Thiadiazatrimethylenemethane and *N,N',P*-Triphenylphosphonothioic Diamide Complexes of Platinum(II)†

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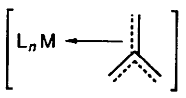
Reaction of *N,N*-diphenylthiourea with *cis*-[$PtCl_2L_2$] [L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_2Ph, $PPh_2(NEt_2)$ or L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe)] in the presence of silver(I) oxide gives the thiadiazatrimethylenemethane complexes [Pt{SC(=NPh)NPh}L_2], an X-ray study on [Pt{SC(=NPh)NPh}(PPh_3)$_2$] establishing the presence of a flat Pt–S–C–N ring. Related Pt–S–P–N ring complexes which contain a reactive nucleophilic P=NPh group are formed upon treatment of PhNHP(S)(Ph)NHPh with *cis*-[$PtCl_2L_2$] [L = PPh_3, L_2 = dppe, $Ph_2P(CH_2)_3PPh_2$ or $Ph_2P(CH_2)_4PPh_2$] and potassium hydroxide. Treatment of [Pt{SP(=NPh)(Ph)NPh}L_2] with MeI afforded an aminophosphonium salt, whilst with substrates containing either C=O or C=S functionalities new complexes of the type [Pt{SP(O)(Ph)NPh}L_2] or [Pt{SP(S)(Ph)S}L_2] were formed respectively.

The successful preparation and the interest in the reactivity of trimethylenemethane metal complexes **1**[1] has led to the investigation of other Y-shaped dianions and their complexes with transition metals. Oxygen **2**,[2] nitrogen **3**[3] and sulfur **4**[4] monosubstituted ligands have been prepared and the use of these systems in metal-mediated cycloaddition reactions has attracted a great deal of activity.[5] Herein we report the first examples of metal complexes of the thiadiazatrimethylenemethane ligand **5** and a related dianionic fragment **6**.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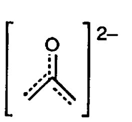
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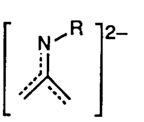
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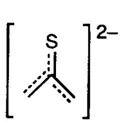
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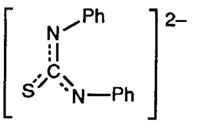
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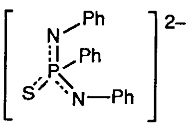
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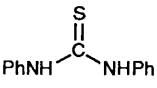
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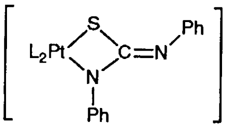

	L
8a	PPh_3
8b	$PMePh_2$
8c	PMe_2Ph
8d	PEt_2Ph
8e	$PPh_2(NEt_2)$
8f	$\frac{1}{2}$dppe

Results and Discussion

Treatment of *cis*-[$PtCl_2L_2$] [L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_2Ph, $PPh_2(NEt_2)$ or L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe)] with 1 mol equivalent of *N,N'*-diphenylthiourea **7** and an excess of silver(I) oxide in refluxing dichloromethane afforded the new complexes **8**. Complex **8a** can also be synthesised by the reaction of *cis*-[$PtCl_2(PPh_3)_2$] with 1 mol equivalent of the 1,3-dianion **5** at low temperature in tetrahydrofuran (thf), or by treatment of the same metal complex with **7** in the presence of an excess of sodium hydroxide in a refluxing mixture of dichloromethane and thf. Complexes **8** were isolated as pale yellow air-stable solids.

Previous studies on oxatrimethylenemethane metal complexes have established the existence of both η^3 and η^4 bonding modes.[6,7] The availability of a series of thiadiazatrimethylenemethane complexes afforded the opportunity to investigate the structure of these systems and accordingly a single-crystal X-ray structure determination of **8a** was carried out. Bond lengths and angles are presented in Tables 1 and 2 respectively and the molecular geometry is illustrated in Fig. 1.

The structure consists of a thiadiazatrimethylenemethane fragment bonded to bis(triphenylphosphine)platinum(II) *via* sulfur and nitrogen, so as to give the metal a distorted square-planar environment. It has also been shown that the dilithium derivative of **5** contains monomeric units effectively formulated as 'Ph$\bar{N}$–C(=NPh)$\bar{S}$' moieties.[8] A similar asymmetric bonding of an η^3-oxatrimethylenemethane fragment to a metal has been observed in the titanium complex **9**, where the preference of titanium to bond to oxygen rather than carbon is apparent.[9] The principal feature of interest in the structure of **8a** concerns the geometry of the platinacyclic ring. Studies on metallacyclobutan-3-ones have established the presence of puckered rings with a transannular M · · · C=O interaction, the systems being best described as η^3 complexes of oxatrimethylenemethane.[10] In contrast, the ring in **8a** is nearly planar, the fold angle

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Selected interatomic bond distances (Å) for [Pt{SC(=NPh)NPh}(PPh$_3$)$_2$] **8a** with estimated standard deviations (e.s.d.s) in parentheses

P(2)–Pt	2.247(1)	P(1)–Pt	2.308(1)
S–Pt	2.331(1)	N(1)–Pt	2.054(3)
C(61)–P(2)	1.839(3)	C(71)–P(2)	1.816(3)
C(81)–P(2)	1.820(2)	C(31)–P(1)	1.820(2)
C(41)–P(1)	1.832(3)	C(51)–P(1)	1.827(2)
C(1)–S	1.782(5)	C(1)–N(1)	1.348(7)
C(21)–N(1)	1.399(5)	C(1)–N(2)	1.277(6)
C(11)–N(2)	1.422(7)		

Table 2 Selected bond angles (°) for [Pt{SC(=NPh)NPh}(PPh$_3$)$_2$] **8a** with e.s.d.s in parentheses

P(2)–Pt–P(1)	97.5(0)	S–Pt–P(2)	94.6(0)
S–Pt–P(1)	167.9(0)	N(1)–Pt–P(2)	165.0(1)
N(1)–Pt–P(1)	97.4(1)	N(1)–Pt–S	70.5(1)
C(61)–P(2)–Pt	114.6(1)	C(71)–P(2)–Pt	110.8(1)
C(71)–P(2)–C(61)	104.1(1)	C(81)–P(2)–Pt	115.6(1)
C(81)–P(2)–C(61)	99.9(1)	C(81)–P(2)–C(71)	110.8(1)
C(31)–P(1)–Pt	112.8(1)	C(41)–P(1)–Pt	112.4(1)
C(41)–P(1)–C(31)	105.8(1)	C(51)–P(1)–Pt	120.5(1)
C(51)–P(1)–C(31)	103.0(1)	C(51)–P(1)–C(41)	100.8(1)
C(1)–S–Pt	80.0(2)	C(1)–N(1)–Pt	101.7(3)
C(21)–N(1)–Pt	138.1(3)	C(21)–N(1)–C(1)	117.3(3)
C(11)–N(2)–C(1)	121.7(5)	N(1)–C(1)–S	107.7(3)
N(2)–C(1)–S	128.2(5)	N(2)–C(1)–N(1)	124.1(5)

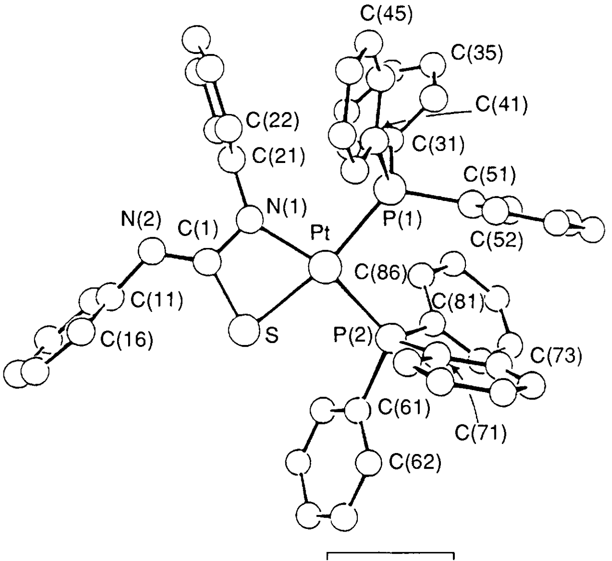
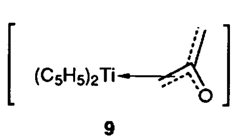


