Synthesis and Reactivity of Phosphonato, Phosphato and Arsonato Complexes of Platinum(II) †

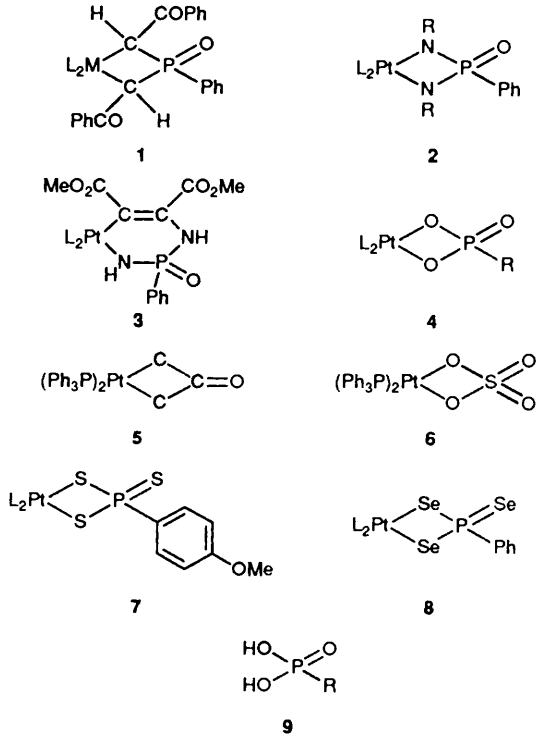
Raymond D. W. Kemmitt,*[a] Simon Mason,[a] John Fawcett[b] and David R. Russell[b]
[a] *Inorganic Research Laboratories, Department of Chemistry, The University, Leicester LE1 7RH, UK*
[b] *X-Ray Crystallography Laboratory, Department of Chemistry, The University, Leicester LE1 7RH, UK*

Treatment of the complexes *cis*-$[PtCl_2L_2]$ (L = donor ligand) with phenylphosphonic acid, methylphosphonic acid, phenyl dihydrogenphosphate or phenylarsonic acid in the presence of an excess of silver(I) oxide in refluxing dichloromethane yielded the new metallacycles $[\overline{Pt\{OP(O)(Ph)O\}}L_2]$, $[\overline{Pt\{OP(O)(Me)O\}}L_2]$, $[\overline{Pt\{OP(O)(OPh)O\}}L_2]$ or $[\overline{Pt\{OAs(O)(Ph)O\}}L_2]$ respectively. The X-ray crystal structure of $[\overline{Pt\{OP(O)(Ph)O\}}(PMePh_2)_2]$ showed the presence of a slightly puckered metallacyclic ring with the phosphoryl oxygen adopting an equatorial position. A decomposition product of the complex $[\overline{Pt\{OP(O)(Ph)O\}}\{P(CH_2Ph)Ph_2\}_2]$ in solution was shown, *via* an X-ray crystal structure determination, to be the diorthometallated complex *cis*-$[\overline{Pt(C_6H_4CH_2PPh_2)_2}]$.

We have previously described the syntheses of the metallaphosphetane oxide **1** and platinadiazaphosphetidine oxide **2** complexes using silver(I) oxide as a base and halide-abstracting agent.[1] The former complexes were shown to contain highly puckered rings with the phosphoryl oxygen occupying an equatorial site.[1] In contrast, complexes **2** (R = Ph) have been shown to contain almost planar metallacyclic rings, with the nitrogen atoms also in an essentially planar environment.[2] In addition, insertion into the metal–nitrogen bond of the complexes **2** (R = H) by dimethyl acetylenedicarboxylate has been shown to yield the novel six-membered metallacyclic products **3**.[1] These results prompted an investigation into the analogous synthesis of complexes of the type **4**, which contain platinum–oxygen bonds, in order to compare their structure and reactivity with those of complexes **1** and **2**.

Other four-membered platinacycles containing two metal–oxygen bonds include the carbonato **5**[3] and sulfato **6**[4] complexes, both of which may be prepared from the respective silver(I) salt and *cis*-$[PtCl_2(PPh_3)_2]$. Also, analogues of **4** containing sulfur **7**[5] or selenium **8**[6] have been prepared by Woollins and co-workers. Crystal structure determinations indicated that both ring systems are puckered with the P=S or P=Se group adopting an equatorial site.[5,6]

Herein, we describe the preparation of metallacyclic complexes of the type **4** (R = Ph, Me or OPh) from the respective dibasic acid **9** (R = Ph, Me or OPh) in the presence of silver(I) oxide together with the syntheses of related complexes using phenylarsonic acid.

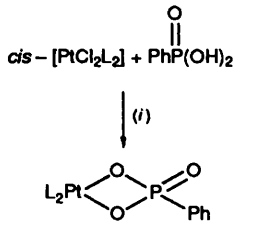


Results and Discussion

Treatment of the complexes *cis*-$[PtCl_2L_2]$ [L = PPh_3, $PMePh_2$, or $P(CH_2Ph)Ph_2$; L_2 = $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) or $Ph_2P(CH_2)_4PPh_2$ (dppb)] {prepared *in situ* by the reaction of $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) with either 2 mole equivalents of L or 1 mole equivalent of L_2} with 1 equivalent of phenylphosphonic acid **9** (R = Ph) and an excess of silver(I) oxide in refluxing dichloromethane gave the complexes **10a**–**10f** in high yield, whilst analogous treatment of *cis*-$[PtCl_2(AsPh_3)_2]$ yielded complex **10g**, Scheme 1. Treatment of the bromide-bridged dimeric complex $[\{PtBr_2(PPr^n_3)\}_2]$ with 1 equivalent of either triphenylphosphine or triphenylarsine and 1 equivalent of phenylphosphonic acid per platinum, in the presence of silver(I) oxide, afforded the mixed-ligand complexes **10h** and **10i** respectively. Similar treatment of $[\{PtBr_2(PEt_3)\}_2]$ with $AsPh_3$ and phenylphosphonic acid gave complex **10j** in good yield.

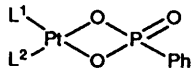
Using a similar methodology, complexes **11** may be prepared using methylphosphonic acid **9** (R = Me), complexes **12** using phenyl dihydrogenphosphate **9** (R = OPh), and complexes **13** using phenylarsonic acid, all products being obtained in good

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

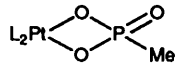


10a L = PPh_3
10b L = $PMePh_2$
10c L = $P(CH_2Ph)Ph_2$
10d L_2 = dppe
10e L_2 = dppp
10f L_2 = dppb
10g L = $AsPh_3$

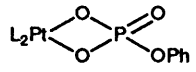
Scheme 1 (*i*) Excess of Ag_2O, refluxing CH_2Cl_2



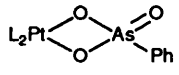
	L^1	L^2
10h	PPr^n_3	PPh_3
10i	PPr^n_3	$AsPh_3$
10j	PEt_3	$AsPh_3$



11a L = PPh_3
11b L = $PMePh_2$
11c L_2 = dppe
11d L_2 = dppp
11e L_2 = dppb
11f L = $AsPh_3$



