Preparation and Reactivity of Platinathiadiazetidine 1,1-Dioxide and Platinadiazaphosphetidine 2-Oxide Complexes†

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Treatment of the complexes cis-[PtCl₂L₂] (L = donor ligand) with either N,N'-diphenylsulfamide or N,N',P-triphenylphosphonic diamide in the presence of an excess of silver(I) oxide in refluxing dichloromethane yielded the new metallacycles [Pt{NPhS(O)₂NPh}L₂] and [Pt{NPhP(O)(Ph)NPh}L₂] respectively. The X-ray crystal structure of [Pt{NPhS(O)₂NPh}(cod)] (cod = cycloocta-1,5-diene) showed the presence of an entirely flat four-membered ring, whereas that of [Pt{NPhP(O)(Ph)NPh}-(PPh₃)₂] exhibits a small puckering angle, but with no substantial Pt···P transannular interaction. tert-Butyl isocyanide displaces a phosphine ligand from [Pt{NPhS(O)₂NPh}(PPh₃)₂].

The preparation of monometallic ureylene chelate complexes can be achieved by the reaction of organic azides or isocyanates with various low-oxidation-state transition-metal complexes. Thus, for example, complexes **1** or **2** may be prepared from [M(NO)(CO)(PPh₃)₂] (M = Rh or Ir) and toluene-p-sulfonyl azide, and **3** or **4** from [M(PPh₃)₄] (M = Pd or Pt) and toluene-p-sulfonyl isocyanate.[1] However, modifications of this procedure in efforts to prepare complexes in which the central carbonyl group has been replaced by an alternative functionality have not appeared in the literature. Nevertheless, monometallic complexes containing the Pt–NH–S(O)₂–NH framework have been prepared by the action of liquid ammonia on sulfamide in the presence of bis(phosphine)platinum dichloride complexes, Scheme 1.[2,3] An X-ray crystal structure determination on complex **5** (L = PMePh₂) established the presence of an almost planar metallacyclic ring, with the NH protons adopting a trans-anti orientation.[2]

We have previously reported the formation of the ring systems Pt–NR–S(O)₂–NR **6** (R = H or Ph) and Pt–NR–P(O)(Ph)–NR **7** (R = H or Ph) by treatment of cis-[PtCl₂L₂] (L = donor ligand) with silver(I) oxide and either sulfamide, N,N'-diphenylsulfamide, phenylphosphonic diamide or N,N',P-triphenylphosphonic diamide respectively.[4] We now describe in detail the preparation of the N,N'-diphenyl-substituted metallacycles **6** (R = Ph) and **7** (R = Ph) and investigations of their structural and spectroscopic properties.

Results and Discussion

Treatment of cis-[PtCl₂L₂] [L = PPh₃, PMePh₂, PEt₂Ph, PEt₃ or P(NEt₂)Ph₂; L₂ = Ph₂PCH₂CH₂PPh₂ (dppe)] with 1 mole equivalent of N,N'-diphenylsulfamide **8** and an excess of silver(I) oxide in refluxing dichloromethane for 3 h yielded the air-stable, white to yellow complexes **9a–9f**. The complexes **9a**, **9c** and **9f** can also be synthesised via treatment of the appropriate cis-[PtCl₂L₂] complex with 1 mole equivalent of **8** and an excess of potassium hydroxide in a refluxing mixture of

R = Me—⟨ ⟩—SO₂—

1 M = Rh
2 M = Ir

3 M = Pd
4 M = Pt

cis-[PtCl₂L₂] + (H₂N)₂SO₂ →(NH₃(l))→ **5**

Scheme 1

6

7
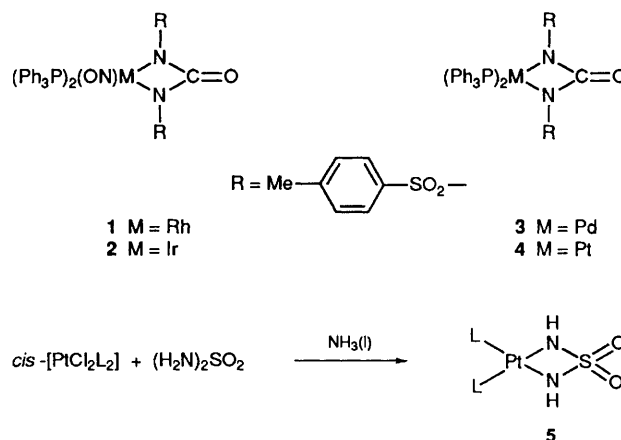
dichloromethane and tetrahydrofuran (thf). Several crystals of the derivative **9g** (cod = cycloocta-1,5-diene), one of which was suitable for an X-ray crystal structure determination, were isolated from one preparation of the chelating phosphine analogue **9f**. Treatment of the complexes cis-[PtCl₂L₂] [L = PPh₃, PMePh₂ or PMe₂Ph; L₂ = Ph₂PCH₂PPh₂ (dppm), dppe, Ph₂P(CH₂)₃PPh₂ (dppp) or Ph₂P(CH₂)₄PPh₂ (dppb)] with 1 equivalent of N,N',P-triphenylphosphonic diamide (RNH)₂P(O)Ph **10** (R = Ph) and an excess of silver(I) oxide in refluxing dichloromethane gave complexes **11a–11g** in high yield, whilst analogous treatment of [PtCl₂(cod)] yielded the complex **11h**, also in high yield. Treatment of the bromide-bridged dimeric complex [{PtBr₂(PPrⁿ₃)}₂] with 1 mole equivalent of **10** (R = Ph) and AsPh₃ per platinum, in the presence of excess of silver(I) oxide in refluxing dichloromethane, afforded the mixed-ligand species **12** in quantitative yield. The

9a PPh₃
9b PMePh₂
9c PEt₂Ph
9d PEt₃
9e P(NEt₂)Ph₂
9f ½ dppe
9g ½ cod

11a PPh₃
11b PMePh₂
11c PMe₂Ph
11d ½ dppm
11e ½ dppe
11f ½ dppp
11g ½ dppb
11h ½ cod