Fig. 1 Molecular structure of [Pt{SC(=NPh)NPh}(PPh$_3$)$_2$] **8a** showing the atom numbering scheme. All hydrogen atoms are omitted

between the planes N(1)–Pt–S and N(1)–C(1)–S being only 5.3(1)°. Furthermore, the transannular Pt–C(1) distance of 2.68(1) Å indicates the absence of any cross-ring metal–carbon interaction. Interestingly, the four-membered ring of 3-phenyl-2-phenylimino-1,3-thiazetidine **10** is also virtually planar.[11] The C(1)–N(2) bond [1.277(6) Å] shows considerable double-bond character, while the C–S bond is single. The phenyl group attached to N(1) is rotated out of the plane of the four-membered ring, presumably to reduce unfavourable steric interactions between this group and the *cis*-tertiary phosphine ligand. Such rotation is also seen in the thioureido systems [RhCl(C$_5$Me$_5$){PhNC[N(R)CH=NR]S}] **11** (R = *p*-MeC$_6$H$_4$) and [RhCl{PhN–C(NMe$_2$)S}(SCNMe$_2$)(PPh$_3$)] **12**, the four-membered rings of which also show little deviation from planarity.[12]



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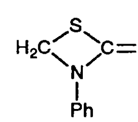

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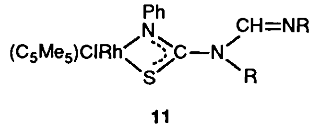

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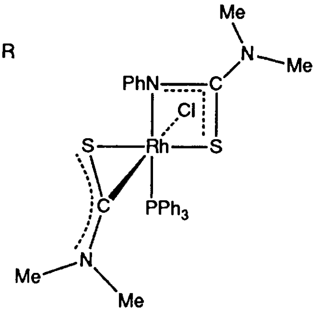

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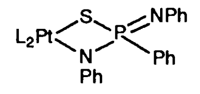
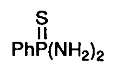


14a L = PPh$_3$
14b L$_2$ = dppe
14c L$_2$ = dppp
14d L$_2$ = dppb



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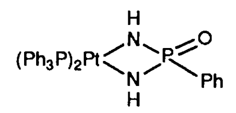

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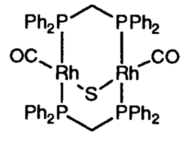

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In an attempt to prepare a related N,S-bonded four-membered ring system, the reactions of *cis*-[PtCl$_2$L$_2$] [L = PPh$_3$; L$_2$ = dppe, Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp) or Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb)] with *N*,*N*′,*P*-triphenylphosphonothioic diamide **13** in the presence of a base were investigated. The reaction of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with **13** in the presence of silver(I) oxide afforded a mixture of products. This result may be due to the oxygenating potential of this reagent which could allow it to react with a P=S or P=NPh group to form a P=O moiety, therefore complicating the reaction. Thus, in the presence of potassium hydroxide rather than silver(I) oxide, quantitative yields of the complexes **14** were obtained. In addition, treatment of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with the new dianion **6**, prepared from **13** with 2 mol equivalents of LiBu^n in thf at low temperature, also gave complex **14a**. Complexes **14** were isolated as yellow, air-stable, microcrystalline solids.

In contrast to its *N*,*N*′-diphenyl-substituted analogue, the reaction of phenylphosphonothioic diamide **15** with *cis*-[PtCl$_2$(PPh$_3$)$_2$] in refluxing dichloromethane in the presence of silver(I) oxide led to the formation of complex **16**[13] in quantitative yield. Use of potassium hydroxide in thf instead of silver(I) oxide in this reaction resulted only in the recovery of unreacted platinum starting material.

It is also interesting that both dianions **5** and **6** react with the dimeric rhodium species [{RhCl(CO)(dppm)}$_2$] (dppm = Ph$_2$PCH$_2$PPh$_2$) in thf at low temperatures to yield the sulfur-bridged system [Rh$_2$(μ-S)(CO)$_2$(dppm)$_2$] **17** in good yield. Abstraction of sulfur by transition-metal complexes has been reported, for example in the formation of [Co$_3$S(CO)$_7$(μ-R′C=NR)] **18** (R = C$_6$H$_{11}$, R = Me or Ph) from [Co$_2$(CO)$_8$] and RNHC(S)R.[14]

The room-temperature ^{31}P-{^{1}H} NMR spectra of complexes **8a**–**8f** consist of simple second-order AB spin-system patterns with corresponding platinum-195 satellites. IR spectra show a

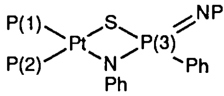
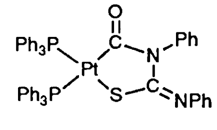


Fig. 2



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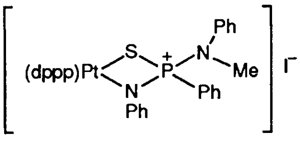

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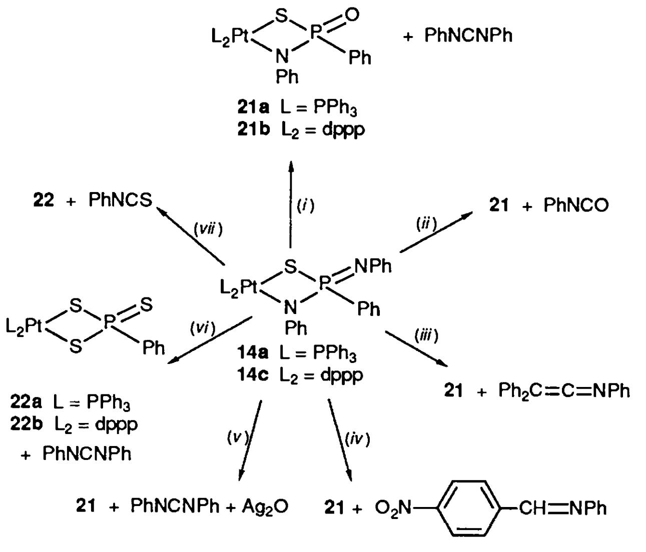
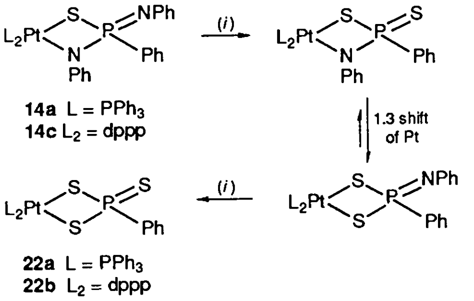
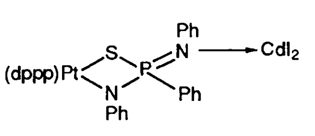


Scheme 1 *Reagents*: (*i*), PhNCO; (*ii*) CO$_2$: (*iii*) Ph$_2$C=C=O; (*iv*) *p*-O$_2$NC$_6$H$_4$CHO; (*v*) Ag$_2$CO$_3$; (*vi*) PhNCS; (*vii*) CS$_2$



Scheme 2 (*i*) CS$_2$ or PhNCS



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strong band in the range 1560–1547 cm^{-1}, attributable to a v(C=N) mode. The room-temperature ^{31}P-{^{1}H} NMR spectra of **14a**, **14c** and **14d** (complex **14b** was too insoluble) are consistent with the basic structure indicated in Fig. 2. The phosphinimine phosphorus P(3) exhibits coupling to both ^{31}P nuclei of the tertiary phosphine donor ligands and to ^{195}Pt, with ^2J[PtP(3)] in the range 181–186 Hz. The IR spectra of these complexes all show a strong band between 1310 and 1320 cm^{-1}, attributed to the stretching vibration of the P=NPh group.[15]

Preliminary studies show that the four-membered ring in complex **8a** undergoes an insertion reaction with carbon monoxide. Thus, passage of carbon monoxide through a solution of **8a** in dichloromethane at room temperature affords a ring-expansion product formulated as **19**. The complex exhibits a carbonyl stretching frequency of 1647 cm^{-1} and its ^{31}P-{^{1}H} NMR spectrum is consistent with phosphorus nuclei *trans* to sulfur and carbon. Interestingly, complex **14a** does not undergo an analogous insertion and can be recovered unchanged after treatment under the above conditions.

