.r. spectra of the dialkyldithiocarbamato-derivatives which showed two magnetically inequivalent alkyl groups at ambient



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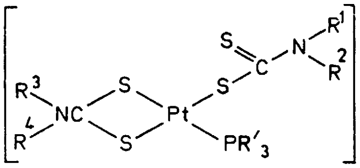

(2)

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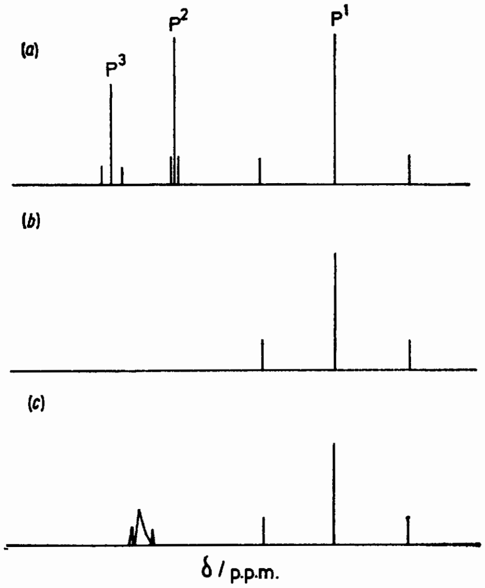
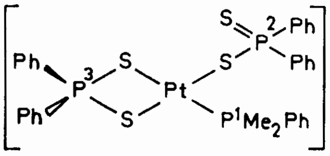
* Recently, N. Sonoda and T. Tanaka, *Inorg. Chim. Acta*, 1975, **12**, 261 have independently reported the synthesis of the related $[PdCl(PR'_3)(XYCNR_2)]$ ($R = Me$ or Et; $PR_3' = PMePh_2$, PPh_3 or PMe_2Ph; $X = S$; $Y = Se$) by reaction of $[\{PdCl_2(PR'_3)\}_2]$ with $SnMe_2Cl(XYCNR_2)$. The complexes $[PdCl(PR'_3)(S_2CNR_2)]$ ($R = Me$ or Et; $PR'_3 = PPh_3$ or $PMePh_2$) are also briefly described.

temperature. As expected for a structure of this type, the $[S_2PMe_2]^-$ complexes exhibited only one methyl resonance from the dithioacid group (Table 2). Up to 330 K (the limit of our studies) the ^1H n.m.r. spectra of the dithiocarbamato-complexes were temperature invariant. However, Fackler[5] showed that, at >390 K, magnetic equivalence of the alkyl groups was obtained and he ascribed this to the onset of facile rotation about the –CN partial double bond.

The observation of magnetically inequivalent dithiocarbamato-alkyl groups in complexes (1) at ambient temperature indicates that our earlier explanation[8] of the apparent magnetic equivalence of R^3 and R^4 in $[Pt(PR'_3)(S_2CNR_2)_2]$ (2) at low temperature [namely that 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] is clearly incorrect. Furthermore, unlike $[NiX(PR'_3)(S_2CNR_2)]$ where the inability to observe magnetically inequivalent dithiocarbamato-alkyl groups at ambient temperature is ascribed to facile phosphine[4] or halide exchange,[5] there is no evidence of facile phosphine exchange in $[Pt(PMePh_2)(S_2CNEt_2)_2]$ since in the ^1H n.m.r. spectrum between 213 and 301 K the $PMePh_2$ group exhibited a sharp triplet of doublets centred at δ 2.28 p.p.m. [with $^3J(PtH)$ 38.0 and $^2J(PH)$ 10.0 Hz].[8] This is also evident from the ^{31}P n.m.r. spectra of $[Pt(PMe_2Ph)(S_2PPh_2)_2]$ (Figure) which show that $^1J(PtP^1)$ remains practically invariant from 218 to 383 K. These spectra also provide good evidence that the solid-state structure (3) is maintained in solution with $^2J(PtP^3)$ 276.6 Hz (P^3 87.8 p.p.m.) and $^2J(PtP^2)$ 105.3 Hz (P^2 57.1 p.p.m.) at 218 K {*cf.* $[Pt(PPh_3)_2(S_2PPh_2)][PF_6]$, $^2J(PtP)$ 254.7 Hz; $S_2\mathit{P}Ph_2$, 92.1 p.p.m.}. At 383 K rapid intramolecular scrambling of uni- and bi-dentate $[S_2PPh_2]^-$ groups produced, as expected, an averaged signal at 70.5 p.p.m. with $^2J(PtP^{2,3})$ 191.0 Hz. This evidence confirming the retention of the four-co-ordinate square-planar structure in solution strongly suggests that the apparent magnetic equivalence of R^3 and R^4 in (2) at low temperature can only be produced by the fortuitously similar electronic effects of the PR'_3 and $[S_2CNR_2]^-$ groups.