12

13

14

15
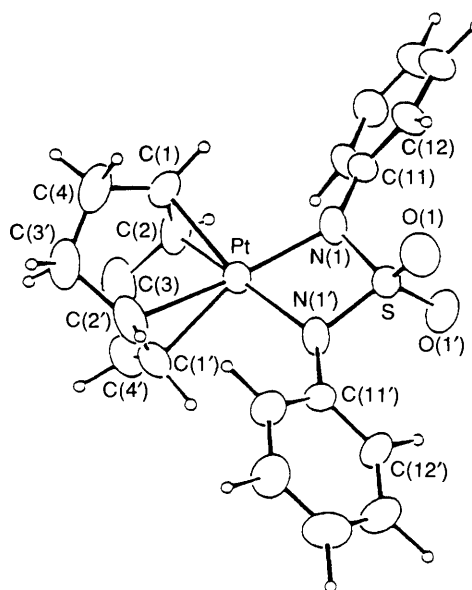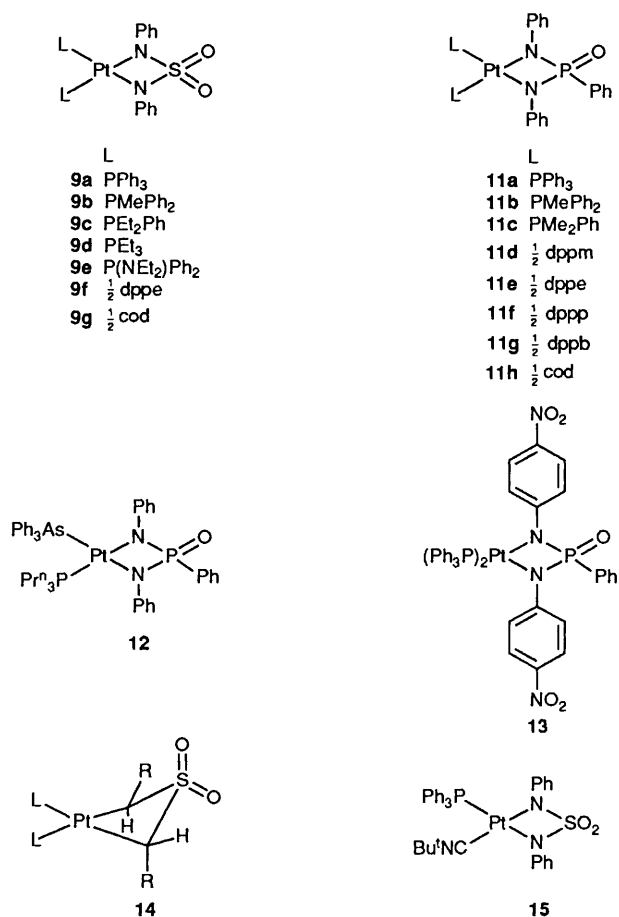
Fig. 1 Molecular structure of [Pt{NPhS(O)₂NPh}(cod)] 9g showing the atom numbering scheme
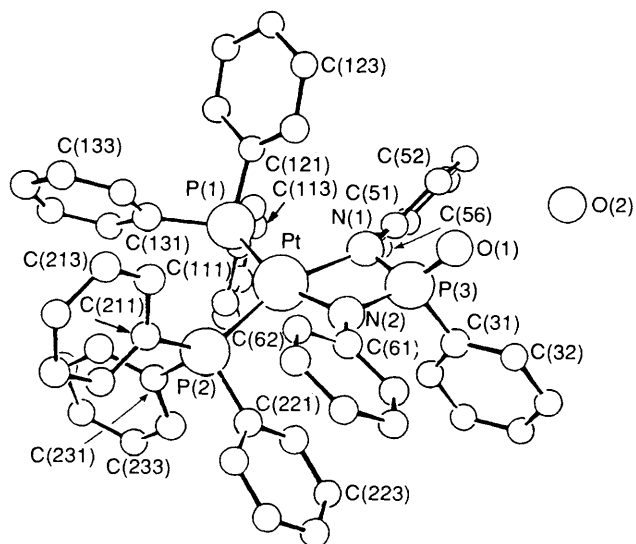
Fig. 2 Molecular structure of [Pt{NPhP(O)(Ph)NPh}(PPh₃)₂] 11a·H₂O·CH₂Cl₂ with all hydrogen atoms and CH₂Cl₂ omitted

Table 1 Selected interatomic bond distances (Å) and angles (°) for [Pt{NPhS(O)₂NPh}(cod)] 9g with estimated standard deviations (e.s.d.s) in parentheses

Pt–N(1)	2.020(3)	Pt–C(1)	2.162(4)
Pt–N(1')	2.020(3)	Pt–C(1')	2.162(4)
N(1)–S	1.617(4)	Pt–C(2)	2.178(4)
N(1')–S	1.617(4)	Pt–C(2')	2.178(4)
S–O(1)	1.435(3)	C(1)–C(2)	1.389(8)
S–O(1')	1.435(3)	C(1')–C(2')	1.389(8)
N(1)–C(11)	1.408(5)		
N(1')–C(11')	1.408(5)		
N(1)–Pt–N(1')	69.6(2)	O(1)–S–O(1')	112.3(3)
Pt–N(1)–S	99.7(2)	C(1)–Pt–C(2)	37.3(2)
Pt–N(1')–S	99.7(2)	C(1')–Pt–C(2')	37.3(2)
N(1)–S–N(1')	91.0(2)	C(1)–Pt–N(1)	98.7(2)
Pt–N(1)–C(11)	137.1(3)	C(1')–Pt–N(1')	98.7(2)
Pt–N(1')–C(11')	137.1(3)	C(2)–Pt–N(1)	104.2(2)
C(11)–N(1)–S	122.3(3)	C(2')–Pt–N(1')	104.2(2)
C(11')–N(1')–S	122.3(3)		

reaction of cis-[PtCl₂(PPh₃)₂] with 1 mole equivalent of 10 (R = p-nitrophenyl) and an excess of silver(I) oxide in refluxing dichloromethane gave complex 13 in good yield. The complexes 11–13 were isolated as golden-yellow to pale green, air-stable, microcrystalline solids.

X-Ray crystal structure determinations of complexes 9g and 11a were carried out in order to investigate and compare their molecular geometries. Important bond lengths and angles for both complexes are presented in Tables 1 and 2, whilst the molecular geometry of 9g is shown in Fig. 1 and that of 11a in Fig. 2, both diagrams depicting the crystallographic numbering systems. The structure of 9g indicates that the compound

possesses a two-fold rotation axis about the Pt · · · S vector. As a result, the four-membered ring is entirely flat, with no fold angle between the N(1)–Pt–N(1') and N(1)–S–N(1') planes. This is in contrast with the sulfone complexes 14, the crystal structures of several such derivatives [5,6] showing extensive puckering of the four-membered rings, with fold angles of 15.3–24.5° between the C–Pt–C and C–S–C planes. To our knowledge, an X-ray crystal structure determination of a monometallic ureylene derivative, containing the fragment M–NR–C(O)–NR, has not been reported, thus preventing a direct comparison of the geometry of such a system with the present cases. The S–O bond lengths are comparable to those found in 5 (L = PMePh₂) by Woollins and co-workers.[2] The sum of the bond angles about nitrogen is equal to 359.1°, very close to the value of 360° expected for a planar co-ordination and very much larger than the 328.5° expected for a pyramidal arrangement. The lone pairs on the nitrogen atoms must therefore reside in 2p orbitals perpendicular to the plane of the four-membered ring. No significant π interaction between these lone pairs and the attached aromatic systems can occur as the phenyl groups are rotated somewhat

Table 2 Selected bond lengths and angles for [Pt{NPhP(O)(Ph)N-Ph}(PPh₃)₂] 11a·H₂O·CH₂Cl₂ᵃ

Pt–P(1)	2.279(2)	P(3)–O(1)	1.478(9)
Pt–P(2)	2.284(2)	P(3)–C(31)	1.826(7)
Pt–N(1)	2.085(7)	N(1)–C(51)	1.431(6)
Pt–N(2)	2.077(6)	N(2)–C(61)	1.411(6)
N(1)–P(3)	1.648(6)	Pt ··· P(3)	2.843(2)
N(2)–P(3)	1.662(7)	O(1)··· O(2)	2.745
P(1)–Pt–P(2)	100.7(1)	C(51)–N(1)–P(3)	121.2(5)
N(1)–Pt–N(2)	70.2(2)	C(61)–N(2)–Pt	137.1(5)
P(1)–Pt–N(1)	96.5(1)	C(61)–N(2)–P(3)	123.7(5)
P(2)–Pt–N(2)	94.6(2)	Twistᵇ	16.1(3)
Pt–N(1)–P(3)	98.5(2)	Foldᶜ	6.2(4)
Pt–N(2)–P(3)	98.4(2)	C(32)–C(31)–P(3)–O(1)	16.5(5)
N(1)–P(3)–N(2)	92.6(3)	C(56)–C(51)–N(1)–Pt	−36.1(10)
O(1)–P(3)–C(31)	106.6(4)	C(62)–C(61)–N(2)–Pt	−34.3(12)
C(51)–N(1)–Pt	137.0(5)		