Organophosphinimines have been shown to exhibit nucleophilic character towards alkyl halides, C=O and C=S functionalities, electron-deficient acetylenes and Lewis acids to form a range of products.[16] The complexes **14a** and **14c** were thus treated with a range of reagents in order to compare their reactivity to that of their non-metal-containing analogues.

(*a*) *With methyl iodide.* Treatment of complex **14c** with methyl iodide in dichloromethane afforded the aminophosphonium salt **20** in good yield. In both the ^{1}H and ^{13}C-{^{1}H} NMR spectra the methyl group on nitrogen appeared as a doublet, due to coupling to P(3). In its ^{31}P-{^{1}H} NMR spectrum, P(3) was, as expected, shifted downfield by nearly 37 ppm, due to the formation of a formal positive charge on this phosphorus. The signals for the dppp phosphorus nuclei were almost unaffected by the reaction. This reaction clearly shows the greater nucleophilicity of the phosphinimine group in comparison to the platinum(II) and sulfur centres.

(*b*) *With double bonds to oxygen or sulfur.* Complexes **14a** and **14c** react with phenyl isocyanate in dichloromethane at room temperature to afford, in high yield, complexes **21a** and **21b** respectively. The reactions proceed with the concomitant formation of diphenylcarbodiimide, the presence of which was established by IR spectroscopy. Scheme 1 shows this and other reactions of complexes **14a** and **14c** with several C=O and C=S containing species to form complexes **21** and **22**. The organic side products shown were all identified by IR spectroscopy.

The metal-containing products **21a** and **21b** were identified by NMR and IR spectroscopy and elemental analysis. The ^{31}P-{^{1}H} NMR spectra showed that P(3) had been shifted downfield by over 12 ppm on formation of the phosphoryl group. The IR spectra of **21a** and **21b** showed bands due to the phosphoryl stretch at 1240 and 1250 cm^{-1} respectively.

The novel reaction with silver(I) carbonate provides an interesting source of diphenylcarbodiimide, the initially formed phenyl isocyanate, which cannot be detected, presumably reacting significantly faster than Ag$_2$CO$_3$ with **14a** or **14c**. It is noteworthy that the treatment of [PtCl$_2$(dppp)] with 1 mol equivalent of **13** and an excess of silver(I) carbonate in refluxing dichloromethane leads to complex **21b** in high yield.

The formation of the trithiophosphonate complexes **22**, from the reaction of **14a** or **14c** with either phenyl isothiocyanate or carbon disulfide, is of interest and presumably occurs *via* a 1,3-shift of platinum from nitrogen to sulfur, Scheme 2, the reaction providing a route for the replacement of both NPh groups present in the two complexes. Compounds containing a Pt–S–P(S)–S ring system have been previously reported,[17] and data for complexes **22** compare well to those of the known compounds. The formation of complexes **21** and **22** illustrates the ability of platinum to control substitution at phosphorus(V).

(*c*) *With dimethyl acetylenedicarboxylate.* The reaction of dimethyl acetylenedicarboxylate with the phosphinimines R$_3$P=NR (R = aryl) has previously been shown to afford products of the type MeO$_2$CC(=PR$_3$)–C(=NR)CO$_2$Me **23**.[18] However, although both complexes **14a** and **14c** reacted with this acetylene in dichloromethane at room temperature, no pure products could be isolated from the reaction mixture. This difference in reactivity is almost certainly due to the additional presence of both the platinum, which can form strong π complexes with this acetylene,[19] and sulfur, whose lone pairs could attack the electron-deficient sites in this reagent.

(*d*) *With cadmium*(II) *iodide.* Complex **14c** reacted with CdI$_2$ in thf to give the co-ordination compound **24**, assigned on the basis of a large downfield shift of the signal for P(3) of over 23 ppm in its ^{31}P-{^{1}H} NMR spectrum. The IR spectrum showed a shift in the frequency of the strong P=NPh band, as seen for the starting complex **14c**, although its new position could not be determined with confidence.

Experimental

Melting points were measured in air on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer, proton NMR spectra on a Varian EM390 spectrometer at 90 MHz or on a Bruker AM300 spectrometer at 300.13 MHz with $SiMe_4$ (δ 0.0) as internal reference, positive values being to high frequency (low field), in $CDCl_3$ unless otherwise stated. $^{13}C-\{^1H\}$ NMR spectra were recorded on a Bruker AM300 spectrometer at 75.47 MHz with $SiMe_4$ as internal reference, in $CDCl_3$. The phenyl carbon region has been omitted for clarity. $^{31}P-\{^1H\}$ NMR spectra were recorded in dichloromethane on a JEOL-FX60 spectrometer at 24.15 MHz, or on a JEOL-FX90 spectrometer at 36.21 MHz, with $[P(OH)_4]^+$ [20] in D_2O (δ 0.0) as external reference; *J* values in Hz.

Experiments were carried out using a dry, oxygen-free, dinitrogen atmosphere, using solvents which were dried and distilled under dinitrogen prior to use. Absolute ethanol was used as supplied. Light petroleum refers to the fraction of b.p. 40–60 °C. All compounds were recrystallised in air. The compounds $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene),[21] *cis*-$[PtCl_2\{PPh_2(NEt_2)\}_2]$,[22] $[PtCl_2(dppe)]$,[23] *cis*-$[PtCl_2(PPh_3)_2]$,[24] $[\{RhCl(CO)(dppm)\}_2]$,[25] $[Rh_2(\mu\text{-}S)(CO)_2(dppm)_2]$,[25] *N,N′,P*-triphenylphosphinothioic diamide,[26] phenylphosphonothioic diamide[27] and PEt_2Ph[28] were prepared as described in the literature.

Preparation of Platinum Thiadiazatrimethylenemethane Complexes using Silver(I) *Oxide; General Method.*—Two equivalents of tertiary phosphine, followed by 1 equivalent of *N,N′*-diphenylthiourea **7** and an excess of silver(I) oxide were added in succession to a stirred solution of $[PtCl_2(cod)]$ in dichloromethane, and the mixture refluxed for 2.5 h. The mixture was filtered through Celite and the filtrate evaporated to dryness under reduced pressure. Dissolution of the residual oil in dichloromethane (*ca.* 5 cm^3) followed by addition of light petroleum gave powdery solids which were recrystallised from dichloromethane–light petroleum and dried *in vacuo*.

(*i*) $[Pt\{SC(=NPh)NPh\}(PPh_3)_2]$ **8a**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and **7** (0.062 g, 0.27 mmol) in dichloromethane (35 cm^3) gave pale yellow *crystals* of **8a** (0.20 g, 78%) (Found: C, 61.4; H, 4.5; N, 2.8. $C_{49}H_{40}N_2P_2PtS$ requires C, 62.2; H, 4.3; N, 3.0%), m.p. >230 °C; ν(C=N)/cm^{-1} 1550vs. $^{31}P-\{^1H\}$ (36 MHz) NMR: second-order AB spin-system, δ 16.1 {d, P(2), $^1J[PtP(2)]$ 3103, $^2J[P(1)P(2)]$ 22} and 11.4 {d, P(1), $^1J[PtP(1)]$ 3261, $^2J[P(2)P(1)]$ 22}. X-Ray-quality crystals were grown slowly from dichloromethane–light petroleum, in air.