12a L = PPh_3
12b L = $PMePh_2$
12c L_2 = dppp
12d L_2 = dppb
12e L = $AsPh_3$



13a L = PPh_3
13b L_2 = dppe
13c L_2 = dppb
13d L = $AsPh_3$

cis – $[\overline{Pt(C_6H_4CH_2PR_2)_2}]$

14

Table 1 Selected bond lengths (Å) and angles (°) for $[\overline{Pt\{OP(O)(Ph)O\}}(PMePh_2)_2]$ **10b**[a]

Pt–P(2)	2.231(1)	P(2)–Pt–P(3)	98.7(1)
Pt–P(3)	2.222(1)	O(2)–Pt–O(3)	71.2(2)
Pt–O(2)	2.070(4)	P(2)–Pt–O(3)	96.5(1)
Pt–O(3)	2.102(4)	P(3)–Pt–O(2)	93.7(1)
O(2)–P(1)	1.576(5)	Pt–O(2)–P(1)	93.4(2)
O(3)–P(1)	1.563(4)	Pt–O(3)–P(1)	92.6(3)
P(1)–O(1)	1.475(5)	O(2)–P(1)–O(3)	101.3(2)
P(1)–C(11)	1.801(5)	O(1)–P(1)–C(11)	108.9(3)
P(2)–C(1)	1.809(5)	O(2)–P(1)–O(1)	116.3(3)
P(2)–C(21)	1.811(3)	O(3)–P(1)–O(1)	115.7(3)
P(2)–C(31)	1.819(4)	Twist[b]	2.2(1)
P(3)–C(2)	1.811(7)	Fold[c]	12.9(2)
P(3)–C(41)	1.810(4)	C(12)–C(11)–P(1)–O(1) Torsion	−1.9(2)
P(3)–C(51)	1.814(4)		
Pt ··· P(1)	2.676(2)		

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

yield. All the new complexes **10–13** were isolated as white to pale yellow, air-stable, microcrystalline solids.

An X-ray crystal structure determination of the bis(phosphine)platinum phosphonato complex **10b** was carried out in order to investigate its molecular conformation for comparison with those of the related sulfur[5] and selenium[6] metallacycles **7** (L = PPh_3) and **8** (L_2 = dppe) and also with those of complexes **1** (M = Pt, L = PPh_3)[1] and **2** (R = Ph, L = PPh_3).[2] Important bond lengths and angles are presented in Table 1 whilst the molecular structure is illustrated in Fig. 1 along with the crystallographic numbering system for the non-

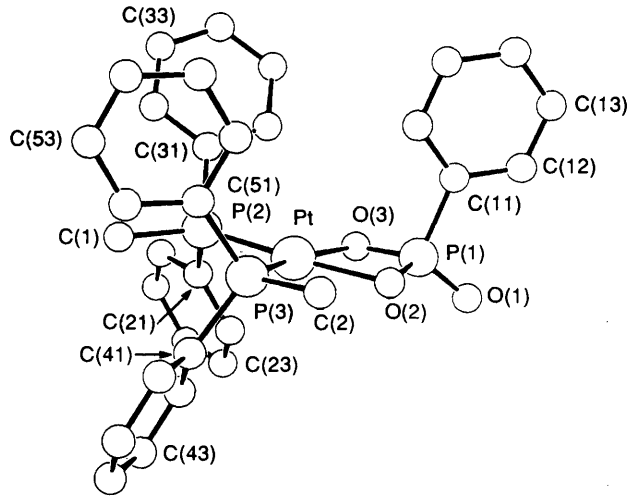
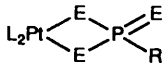


Fig. 1 Molecular structure of $[\overline{Pt\{OP(O)(Ph)O\}}(PMePh_2)_2]$ **10b**, showing the atom numbering scheme. All hydrogen atoms are omitted for clarity

Table 2 Selected structural data for complexes **8** (L_2 = dppe), **7** (L = PPh_3) and **10b**



Bond length (Å) or angle (°)	E = Se, R = Ph, L_2 = dppe **8**	E = S, R = C_6H_4OMe, L = PPh_3 **7**	E = O, R = Ph, L = $PMePh_2$ **10b**
Pt–P	2.253(2)	2.293(2)	2.231(1)
	2.249(2)	2.291(2)	2.222(1)
Pt–E	2.471(1)	2.369(2)	2.102(4)
	2.465(1)	2.351(2)	2.070(4)
P–E	2.239(3)	2.065(2)	1.576(5)
	2.215(3)	2.063(2)	1.563(4)
P=E	2.104(3)	1.945(3)	1.475(5)
E–Pt–E	85.3(1)	81.7(1)	71.2(2)
E–P–E	97.3(1)	96.8(1)	101.3(2)
Pt–E–P	88.3(1)	89.3(1)	93.4(2)
	87.6(1)	88.9(1)	92.6(2)
Fold*	13.2	19.4	12.9(2)

* E–Pt–E/E–P–E.

hydrogen atoms. Selected structural data for complexes **7** (L = PPh_3), **8** (L_2 = dppe) and **10b** are presented in Table 2 for comparison.

The structure consists of a four-membered metallacyclic ring containing two metal–oxygen and two phosphorus–oxygen bonds, with two co-ordinating methyldiphenylphosphine ligands giving the metal a slightly distorted square-planar environment. The twist angle between planes P(2)–Pt–P(3) and O(2)–Pt–O(3) is 2.2(1)° and the fold angle between planes O(2)–Pt–O(3) and O(2)–P(1)–O(3) is 12.9(2)° with the phosphoryl group adopting the pseudo-equatorial position. This latter behaviour compares well with the molecular structures of **7** (L = PPh_3) and **8** (L_2 = dppe), which also have fold angles of a similar magnitude.[5,6]

The metal–phosphine distances in complex **10b** are noticeably shorter than those in **7** (L = PPh_3)[5] and **8** (L_2 = dppe).[6] By comparison with the Pt–P distances in the respective bis(phosphine)platinum dichloride complexes, $[PtCl_2(dppe)]$ [2.208(6) Å],[7] $[PtCl_2(PPh_3)_2]$ [average 2.258(9) Å][8] and $[PtCl_2(PMePh_2)_2]$ [average 2.247(2) Å],[9] the series Se > S > Cl > O becomes apparent, for the magnitude of the *trans* influence of the respective atoms with a platinum(II) centre.

The Pt–O(3) bond is significantly longer (*ca.* 0.03 Å) than

Table 3 Selected bond lengths (Å) and angles (°) for *cis*-[Pt(C$_6$H$_4$CH$_2$PPh$_2$)$_2$] **14** (R = Ph)[a]

Pt–P(1)	2.282(1)	P(1)–Pt–P(1′)	105.4(1)
Pt–C(11)	2.064(4)	P(1)–Pt–C(11)	81.2(1)
P(1)–C(1)	1.831(4)	C(11)–Pt–C(11′)	94.2(2)
P(1)–C(21)	1.828(2)	Pt–P(1)–C(1)	101.4(2)
P(1)–C(31)	1.822(2)	P(1)–C(1)–C(12)	105.9(3)
C(1)–C(12)	1.512(6)	C(1)–C(12)–C(11)	118.5(4)
C(11)–C(12)	1.410(6)	C(12)–C(11)–Pt	119.9(3)
C(12)–C(13)	1.389(6)	C(11)–C(12)–C(13)	121.6(4)
C(13)–C(14)	1.383(7)	C(12)–C(13)–C(14)	120.1(5)
C(14)–C(15)	1.388(8)	C(13)–C(14)–C(15)	120.5(5)
C(15)–C(16)	1.391(7)	C(14)–C(15)–C(16)	118.9(5)
C(11)–C(16)	1.406(6)	C(15)–C(16)–C(11)	122.7(5)
		C(16)–C(11)–C(12)	116.2(4)
		Twist[b]	16.4(1)

[a] See Fig. 2 for crystallographic numbering system. [b] P(1)–Pt–C(11)/P(1′)–Pt–C(11′).