ᵃ See Fig. 2 for crystallographic numbering system. ᵇ P(1)–Pt–P(2)/N(1)–Pt–N(2). ᶜ N(1)–Pt–N(2)/N(1)–P(3)–N(2).

out of the plane of the ring. The double bonds co-ordinated to the platinum atom have lengths similar to the corresponding bonds in [PtCl₂(cod)].[7] In addition, the Pt–C(1) and Pt–C(2) bond lengths are not greatly different from one another and are similar to the Pt–C bond lengths in [PtCl₂(cod)]. These values indicate that the diene ligand is essentially symmetrically co-ordinated to the platinum atom. There has been much controversy over the extent of unsymmetrical bonding of the diene ligand in [PtCl₂(cod)],[7,8] although an effectively symmetrical co-ordination seems more likely on the basis of X-ray crystal structure studies conducted thus far.[7,8]

The structure of complex 11a consists of a four-membered platinacyclic ring containing two metal–nitrogen and two phosphorus–nitrogen single bonds with two triphenylphosphine ligands attached to the metal, to give a distorted square-planar environment. The platinum lies in the least-squares plane defined by itself and its nearest neighbours, though the twist angle between the planes P(1)–Pt–P(2) and N(1)–Pt–N(2) is quite large at 16.1(3)°. The reason for this significant deviation from planar geometry is probably associated with steric interactions between the phosphine ligands and the phenyl groups attached to N(1) and N(2). The four-membered ring itself is almost planar, the fold angle between planes N(1)–Pt–N(2) and N(1)–P(3)–N(2) being just 6.2(4)°. A consequence of the near-planarity of the ring is that the trans-annular Pt ··· P(3) distance of 2.843(2) Å is well outside the sum of the covalent radii of the two atoms, thus indicating no significant interaction between them. The oxygen atom O(1) occupies a pseudo-equatorial position. As found for 9g, the two nitrogen atoms are again in effectively planar environments, the bond angles around N(1) and N(2) adding to 356.7 and 359.2° respectively. This suggests the occupation of a 2p orbital on nitrogen by the lone pairs on these atoms, as postulated for 9g. The phenyl groups attached to N(1) and N(2) are each rotated out of the plane of the metallacyclic ring by about 35°. Each molecule of complex 11a crystallises with one molecule of dichloromethane and one molecule of water; the latter containing O(2) is hydrogen-bonded to the phosphoryl group, and probably originates from the synthesis stage of the metallacycle.

The room-temperature ¹H NMR spectra of complexes 11 are consistent with the static structures shown above. In complex 11d the dppm methylene protons are inequivalent, since they are either cis or trans to the phosphoryl group in the opposing ring. They each appear as a doublet of triplets owing to coupling to each other and to the adjacent equivalent phosphorus nuclei. The spectrum of 11h shows only two sets of signals for the cycloocta-1,5-diene olefinic protons, which indicates the presence of a mirror plane passing through the platinum,

phosphorus and oxygen atoms. The ¹³C-{¹H} NMR spectra of complexes 11 are also consistent with the above structures.

The room-temperature ³¹P-{¹H} NMR spectra of the phosphorus-containing derivatives of 9 all consist of single phosphorus resonances with corresponding platinum-195 satellites. The room-temperature ³¹P-{¹H} NMR spectra of 11 are highly distinctive, the donor-ligand phosphorus nuclei appearing as a singlet, with ¹J(PtP) in the range 2800–3440 Hz, with the ring phosphorus also being observed as a singlet, but with a two-bond coupling to platinum-195 in the range 132–186 Hz. No three-bond phosphorus–phosphorus coupling is seen in any of the spectra.

The IR spectra of complexes 9a–9f exhibit very strong bands in the regions 1261–1245 and 1142–1093 cm⁻¹, corresponding to $v_{asym}(SO)_2$ and $v_{sym}(SO)_2$ vibrations respectively. The spectra of 11 clearly show the characteristic band of the phosphoryl stretch between 1280 and 1250 cm⁻¹. For such a group these values are quite high, one probable explanation being the fact that the phosphorus forms part of a strained ring system. Increases in the frequency of phosphoryl stretches when the phosphorus atom is contained in a cyclic structure have been noted previously.[9] The spectrum of 13, in addition, shows two strong bands at 1490 and 1350 cm⁻¹, corresponding to asymmetric and symmetric stretching respectively of the two nitro groups.

One triphenylphosphine ligand can be replaced by tert-butyl isocyanide on treatment of complex 9a with an excess of this reagent in dichloromethane at room temperature to yield complex 15. No evidence for insertion of an isocyanide molecule into a platinum–nitrogen bond was observed. The cycloocta-1,5-diene complex 11h readily undergoes simple diene-displacement reactions with mono- or bi-dentate tertiary phosphines to yield the corresponding phosphine analogues. Thus, treatment of 11h with 2 mole equivalents of triphenylphosphine in dichloromethane at room temperature afforded complex 11a, whereas similar treatment with 1 mole equivalent of either dppe or dppp gave complexes 11e and 11f respectively, in good yield.

The compounds 5 (L = PMePh₂) and 7 (R = H, L = PPh₃ or PMePh₂; L₂ = dppp or dppb) are able to insert a molecule of dimethyl acetylenedicarboxylate (dmad) into a metal–nitrogen bond to form six-membered metallacycles.[4] However, the N,N'-diphenyl-substituted derivatives 9a, 11a, 11c or 11h do not react with dmad in dichloromethane. This suggests that the nucleophilicity of the nitrogen lone pairs is an important factor governing these reactions, since, as can be inferred from the X-ray crystal structures of 9g and 11a, the nitrogen lone pairs in these complexes reside in 2p orbitals and therefore have reduced nucleophilic character. In contrast, the X-ray crystal structure of 5 (L = PMePh₂) showed the nitrogen atoms to be in pyramidal environments,[2] with the lone pairs retaining their nucleophilicity. It should be noted, however, that steric factors may also inhibit these insertion reactions. We also note that complexes 9a, 11a and 11h do not react with methyl iodide at room temperature, whereas 7 (R = H, L = PPh₃) reacts almost instantaneously to yield cis-[PtI₂(PPh₃)₂] and PhP(O)(NHMe)₂.[10]

Experimental

Tables 3 and 4 show m.p.s, analytical and selected IR data for complexes **9** and **11–13** respectively. 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 SiMe₄ (0.0 ppm) as internal reference, positive values being to high frequency (low field), in CDCl₃ unless otherwise stated. ¹³C-{¹H} NMR spectra were recorded on a Bruker AM300 spectrometer at 75.47 MHz with SiMe₄ (0.0 ppm) as internal reference, in

Table 3 M.p.s, analytical[a] and selected IR[b] data for complexes 9

| Complex | M.p.[c]/°C | Elemental analysis (%) | | | v(SO$_2$)[d]/cm^{-1} | |
		C	H	N	asym	sym
9a	205–211	59.9 (59.7)	4.2 (4.2)	2.9 (2.9)	1258	1130, 1100
9b	217–220	53.9 (54.2)	4.3 (4.3)	3.2 (3.3)	1260	1135, 1107
9c·0.5CH$_2$Cl$_2$	218–220	47.8 (47.8)	5.3 (5.1)	3.5 (3.4)	1245	1142, 1114
9d·0.5H$_2$O	>220	40.0 (40.4)	5.8 (5.8)	4.2 (3.9)	1261	1142
9e	175–176	55.3 (55.3)	5.4 (5.3)	5.8 (5.9)	1260	1132, 1093
9f	>220	54.1 (54.4)	4.1 (4.1)	3.5 (3.4)	1246	1132, 1114

[a] Calculated values given in parentheses. [b] Recorded as KBr discs. [c] All with decomposition except 9f. [d] All bands very strong.