Phosphorus-31 n.m.r. spectrum (proton decoupled) of $[Pt(PMe_2Ph)(S_2PPh_2)_2]$ in $CDCl_3$ at: (*a*) 218 K, P^1 −14.3 p.p.m., $^1J(PtP^1)$ 3 563.9 Hz, P^2 57.1 p.p.m., $^2J(PtP^2)$ 105.3 Hz, P^3 87.8 p.p.m., $^2J(PtP^3)$ 276.6 Hz, $^3J(P^3P^1)$ 7.0 Hz; (*b*) 302 K, P^1 −16.2 p.p.m., $^1J(PtP^1)$ 3 639.4 Hz; (*c*) 373 K, P^1 −17.0 p.p.m., $^1J(PtP^1)$ 3 679.0 Hz, average of P^2 and P^3 70.5 p.p.m., $^2J(PtP^{2,3})$ 191.0 Hz.



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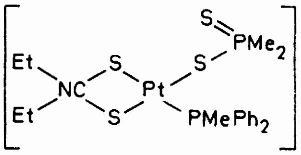

(4)

Reaction of excess of $Na[S_2CNR_2]\cdot3H_2O$ (R = Et or Pr^i) with $[\{MCl_2(PR'_3)\}_2]$ gave $[M(S_2CNR_2)_2]$,* whereas excess of $Na[S_2PMe_2]\cdot2H_2O$ gave the well known[2] $[M(PR'_3)(S_2PMe_2)_2]$. The difference in behaviour is again presumably a reflection of the higher nucleophilicity of $[S_2CNR_2]^-$ compared to $[S_2PMe_2]^-$. In contrast, reaction of $[\{MX_2(PR'_3)\}_2]$ with silver carboxylates gives the dimeric $[\{MX(O_2CR)(PR'_3)\}_2]$ (1 : 2 molar ratio)[9] and $[\{M(O_2CR)_2(PR'_3)\}_2]$ (1 : 4 molar ratio)[10] respectively.

The complexes $[MX(PR'_3)(S{-}S)]$ are useful starting materials for a number of reactions. For example, reaction of $[PtCl(PMePh_2)(S_2CNEt_2)]$ with $Na[S_2PMe_2]\cdot2H_2O$ gave the mixed dithio-complex $[Pt(PMePh_2)(S_2CNEt_2)(S_2PMe_2)]$. The i.r. spectrum of this complex had bands at 600 and 1 530 cm^{-1} indicative of unidentate $[S_2PMe_2]^-$ (ref. 2) and bidentate $[S_2CNEt_2]^-$ co-ordination[11] respectively. The ^1H n.m.r. spectrum (Table 2) confirmed structure (4) with bidentate $[S_2CNEt_2]^-$ and unidentate $[S_2PMe_2]^-$ groups. Unlike the corresponding $[Pt(PMePh_2)(S_2CNEt_2)_2]$[8] and $[Pt(PMePh_2)(S_2PMe_2)_2]$,[2] this complex is stereochemically rigid even at 330 K. In contrast, reaction of $[PtCl(PMePh_2)(S_2PMe_2)]$ with $Na[S_2CNEt_2]\cdot3H_2O$ gave $[Pt(S_2CNEt_2)_2]$, indicating the greater nucleophilicity of $[S_2CNEt_2]^-$ compared to $[S_2PMe_2]^-$. Similarly, reaction of $[NiCl(PPh_3)(S_2CNR_2)]$ and $Na[S_2CNR_2]\cdot3H_2O$ (R = Me or Et) gave only $[Ni(S_2CNR_2)_2]$.[4]

Finally, reaction of $[PdCl(PMe_2Ph)(S_2CNEt_2)]$ with

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* For $Na[S_2CNMe_2]$, the only product at all molar ratios of $[\{MCl_2(PR'_3)\}_2]$ to $[S_2CNMe_2]^-$ is $[M(S_2CNMe_2)_2]$ which can be attributed to a combination of the insolubility of $[M(S_2CNMe_2)_2]$ and the high nucleophilicity of the dithioacid anion.