(*ii*) $[Pt\{SC(=NPh)NPh\}(PMePh_2)_2]\cdot CH_2Cl_2$ **8b**$\cdot CH_2Cl_2$. The complex $[PtCl_2(cod)]$ (0.30 g, 0.80 mmol) with methyldiphenylphosphine (0.34 g, 1.70 mmol) and **7** (0.19 g, 0.83 mmol) in dichloromethane (*ca.* 70 cm^3) gave dark yellow *crystals* of **8b**$\cdot CH_2Cl_2$ (0.39 g, 54%) (Found: C, 52.9; H, 4.3; N, 3.2. $C_{39}H_{36}N_2P_2PtS\cdot CH_2Cl_2$ requires C, 53.0; H, 4.2; N, 3.1%), m.p. 128–135 °C; ν(C=N)/cm^{-1} 1547vs. NMR: ^1H (300 MHz), δ 7.80–6.50 (m, 30 H, Ph), 5.22 (s, 2 H, CH_2Cl_2), 1.63 [d, second order, 3 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 9.96, $^3J(PtH)$ 29.7], and 1.27 [d, second order, 3 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 9.84, $^3J(PtH)$ 28.1]; $^{13}C-\{^1H\}$ (75.5 MHz), δ 148.03 (s, C=N), 15.66 (dd, second order, Me, $PMePh_2$, no *J* values discernible), and 14.25 (dd, second order, Me, $PMePh_2$, no *J* values discernible); $^{31}P-\{^1H\}$ (24 MHz), second-order AB spin system, δ 1.8 {d, P(2), $^1J[PtP(2)]$ 3090, $^2J[P(1)P(2)]$ 22} and −9.1 {d, P(1), $^1J[PtP(1)]$ 3125, $^2J[P(2)P(1)]$ 22}.

(*iii*) $[Pt\{SC(=NPh)NPh\}(PMe_2Ph)_2]\cdot 2CH_2Cl_2$ **8c**$\cdot 2CH_2Cl_2$. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with dimethylphenylphosphine (0.075 g, 0.54 mmol) and **7** (0.062 g, 0.27 mmol) in dichloromethane (35 cm^3) gave dark yellow *crystals* of **8c**$\cdot 2CH_2Cl_2$ (0.16 g, 68%) (Found: C, 42.8; H, 4.1; N, 3.3. $C_{29}H_{32}N_2P_2PtS\cdot 2CH_2Cl_2$ requires C, 42.9; H, 4.2; N, 3.2%), m.p. 190–200 °C (decomp.); ν(C=N)/cm^{-1} 1555vs. NMR: ^1H (300 MHz), δ 7.56–6.89 (m, 20 H, Ph), 5.36 (s, 4 H, CH_2Cl_2), 1.63 [d, second order, 6 H, Me, PMe_2Ph, $|^2J(PH) + {}^4J(PH)|$ 10.38, $^3J(PtH)$ 33.2], and 1.09 [d, second order, 6 H, Me, PMe_2Ph, $|^2J(PH) + {}^4J(PH)|$ 10.15, $^3J(PtH)$ 27.8]; $^{13}C-\{^1H\}$ (75.5 MHz), δ 148.28 (s, C=N), 16.04 [dd, second order, Me, PMe_2Ph, no *J* values discernible], and 14.43 [dd, second order, Me, PMe_2Ph, $|^1J(PC) + {}^3J(PC)|$ 60.38, $^2J(PtC)$ not discernible]; $^{31}P-\{^1H\}$ (24 MHz), second-order AB spin system, δ −13.8 {d, P(2), $^1J[PtP(2)]$ 3047, $^2J[P(1)P(2)]$ 24} and −24.7 {d, P(1) $^1J[PtP(1)]$ 3057, $^2J[P(2)P(1)]$ 24}.

(*iv*) $[Pt\{SC(=NPh)NPh\}(PEt_2Ph)_2]$ **8d**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with diethylphenylphosphine (0.093 g, 0.56 mmol) and **7** (0.062 g, 0.27 mmol) in dichloromethane (35 cm^3) gave pale yellow *crystals* of **8d** (0.18 g, 89%), compound not obtained analytically pure; m.p. semi-melts 142–155 °C, complete melting 210–212 °C (decomp.); ν(C=N)/cm^{-1} 1550vs. NMR: ^1H, showed some decomposition of the compound; $^{13}C-\{^1H\}$ [75.5 MHz, distortionless enhancement of polarisation transfer (DEPT)], δ 147.99 (s, C=N), 16.90–14.84 (m, CH_2, PEt_2Ph), and 7.98–7.85 (m, Me, PEt_2Ph); $^{31}P-\{^1H\}$ (24 MHz), second-order AB spin system, δ 5.8 {d, P(2), $^1J[PtP(2)]$ 3027, $^2J[P(1)P(2)]$ 24} and −5.1 {d, P(1), $^1J[PtP(1)]$ 3120, $^2J[P(2)P(1)]$ 24}.

Preparation of $[Pt\{SC(=NPh)NPh\}\{PPh_2(NEt_2)\}_2]$ **8e**.—Compound **7** (0.062 g, 0.27 mmol) and silver(I) oxide (0.38 g, 1.64 mmol) were added in succession to a stirred solution of *cis*-$[PtCl_2\{PPh_2(NEt_2)\}_2]$ (0.20 g, 0.26 mmol) in dichloromethane (70 cm^3), and the mixture refluxed for 3 h. The silver salts were filtered off on a pad of Celite to yield a dark yellow solution, which was reduced in volume to *ca.* 3 cm^3. Addition of light petroleum gave a pale yellow solid, which was recrystallised from dichloromethane–light petroleum and dried *in vacuo* to give yellow *microcrystals* of complex **8e** (0.125 g, 51%) (Found: C, 57.4; H, 5.4; N, 5.6. $C_{45}H_{50}N_4P_2PtS$ requires C, 57.7; H, 5.4; N, 6.0%), m.p. semi-melts >100 °C, complete melting 122 °C (decomp.); ν(C=N)/cm^{-1} 1552s. NMR: ^1H (300 MHz), δ 7.45–6.60 (m, 30 H, Ph), 3.25–2.85 (m, 8 H, CH_2, PPh_2NEt_2), 1.03 [t, 6 H, Me, PPh_2NEt_2, $^3J(HH)$ 6.80] and 0.85 [t, 6 H, Me, PPh_2NEt_2, $^3J(HH)$ 6.37]; $^{31}P-\{^1H\}$ (36 MHz), second-order AB spin system, δ 61.9 {d, P(2), $^1J[PtP(2)]$ 3408, $^2J[P(1)P(2)]$ 24} and 54.9 {d, P(1), $^1J[PtP(1)]$ 3572, $^2J[P(2)P(1)]$ 24}.

Preparation of $[Pt\{SC(=NPh)NPh\}(dppe)]$ **8f**.—Compound **7** (0.070 g, 0.31 mmol) and silver(I) oxide (0.42 g, 1.81 mmol) were added in succession to a stirred solution of $[PtCl_2(dppe)]$ (0.186 g, 0.28 mmol) in dichloromethane (50 cm^3), and the mixture refluxed for 2.5 h. The insoluble silver salts were removed by filtration through a pad of Celite, the filtrate being reduced in volume to *ca.* 2 cm^3 under reduced pressure. Addition of light petroleum afforded a pale yellow powdery solid, which was filtered off and washed with light petroleum and diethyl ether to give complex **8f** (0.163 g, 71%) (Found: C, 56.3; H, 4.9; N, 2.5. $C_{39}H_{34}N_2P_2PtS$ requires, C, 57.1; H, 4.2; N, 3.4%), m.p. semi-melts 120 °C (decomp.), >150 °C; ν(C=N)/cm^{-1} 1551. NMR: ^1H (300 MHz), δ 7.79–6.49 (m, 30 H, Ph) and 2.27–2.13 (m, 4 H, CH_2, dppe); $^{13}C-\{^1H\}$ (75.5 MHz), δ 148.22 (s, C=N) and *ca.* 31–27 (m, CH_2, dppe); $^{31}P-\{^1H\}$ (36 MHz), second-order AB spin system, δ 43.4 {d, P(2), $^1J[PtP(2)]$ 3091, $^2J[P(1)P(2)]$ 10} and 37.0 {d, P(1) $^1JPtP(1)]$ 3054, $^2J[P(2)P(1)]$ 10}.

Reaction of cis-$[PtCl_2(PPh_3)_2]$ *with Dianion* **5**.—One mol equivalent of dianion **5** was added to a stirred suspension of *cis*-

$[PtCl_2(PPh_3)_2]$ (0.15 g, 0.19 mmol) in thf (*ca.* 40 cm^3) at −78 °C. The mixture was stirred at this temperature for 15 min and then allowed to warm slowly to room temperature, whereupon it was stirred overnight, to give a pale yellow solution. The solution was evaporated to dryness under reduced pressure, and the residue extracted with toluene, the resulting solution being filtered. The filtrate was evaporated to dryness, the residue dissolved in dichloromethane (*ca.* 5 cm^3), and addition of light petroleum yielded a pale yellow solid, which was filtered off and dried *in vacuo* to give complex **8a** (0.10 g, 56%), identified by comparison of its ^{31}P-{^1H} NMR and IR spectra with those of an authentic sample.