Table 4 M.p.s, analytical[a] and selected IR[b] data for complexes 11–13

| Complex | M.p./°C | Elemental analysis (%) | | | v(P=O)[c]/ cm^{-1} |
		C	H	N	
11a·H$_2$O	126	61.5 (62.1)	4.5 (4.5)	2.6 (2.7)	1250
11b·H$_2$O	>220	57.8 (57.5)	4.6 (4.7)	3.3 (3.1)	1260
11c	116	52.3 (52.5)	4.9 (4.8)	3.6 (3.6)	1260
11d	>220	58.1 (58.2)	4.0 (4.2)	3.1 (3.2)	1270
11e	123	58.4 (58.7)	4.4 (4.3)	3.1 (3.1)	1280
11f·H$_2$O	>220	58.0 (58.0)	4.5 (4.6)	3.1 (3.0)	1270
11g·CH$_2$Cl$_2$	127	56.1 (55.7)	4.6 (4.5)	2.9 (2.8)	1260
11h·CHCl$_3$	205	44.8 (44.5)	3.7 (3.8)	3.9 (3.8)	1270
12·H$_2$O	97	54.9 (54.8)	5.4 (5.4)	3.4 (2.9)	1260
13·H$_2$O	160	56.9 (57.2)	3.9 (4.0)	4.9 (4.9)	1260

[a] Calculated values given in parentheses. [b] Recorded as KBr discs. [c] All bands strong.

CDCl$_3$. The phenyl carbon region has been omitted for clarity. ^{31}P-{^{1}H} NMR spectra were recorded in dichloromethane on a JEOL-FX90 spectrometer at 36.2 MHz, with [P(OH)$_4$]$^+$ in D$_2$O (0.0 ppm) as external reference.

Experiments were carried out using a dry, oxygen-free, dinitrogen atmosphere, using solvents which were dried and distilled under dinitrogen prior to use. Light petroleum refers to the fraction of b.p. 40–60 °C. All compounds were recrystallised in air. The compounds methyl iodide, dimethyl acetylene-dicarboxylate (Aldrich), potassium hydroxide (BDH) and *tert*-butyl isocyanide (Fluka) were used as supplied from commercial sources. The compounds [PtCl$_2$(cod)],[11] *cis*-[PtCl$_2${P(NEt$_2$)Ph$_2$}$_2$],[12] [{PtBr$_2$(PPr^n$_3$)}$_2$],[13] N,N'-diphenyl-sulfamide 8,[14] N,N',P-triphenylphosphonic diamide 10 (R = Ph),[15] N,N'-di-p-nitrophenyl-P-phenylphosphonic diamide 10 (R = p-C$_6$H$_4$NO$_2$)[15] and diethylphenylphosphine[16] were prepared as described in the literature.

Preparation of Platinum 2,4-Diphenyl-1,2,4-thiadiazetidine 1,1-Dioxide Complexes 9.—(a) Using silver(ı) oxide: general method. Two equivalents of tertiary monodentate phosphine or 1 equivalent of bidentate phosphine, followed by 1 equivalent of N,N'-diphenylsulfamide 8 and an excess of silver(ı) oxide, were added in succession to a stirred solution of [PtCl$_2$(cod)] in dichloromethane and the mixture refluxed for 3 h. The mixture was filtered through Celite and the filtrate evaporated to dryness under reduced pressure. Dissolution of the resulting oil in dichloromethane (ca. 1 cm^3) and addition of light petroleum gave a microcrystalline *solid* which was recrystallised from dichloromethane–light petroleum, unless stated otherwise, and dried *in vacuo*.

(*i*) [Pt{NPhS(O)$_2$NPh}(PPh$_3$)$_2$] 9a. The complex [PtCl$_2$-(cod)] (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and N,N'-diphenylsulfamide (0.067 g, 0.27 mmol) in dichloromethane (30 cm^3) gave, on recrystallisation of the solid product from dichloromethane–diethyl ether, pale yellow *crystals* of complex 9a (0.154 g, 59%). ^{31}P-{^{1}H} NMR spectrum (36 MHz): δ 7.81 [s, ^{1}J(PtP) 3501 Hz].

(*ii*) [Pt{NPhS(O)$_2$NPh}(PMePh$_2$)$_2$] 9b. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with methyldiphenylphosphine (0.108 g, 0.54 mmol) and N,N'-diphenylsulfamide (0.067 g, 0.27 mmol) in dichloromethane (35 cm^3) gave, on recrystallisation of the solid product from dichloromethane–diethyl ether, white *microcrystals* of 9b (0.070 g, 31%). NMR spectra: ^{1}H (300 MHz), δ 7.39–6.82 (m, 30 H, Ph) and 1.62 (m, 6 H, Me, PMePh$_2$); ^{31}P-{^{1}H} (36 MHz), δ −8.21 [s, ^{1}J(PtP) 3394 Hz].

(*iii*) [Pt{NPhS(O)$_2$NPh}(PEt$_2$Ph)$_2$] 9c·0.5CH$_2$Cl$_2$. The complex [PtCl$_2$(cod)] (0.15 g, 0.40 mmol) with diethylphenyl-phosphine (0.134 g, 0.81 mmol) and N,N'-diphenylsulfamide (0.10 g, 0.40 mmol) in dichloromethane (50 cm^3) gave white *microcrystals* of 9c·0.5CH$_2$Cl$_2$ (0.050 g, 15%). NMR spectra: ^{1}H (300 MHz), δ 7.48–7.09 (m, 20 H, Ph), 5.31 (s, 1 H, CH$_2$Cl$_2$), 1.57 (m, 4 H, CH$_2$, PEt$_2$Ph), 1.20 (m, 4 H, CH$_2$, PEt$_2$Ph) and 0.69 (m, 12 H, Me, PEt$_2$Ph); ^{31}P-{^{1}H} (36 MHz), δ −4.58 [s, ^{1}J(PtP) 3313 Hz].

(*iv*) [Pt{NPhS(O)$_2$NPh}(PEt$_3$)$_2$] 9d·0.5H$_2$O. The complex [PtCl$_2$(cod)] (0.15 g, 0.40 mmol) with triethylphosphine (0.096 g, 0.81 mmol) and N,N'-diphenylsulfamide (0.101 g, 0.407 mmol) in dichloromethane (35 cm^3) gave, on stirring the initially obtained oil with light petroleum overnight, sandy coloured *microcrystals* of 9d·0.5H$_2$O (0.21 g, 78%). NMR spectra: ^{1}H (300 MHz), δ 7.46–7.05 (m, 10 H, Ph), 1.87 (s, br, 1 H, H$_2$O), 1.52 (m, 12 H, CH$_2$, PEt$_3$) and 1.05 (m, 18 H, Me, PEt$_3$); ^{31}P-{^{1}H} (36 MHz), δ −0.67 [s, ^{1}J(PtP) 3286 Hz].