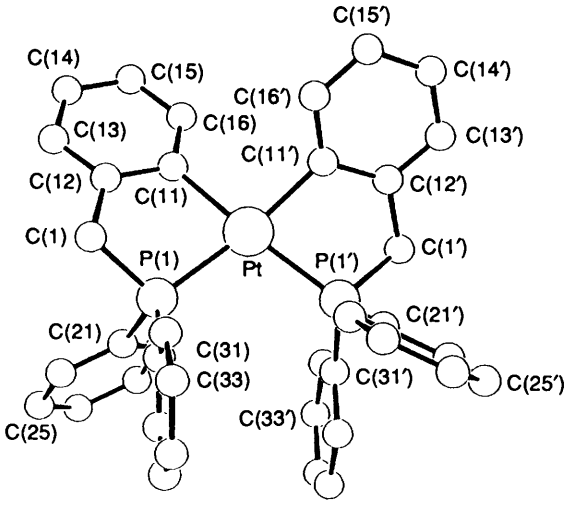


Fig. 2 Molecular structure of *cis*-[Pt(C$_6$H$_4$CH$_2$PPh$_2$)$_2$] **14** (R = Ph) showing the atom numbering scheme. All hydrogen atoms are omitted for clarity

Pt–O(2), however the expected trend of the bond lengths Pt–E, P–E and P=E increasing down Group 16 as E = O ⟶ S ⟶ Se can be seen in Table 2. The E–Pt–E angle also increases as E = O ⟶ S ⟶ Se, however no trend is discernible for the E–P–E angle. The internal ring angles at E, *i.e.* Pt–E–P, decrease as E = O ⟶ S ⟶ Se.

As was observed for the P–S and P–Se distance in complexes **7** (L = PPh$_3$)[5] and **8** (L$_2$ = dppe),[6] the exocyclic P=O length in **10b** is only *ca.* 0.1 Å shorter than the P–O bond distances in the ring. In the discussion of the structures of **7** (L = PPh$_3$) and **8** (L$_2$ = dppe) the proximity of the P–E (E = S or Se) bond lengths to that of the P=E (E = S or Se) bond length was accounted for by suggesting significant electron delocalisation in the rings.[5,6] To what extent this may occur in complex **10b** is unclear, and comparisons with the structure of phenylphosphonic acid, in which electron delocalisation is clearly possible, are complicated by the presence of hydrogen bonding.[10]

A comparison of the X-ray crystal structures of complexes **1** (M = Pt, L = PPh$_3$),[1] **2** (R = Ph, L = PPh$_3$)[2] and **10b** indicates several important points with respect to these systems. The basic feature of all the Pt–X–P–X (X = C, N or O) rings is the fold angle about the X–X axis [X = C, fold angle 31.1(2)°;[1] N, 6.2(4)°,[2] and O, 12.9(2)°]. Substitution of more electronegative oxygen atoms for the CH(COPh) groups in **1** (M = Pt, L = PPh$_3$) causes the ring to be less puckered.[11] The smaller fold angle in the platinadiazaphosphetidine oxide complex **2** (R = Ph, L = PPh$_3$) is presumably associated with the presence of three bulky groups attached to the nitrogen atoms. In addition, in all three cases the phosphoryl group on the ring is equatorial and its attached phenyl ring is orientated such that its plane is almost coincidental with the P=O moiety.[1,2]

The metal–phosphine distances are indicative of the *trans* influences of the atoms X and thus decrease in the order X = C > N > O.[1,2] However steric effects, especially for the platinadiazaphosphetidine complex **2** (R = Ph, L = PPh$_3$), also affect this distance and so a quantitative relationship based on these bond lengths cannot be made.

The transannular Pt ··· P distances are all outside the sum of the covalent radii of the two atoms, and indicate no significant interaction between the platinum and phosphorus.

There are no apparent trends in the comparison of the bond angles of these complexes, however the increase in the ring angle X–P–X as X = N ⟶ C ⟶ O is a possible indication of decreasing ring strain along this series.[1,2]

The room-temperature ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of the new complexes are consistent with the structures shown above. The ^{31}P-{^{1}H} NMR spectra of the bis(phosphine) complexes **10a–10f**, **11a–11e** and **12a–12d** show the presence of two inequivalent phosphorus environments. The signal due to the two equivalent donor-ligand phosphorus nuclei shows a one-bond coupling to platinum-195 in excess of 3500 Hz, characteristic of phosphine ligands opposite oxygen, and for complexes **10d–10f**, **11a** and **11d** they appear as a doublet due to three-bond coupling to the phosphorus atom of the four-membered ring. This atom therefore appears as either a singlet or a triplet, with a two-bond coupling to platinum-195 in the range 107–147 Hz. Despite the inequivalence of the phosphine ligands of **10b** in the solid state, they appear equivalent in its solution ^{31}P-{^{1}H} NMR spectrum. A similar effect was also noted for complexes **7** (L = PPh$_3$)[5] and **8** (L$_2$ = dppe).[6] The spectra of the triphenylarsine complexes **10g**, **11f** and **12e** show a singlet with corresponding platinum-195 satellites, with ^2J(PtP) in the range 147–181 Hz.

The IR spectra of complexes **10–12** all show a band corresponding to the stretching mode of the phosphoryl group. For complexes **10a–10j** and **11a–11f** this absorption appears in the region 1190–1235 cm^{-1}, whilst for **12a–12e** it appears in the slightly higher range 1240–1260 cm^{-1}, as expected due to the presence of the more electronegative phenoxy substituent on the phosphorus atom.[12] The spectra for complexes **13a–13d** all show a band in the region 900–930 cm^{-1} which can be assigned to the As=O stretching vibration.

All the new complexes are air stable in the solid phase, however during NMR studies the benzyldiphenylphosphine complex **10c** was found to decompose in either chloroform or dichloromethane solution. ^{31}P-{^{1}H} NMR studies showed the decomposition products to be numerous, even though some of the other phosphonato complexes were stable in solution for several weeks. Attempts to isolate any of the decomposition products resulted in the collection of colourless crystals in *ca.* 17% yield. An X-ray crystal structure determination was carried out in order to establish the identity of the product, which may provide information on the cause of decomposition. Important bond lengths and angles are presented in Table 3, whilst the molecular structure is illustrated in Fig. 2 along with the crystallographic numbering system for the non-hydrogen atoms.