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

[9] J. Powell and T. R. Jack, *Inorg. Chem.*, 1972, **11**, 1039.

[10] T. R. Jack and J. Powell, *Canad. J. Chem.*, 1975, **53**, 2558.

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

$Ag[BF_4]$ in tetrahydrofuran (thf) produces a white precipitate of AgCl and a yellow solution which probably contains the solvated cation $[Pd(thf)(PMe_2Ph)(S_2CNEt_2)]^+$. Addition of various ligands (L) to this solution followed by treatment with $Na[BPh_4]$ then gave the mixed-ligand cationic complexes $[PdL(PMe_2Ph)(S_2CNEt_2)][BPh_4]$ (L = PPh_3 or C_5H_5N) which, as expected, showed magnetically inequivalent ethyl groups in their ^1H n.m.r. spectra at ambient temperature (Table 2). The related mixed-ligand complex $[Pt(AsPh_3)(PPh_3)(S_2PMe_2)][BPh_4]$ can be synthesised by reaction of $[Pt(PPh_3)(S_2PMe_2)_2]$, $AsPh_3$, and $Na[BPh_4]$.

EXPERIMENTAL

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Conductivity measurements were made on a Portland Electronics 310 conductivity bridge. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe, and ^{31}P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4). Mass spectra were obtained on an A.E.I. MS9 spectrometer. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson, Matthey Ltd.), triphenylphosphine, sodium diethyldithiocarbamate, and sodium tetraphenylborate (B.D.H.), dimethylphenylphosphine and methyldiphenylphosphine (Maybridge Chemical Company) were obtained as indicated. The compounds $Na[S_2PMe_2]\cdot2H_2O$,[12] $[\{PdX_2(PMe_2Ph)\}_2]$ (X = Cl, Br, or I),[13] $[\{PtCl_2(PR_3)\}_2]$ (PR'_3 = $PMePh_2$ or PMe_2Ph),[14] $[Pd(PPh_3)(S_2PPh_2)_2]$,[15] $[Pd(PMe_2Ph)(S_2PPh_2)_2]$,[15] $[Pt(PPh_3)(S_2PPh_2)_2]$[16] $[Pt(PMe_2Ph)(S_2PPh_2)_2]$,[16] and $[Pt(PPh_3)(S_2PMe_2)_2]$[2] were synthesised as described earlier.

Infrared bands diagnostic of bidentate $[S_2PPh_2]^-$,[16] $[S_2PMe_2]^-$,[2] and $[S_2CNR_2]^-$ co-ordination[11] are listed for each complex.

Palladium Complexes.—*Diphenylphosphinodithioato(thiocyanato)(triphenylphosphine)palladium*(II). The complex $[\{Pd(PPh_3)(S_2PPh_2)\}_2]$ and Ag[SCN] (1 : 6 molar ratio) were shaken together in acetone for 1 h after which the solution was filtered to remove insoluble silver salts. Removal of solvent *in vacuo* then yielded a yellow *solid* which was recrystallised from benzene–light petroleum (b.p. 60—80 °C), m.p. 216—218 °C, $\nu(PS_2)$ at 603 and 570 cm^{-1}, ν(CN) at 2 100 cm^{-1}. Similarly, *bromo(diphenylphosphinodithioato)(triphenylphosphine)palladium*(II), m.p. 211—213 °C, $\nu(PS_2)$ at 600 and 570 cm^{-1}, *diphenylphosphinodithioato(iodo)(triphenylphosphine)palladium*(II), $\nu(PS_2)$ at 603 and 570 cm^{-1}, *dimethylphenylphosphine(diphenylphosphinodithioato)iodopalladium*(II), $\nu(PS_2)$ at 602 and 570 cm^{-1}, and *dimethylphenylphosphine(diphenylphosphinodithioato)thiocyanatopalladium*(II), $\nu(PS_2)$ at 603 and 572 cm^{-1} were prepared by reaction of $[Pd(PR'_3)(S_2PPh_2)_2]$ with the appropriate silver salt.