(*v*) [Pt{NPhS(O)$_2$NPh}{P(NEt$_2$)Ph$_2$}$_2$] 9e. N,N'-Diphenyl-sulfamide (0.048 g, 0.19 mmol) and silver(ı) oxide (0.17 g, 0.73 mmol) were added in succession to a stirred solution of *cis*-[PtCl$_2${P(NEt$_2$)Ph$_2$}$_2$] (0.15 g, 0.19 mmol) in dichloromethane (35 cm^3) and the mixture refluxed for 2.5 h. The insoluble silver salts were removed by filtration, and the resulting solution evaporated to dryness under reduced pressure to afford a colourless oil. Dissolution of the oil in dichloromethane (ca. 2 cm^3) and addition of light petroleum gave a pale yellow powdery solid which was recrystallised from dichloromethane–light petroleum to give pale yellow *microcrystals* of complex 9e (0.12 g, 66%). NMR spectra: ^{1}H (300 MHz), δ 7.35–6.74 (m, 30 H, Ph), 3.18–3.10 [m, 8 H, CH$_2$, P(NEt$_2$)Ph$_2$] and 0.97 [t, 12 H, Me, P(NEt$_2$)Ph$_2$, ^{3}J(HH) 7.0]; ^{13}C-{^{1}H} [75.5 MHz, distortionless enhancement of polarisation transfer (DEPT)], δ 132.96–122.64 (m, Ph), 43.46 [s, CH$_2$, P(NEt$_2$)Ph$_2$] and 12.85 [s, Me, P(NEt$_2$)Ph$_2$]; ^{31}P-{^{1}H} (36 MHz), δ 52.03 [s, ^{1}J(PtP) 3809 Hz].

(*vi*) [Pt{NPhS(O)$_2$NPh}(dppe)] 9f. The complex [PtCl$_2$-(cod)] (0.10 g, 0.27 mmol) with 1,2-bis(diphenylphosphino)-ethane (0.11 g, 0.28 mmol) and N,N'-diphenylsulfamide (0.067 g, 0.27 mmol) in dichloromethane (30 cm^3) gave yellow *crystals* of 9f (0.18 g, 79%). NMR spectra: ^{1}H (300 MHz), δ 7.59–6.60 (m, 30 H, Ph) and 2.24–2.08 (m, 4 H, CH$_2$, dppe); ^{31}P-{^{1}H} (36 MHz), δ 37.92 [s, ^{1}J(PtP) 3384 Hz].

Several *crystals* of [Pt{NPhS(O)$_2$NPh}(cod)] 9g, one of which was suitable for a single-crystal X-ray diffraction study,

were isolated from a subsequent preparation of the chelating phosphine analogue **9f**.

(*b*) *Using potassium hydroxide; general method.* Two equivalents of tertiary monodentate phosphine or 1 equivalent of bidentate phosphine, followed by one equivalent of *N,N'*-diphenylsulfamide **8** and an excess of potassium hydroxide, were added in succession to a stirred suspension of [PtCl$_2$(cod)] in a mixture of dichloromethane (*ca.* 10 cm^3) and thf (*ca.* 30 cm^3) and the mixture refluxed for 1.5 h. The mixture was filtered to remove excess of potassium hydroxide 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.* 20 cm^3). The organic layer was separated off and dried over anhydrous MgSO$_4$. The mixture was filtered and the solution reduced in volume to *ca.* 2 cm^3, addition of diethyl ether yielding a microcrystalline *solid* which was filtered off and dried *in vacuo*.

(*i*) *Complex* **9a**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and *N,N'*-diphenyl-sulfamide (0.067 g, 0.27 mmol) gave yellow *microcrystals* of complex **9a** (0.09 g, 35%), identified by comparison of their ^{31}P-$\{^1$H$\}$ NMR spectrum with that of an authentic sample.

(*ii*) *Complex* **9c·0.5CH$_2$Cl$_2$**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PEt$_2$Ph (0.091 g, 0.55 mmol) and *N,N'*-diphenylsulfamide (0.067 g, 0.27 mmol) gave white *micro-crystals* of complex **9c·0.5CH$_2$Cl$_2$** (0.13 g, 59%), identified by comparison of their ^{31}P-$\{^1$H$\}$ NMR spectrum with that of an authentic sample.

(*iii*) *Complex* **9f**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.108 g, 0.27 mmol) and *N,N'*-diphenylsulfa-mide (0.067 g, 0.27 mmol) gave pale yellow *microcrystals* of complex **9f** (0.163 g, 72%), identified by comparison of their ^{31}P-$\{^1$H$\}$ NMR spectrum with that of an authentic sample.

Preparation of Platinum 1,2,3-Triphenyl-1,3,2-diazaphosphet-idine 2-Oxide Complexes; General Method.—Two mole equivalents of tertiary phosphine or 1 mole equivalent of chelating tertiary phosphine, followed by 1 equivalent of *N,N',P*-triphenylphosphonic diamide **10** (R = Ph) and an excess of silver(ı) oxide, were added in succession to a stirred solution of [PtCl$_2$(cod)] in dichloromethane (*ca.* 45 cm^3) and the mixture refluxed for 15 h. The cooled reaction mixture was filtered through Celite and the filtrate evaporated to dryness under reduced pressure to afford a yellowish brown oil. Dissolution of the oil in dichloromethane (*ca.* 5 cm^3) followed by addition of light petroleum afforded, on standing, a yellow to pale green microcrystalline *solid*, which was recrystallised from dichloromethane–light petroleum and dried *in vacuo*.

(*i*) [Pt{NPhP(O)(Ph)NPh}(PPh$_3$)$_2$] **11a·H$_2$O**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and *N,N',P*-triphenylphosphonic diamide **10** (R = Ph) (0.09 g, 0.29 mmol) gave greeny yellow *microcrystals* of **11a·H$_2$O** (0.27 g, 96%). NMR spectra: ^{1}H (90 MHz), δ 8.2–6.1 (m, 45 H, Ph) and 2.1 (s, br, 2 H, H$_2$O); ^{31}P-$\{^1$H$\}$, δ 46.51 [s, P=O, ^2J(PtP) 151] and 9.15 [s, PPh$_3$, ^1J(PtP) 3401 Hz]. X-Ray quality *crystals* of **11a·H$_2$O·CH$_2$Cl$_2$** were grown slowly from dichloromethane–light petroleum, in air.

(*ii*) [Pt{NPhP(O)(Ph)NPh}(PMePh$_2$)$_2$] **11b·H$_2$O**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PMePh$_2$ (0.11 g, 0.55 mmol) and *N,N',P*-triphenylphosphonic diamide **10** (R = Ph) (0.09 g, 0.29 mmol) gave greeny yellow *microcrystals* of **11b·H$_2$O** (0.23 g, 93%). NMR spectra: ^{1}H (300 MHz), δ 8.08–6.48 (m, 35 H, Ph), 2.37 (s, br, 2 H, H$_2$O), 1.57 [d, 6 H, Me, PMePh$_2$, |^2J(PH) + ^4J(PH)| 10]; ^{13}C-$\{^1$H$\}$, δ 15.08 [d, Me, PMePh$_2$, |^1J(PC) + ^3J(PC)| 42]; ^{31}P-$\{^1$H$\}$, δ 43.48 [s, P=O, ^2J(PtP) 152] and −7.20 [s, PMePh$_2$, ^1J(PtP) 3308 Hz].

(*iii*) [Pt{NPhP(O)(Ph)NPh}(PMe$_2$Ph)$_2$] **11c**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PMe$_2$Ph (0.08 g, 0.58 mmol) and *N,N',P*-triphenylphosphonic diamide (0.09 g, 0.29

mmol) gave greeny yellow *microcrystals* of **11c** (0.29 g, 95%). NMR spectra: ^{1}H (300 MHz), δ 8.03–6.66 (m, 25 H, Ph) and 1.14 (m, 12 H, Me, PMe$_2$Ph); ^{13}C-$\{^1$H$\}$, δ 13.77 (m, Me, PMe$_2$Ph); ^{31}P-$\{^1$H$\}$, δ 40.72 [s, P=O, ^2J(PtP) 156] and −23.69 [s, PMe$_2$Ph, ^1J(PtP) 3241 Hz].