The structure of complex **14** (R = Ph) consists of two *cis*-metallated benzyldiphenylphosphine ligands bound to a platinum(II) centre, so as to give the metal a distorted square-planar geometry. The phosphines thus act as chelating ligands, each forming a five-membered ring. It should be noted that the molecule has a two-fold rotational symmetry axis passing through the platinum such that P(1) maps onto P(1′), C(1) onto C(1′) and C(11) onto C(11′), *etc.* This also means that the bond lengths on one side of the molecule are equal to their

Table 4 M.p.s, analytical[a] and selected IR[b] data for the platinaphosphonato, phosphato and arsonato complexes **10a–13d**

Complex	M.p. (°C)	Analysis (%) C	H	ν(P=O) [or ν(As=O)][c]/ cm^{-1}
10a	143	57.7 (57.6)	4.4 (4.0)	1220
10b	>220	51.0 (51.1)	4.1 (4.1)	1225
10c·H_2O	132	—	—	1220
10d·H_2O	178	50.2 (50.1)	4.0 (4.0)	1200
10e·CH_2Cl_2	137	48.1 (48.1)	3.8 (3.9)	1210
10f	183	52.2 (52.5)	4.1 (4.2)	1220
10g·H_2O	>220	51.6 (51.4)	3.6 (3.8)	1235
10h	175	51.2 (51.2)	5.4 (5.3)	1210
10i	216	48.2 (48.5)	5.1 (5.0)	1215
10j	208	46.5 (46.5)	4.7 (4.5)	1225
11a·H_2O	>220	53.7 (53.4)	4.4 (4.2)	1220
11b·CH_2Cl_2	>220	43.0 (43.4)	3.5 (3.7)	1220
11c·H_2O	>220	46.2 (46.0)	3.9 (4.1)	1190
11d·CH_2Cl_2	>220	44.4 (44.2)	3.7 (3.9)	1210
11e	>220	48.1 (48.7)	4.3 (4.3)	1205
11f·H_2O	173	48.3 (48.3)	3.9 (3.8)	1210
12a·H_2O	>220	54.8 (55.4)	3.9 (4.1)	1250
12b·H_2O	183	49.2 (48.9)	4.1 (4.2)	1250
12c·CH_2Cl_2	>220	47.1 (47.2)	3.8 (3.8)	1240
12d·H_2O	>220	50.6 (50.3)	4.2 (4.3)	1240
12e·H_2O	>220	50.7 (50.6)	3.7 (3.7)	1260
13a	177	54.9 (54.9)	4.2 (3.8)	[930]
13b·CH_2Cl_2	174	45.9 (45.1)	3.8 (3.5)	[900]
13c·H_2O	151	48.9 (48.6)	4.2 (4.2)	[910]
13d	200	50.9 (50.1)	3.8 (3.5)	[930]

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

counterparts on the other. The twist angle about the platinum between planes P(1)–Pt–C(11) and P(1′)–Pt–C(11′) is large at 16.4(1)° and the four valence angles around the metal are considerably displaced from 90°, presumably to accommodate the two five-membered rings. These two rings show an 'envelope'-type conformation: the Pt and C atoms lie in the plane whilst the P atom deviates from it. This behaviour was also seen in the structure of complex **14** (R = CH_2Ph), whose bond lengths and angles compare well to those of the present study.[13]

The driving force behind the decomposition of complex **10c** may be the formation of a thermodynamically more stable product **14** (R = Ph) or perhaps the relief of ring strain. The benzyl group on each phosphine ligand possibly provides an energetically favourable route to decomposition, as the final product contains two relatively stress-free, five-membered rings. With phenyl-substituted phosphines any orthometallation would lead to a four-membered ring, which would not be such a stable product.

Complex **14** (R = Ph) was originally prepared in >80% yield by the action of (σ-lithiobenzyl)diphenylphosphine on $[PtCl_2(SEt_2)_2]$.[14] Therefore, the decomposition of complex **10c** under the stated conditions does not constitute a primary synthetic route to **14** (R = Ph).

Finally, the phosphonato complex **10a** did not react with dimethyl acetylenedicarboxylate when treated with this reagent in dichloromethane at room temperature. This is in contrast to the reactivity of complexes **2** (R = H) which, as mentioned above, readily insert a molecule of this acetylene into the metallacyclic ring.[1]

Experimental

Table 4 shows m.p.s, analytical and selected IR data for complexes **10–13**. 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. The ^{13}C-{^1H} NMR spectra were recorded on a Bruker AM300 spectrometer at 75.47 MHz with $SiMe_4$ (δ 0.0) as internal reference, in $CDCl_3$. The phenylcarbon region has been omitted for clarity. The ^{31}P-{^1H} NMR spectra were recorded in dichloromethane on a JEOL-FX90 spectrometer at 36.21 MHz, with $[P(OH)_4]^+$ in D_2O (δ 0.0) 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. Phenylphosphonic acid, methylphosphonic acid, phenylarsonic acid and dimethyl acetylenedicarboxylate (Aldrich) were used as supplied from commercial sources. The compounds $[PtCl_2(cod)]$,[15] *cis*-$[PtCl_2(PPh_3)_2]$,[16] *cis*-$[PtCl_2(AsPh_3)_2]$,[17] $[\{PtBr_2(PPr_3)\}_2]$,[18] $[\{PtBr_2(PEt_3)\}_2]$,[18] benzyldiphenylphosphine,[19] and phenyl dihydrogenphosphate[20] were prepared as described in the literature.

Preparation of Phosphonato, Phosphato and Arsonato Complexes of Platinum(II): *General Method.*—Two mole equivalents of tertiary phosphine or 1 mole equivalent of chelating tertiary phosphine, followed by 1 mole equivalent of the appropriate acid, and an excess of silver(I) oxide were added in succession to a stirred solution of $[PtCl_2(cod)]$ in dichloromethane (*ca.* 45 cm^3), and the mixture was refluxed for 4 h. The cooled reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a colourless to yellowish brown oil. Dissolution of the oil in dichloromethane (*ca.* 10 cm^3) followed by addition of light petroleum afforded, on standing, a white to pale yellow microcrystalline *solid*, which was recrystallised from dichloromethane–light petroleum and dried *in vacuo*.

(*i*) $[Pt\{OP(O)(Ph)O\}(PPh_3)_2]$ **10a**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and phenylphosphonic acid **9** (R = Ph) (0.045 g, 0.28 mmol) gave white *microcrystals* of **10a** (0.23 g, 97%). NMR spectra: ^1H (90 MHz), δ 8.0–7.0 (m, 35 H, Ph); ^{31}P-{^1H}, δ 35.50 {s, P(1), ^2J[PtP(1)] 27} and 7.26 [s, PPh_3, ^1J(PtP) 3877 Hz].

(*ii*) $[Pt\{OP(O)(Ph)O\}(PMePh_2)_2]$ **10b**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with methyldiphenylphosphine (0.11 g, 0.55 mmol) and phenylphosphonic acid (0.045 g, 0.28 mmol) gave white *microcrystals* of **10b** (0.18 g, 89%). NMR spectra: ^1H (300 MHz), δ 7.98–6.86 (m, 25 H, Ph) and 1.78 [d, 6 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 11]; ^{13}C-{^1H}, δ 14.33 (m, Me, $PMePh_2$); ^{31}P-{^1H}, δ 36.50 {s, P(1), ^2J[PtP(1)] 122} and −7.26 [s, $PMePh_2$, ^1J(PtP) 3755 Hz]. X-Ray-quality *crystals* of **10b** were grown slowly from dichloromethane–light petroleum in air.