Chloro(dimethylphenylphosphine)(dimethylphosphinodithioato)palladium(II). The salt $Na[S_2PMe_2]\cdot2H_2O$ (0.03 g) was added to an acetone solution of $[\{PdCl_2(PMe_2Ph)\}_2]$ (0.10 g) (2 : 1 molar ratio) and the mixture shaken for *ca.* 2 h. The resulting cloudy yellow solution was filtered through Celite to give a bright yellow filtrate. Removal of solvent gave a yellow solid which was recrystallised from acetone–light petroleum (b.p. 60—80 °C), $\nu(PS_2)$ at 570 cm^{-1}, ν(PdCl) at 340 cm^{-1}. Similarly, *bromo(dimethylphenylphosphine)(dimethylphosphinodithioato)palladium*(II), $\nu(PS_2)$ at 570 cm^{-1}, and *dimethylphenylphosphine(dimethylphosphinodithioato)iodopalladium*(II), m.p. 238—240 °C, $\nu(PS_2)$ at 570 cm^{-1}, were prepared from $[\{PdBr_2(PMe_2Ph)\}_2]$ and $[\{PdI_2(PMe_2Ph)\}_2]$ respectively.

Chloro(diethyldithiocarbamato)(dimethylphenylphosphine)palladium(II). The complex $[\{PdCl_2(PMe_2Ph)\}_2]$ and $Na[S_2CNEt_2]\cdot3H_2O$ (1 : 2 molar ratio) were shaken in acetone for *ca.* 1 h to give a white precipitate of sodium chloride and a yellow solution. After filtering through Celite, the filtrate was evaporated to dryness to give a yellow-orange *solid* which was recrystallised from acetone–light petroleum (b.p. 60—80 °C), m.p. 162—164 °C, ν(CN) at 1 530 cm^{-1}, ν(PdCl) at 300 cm^{-1}. Similarly, *bromo(diethyldithiocarbamato)(dimethylphenylphosphine)palladium*(II), m.p. 164—166 °C, ν(CN) at 1 530 cm^{-1}, and *diethyldithiocarbamato(dimethylphenylphosphine)iodopalladium*(II), m.p. 145—147 °C, ν(CN) at 1 530 cm^{-1}, were prepared from $[\{PdBr_2(PMe_2Ph)\}_2]$ and $[\{PdI_2(PMe_2Ph)\}_2]$ respectively, and *chloro(di-isopropyldithiocarbamato)(dimethylphenylphosphine)palladium*(II), ν(CN) at 1 500 cm^{-1}, was obtained from $[\{PdCl_2(PMe_2Ph)\}_2]$ and $Na[S_2CNPr^i_2]\cdot3H_2O$. Likewise, reaction of $[\{PdCl_2(PMe_2Ph)\}_2]$ and $K[S_2COEt]$ (1 : 2 molar ratio) gave *chloro(dimethylphenylphosphine)(O-ethyldithiocarbonato)palladium*(II), m.p. 148—150 °C (decomp.), ν(CO) at 1 260 cm^{-1}, ν(PdCl) at 300 cm^{-1}.

Diethyldithiocarbamato(dimethylphenylphosphine)(triphenylphosphine)palladium(II) *tetraphenylborate*. The complex $[PdCl(PMe_2Ph)(S_2CNEt_2)]$ (0.10 g) and $Ag[BF_4]$ (0.04 g) in tetrahydrofuran were shaken together to give a white precipitate of AgCl and an orange solution. After filtering through Celite, an excess of triphenylphosphine was added to the filtrate to give a pale yellow solution. Removal of the solvent *in vacuo* produced a yellow oil. Methanol was then added to give a white solid (unchanged PPh_3) and a yellow solution which was filtered into a methanolic solution of $Na[BPh_4]$ to give the pale yellow *product*, m.p. 78—80 °C, ν(CN) at 1 525 cm^{-1}, $\Lambda(1 \times 10^{-3}$ mol $dm^{-3})$ in CH_2Cl_2 = 38.0 S cm^2 mol^{-1}.