(*iv*) [Pt{NPhP(O)(Ph)NPh}(dppm)] **11d**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppm (0.11 g, 0.29 mmol) and *N,N',P*-triphenylphosphonic diamide (0.09 g, 0.29 mmol) gave pale green *microcrystals* of **11d** (0.22 g, 92%). NMR spectra: ^{1}H (300 MHz), δ 8.20–6.32 (m, 35 H, Ph), 4.54 [dt, 1 H, CH$_2$, dppm, ^2J(HH) 16, ^2J(PH) 11], 4.38 [dt, 1 H, CH$_2$, dppm, ^2J(HH) 16, ^2J(PH) 11]; ^{13}C-$\{^1$H$\}$, δ 49.94 [t, CH$_2$, dppm, ^1J(PC) 34]; ^{31}P-$\{^1$H$\}$, δ 38.91 [s, P=O, ^2J(PtP) 186] and −57.62 [s, dppm, ^1J(PtP) 2803 Hz].

(*v*) [Pt{NPhP(O)(Ph)NPh}(dppe)] **11e**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and *N,N',P*-triphenylphosphonic diamide (0.09 g, 0.29 mmol) gave greeny yellow *microcrystals* of **11e** (0.23 g, 95%). NMR spectra: ^{1}H (300 MHz), δ 8.16–6.37 (m, 35 H, Ph) and 2.20–1.98 (m, 4 H, CH$_2$, dppe); ^{13}C-$\{^1$H$\}$, δ 30.29 [dd, CH$_2$, dppe, ^1J(PC) 45, ^2J(PC) 8]; ^{31}P-$\{^1$H$\}$, δ 39.53 [s, P=O, ^2J(PtP) 142] and −38.12 [s, dppe, ^1J(PtP) 3291 Hz].

(*vi*) [Pt{NPhP(O)(Ph)NPh}(dppp)] **11f·H$_2$O**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and *N,N',P*-triphenylphosphonic diamide (0.09 g, 0.29 mmol) gave greeny yellow *microcrystals* of **11f·H$_2$O** (0.24 g, 95%). NMR spectra: ^{1}H (300 MHz), δ 8.08–6.34 (m, 35 H, Ph), 2.?2 (m, 4 H, PCH$_2$, dppp), 2.01 (s, br, 2 H, H$_2$O) and 1.74 (m, 2 H, CH$_2$, dppp); ^{13}C-$\{^1$H$\}$, too insoluble; ^{31}P-$\{^1$H$\}$, δ 41.46 [s, P=O, ^2J(PtP) 142] and −7.20 [s, dppp, ^1J(PtP) 3157 Hz].

(*vii*) [Pt{NPhP(O)(Ph)NPh}(dppb)] **11g·CH$_2$Cl$_2$**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and *N,N',P*-triphenylphosphonic diamide (0.09 g, 0.29 mmol) gave pale green *microcrystals* of **11g·CH$_2$Cl$_2$** (0.25 g, 91%). NMR spectra: ^{1}H (300 MHz), δ 8.00–6.32 (m, 35 H, Ph), 5.22 (s, 2 H, CH$_2$Cl$_2$), 2.48 (m, 4 H, PCH$_2$, dppb) and 1.52 (m, 4 H, CH$_2$, dppb); ^{13}C-$\{^1$H$\}$, δ 53.11 (s, CH$_2$Cl$_2$), 32.81 (m, PCH$_2$, dppb) and 23.53 (s, CH$_2$, dppb); ^{31}P-$\{^1$H$\}$, δ 43.75 [s, P=O, ^2J(PtP) 154] and −7.07 [s, dppb, ^1J(PtP) 3256 Hz].

(*viii*) [Pt{NPhP(O)(Ph)NPh}(cod)] **11h·CHCl$_3$**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with *N,N',P*-triphenylphosphonic diamide (0.09 g, 0.29 mmol) gave greeny yellow *microcrystals* which were recrystallised from a saturated chloro-form solution to give greeny yellow *crystals* of **11h·CHCl$_3$** (0.18 g, 92%). NMR spectra: ^{1}H (300 MHz), δ 8.08–6.84 (m, 16 H, Ph + CHCl$_3$), 4.97 [m, 2 H, CH, cod, ^2J(PtH) 54], 4.88 [m, 2 H, CH, cod, ^2J(PtH) 54], 2.64 (m, 4 H, CH$_2$, cod) and 2.26 (m, 4 H, CH$_2$, cod); ^{13}C-$\{^1$H$\}$, δ 92.22 [s, CH, cod, ^1J(PtC) 151], 90.81 [s, CH, cod, ^1J(PtC) 151], 77.21 (s, CHCl$_3$), 30.45 (s, CH$_2$, cod) and 30.12 (s, CH$_2$, cod); ^{31}P-$\{^1$H$\}$, δ 44.15 [s, P=O, ^2J(PtP) 149 Hz].

(*ix*) [Pt{NPhP(O)(Ph)NPh}(PPr$^n_3$)(AsPh$_3$)] **12·H$_2$O**. The complex [{PtBr$_2$(PPr$^n_3$)}$_2$] (0.20 g, 0.19 mmol) with AsPh$_3$ (0.12 g, 0.39 mmol) and *N,N',P*-triphenylphosphonic diamide (0.12 g, 0.39 mmol) gave yellow *microcrystals* of **12·H$_2$O** (0.36 g, 96%). NMR spectra: ^{1}H (300 MHz), δ 8.05–6.24 (m, 30 H, Ph), 2.41 (s, br, 2 H, H$_2$O), 1.36 (m, 6 H, PCH$_2$, PPr$^n_3$), 1.13 (m, 6 H, CH$_2$, PPr$^n_3$), and 0.74 [t, 9 H, CH$_3$, PPr$^n_3$, ^3J(HH) 7]; ^{13}C-$\{^1$H$\}$, 26.07 [d, PCH$_2$, PPr$^n_3$, ^1J(PC) 34], 17.94 (s, CH$_2$, PPr$^n_3$) and 15.45 [d, CH$_3$, PPr$^n_3$, ^3J(PC) 15]; ^{31}P-$\{^1$H$\}$, δ 44.37 [s, P=O, ^2J(PtP) 166] and −12.91 [s, PPr$^n_3$, ^1J(PtP) 3174 Hz].

(*x*) [Pt{N(*p*-NO$_2$C$_6$H$_4$)P(O)(Ph)N(*p*-NO$_2$C$_6$H$_4$)}(PPh$_3$)$_2$] **13·H$_2$O**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and *N,N'*-di-*p*-nitrophenyl-*P*-phenylphosphonic diamide **10** (R = *p*-nitrophenyl) (0.11 g, 0.28 mmol) gave golden-yellow *microcrystals* of **13·H$_2$O** (0.29 g, 95%). IR spectra: v_{NO_2} at 1490 (asym) and 1350 (sym) cm^{-1}. NMR spectra: ^{1}H (90 MHz), δ 8.2–6.4 (m, 43 H, Ph) and 1.9