(*iii*) $[Pt\{OP(O)(Ph)O\}\{P(CH_2Ph)Ph_2\}_2]$ **10c**·H_2O. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with benzyldiphenylphosphine (0.16 g, 0.58 mmol) and phenylphosphonic acid (0.045 g, 0.28 mmol) gave white *microcrystals* of **10c**·H_2O (0.22 g, 90%). NMR spectra: ^1H (300 MHz), δ 7.96–6.68 (m, 35 H, Ph), 3.66 [m, 4 H, CH_2, $P(CH_2Ph)Ph_2$] and 3.03 (s br, 2 H, H_2O); ^{13}C-{^1H}, δ 33.65 [m, CH_2, $P(CH_2Ph)Ph_2$]; ^{31}P-{^1H}, δ 36.82 {t, P(1), ^2J[PtP(1)] 117, ^3J[PP(1)] 7} and 3.93 {d, $P(CH_2Ph)Ph_2$, ^1J(PtP) 3865, ^3J[P(1)] 7 Hz}.

(*iv*) $[Pt\{OP(O)(Ph)O\}(dppe)]$ **10d**·H_2O. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and phenylphosphonic acid (0.045 g, 0.28 mmol) gave white *microcrystals* of **10d**·H_2O (0.20 g, 97%). NMR spectra: ^1H (300 MHz), δ 8.13–6.76 (m, 25 H, Ph), 3.27 (s, br, 2 H, H_2O), and 2.89–2.00 (m, 4 H, CH_2, dppe); ^{13}C-{^1H}, too insoluble; ^{31}P-{^1H}, δ 40.38 {t, P(1), ^2J[PtP(1)] 128, ^3J[PP(1)] 7} and 31.80 {d, dppe, ^1J(PtP) 3709, ^3J[P(1)P] 7 Hz}.

(*v*) [Pt{OP(O)(Ph)O}(dppp)] **10e**·CH_2Cl_2. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and phenylphosphonic acid (0.045 g, 0.28 mmol) gave white *microcrystals* of **10e**·CH_2Cl_2 (0.22 g, 96%). NMR spectra: ^1H (300 MHz), δ 7.84–7.16 (m, 25 H, Ph), 5.26 (s, 2 H, CH_2Cl_2), 2.35 (m, 4 H, PCH_2, dppp), and 2.06 (m, 2 H, CH_2, dppp); ^{13}C-{^1H}, δ 53.48 (s, CH_2Cl_2), 23.72 [d, PCH_2, dppp, ^1J(PC) 49], and 19.41 (s, CH_2, dppp); ^{31}P-{^1H}, δ 37.42 {t, P(1), ^2J[PtP(1)] 124, ^3J[PP(1)] 5} and −11.71 {d, dppp, ^1J(PtP) 3556, ^3J[P(1)P] 5 Hz}.

(*vi*) [Pt{OP(O)(Ph)O}(dppb)] **10f**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and phenylphosphonic acid (0.045 g, 0.28 mmol) gave white *microcrystals* of **10f** (0.20 g, 95%). NMR spectra: ^1H (300 MHz), δ 7.78–7.15 (m, 25 H, Ph), 2.43 (m, 4 H, PCH_2, dppb), and 1.84 (m, 4 H, CH_2, dppb); ^{13}C-{^1H}, δ 24.99 [d, PCH_2, dppb, ^1J(PC) 40], 22.47 (s, CH_2, dppb); ^{31}P-{^1H}, δ 37.92 {t, P(1), ^2J[PtP(1)] 117, ^3J[PP(1)] 10} and 2.82 {d, dppb, ^1J(PtP) 3701, ^3J[P(1)P] 10 Hz}.

(*vii*) [Pt{OP(O)(Ph)O}$(AsPh_3)_2$] **10g**·H_2O. The complex *cis*-[$PtCl_2(AsPh_3)_2$] (0.30 g, 0.34 mmol) with phenylphosphonic acid (0.055 g, 0.35 mmol) gave pale yellow *microcrystals* of **10g**·H_2O (0.31 g, 93%). NMR spectra: ^1H (90 MHz), δ 8.2–6.9 (m, 35 H, Ph) and 3.1 (s, br, 2 H, H_2O); ^{31}P-{^1H}, δ 40.94 {s, P(1), ^2J[PtP(1)] 147 Hz}.

(*viii*) [Pt{OP(O)(Ph)O}$(PPr^n_3)(PPh_3)$] **10h**. The complex [{$PtBr_2(PPr^n_3)$}$_2$] (0.20 g, 0.19 mmol) with triphenylphosphine (0.11 g, 0.42 mmol) and phenylphosphonic acid (0.06 g, 0.38 mmol) gave white *microcrystals* of **10h** (0.29 g, 98%). NMR spectra: ^1H (300 MHz), δ 7.98–7.29 (m, 20 H, Ph), 1.43 (m, 6 H, PCH_2, PPr^n_3), 1.29 (m, 6 H, CH_2, PPr^n_3), and 0.86 [t, 9 H, CH_3, PPr^n_3, ^3J(HH) 7]; ^{13}C-{^1H}, δ 23.58 [d, PCH_2, PPr^n_3, ^1J(PC) 37], 17.74 [d, CH_2, PPr^n_3, ^2J(PC) 1], and 15.43 [d, CH_3, PPr^n_3, ^3J(PC) 15]; ^{31}P-{^1H}, δ 38.16 {s, P(1), ^2J[PtP(1)] 115}, 3.95 [d, PPh_3, ^1J(PtP) 3928, ^2J(PP) 32] and −3.77 [d, PPr^n_3, ^1J(PtP) 3591, ^2J(PP) 32 Hz].

(*ix*) [Pt{OP(O)(Ph)O}$(PPr^n_3)(AsPh_3)$] **10i**. The complex [{$PtBr_2(PPr^n_3)$}$_2$] (0.20 g, 0.19 mmol) with triphenylarsine (0.12 g, 0.39 mmol) and phenylphosphonic acid (0.06 g, 0.38 mmol) gave white *microcrystals* of **10i** (0.30 g, 97%). NMR spectra: ^1H (300 MHz), δ 8.08–7.30 (m, 20 H, Ph), 1.52–1.26 (m, 12 H, CH_2, PPr^n_3), and 0.87 [t, 9 H, CH_3, PPr^n_3, ^3J(HH) 7]; ^{13}C-{^1H}, δ 23.96 [d, PCH_2, PPr^n_3, ^1J(PC) 37], 17.61 [d, CH_2, PPr^n_3, ^2J(PC) 2], and 15.24 [d, CH_3, PPr^n_3, ^3J(PC) 15]; ^{31}P-{^1H}, δ 38.72 {s, P(1), ^2J[PtP(1)] 137} and −6.66 [s, PPr^n_3, ^1J(PtP) 3550 Hz].