Preparation of $[Pt\{SC(=NPh)NPh\}(PPh_3)_2]$ **8a** *from cis-*$[PtCl_2(PPh_3)_2]$ *and* **7** *in the Presence of Sodium Hydroxide.*—Triphenylphosphine (0.15 g, 0.57 mmol), compound **7** (0.062 g, 0.27 mmol) and an excess of sodium hydroxide were added in succession to a stirred suspension of $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) in a mixture of dichloromethane (*ca.* 10 cm^3) and thf (*ca.* 30 cm^3), and the mixture refluxed for 1 h, yielding a lemon-yellow solution. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (*ca.* 20 cm^3) and the solution washed with water (*ca.* 10 cm^3). The organic layer was separated and dried over anhydrous $MgSO_4$. The mixture was filtered, reduced to *ca.* 2 cm^3 under reduced pressure, and light petroleum added to yield pale yellow *microcrystals* of complex **8a** (0.162 g, 63%), identified by comparison of its ^{31}P-{^1H} NMR spectrum with that of an authentic sample.

Reaction of cis-$[PtCl_2(PPh_3)_2]$ *with* N,N′,P-*triphenylphosphonothioic Diamide* **13** *in the Presence of Silver*(I) *Oxide.*—Triphenylphosphine (0.15 g, 0.57 mmol), *N,N′,P*-triphenylphosphonothioic diamide **13** (0.09 g, 0.28 mmol) and an excess of silver(I) oxide were added in succession to a stirred solution of $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) in dichloromethane, and the mixture refluxed for 5 h. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure to give a brown oil, which was shown by ^{31}P-{^1H} NMR spectroscopy to contain several products.

Preparation of Platinacyclophosphinimine Complexes using Potassium Hydroxide; General Method.—To a stirred solution of *cis*-$[PtCl_2L_2]$ ($L = PPh_3$; L_2 = dppe, dppp or dppb) {prepared by the reaction in dichloromethane of $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with 2 mol equivalents of triphenylphosphine (0.15 g, 0.57 mmol) or 1 mol equivalent of either dppe (0.11 g, 0.28 mmol), dppp (0.12 g, 0.29 mmol) or dppb (0.12 g, 0.28 mmol)} was added 1 mol equivalent of the respective diamide and an excess of potassium hydroxide pellets, and the mixture refluxed for 5 h. The mixture was filtered, and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (*ca.* 5 cm^3), and addition of light petroleum yielded a microcrystalline *solid* which was filtered off and dried *in vacuo*.

(*i*) $[Pt\{SP(=NPh)(Ph)NPh\}(PPh_3)_2]\cdot H_2O$ **14a**·H_2O. The complex *cis*-$[PtCl_2(PPh_3)_2]$ (0.27 mmol) with **13** (0.09 g, 0.28 mmol) gave yellow *microcrystals* of **14a**·H_2O (0.27 g, 94%) (Found: C, 60.6; H, 4.3; N, 2.7. $C_{54}H_{45}N_2P_3PtS\cdot H_2O$ requires C, 61.2; H, 4.4; N, 2.6%), m.p. 188 °C; ν(P=NPh)/cm^{-1} 1320s. NMR: ^1H (90 MHz), δ 8.1–6.2 (m, 45 H, Ph) and 2.0 (s, br, 2 H, H_2O); ^{31}P-{^1H} (36 MHz), δ 35.6 {dd, P(3), ^2J[PtP(3)] 186, ^3J[P(1)P(3)] 24, ^3J[P(2)P(3)] 10}, 17.0 {dd, P(2), ^1J[PtP(2)] 3472, ^2J[P(1)P(2)] 24, ^3J[P(3)P(2)] 10} and 8.5 {dd, P(1), ^1J[PtP(1)] 3184, ^2J[P(2)P(1)] 24, ^3J[P(3)P(1)] 24}.

(*ii*) $[Pt\{SP(=NPh)(Ph)NPh\}(dppe)]\cdot H_2O$ **14b**·H_2O. The complex $[PtCl_2(dppe)]$ (0.27 mmol) with **13** (0.09 g, 0.28 mmol) gave yellow *microcrystals* of **14b**·H_2O (0.24 g, 95%) (Found: C, 56.9; H, 4.1; N, 3.0. $C_{44}H_{39}N_2P_3PtS\cdot H_2O$ requires C, 56.6; H, 4.4; N, 3.0%), m.p. >220 °C; ν(P=NPh)/cm^{-1} 1310s. Complex **14**·$6H_2O$ was too insoluble for NMR spectroscopy.

(*iii*) $[Pt\{SP(=NPh)(Ph)NPh\}(dppp)]\cdot H_2O$ **14c**·H_2O. The complex $[PtCl_2(dppp)]$ (0.27 mmol) with **13** (0.09 g, 0.28 mmol) gave yellow *microcrystals* of **14c**·H_2O (0.25 g, 98%) (Found: C, 57.0; H, 4.4; N, 2.8. $C_{45}H_{41}N_2P_3PtS\cdot H_2O$ requires C, 57.0; H, 4.5; N, 3.0%), m.p. 129 °C; ν(P=NPh)/cm^{-1} 1320s. NMR: ^1H (300 MHz), δ 8.12–6.17 (m, 35 H, Ph), 2.35 (m, 4 H, PCH_2, dppp), 2.08 (s, br, 2 H, H_2O) and 1.88 (m, 2 H, CH_2, dppp); ^{13}C-{^1H} (75.5 MHz), δ 28.90 (m, PCH_2, dppp), 24.66 (m, PCH_2, dppp) and 18.80 (s, CH_2, dppp); ^{31}P-{^1H} (36 MHz), δ 35.7 {dd, P(3), ^2J[PtP(3)] 183, ^3J[P(1)P(3)] 24, ^3J[P(2)P(3)] 7}, −1.5 {dd, P(2), ^1J[PtP(2)] 3225, ^2J[P(1)P(2)] 34, ^3J[P(3)P(2)] 7} and −11.6 {dd, P(1), ^1J[PtP(1)] 2908, ^2J[P(2)P(1)] 34, ^3J[P(3)P(1)] 24}.

(*iv*) $[Pt\{SP(=NPh)(Ph)NPh\}(dppb)]\cdot CH_2Cl_2$ **14d**·CH_2Cl_2. The complex $[PtCl_2(dppb)]$ (0.27 mmol) with **13** (0.09 g, 0.28 mmol) gave yellow *microcrystals* of **14d**·CH_2Cl_2 (0.26 g, 94%) (Found: C, 55.2; H, 4.8; N, 2.4. $C_{46}H_{43}N_2P_3PtS\cdot CH_2Cl_2$ requires C, 54.9; H, 4.4; N, 2.7%), m.p. 140 °C; ν(P=NPh)/cm^{-1} 1320s. NMR: ^1H (300 MHz), δ 7.98–6.25 (m, 35 H, Ph), 5.28 (s, 2 H, CH_2Cl_2), 2.62–2.37 (m, 4 H, PCH_2, dppb), 2.04 (m, 2 H, CH_2, dppb) and 1.56 (m, 2 H, CH_2, dppb); ^{13}C-{^1H} (75.5 MHz), too insoluble; ^{31}P-{^1H} (36 MHz), δ 36.2 {dd, P(3), ^2J[PtP(3)] 181, ^3J[P(1)P(3)] 22, ^3J[P(2)P(3)] 10}, 16.6 {dd, P(2), ^1J[PtP(2)] 3384, ^2J[P(1)P(2)] 27, ^3J[P(3)P(2)] 10} and 0.0 {dd, P(1), ^1J[PtP(1)] 3001, ^2J[P(2)P(1)] 27, ^3J[P(3)P(1)] 22}.

Reaction of cis-$[PtCl_2(PPh_3)_2]$ *with Phenylphosphonothioic Diamide* **15** *in the Presence of Silver*(I) *Oxide.*—The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol), **15** (0.05 g, 0.29 mmol) and excess of silver(I) oxide in refluxing dichloromethane (*ca.* 30 cm^3) gave white *microcrystals* of complex **16** (0.21 g, 89%) as shown by ^1H and ^{31}P-{^1H} NMR spectroscopy.