Diethyldithiocarbamato(dimethylphenylphosphine)pyridinepalladium(II) *tetraphenylborate* was prepared as above by adding an excess of pyridine to the orange solution of $[Pd(thf)(PMe_2Ph)(S_2CNEt_2)][BF_4]$ to give a pale yellow solution. Removal of solvent followed by addition of $Na[BPh_4]$ in methanol then gave a yellow *precipitate* which was washed with water, methanol, and diethyl ether, m.p. 126—128 °C, ν(CN) at 1 520 cm^{-1}, $\Lambda(1 \times 10^{-3}$ mol $dm^{-3})$ in CH_2Cl_2 = 35.0 S cm^2 mol^{-1}.

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Platinum Complexes.—Diphenylphosphinodithioato(thiocyanato)(triphenylphosphine)platinum(II). The complex [Pt(PPh$_3$)(S$_2$PPh$_2$)$_2$] and an excess of Ag[SCN] in acetone were heated under reflux for 2 h. After filtration and removal of solvent, the pale yellow solid was dissolved in a minimum volume of benzene and reprecipitated with light petroleum (b.p. 60—80 °C) to give the pale yellow *product*, ν(PS$_2$) at 600 and 570 cm^{-1},ν(CN) at 2 100 cm^{-1}. Similarly, *bromo(diphenylphosphinodithioato)(triphenylphosphine)platinum*(II) was prepared from [Pt(PPh$_3$)(S$_2$PPh$_2$)$_2$] and AgBr, ν(PS$_2$) at 600 and 570 cm^{-1}.

Dimethylphosphinodithioato(triphenylarsine)(triphenylphosphine)platinum(II) *tetraphenylborate*. The complex [Pt(PPh$_3$)(S$_2$PMe$_2$)$_2$] was dissolved in acetone–methanol and a slight excess of AsPh$_3$ was added followed immediately by an excess of Na[BPh$_4$]. Removal of acetone then gave an off-white *precipitate* which was washed with methanol and light petroleum (b.p. 60—80 °C), ν(PS$_2$) at 574 cm^{-1}.

Chloro(diethyldithiocarbamato)(methyldiphenylphosphine)platinum(II). The salt Na[S$_2$CNEt$_2$]·3H$_2$O (0.045 g) was dissolved in acetone, added to [{PtCl$_2$(PMePh$_2$)}$_2$] (0.10 g) in dichloromethane (2 : 1 molar ratio), and the mixture shaken for 1 h. A white precipitate of sodium chloride formed together with a yellow solution. After filtration, evaporation of the solution almost to dryness followed by addition of light petroleum (b.p. 60—80 °C) gave a pale yellow *precipitate* which was washed with water, methanol, and diethyl ether, ν(CN) at 1 534 cm^{-1}, ν(PtCl) at 310 cm^{-1}. Similarly, *chloro(diethyldithiocarbamato)(dimethylphenylphosphine)platinum*(II) was prepared from [{PtCl$_2$(PMe$_2$Ph)}$_2$] and Na[S$_2$CNEt$_2$]·3H$_2$O, m.p. 163—165 °C, ν(CN) at 1530 cm^{-1}, and *chloro(dimethylphosphinodithioato)(methyldiphenylphosphine)platinum*(II) was obtained from [{PtCl$_2$(PMePh$_2$)}$_2$] and Na[S$_2$PMe$_2$]·2H$_2$O, ν(PS$_2$) at 573 cm^{-1}.

Diethyldithiocarbamato(dimethylphosphinodithioato)(methyldiphenylphosphine)platinum(II). The complex [PtCl(PMePh$_2$)(S$_2$CNEt$_2$)] (0.06 g) and Na[S$_2$PMe$_2$]·2H$_2$O (0.02 g) were shaken in acetone–dichloromethane for *ca.* 1 h. A white precipitate of NaCl was then filtered off and the yellow filtrate was evaporated almost to dryness. Addition of diethyl ether–pentane gave a yellow *solid* which was washed with water, methanol, and diethyl ether, ν(CN) at 1 530 cm^{-1}, ν(PS$_2$) at 600 cm^{-1}.

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