(*x*) [Pt{OP(O)(Ph)O}$(PEt_3)(AsPh_3)$] **10j**. The complex [{$PtBr_2(PEt_3)$}$_2$] (0.20 g, 0.21 mmol) with triphenylarsine (0.13 g, 0.43 mmol) and phenylphosphonic acid (0.07 g, 0.44 mmol) gave white *microcrystals* of **10j** (0.32 g, 98%). NMR spectra: ^1H (300 MHz), δ 8.10–7.32 (m, 20 H, Ph), 1.38 (m, 6 H, PCH_2, PEt_3), and 0.99 [dt, 9 H, CH_3, PEt_3, ^3J(PH) 17, ^3J(HH) 7]; ^{13}C-{^1H}, δ 14.19 [d, PCH_2, PEt_3, ^1J(PC) 39] and 7.93 [d, CH_3, PEt_3, ^2J(PC) 3]; ^{31}P-{^1H}, δ 38.72 {s, P(1), ^2J[PtP(1)] 137} and 2.82 [s, PEt_3, ^1J(PtP) 3564 Hz].

(*xi*) [Pt{OP(O)(Me)O}$(PPh_3)_2$] **11a**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and methylphosphonic acid **9** (R = Me) (0.03 g, 0.31 mmol) gave white *microcrystals* of **11a**·H_2O (0.20 g, 89%). NMR spectra: ^1H (300 MHz), δ 7.89–6.63 (m, 30 H, Ph), 3.21 (s, br, 2 H, H_2O), and 1.40 {d, 3 H, Me, ^2J[P(1)H] 16}; ^{13}C-{^1H}, δ 17.09 {d, Me, ^1J[P(1)C] 124}; ^{31}P-{^1H}, δ 46.80 {t, P(1), ^2J[PtP(1)] 122, ^3J[PP(1)] 10} and 7.25 {d, PPh_3, ^1J(PtP) 3848, ^3J[P(1)P] 10 Hz}.

(*xii*) [Pt{OP(O)(Me)O}$(PMePh_2)_2$] **11b**·CH_2Cl_2. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with methyldiphenylphosphine (0.11 g, 0.55 mmol) and methylphosphonic acid (0.03 g, 0.31 mmol) gave white *microcrystals* of **11b**·CH_2Cl_2 (0.19 g, 91%). NMR spectra: ^1H (300 MHz), δ 7.76–7.18 (m, 20 H, Ph), 5.29 (s, 2 H, CH_2Cl_2), 1.76 [d, 6 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 11, ^3J(PtH) 50], and 1.43 {d, 3 H, Me, ^2J[P(1)H] 16}; ^{13}C-{^1H}, δ 53.37 (s, CH_2Cl_2), 17.24 {d, Me, ^1J[P(1)C] 124}, and 14.08 [d, Me, $PMePh_2$, $|^1J(PC) + {}^3J(PC)|$ 44]; ^{31}P-{^1H}, δ 47.32 {s, P(1), ^2J[PtP(1)] 112} and −7.47 [s, $PMePh_2$, ^1J(PtP) 3755 Hz].

(*xiii*) [Pt{OP(O)(Me)O}(dppe)] **11c**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and methylphosphonic acid (0.03 g, 0.31 mmol) gave white *microcrystals* of **11c**·H_2O (0.18 g, 95%). NMR spectra: ^1H (300 MHz), δ 8.11–7.09 (m, 20 H, Ph), 2.96–2.15 (m, br, 4 H, CH_2, dppe), 2.20 (s, br, 2 H, H_2O), and 1.47 {d, 3 H, Me, ^2J[P(1)H] 16}; ^{13}C-{^1H}, too insoluble; ^{31}P-{^1H}, δ 50.68 {s, P(1), ^2J[PtP(1)] 107} and 31.26 [s, dppe, ^1J(PtP) 3696 Hz].

(*xiv*) [Pt{OP(O)(Me)O}(dppp)] **11d**·CH_2Cl_2. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and methylphosphonic acid (0.03 g, 0.31 mmol) gave white *microcrystals* of **11d**·CH_2Cl_2 (0.20 g, 94%). NMR spectra: ^1H (300 MHz), δ 7.79–7.20 (m, 20 H, Ph), 5.23 (s, 2 H, CH_2Cl_2), 2.52–2.09 (m, 6 H, CH_2, dppp), and 1.37 {d, 3 H, Me, ^2J[P(1)H] 16}; ^{13}C-{^1H}, δ 53.30 (s, CH_2Cl_2), 23.87 [d, PCH_2, dppp, ^1J(PC) 47], 19.45 (s, CH_2, dppp), and 17.12 {d, Me, ^1J[P(1)C] 124}; ^{31}P-{^1H}, δ 49.47 {t, P(1), ^2J[PtP(1)] 112, ^3J[PP(1)] 5} and −12.25 {d, dppp, ^1J(PtP) 3547, ^3J[P(1)P] 5 Hz}.

(*xv*) [Pt{OP(O)(Me)O}(dppb)] **11e**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and methylphosphonic acid (0.03 g, 0.31 mmol) gave white *microcrystals* of **11e** (0.18 g, 93%). Complex **11e** was too insoluble for NMR spectroscopy.

(*xvi*) [Pt{OP(O)(Me)O}$(AsPh_3)_2$] **11f**·H_2O. The complex *cis*-[$PtCl_2(AsPh_3)_2$] (0.30 g, 0.34 mmol) with methylphosphonic acid (0.035 g, 0.37 mmol) gave pale yellow *microcrystals* of **11f**·H_2O (0.30 g, 96%). NMR spectra: ^1H (300 MHz), δ 7.88–6.97 (m, 30 H, Ph), 3.12 (s, br, 2 H, H_2O), and 1.47 {d, 3 H, Me, ^2J[P(1)H] 16}; ^{13}C-{^1H}, δ 17.55 {d, Me, ^1J[P(1)C] 124}; ^{31}P-{^1H}, δ 52.03 {s, P(1), ^2J[PtP(1)] 156 Hz}.

(*xvii*) [Pt{OP(O)(OPh)O}$(PPh_3)_2$] **12a**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and phenyl dihydrogenphosphate **9** (R = OPh) (0.05 g, 0.29 mmol) gave white *microcrystals* of **12a**·H_2O (0.24 g, 98%). NMR spectra: ^1H (90 MHz), δ 8.2–6.8 (m, 35 H, Ph) and 2.7 (s, br, 2 H, H_2O); ^{31}P-{^1H}, δ 18.96 {s, P(1), ^2J[PtP(1)] 147} and 6.66 [s, PPh_3, ^1J(PtP) 3936 Hz].

(*xviii*) [Pt{OP(O)(OPh)O}$(PMePh_2)_2$] **12b**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with methyldiphenylphosphine (0.11 g, 0.55 mmol) and phenyl dihydrogenphosphate (0.05 g, 0.29 mmol) gave white *microcrystals* of **12b**·H_2O (0.20 g, 94%). NMR spectra: ^1H (300 MHz), δ 7.42–6.66 (m, 25 H, Ph), 3.23 (s, br, 2 H, H_2O), and 1.67 [d, 6 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 11]; ^{13}C-{^1H}, δ 14.00 [d, Me, $PMePh_2$, $|^1J(PC) + {}^3J(PC)|$ 44]; ^{31}P-{^1H}, δ 18.78 {s, P(1), ^2J[PtP(1)] 142} and −8.01 [s, $PMePh_2$, ^1J(PtP) 3823 Hz].