Table 5 Fractional atomic coordinates for [Pt{NPhS(O)₂NPh}(cod)] **9g**

Atom	x	y	z
Pt	0.000 00(0)	0.092 30(1)	0.250 00(0)
S	0.000 00(0)	−0.108 59(9)	0.250 00(0)
O(1)	0.045 93(29)	−0.166 07(22)	0.362 3(3)
N(1)	−0.082 7(3)	−0.027 03(25)	0.268 7(4)
C(1)	−0.133 4(4)	0.195 2(3)	0.213 6(5)
C(2)	−0.064 8(5)	0.205 3(3)	0.339 4(5)
C(3)	0.018 0(5)	0.286 3(3)	0.390 8(5)
C(4)	0.134 1(5)	0.258 7(4)	0.396 0(6)
C(11)	−0.172 4(3)	−0.049 43(29)	0.308 5(4)
C(12)	−0.252 0(4)	−0.117 1(3)	0.241 1(5)
C(13)	−0.341 3(4)	−0.138 3(4)	0.278 1(5)
C(14)	−0.353 8(5)	−0.091 6(4)	0.381 6(6)
C(15)	−0.275 1(5)	−0.025 5(4)	0.449 3(5)
C(16)	−0.183 8(4)	−0.006 39(29)	0.415 1(4)
H(1)	−0.200(6)	0.146(5)	0.191(6)
H(2)	−0.085(5)	0.174(4)	0.394(6)
H(12)	−0.243 4(4)	−0.152 8(3)	0.159 6(5)
H(13)	−0.401 4(4)	−0.191 4(4)	0.226 5(5)
H(14)	−0.424 7(5)	−0.106 8(4)	0.409 3(6)
H(15)	−0.285 2(5)	0.011 4(4)	0.529 3(5)
H(16)	−0.120 8(4)	0.042 46(29)	0.471 7(4)
H(31)	−0.009 1(5)	0.348 4(3)	0.330 1(5)
H(32)	0.020 6(5)	0.304 0(3)	0.485 5(5)
H(41)	0.178 3(5)	0.215 1(4)	0.477 3(6)
H(42)	0.183 6(5)	0.320 7(4)	0.392 4(6)

(s, br, 2 H, H₂O); ³¹P-{¹H}, δ 43.41 [s, P=O, ²J(PtP) 132] and 7.67 [s, PPh₃, ¹J(PtP) 3440 Hz].

Reactions of New Metallacyclic Complexes.—(i) *Complex* **9a** *with* BuⁱNC. *tert*-Butyl isocyanide (0.07 g, 0.84 mmol) was added to a solution of complex **9a** (0.20 g, 0.21 mmol) in dichloromethane (40 cm³) and the mixture stirred for 2 h at room temperature. It was reduced in volume to *ca.* 2 cm³ under reduced pressure, and diethyl ether added to precipitate a white solid. The mixture was evaporated to dryness, the solid being stirred with diethyl ether for 1 h. The mother-liquor was decanted off and the solid dissolved in dichloromethane (*ca.* 1 cm³). Addition of light petroleum afforded a creamy-white powder which was filtered off and dried *in vacuo* to give [Pt{NPhS(O)₂NPh}(CNBuⁱ)(PPh₃)] **15** (0.073 g, 44%), m.p. >230 °C; ν(C≡N) at 2205vs, ν_asym(SO₂) at 1260s and ν_sym(SO₂) at 1133s cm⁻¹. NMR spectra: ¹H (300 MHz), δ 7.59–6.71 (m, 25 H, Ph) and 1.01 (s, 9 H, Buⁱ); ³¹P-{¹H} (36 MHz), δ 5.99 [s, ¹J(PtP) 3262 Hz]. The compound was not obtained analytically pure.

(ii) *Ligand substitutions of complex* **11h·CHCl₃**. (a) *With* PPh₃. A solution of [Pt{NPhP(O)(Ph)NPh}(cod)] **11h·** CHCl₃ (0.10 g, 0.14 mmol) in dichloromethane (30 cm³) with PPh₃ (0.08 g, 0.30 mmol) was stirred for 30 min at room temperature. The mixture was evaporated to dryness under reduced pressure to afford an oil which was crystallised from dichloromethane–light petroleum to afford greeny yellow *microcrystals* of [Pt{NPhP(O)(Ph)NPh}(PPh₃)₂] **11a** (0.14 g, 98%), identified by ³¹P-{¹H} NMR spectroscopy.

(b) *With* dppe. A solution of complex **11h·CHCl₃** (0.10 g, 0.14 mmol) in dichloromethane (30 cm³) with dppe (0.06 g, 0.15 mmol) was stirred for 30 min at room temperature. Work-up as in (a) afforded greeny yellow *microcrystals* of [Pt{NPhP(O)(Ph)NPh}(dppe)] **11e** (0.12 g, 95%), identified by ³¹P-{¹H} NMR spectroscopy.

(c) *With* dppp. A solution of complex **11h·CHCl₃** (0.10 g, 0.14 mmol) in dichloromethane (30 cm³) with dppp (0.06 g, 0.15 mmol) was stirred for 30 min at room temperature. Work-up as in (a) afforded greeny-yellow *microcrystals* of

[Pt{NPhP(O)(Ph)NPh}(dppp)] **11f** (0.12 g, 94%), identified by ³¹P-{¹H} NMR spectroscopy.

(iii) *With dimethyl acetylenedicarboxylate.* A solution of one of the complexes **9a**, **11a**, **11c** or **11h** (0.10 g) in dichloromethane (25 cm³) with dimethyl acetylenedicarboxylate (0.10 g, 0.70 mmol) was stirred for 15 h at room temperature. Evaporation to dryness under reduced pressure afforded in each case a pale green oil which was shown by ³¹P-{¹H} NMR spectroscopy to contain mainly unreacted starting material.

(iv) *With methyl iodide.* A solution of one of the complexes **9a**, **11a** or **11h** (0.10 g) in dichloromethane (25 cm³) with methyl iodide (1.5 cm³) was stirred for 4 h at room temperature. Evaporation to dryness under reduced pressure afforded in each case a pale green oil which was shown by ³¹P-{¹H} NMR spectroscopy to contain mainly unreacted starting material.

X-Ray Crystallography.—(a) [Pt{NPhS(O)₂NPh}(cod)] **9g**. The approximate unit-cell dimensions were obtained from oscillation and Weissenberg photographs along the *c* axis, and final cell dimensions were determined by least-squares refinement of observed ω angles for 417 reflections from zero and upper layers measured on the Weissenberg diffractometer. Data were collected from the layers *hk*0 to *hk*13 on a Weissenberg diffractometer, in the two quadrants +*h*, +*k*, and −*h*, +*k*. The intensity data were collected at room temperature on a Stöe Stadi-2 Weissenberg diffractometer using an ω-scan technique in the range 7 < 2θ < 54°. The unique 2208 reflections, having *I* ≥ 3σ(*I*), were corrected for Lorentz and polarisation effects. An absorption correction was also applied, the maximum and minimum transmission factors being 0.3033 and 0.2118 respectively.

Crystal data. C₂₀H₂₂N₂O₂PtS, *M* = 549.42, 0.32 × 0.23 × 0.22 mm monoclinic, space group *I*2/*c* (non-standard setting of *C*2/*c*), *a* = 12.862(4), *b* = 13.901(4), *c* = 11.220(1) Å, β = 110.21(1)°, *U* = 1882.57(1.26) Å³, *Z* = 4, *D*_c = 1.94 g cm⁻³, *F*(000) = 1063.8, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 72.71 cm⁻¹.

The heavy atom method was employed to solve the structure. The program SHELXS 86 ¹⁷ was used for Patterson summation to locate the platinum atom, and the program SHELX 76 ¹⁸ for the rest of the analysis. Scattering factors used in the program SHELX 76 were obtained from ref. 19. In the final cycles of refinement all atoms were given anisotropic thermal parameters. The final cycles with all hydrogen atoms in fixed positions employed a weighting parameter $w = 1.2571/(\sigma^2 F + gF^2)$, where $g = 0.000\ 527$. The final residual indices for 2208 reflections were $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.0254$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.0261$. The final Fourier difference map revealed no major features and an analysis of the weighting scheme over $|F_o|$ and (sin θ)/λ was satisfactory. The atomic coordinates are given in Table 5 (owing to the symmetry of the molecule, only coordinates for one side of the molecule are given).