Attempted Preparation of $[Pt\{SP(=NH)(Ph)NH\}(PPh_3)_2]$ *using Potassium Hydroxide.*—The complex *cis*-$[PtCl_2(PPh_3)_2]$ with **15** (0.05 g, 0.29 mmol) and an excess of potassium hydroxide in thf gave, after evaporation of the filtrate, a colourless oil, which was shown by ^{31}P-{^1H} NMR spectroscopy to contain *cis*-$[PtCl_2(PPh_3)_2]$.

Reaction of cis-$[PtCl_2(PPh_3)_2]$ *with Dianion* **6**.—(*i*) *Preparation of* **6**. Compound **13** (0.50 g, 1.54 mmol) was dissolved in thf (*ca.* 45 cm^3) and the solution was cooled to −78 °C. Butyllithium (1.8 cm^3, 1.8 mol dm^{-3}, 3.24 mmol) was added slowly, under nitrogen, to the cooled solution, which was then stirred for 15 min at −78 °C. The solution was allowed to warm slowly to room temperature and then stirred overnight. The dark red solution was estimated for total base content by hydrolysis of an aliquot (5.0 cm^3) in water (*ca.* 20 cm^3), followed by titration of the liberated hydroxide with hydrochloric acid, using phenolphthalein indicator.

(*ii*) *Preparation of* **14a**·H_2O. One mol equivalent of dianion **6** was added dropwise to a stirred suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.20 g, 0.25 mmol) in thf (*ca.* 40 cm^3) at −78 °C. The mixture was stirred for 15 min at this temperature and for 5 h at room temperature, to give a pale yellow solution. Evaporation to dryness under reduced pressure gave an oil, which was extracted into dichloromethane (20 cm^3) and the solution filtered. The volume of the filtrate was reduced to *ca.* 5 cm^3 and the addition of light petroleum afforded yellow *microcrystals* of complex **14a**·H_2O (0.19 g, 73%), identified by comparison of IR and ^{31}P-{^1H} NMR spectra with those of an authentic sample.

Reaction of $[\{RhCl(CO)(dppm)\}_2]$ *with Dianion* **5**.—1.45 Mol equivalents of dianion **5** were added to a stirred suspension of $[\{RhCl(CO)(dppm)\}_2]$ (0.270 g, 0.245 mmol) in thf (40 cm^3) at room temperature, and the mixture stirred for 3 h, resulting in a deep red solution. The mixture was evaporated to dryness under reduced pressure, and the residue extracted into diethyl ether. The mixture was filtered and the dark red solution evaporated to dryness, the minimum quantity of dichloromethane being added to dissolve the residue. Light petroleum was slowly added until the solution started to cloud over, and the mixture was left to stand overnight. The red-orange *crystals* which had formed were filtered off and dried *in vacuo*, to give $[Rh_2(\mu\text{-}S)(CO)_2(dppm)_2]$ **17** (0.105 g, 41%), identified by comparison of its $^{31}P\text{-}\{^1H\}$ NMR spectrum with that of an authentic sample made by the literature procedure.[25] $^{31}P\text{-}\{^1H\}$ (24 MHz) NMR: δ 17.0 [d, $^1J(RhP)$ 132].

Reaction of $[\{RhCl(CO)(dppm)\}_2]$ *with Dianion* **6**.—One mol equivalent of dianion **6** was added dropwise to a stirred suspension of $[\{RhCl(CO)(dppm)\}_2]$ (0.30 g, 0.27 mmol) in thf at −78 °C. The mixture was stirred for 15 min at this temperature and for 15 h at room temperature, to give an orange solution. Evaporation to dryness under reduced pressure gave an orange solid, which was extracted into dichloromethane and the solution filtered. The volume of the filtrate was reduced and the addition of light petroleum afforded the orange powder $[Rh_2(u\text{-}S)(CO)_2(dppm)_2]$ **17** (0.20 g, 70%), identified as before.

Reaction of $[Pt\{SC(=NPh)NPh\}(PPh_3)_2]$ **8a** *with Carbon monoxide*—Carbon monoxide was bubbled through a solution of complex **8a** (0.20 g, 0.22 mmol) in dichlororomethane (40 cm^3) and the reaction monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. After 13.5 h the reaction was complete. and the solution was reduced in volume to *ca.* 1 cm^3. Addition of diethyl ether gave a dirty green *microcrystalline solid*, which was recrystallised three times from dichloromethane–diethyl ether, to yield grey *microcrystals* of complex **19** (0.070 g, 34%). The purified compound was found to be insoluble in all common organic solvents, and could not be obtained analytically pure; m.p. > 230 °C (decomp.); ν(C=O) 1647s, ν(C=N) 1578s cm^{-1}. $^{31}P\text{-}\{^1H\}$ (36 MHz) NMR: second order AB spin system, 24.1 {d, P(2), $^1J[PtP(2)]$ 3547, $^2J[P(1)P(2)]$ 22} and 17.1 {d, P(1), $^1J[PtP(1)]$ 1846, $^2J[P(2)P(1)]$ 22}.

Reaction of $[Pt\{SP(=NPh)(Ph)NPh\}(PPh_3)_2]\cdot H_2O$ **14a**·H_2O *with Carbon Monoxide*.—In a similar experiment to that described above, a slow stream of carbon monoxide was bubbled through a solution of complex **14a** (0.15 g, 0.14 mmol) in dichloromethane (40 cm^3) for 15 h. Evaporation to dryness under reduced pressure afforded an oil, which contained only starting material **14a**, as shown by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

Reactions of Platinacyclophosphinimine Complexes.—(*i*) *With methyl iodide*. A solution of $[Pt\{SP(=NPh)(Ph)NPh\}(dppp)]\cdot H_2O$ **14c**·H_2O (0.12 g, 0.13 mmol) in dichloromethane (25 cm^3) with methyl iodide (0.07 g, 0.49 mmol) was stirred for 6 h at room temperature. Evaporation to dryness under reduced pressure afforded a pale yellow oil. Dissolution of the oil in dichloromethane (*ca.* 3 cm^3) followed by addition of light petroleum gave, on standing, pale yellow *microcrystals* of $[Pt\{SP(NMePh)(Ph)NPh\}(dppp)]I$ **20**·H_2O (0.12 g, 85%) (Found: C, 50.9; H, 4.4; N, 2.4. $C_{46}H_{44}IN_2P_3PtS\cdot H_2O$ requires C, 50.6; H, 4.2; N, 2.6%), m.p. 141 °C. NMR: ^1H (300 MHz), δ 8.04–6.06 (m, 35 H, Ph), 3.13 [d, 3 H, Me, $^3J(PH)$ 11] and 2.85–1.68 (m, br, 8 H, CH_2, dppp + H_2O); $^{13}C\text{-}\{^1H\}$ (75.5 MHz), δ 39.14 [d, Me, $^2J(PC)$ 5], 27.75 [dd, PCH_2, dppp, $^1J(PC)$ 42, $^3J(PC)$ 5], 23.92 [dd, PCH_2, dppp, $^1J(PC)$ 35, $^3J(PC)$ 3] and 18.81 (s, CH_2, dppp); $^{31}P\text{-}\{^1H\}$ (36 MHz), δ 72.6 [dd, PNMePh, $^2J(PtP)$ 249, $^3J(PP)$ 10, 27], −1.6 [dd, dppp, $^1J(PtP)$ 3357, $^2J(PP)$ 34, $^3J(PP)$ 10] and −12.7 [dd, dppp, $^1J(PtP)$ 2991, $^2J(PP)$ 34, $^3J(PP)$ 27 Hz].

(*ii*) *With double bonds to oxygen or sulfur; general method*. A solution of the metallacyclic complex in dichloromethane (25 cm^3) with excess of the respective substrate was stirred overnight at room temperature. The solution was then filtered and evaporation of the filtrate to dryness under reduced pressure afforded a pale yellow to pale brown oil. Dissolution of the oil in dichloromethane (*ca.* 3 cm^3) followed by the addition of light petroleum gave, on standing, pale yellow *microcrystals* which were dried *in vacuo*.