(*xix*) [Pt{OP(O)(OPh)O}(dppp)] **12c**·CH_2Cl_2. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and phenyl dihydrogenphosphate (0.05 g, 0.29 mmol) gave white *microcrystals* of **12c**·CH_2Cl_2 (0.22 g, 94%). NMR spectra: ^1H (300 MHz), δ 7.93–6.69 (m, 25 H, Ph), 5.27 (s, 2 H, CH_2Cl_2), 2.81–1.92 (m, 6 H, CH_2, dppp); ^{13}C-{^1H}, too insoluble; ^{13}P-{^1H}, δ 19.56 {s, P(1), ^2J[PtP(1)] 146} and −11.50 [s, dppp, ^1J(PtP) 3594 Hz].

(*xx*) [Pt{OP(O)(OPh)O}(dppb)] **12d**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and phenyl dihydrogenphosphate (0.05 g, 0.29 mmol) gave white *microcrystals* of **12d**·H_2O (0.21 g, 96%). Complex **12d**·H_2O was too insoluble for NMR spectroscopy.

(*xxi*) [Pt{OP(O)(OPh)O}$(AsPh_3)_2$] **12e**·H_2O. The complex *cis*-[$PtCl_2(AsPh_3)_2$] (0.30 g, 0.34 mmol) with phenyl dihydro-

Table 5 Fractional atomic coordinates for the non-hydrogen atoms of [Pt{OP(O)(Ph)O}(PMePh$_2$)$_2$] **10b** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.207 11(1)	0.011 93(2)	0.494 56(2)	C(26)	0.166 41(19)	0.375 58(25)	0.542 10(27)
P(1)	0.234 88(10)	−0.035 74(12)	0.301 62(12)	C(31)	0.302 69(20)	0.224 9(4)	0.574 5(3)
P(2)	0.213 58(8)	0.166 89(10)	0.580 34(10)	C(32)	0.334 22(20)	0.275 2(4)	0.657 5(3)
P(3)	0.186 91(9)	−0.099 41(12)	0.622 94(12)	C(33)	0.401 58(20)	0.322 0(4)	0.648 4(3)
O(1)	0.199 9(3)	−0.047 0(4)	0.202 5(4)	C(34)	0.437 48(20)	0.318 5(4)	0.556 3(3)
O(2)	0.206 02(25)	−0.110 9(3)	0.388 5(3)	C(35)	0.405 94(20)	0.268 3(4)	0.473 3(3)
O(3)	0.228 93(23)	0.078 25(29)	0.351 85(27)	C(36)	0.338 56(20)	0.221 4(4)	0.482 4(3)
C(1)	0.188 7(4)	0.176 3(5)	0.711 9(4)	C(41)	0.099 70(18)	−0.092 2(3)	0.681 1(3)
C(2)	0.191 6(5)	−0.236 1(5)	0.574 3(6)	C(42)	0.050 82(18)	−0.016 1(3)	0.645 6(3)
C(11)	0.328 50(24)	−0.064 9(5)	0.288 0(4)	C(43)	−0.018 18(18)	−0.013 3(3)	0.684 9(3)
C(12)	0.353 97(24)	−0.095 7(5)	0.193 4(4)	C(44)	−0.038 33(18)	−0.086 7(3)	0.759 5(3)
C(13)	0.426 45(24)	−0.116 7(5)	0.180 0(4)	C(45)	0.010 56(18)	−0.162 8(3)	0.795 0(3)
C(14)	0.473 47(24)	−0.107 0(5)	0.261 1(4)	C(46)	0.079 56(18)	−0.165 6(3)	0.755 8(3)
C(15)	0.447 97(24)	−0.076 2(5)	0.355 6(4)	C(51)	0.253 53(24)	−0.092 5(4)	0.722 1(4)
C(16)	0.375 48(24)	−0.055 2(5)	0.369 1(4)	C(52)	0.236 55(24)	−0.072 2(4)	0.822 7(4)
C(21)	0.156 38(19)	0.266 15(25)	0.520 65(27)	C(53)	0.290 71(24)	−0.063 3(4)	0.894 5(4)
C(22)	0.100 07(19)	0.233 79(25)	0.458 76(27)	C(54)	0.361 86(24)	−0.074 9(4)	0.865 7(4)
C(23)	0.053 80(19)	0.310 85(25)	0.418 30(27)	C(55)	0.378 83(24)	−0.095 3(4)	0.765 0(4)
C(24)	0.063 86(19)	0.420 24(25)	0.439 74(27)	C(56)	0.324 70(24)	−0.104 1(4)	0.693 2(4)
C(25)	0.120 16(19)	0.452 63(25)	0.501 62(27)				

genphosphate (0.06 g, 0.34 mmol) gave pale yellow *microcrystals* of **12e**·H_2O (0.33 g, 97%). NMR spectra: ^{1}H (90 MHz), δ 7.7–7.0 (m, 35 H, Ph) and 2.1 (s, br, 2 H, H_2O); ^{31}P-{^{1}H}, δ 23.60 {s, P(1), ^2J[PtP(1)] 181 Hz}.

(*xxii*) [Pt{OAs(O)(Ph)O}(PPh$_3$)$_2$] **13a**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and phenylarsonic acid (0.06 g, 0.30 mmol) gave white *microcrystals* of **13a** (0.24 g, 97%). NMR spectra: ^{1}H (90 MHz), δ 8.2–6.9 (m, 35 H, Ph); ^{31}P-{^{1}H}, δ 8.27 [s, PPh$_3$, ^1J(PtP) 3690 Hz].

(*xxiii*) [Pt{OAs(O)(Ph)O}(dppe)] **13b**·CH_2Cl_2. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and phenylarsonic acid (0.06 g, 0.30 mmol) gave white *microcrystals* of **13b**·CH_2Cl_2 (0.23 g, 97%). NMR spectra: ^{1}H (300 MHz), δ 8.11–6.73 (m, 25 H, Ph), 5.27 (s, 2 H, CH_2Cl_2), and 2.66–2.15 (m, 4 H, CH_2, dppe); ^{13}C-{^{1}H}, δ 53.17 (s, CH_2Cl_2) and 26.28 [d, PCH_2, dppe, |^1J(PC) + ^3J(PC)| 51]; ^{31}P-{^{1}H}, δ 30.05 [s, dppe, ^1J(PtP) 3560 Hz].

(*xxiv*) [Pt{OAs(O)(Ph)O}(dppb)] **13c**·H_2O. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and phenylarsonic acid (0.06 g, 0.30 mmol) gave white *microcrystals* of **13c**·H_2O (0.22 g, 97%). NMR spectra: ^{1}H (300 MHz), δ 7.87–7.17 (m, 25 H, Ph), 3.36 (s, br, 2 H, H_2O), 2.45 (m, 4 H, PCH_2, dppb), and 2.03–1.90 (m, 4 H, CH_2, dppb); ^{13}C-{^{1}H}, δ 25.58 [d, PCH_2, dppb), ^1J(PC) 40] and 22.85 (s, CH_2, dppb); ^{31}P-{^{1}H}, δ 3.23 [s, dppb, ^1J(PtP) 3525 Hz].