(b) [Pt{NPhP(O)(Ph)NPh}(PPh₃)₂] **11a·CH₂Cl₂·H₂O**. The crystal was glued to a glass fibre. The unit-cell parameters were determined by least-squares refinement of ω measurements for 835 strong reflections from different layers. The intensities of 7881 unique reflections with 7 < 2θ < 54° and (±*h*, ±*k*, +*l*) were collected at room temperature on a Stöe Stadi-2 Weissenberg diffractometer using an ω-scan technique. The data were corrected for Lorentz and polarisation effects to yield 7625 reflections with *I* > 3σ(*I*). No absorption correction was applied. All subsequent computations were carried out using the computer program SHELX 76.¹⁸

Crystal data. C₅₄H₄₅N₂OP₃Pt·CH₂Cl₂·H₂O, *M* = 1128.9, 0.60 × 0.15 × 0.15 mm, triclinic, space group *P*1, *a* = 18.872(8), *b* = 12.461(6), *c* = 13.573(3) Å, α = 116.87(2), β = 116.07(1), γ = 91.51(1)°, *U* = 2455(2) Å³, *Z* = 2, *D*_c = 1.53 g cm⁻³, *F*(000) = 1132.0, Mo-Kα X-radiation, λ = 0.7107 Å, μ(Mo-Kα) = 31 cm⁻¹.

Table 6 Fractional atomic coordinates for [Pt{NPhP(O)PhNPh}(PPh₃)₂] 11a·H₂O·CH₂Cl₂

Atom	x	y	z	Atom	x	y	z
Pt	0.212 01(2)	0.101 86(2)	0.021 96(3)	C(123)	0.266 5(3)	0.279 5(5)	0.459 8(4)
P(1)	0.258 34(12)	0.312 14(16)	0.165 54(19)	C(124)	0.281 3(3)	0.403 6(5)	0.550 9(4)
P(2)	0.119 48(11)	0.096 62(17)	−0.160 10(19)	C(125)	0.292 3(3)	0.499 2(5)	0.527 7(4)
P(3)	0.261 69(11)	−0.101 55(17)	0.048 27(19)	C(126)	0.288 6(3)	0.470 7(5)	0.413 3(4)
N(1)	0.299 7(3)	0.051 9(5)	0.141 0(6)	C(131)	0.192 62(29)	0.414 9(4)	0.144 6(6)
N(2)	0.179 0(3)	−0.091 3(5)	−0.059 4(6)	C(132)	0.117 84(29)	0.387 0(4)	0.137 5(6)
O(1)	0.248 8(3)	−0.176 5(5)	0.100 9(6)	C(133)	0.068 83(29)	0.468 8(4)	0.136 1(6)
C(31)	0.328 9(3)	−0.163 3(5)	−0.014 3(5)	C(134)	0.094 59(29)	0.578 4(4)	0.141 8(6)
C(32)	0.339 0(3)	−0.280 8(5)	−0.035 5(5)	C(135)	0.169 37(29)	0.606 3(4)	0.148 9(6)
C(33)	0.386 5(3)	−0.332 9(5)	−0.089 8(5)	C(136)	0.218 38(29)	0.524 5(4)	0.150 3(6)
C(34)	0.423 9(3)	−0.267 4(5)	−0.123 0(5)	C(211)	0.013 71(23)	0.095 3(5)	−0.199 0(5)
C(35)	0.413 8(3)	−0.149 9(5)	−0.101 9(5)	C(212)	−0.011 93(23)	0.097 9(5)	−0.116 1(5)
C(36)	0.366 3(3)	−0.097 8(5)	−0.047 5(5)	C(213)	−0.093 71(23)	0.090 8(5)	−0.148 3(5)
C(51)	0.382 77(23)	0.108 3(5)	0.245 3(4)	C(214)	−0.149 86(23)	0.081 2(5)	−0.263 4(5)
C(52)	0.407 30(23)	0.081 2(5)	0.342 5(4)	C(215)	−0.124 22(23)	0.078 6(5)	−0.346 3(5)
C(53)	0.488 48(23)	0.132 2(5)	0.443 6(4)	C(216)	−0.042 43(23)	0.085 6(5)	−0.314 1(5)
C(54)	0.545 12(23)	0.210 4(5)	0.447 4(4)	C(221)	0.114 6(3)	−0.048 0(4)	−0.292 8(5)
C(55)	0.520 59(23)	0.237 6(5)	0.350 2(4)	C(222)	0.189 8(3)	−0.069 1(4)	−0.278 9(5)
C(56)	0.439 41(23)	0.186 5(5)	0.249 1(4)	C(223)	0.191 8(3)	−0.173 6(4)	−0.376 9(5)
C(61)	0.108 06(25)	−0.192 9(4)	−0.158 0(5)	C(224)	0.118 6(3)	−0.256 9(4)	−0.488 7(5)
C(62)	0.030 99(25)	−0.175 2(4)	−0.180 3(5)	C(225)	0.043 4(3)	−0.235 7(4)	−0.502 6(5)
C(63)	−0.039 96(25)	−0.273 7(4)	−0.279 3(5)	C(226)	0.041 5(3)	−0.131 3(4)	−0.404 6(5)
C(64)	−0.033 84(25)	−0.389 8(4)	−0.356 1(5)	C(231)	0.145 8(3)	0.217 5(4)	−0.191 0(6)
C(65)	0.043 23(25)	−0.407 5(4)	−0.333 9(5)	C(232)	0.190 5(3)	0.200 9(4)	−0.253 3(6)
C(66)	0.114 17(25)	−0.309 0(4)	−0.234 8(5)	C(233)	0.211 8(3)	0.294 2(4)	−0.273 4(6)
C(111)	0.353 74(27)	0.395 1(5)	0.196 6(5)	C(234)	0.188 4(3)	0.404 2(4)	−0.231 2(6)
C(112)	0.420 67(27)	0.475 0(5)	0.319 3(5)	C(235)	0.143 7(3)	0.420 8(4)	−0.168 8(6)
C(113)	0.488 97(27)	0.542 6(5)	0.335 4(5)	C(236)	0.122 4(3)	0.327 5(4)	−0.148 8(6)
C(114)	0.490 33(27)	0.530 3(5)	0.228 9(5)	O(2)	0.627 5(11)	0.231 6(16)	0.741 1(21)
C(115)	0.423 40(27)	0.450 3(5)	0.106 2(5)	C(1)	0.439 7(10)	0.100 3(22)	0.736 0(18)
C(116)	0.355 10(27)	0.382 8(5)	0.090 1(5)	Cl(1)	0.390 3(4)	0.127 2(10)	0.825 5(7)
C(121)	0.273 8(3)	0.346 6(5)	0.322 1(4)	Cl(2)	0.379 1(7)	0.095 0(13)	0.603 9(10)
C(122)	0.262 8(3)	0.251 0(5)	0.345 4(4)				

The structure was solved using conventional heavy-atom methods. A molecule of H₂O and one of CH₂Cl₂ were identified in later Fourier difference maps. Phenyl rings were included as rigid groups with D_{6h} symmetry, and C–C distances of 1.395 Å. No hydrogen atoms were included due to computer program restrictions. All other atoms were refined with anisotropic thermal parameters. Final cycles of refinement employed a weighting parameter $w = 1/(\sigma^2 F + gF^2)$ ($g = 0.001$) and gave the final residual indices R 0.0526 and R' 0.0546. The final Fourier difference map was featureless except for peaks at +0.9 e Å⁻³ close to the platinum atom, and two isolated peaks at 1.3 e Å⁻³ which could be further disordered solvent atoms. An analysis of the weighting scheme over $|F_o|$ and $(\sin \theta)/\lambda$ was satisfactory. The atomic coordinates are given in Table 6.

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

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