(*a*) $[Pt\{SP(=NPh)(Ph)NPh\}(PPh_3)_2]$ **14a**·H_2O *with phenyl isocyanate*. Complex **14a**·H_2O (0.15 g, 0.14 mmol) with phenyl isocyanate (0.03 g, 0.25 mmol) gave pale yellow *microcrystals* of $[Pt\{SP(O)(Ph)NPh\}(PPh_3)_2]$ **21a**·H_2O (0.13 g, 94%) (Found: C, 58.0; H, 4.2; N, 1.6. $C_{48}H_{40}NOP_3PtS\cdot H_2O$ requires C, 58.5; H, 4.3; N, 1.4%), m.p. 130 °C; ν(P=O)/cm^{-1} 1240s. NMR: ^1H (90 MHz), δ 8.3–6.2 (m, 40 H, Ph) and 2.2 (s, br, 2 H, H_2O); $^{31}P\text{-}\{^1H\}$ (36 MHz), δ 47.7 [dd, P=O, $^2J(PtP)$ 239, $^3J(PP)$ 10, 20], 18.0 [dd, PPh_3, $^1J(PtP)$ 3508, $^2J(PP)$ 25, $^3J(PP)$ 10] and 8.1 [dd, PPh_3, $^1J(PtP)$ 3184, $^2J(PP)$ 25, $^3J(PP)$ 20].

(*b*) $[Pt\{SP(=NPh)(Ph)NPh\}(dppp)]$ **14c**·H_2O *with phenyl isocyanate*. Complex **14c**·H_2O (0.15 g, 0.16 mmol) with phenyl isocyanate (0.04 g, 0.34 mmol) gave yellow *microcrystals* of $[Pt\{SP(O)(Ph)NPh\}(dppp)]$ **21b**·H_2O (0.13 g, 93%) (Found: C, 53.9; H, 4.0; N, 1.6. $C_{39}H_{36}NOP_3PtS\cdot H_2O$ requires C, 53.6; H, 4.3; N, 1.6%), m.p. 125 °C; ν(P=O)/cm^{-1} 1250s. NMR: ^1H (90 MHz), δ 8.3–6.1 (m, 30 H, Ph) and 2.8–1.6 (m, br, 8 H, CH_2, dppp + H_2O); $^{31}P\text{-}\{^1H\}$ (36 MHz), δ 49.4 [dd, P=O, $^2J(PtP)$ 220, $^3J(PP)$ 10, 27], −1.6 [dd, dppp, $^1J(PtP)$ 3247, $^2J(PP)$ 34, $^3J(PP)$ 10] and −11.4 [dd, dppp, $^1J(PtP)$ 2900, $^2J(PP)$ 34, $^3J(PP)$ 27].

(*c*) **14a**·H_2O *with carbon dioxide*. A slow stream of carbon dioxide was bubbled through a dichloromethane solution of complex **14a**·H_2O (0.15 g, 0.14 mmol) for 5 h at room temperature. Work-up as above gave pale yellow *microcrystals* of complex **21a**·H_2O (0.13 g, 94%), identified by $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy.

(*d*) **14c**·H_2O *with carbon dioxide*. A slow stream of carbon dioxide was bubbled through a dichloromethane solution of complex **14c**·H_2O (0.15 g, 0.16 mmol) for 5 h at room temperature. Work-up as above gave pale yellow *microcrystals* of complex **21b**·H_2O (0.13 g, 93%), identified by $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy.

(*e*) **14c**·H_2O *with* p-*nitrobenzaldehyde*. Complex **14c**·H_2O (0.15 g, 0.16 mmol) with *p*-nitrobenzaldehyde (0.05 g, 0.33 mmol) gave pale yellow *microcrystals* of **21b**·H_2O (0.13 g, 93%), identified as above.

(*f*) **14c**·H_2O *with diphenylketene*. Complex **14c**·H_2O (0.15 g, 0.16 mmol) with diphenylketene (0.06 g, 0.31 mmol) gave pale yellow *microcrystals* of **21b**·H_2O (0.13 g, 93%), identified as above.

(*g*) **14a**·H_2O *with silver*(I) *carbonate*. Complex **14a**·H_2O (0.15 g, 0.14 mmol) with silver(I) carbonate (0.08 g, 0.29 mmol) gave pale yellow *microcrystals* of **21a**·H_2O (0.13 g, 94%), identified by $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy.

(*h*) **14c**·H_2O *with silver*(I) *carbonate*. Complex **14c**·H_2O (0.15 g, 0.16 mmol) with silver(I) carbonate (0.09 g, 0.33 mmol) gave pale yellow *microcrystals* of **21b**·H_2O (0.13 g, 93%), identified as above.

(*i*) **14a**·H_2O *with phenyl isothiocyanate*. Complex **14a**·H_2O (0.15 g, 0.14 mmol) with phenyl isothiocyanate (0.08 g, 0.60 mmol) gave yellow *microcrystals* of $[Pt\{SP(S)(Ph)S\}(PPh_3)_2]$ **22a** (0.12 g, 93%), ν(P=S)/cm^{-1} 680m. $^{31}P\text{-}\{^1H\}$ (36 MHz), NMR: δ 88.0 [s, P=S, $^2J(PtP)$ 225] and 18.6 [s, PPh_3, $^1J(PtP)$ 3262].

(*j*) **14c**·H_2O *with phenyl isothiocyanate*. Complex **14c**·H_2O (0.15 g, 0.16 mmol) with phenyl isothiocyanate (0.09 g, 0.67 mmol) gave yellow *microcrystals* of $[Pt\{SP(S)(Ph)S\}(dppp)]$ **22b** (0.12 g, 92%), ν(P=S)/cm^{-1} at 670m. $^{31}P\text{-}\{^1H\}$ (24 MHz) NMR: δ 92.7 [s, P=S, $^2J(PtP)$ 220] and −3.6 [s, dppp, $^1J(PtP)$ 2996 Hz].

(*k*) **14a**·H_2O *with carbon disulfide*. Complex **14a**·H_2O (0.15 g, 0.14 mmol) with carbon disulfide (0.02 g, 0.26 mmol) gave