(*xxv*) [Pt{OAs(O)(Ph)O}(AsPh$_3$)$_2$] **13d**. The complex *cis*-[PtCl$_2$(AsPh$_3$)$_2$] (0.30 g, 0.34 mmol) with phenylarsonic acid (0.07 g, 0.35 mmol) gave pale yellow *microcrystals* of **13d** (0.33 g, 96%). ^{1}H NMR spectrum (90 MHz): δ 8.2–6.9 (m, 35 H, Ph).

Reactions of Platinaphosphonato Complexes.—(*i*) *Decomposition of complex* **10c**·H_2O. A solution of [Pt{OP(O)(Ph)O}{P(CH$_2$Ph)Ph$_2$}$_2$] **10c**·H_2O (0.10 g, 0.11 mmol) in dichloromethane (30 cm^3) was stirred in air for 48 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. The oil was dissolved in dichloromethane (*ca.* 5 cm^3) and light petroleum was added until the cloud-point was reached. On standing, colourless *crystals* were formed, which were filtered off, washed with light petroleum and dried *in vacuo*. An X-ray crystal structure determination identified the product as *cis*-[Pt(C$_6$H$_4$CH$_2$PPh$_2$)$_2$] **14** (R = Ph) (*ca.* 0.015 g, 17%).

(*ii*) *Attempted reaction with dimethyl acetylenedicarboxylate.* A solution of [Pt{OP(O)(Ph)O}(PPh$_3$)$_2$] **10a** (0.10 g, 0.11 mmol) in dichloromethane (30 cm^3) with dimethyl acetylenedicarboxylate (0.10 g, 0.70 mmol) was stirred for 8 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 mainly unreacted starting material **10a**.

X-Ray Crystal Structures.—(*a*) [Pt{OP(O)(Ph)O}(PMePh$_2$)$_2$] **10b**. The crystal was mounted in air. The unit-cell parameters were determined by least-squares refinement of ω measurements for different layers. The intensity data were collected using a Stöe Stadi-2 Weissenberg diffractometer at room temperature, for 12 273 reflections ($\pm h$, $\pm k$, $+l$, $7 \leqslant 2\theta \leqslant 54°$) of a triclinic cell and then transformed to a monoclinic cell found to be appropriate by the matrix (0 −1 0, 0.5 0 0.5, −0.5 0 0.5), to yield 5050 unique reflections. The data were corrected for Lorentz and polarisation effects to yield 4374 unique reflections with $I > 3\sigma(I)$. An absorption correction was also applied to the data, the maximum and minimum transmission factors being 0.335 and 0.135 respectively. All subsequent computations were carried out using the computer program SHELX 76.[21]

Crystal data. $C_{32}H_{31}O_3P_3Pt$, M = 751.6, 0.50 × 0.50 × 0.26 mm, monoclinic, space group = $P2_1/c$, a = 18.746(13), b = 12.364(8), c = 13.256(8) Å, β = 90.05(10)°, U = 3072.6 Å^3, Z = 4, D_c = 1.62 g cm^{-3}, F(000) = 1480.0, Mo-Kα X-radiation, λ = 0.7107 Å, μ(Mo-Kα) = 45.8 cm^{-1}.

The structure was solved using standard 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, but were included in calculated positions (C–H 1.08 Å) with a common fixed isotropic thermal parameter (0.05 Å^2). All other atoms were refined with anisotropic thermal parameters. Final cycles of refinement employed a weighting parameter $w = 1/(\sigma^2F + gF^2)$ (g = 0.0038) and gave the final residual indices R[= $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$] 0.029 and R'\{= $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$\} 0.033. The final difference map was featureless. An analysis of the weighting scheme over $|F_o|$ and sin λ/θ was satisfactory. The atomic coordinates for the structure are given in Table 5.

(*b*) *cis*-[Pt(C$_6$H$_4$CH$_2$PPh$_2$)$_2$] **14** (R = Ph). Conditions were as for complex **10b**, except as follows. The crystal was aligned about the *c* axis of the monoclinic cell. The intensities of 3508 unique reflections with $7 \leqslant 2\theta \leqslant 54°$ and [$\pm h$, $+k$, $+l$, (0–17)]

Table 6 Fractional atomic coordinates for *cis*-[$\overline{Pt(C_6H_4CH_2PPh_2)_2}$] **14**, (R = Ph) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pt	0.000 00(0)	−0.086 08(3)	0.250 00(0)
P(1)	0.093 53(6)	0.049 42(11)	0.221 94(7)
C(1)	0.167 74(23)	−0.062 8(4)	0.233 6(3)
C(11)	0.071 56(23)	−0.223 8(4)	0.205 30(27)
C(12)	0.144 05(24)	−0.193 4(4)	0.200 25(28)
C(13)	0.193 19(27)	−0.278 9(5)	0.164 0(3)
C(14)	0.171 4(3)	−0.395 9(5)	0.130 1(3)
C(15)	0.100 4(3)	−0.428 5(5)	0.131 43(28)
C(16)	0.051 84(27)	−0.343 0(5)	0.169 08(28)
C(21)	0.107 51(15)	0.123 4(3)	0.119 06(15)
C(22)	0.052 22(15)	0.118 9(3)	0.064 51(15)
C(23)	0.060 28(15)	0.175 0(3)	−0.014 43(15)
C(24)	0.123 61(15)	0.235 6(3)	−0.038 84(15)
C(25)	0.178 88(15)	0.240 1(3)	0.015 71(15)
C(26)	0.170 83(15)	0.184 0(3)	0.094 65(15)
C(31)	0.109 69(17)	0.182 13(26)	0.294 59(16)
C(32)	0.123 09(17)	0.150 72(26)	0.376 91(16)
C(33)	0.131 34(17)	0.250 18(26)	0.435 24(16)
C(34)	0.126 19(17)	0.381 04(26)	0.411 25(16)
C(35)	0.112 77(17)	0.412 44(26)	0.328 91(16)
C(36)	0.104 52(17)	0.312 99(26)	0.270 57(16)

were measured and corrected for Lorentz and polarisation effects to yield 2680 reflections with $I > 3\sigma(I)$. An absorption correction was also applied, the maximum and minimum transmission factors being 0.5164 and 0.4275 respectively.

Crystal data. $C_{38}H_{32}P_2Pt$, $M = 745.7$, 0.33 × 0.19 × 0.19 mm, monoclinic, space group = $I2/c$ (non-standard setting of $C2/c$), $a = 18.993(24)$, $b = 10.208(13)$, $c = 16.075(8)$ Å, $\beta = 87.73(6)°$, $U = 3114.19$ Å^3, $Z = 4$, $D_c = 1.59$ g cm^{-3}, $F(000) = 1800.0$, Mo-Kα X-radiation, μ(Mo-Kα) = 44.94 cm^{-1}.

All hydrogen atoms were included in calculated positions (C–H 1.08 Å) with group-refined isotropic thermal parameters. Final cycles of refinement employed a weighting parameter $w = 1/(\sigma^2F + gF^2)$ ($g = 0.000\,162$) and gave the final residual indices R 0.0311 and R' 0.0279. The atomic coordinates are given in Table 6.

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

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