Table 3 Fractional atomic co-ordinates for [Pt{SC(=NPh)NPh}(PPh$_3$)$_2$] **8a**, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.204 53(1)	0.179 49(2)	0.207 69(1)	C(44)	0.242 03(11)	0.244 53(27)	0.533 48(13)
P(1)	0.122 08(4)	0.175 59(10)	0.149 79(6)	C(45)	0.240 58(11)	0.098 94(27)	0.525 34(13)
P(2)	0.176 49(4)	0.044 28(10)	0.310 59(6)	C(46)	0.221 75(11)	0.035 86(27)	0.458 22(13)
S	0.250 85(4)	0.320 19(12)	0.116 65(7)	C(51)	0.103 15(8)	0.014 83(27)	0.334 34(17)
N(1)	0.285 67(14)	0.220 7(4)	0.238 93(24)	C(52)	0.079 38(8)	0.108 33(27)	0.382 64(17)
N(2)	0.357 53(16)	0.338 0(6)	0.172 3(3)	C(53)	0.023 27(8)	0.088 59(27)	0.400 22(17)
C(1)	0.306 73(17)	0.294 4(5)	0.179 0(3)	C(54)	−0.009 07(8)	−0.024 62(27)	0.369 51(17)
C(11)	0.377 88(13)	0.407 8(5)	0.105 90(23)	C(55)	0.014 72(8)	−0.118 11(27)	0.321 22(17)
C(12)	0.397 76(13)	0.331 6(5)	0.046 03(23)	C(56)	0.070 82(8)	−0.098 37(27)	0.303 62(17)
C(13)	0.423 34(13)	0.402 0(5)	−0.015 07(23)	C(61)	0.123 33(11)	0.263 33(26)	0.057 43(13)
C(14)	0.429 04(13)	0.548 5(5)	−0.016 33(23)	C(62)	0.092 61(11)	0.377 69(26)	0.042 66(13)
C(15)	0.409 16(13)	0.624 7(5)	0.043 54(23)	C(63)	0.095 28(11)	0.441 10(26)	−0.028 22(13)
C(16)	0.383 58(13)	0.554 3(5)	0.104 66(23)	C(64)	0.128 66(11)	0.390 13(26)	−0.084 31(13)
C(21)	0.323 41(11)	0.167 2(3)	0.289 03(19)	C(65)	0.159 37(11)	0.275 77(26)	−0.069 51(13)
C(22)	0.331 48(11)	0.230 9(3)	0.359 31(19)	C(66)	0.156 71(11)	0.212 36(26)	0.001 34(13)
C(23)	0.368 20(11)	0.178 7(3)	0.410 72(19)	C(71)	0.073 72(9)	0.269 29(25)	0.204 74(17)
C(24)	0.396 86(11)	0.062 6(3)	0.391 82(19)	C(72)	0.017 90(9)	0.226 40(25)	0.214 94(17)
C(25)	0.388 80(11)	−0.001 1(3)	0.321 53(19)	C(73)	−0.016 23(9)	0.312 21(25)	0.254 02(17)
C(26)	0.352 07(11)	0.051 1(3)	0.270 13(19)	C(74)	0.005 43(9)	0.440 95(25)	0.282 87(17)
C(31)	0.198 74(10)	−0.133 05(20)	0.305 82(16)	C(75)	0.061 23(9)	0.483 85(25)	0.272 65(17)
C(32)	0.237 25(10)	−0.163 62(20)	0.251 07(16)	C(76)	0.095 37(9)	0.398 04(25)	0.233 59(17)
C(33)	0.254 78(10)	−0.298 94(20)	0.254 71(16)	C(81)	0.091 60(10)	0.002 53(20)	0.122 81(18)
C(34)	0.233 78(10)	−0.403 66(20)	0.295 08(16)	C(82)	0.037 95(10)	−0.017 62(20)	0.094 43(18)
C(35)	0.195 28(10)	−0.373 07(20)	0.349 83(16)	C(83)	0.015 44(10)	−0.152 76(20)	0.077 05(18)
C(36)	0.177 75(10)	−0.237 76(20)	0.355 20(16)	C(84)	0.046 57(10)	−0.267 74(20)	0.088 05(18)
C(41)	0.204 38(11)	0.118 38(27)	0.399 25(13)	C(85)	0.100 21(10)	−0.247 60(20)	0.116 42(18)
C(42)	0.205 83(11)	0.263 96(27)	0.407 40(13)	C(86)	0.122 74(10)	−0.112 47(20)	0.133 81(18)
C(43)	0.224 66(11)	0.327 03(27)	0.474 50(13)				

yellow *microcrystals* of **22a** (0.12 g, 93%), identified by ^{31}P-{^{1}H} NMR and IR spectroscopy.

(*l*) **14c**·H$_2$O *with carbon disulfide.* Complex **14c**·H$_2$O (0.15 g, 0.16 mmol) with carbon disulfide (0.03 g, 0.39 mmol) gave yellow *microcrystals* of **22b** (0.12 g, 92%), identified by ^{31}P-{^{1}H} NMR and IR spectroscopy.

(*m*) *Formation of* [Pt{SP(O)(Ph)NPh}(PPh$_3$)$_2$] **21a**·H$_2$O *from cis*-[PtCl$_2$(PPh$_3$)$_2$] *using silver*(I) *carbonate with* **13**. Compound **13** (0.085 g, 0.26 mmol) and excess of silver(I) carbonate were added in succession to a stirred solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.20 g, 0.25 mmol) in dichloromethane (*ca.* 45 cm^3), and the mixture refluxed for 15 h. The cooled reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (*ca.* 5 cm^3) followed by the addition of light petroleum afforded, on standing, pale yellow *microcrystals* of [Pt{SP(O)(Ph)NPh}(PPh$_3$)$_2$] **21a**·H$_2$O (0.24 g, 97%), identified by ^{31}P-{^{1}H} NMR and IR spectroscopy.

(*iii*) *Reaction of* [Pt{SP(=NPh)(Ph)NPh}(PPh$_3$)$_2$] **14a**·H$_2$O *with dimethyl acetylenedicarboxylate.* A solution of [Pt{SP(=NPh)(Ph)NPh}(PPh$_3$)$_2$] **14a**·H$_2$O (0.15 g, 0.14 mmol) in dichloromethane (25 cm^3) with dimethyl acetylenedicarboxylate (dmad) (0.04 g, 0.28 mmol) was stirred for 2 h at room temperature. Evaporation to dryness under reduced pressure afforded an oil which was shown by ^{31}P-{^{1}H} NMR spectroscopy to contain several products.

Reaction of [Pt{SP(=NPh)(Ph)NPh}(dppp)] **14c**·H$_2$O *with dimethyl acetylenedicarboxylate.* A solution of [Pt{SP(=NPh)(Ph)NPh}(dppp)] **14c**·H$_2$O (0.12 g, 0.13 mmol) in dichloromethane (25 cm^3) with dmad (0.04 g, 0.28 mmol) was stirred for 2 h at room temperature. Evaporation to dryness under reduced pressure afforded a pale brown oil which was shown by ^{31}P-{^{1}H} NMR spectroscopy to contain several products.

(*iv*) *Reaction of* [Pt{SP(=NPh)(Ph)NPh}(dppp)] **14c**·H$_2$O *with cadmium*(II) *iodide.* A solution of [Pt{SP(=NPh)(Ph)NPh}(dppp)] **14c**·H$_2$O (0.12 g, 0.13 mmol) in thf (30 cm^3) with cadmium(II) iodide (0.10 g, 0.27 mmol) was stirred for 4 h at room temperature. The solution was filtered and evaporation of the filtrate to dryness under reduced pressure afforded a pale brown solid. The product was recrystallised from dichloromethane–light petroleum to afford the pale brown powdery solid [Pt{SP(=NPhCdI$_2$)(Ph)NPh}(dppp)] **24**·H$_2$O (0.14 g, 83%). ^{31}P-{^{1}H} (24 MHz) NMR: δ 59.0 [dd, P=NPh, ^2J(PtP) 250, ^3J(PP) 12, 29], −1.5 [dd, dppp, ^1J(PtP) 3360, ^2J(PP) 34, ^3J(PP) 12] and −12.6 [dd, dppp, ^1J(PtP) 3005, ^2J(PP) 34, ^3J(PP) 29 Hz].

X-Ray Crystal Structure Determination of [Pt{SC(=NPh)NPh}(PPh$_3$)$_2$] **8a**.—The crystal was mounted in air. The unit-cell parameters were determined by least-squares refinement of ω measurements for different layers. The intensities of 10 450 unique reflections with $7 < 2\theta < 54°$ and ($\pm h$, $\pm k$, $+l$) were collected at room temperature on a Stoe Stadi-2 Weissenberg diffractometer using an ω-scan technique. The data were corrected for Lorentz and polarisation effects to yield 6225 reflections with [$I > 3\sigma(I)$]. An absorption correction was also applied to the data, the maximum and minimum transmission factors being 0.7013 and 0.4385 respectively. All subsequent computations were carried out using the computer program SHELX.[29]

Crystal data. C$_{49}$H$_{40}$N$_2$P$_2$PtS, $M = 945.97$, 0.76 × 0.28 × 0.12 mm, monoclinic, space group $P2_1/a$, $a = 24.267(20)$, $b = 9.547(13)$, $c = 17.746(15)$ Å, $\gamma = 94.56(10)°$ (unique axis = c), $U = 4098.2$ Å^3, $Z = 4$, $D_c = 1.533$ g cm^{-3}, $F(000) = 1888$, Mo-Kα X-radiation, $\lambda = 0.7107$ Å, μ(Mo-Kα) = 34.25 cm^{-1}.

The structure was solved using the Patterson and Fourier techniques. Phenyl rings were included as rigid groups with D_{6h} symmetry, and C–C distances of 1.395 Å. Hydrogen atoms were not located on the Fourier difference map, and all hydrogens were included in calculated positions (C–H 1.08 Å). The isotropic thermal parameters of the phenyl hydrogen atoms were refined as groups. All other atoms were refined with anisotropic thermal parameters. Final cycles of refinement employed a weighting parameter $w = 1/(\sigma^2F + gF^2)$ (g = 0.0001) and gave the final residual indices $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0297$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.027$. The final Fourier difference map was featureless. The atomic co-ordinates for the structure are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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