Bimetallic Systems. Part 2.† Synthesis and Interconversion of Monodentate- and Bridging-bis(diphenylphosphino)methane Platinum, Diplatinum, and Mercury–Platinum Acetylides

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Treatment of $[PtCl_2(dppm\text{-}PP')]$ [dppm = bis(diphenylphosphino)methane] with $LiC{\equiv}CR$ gives good yields of the diplatinum 'face-to-face' complexes *trans,trans*-$[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ (2a), (2b), (2d), or (2e), with R = $C_6H_4Me\text{-}p$, Ph, CH_2CH_2Ph, or $C(Me){=}CH_2$ respectively. These diplatinum complexes react with more dppm to give the mononuclear fluxional complexes *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (3a), (3b), (3d), or (3e). A more convenient method of making the mononuclear complexes (3a)—(3e) is to treat $[PtCl_2(dppm\text{-}PP')]$ with $LiC{\equiv}CR$ in the presence of dppm. Treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ with $LiC{\equiv}CPh$ gives (3b) but deprotonation to give $[Pt(Ph_2PCHPPh_2)_2]$ also occurs. Treatment of $[PtCl_2(dppm\text{-}PP')]$ with an excess of $LiC{\equiv}CPh$ gives (3b) and $[Pt(C{\equiv}CPh)_4]^{2-}$, isolated as its $[NBu^n_4]^+$ salt. Treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ with $Hg(C{\equiv}CR)_2$ rapidly gives the platinum–mercury complexes $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (4a)—(4d) in very high yields, with R = $C_6H_4Me\text{-}p$, Ph, Me, or Pr^n respectively. Treatment of the platinum–mercury complexes (4a)—(4c) with $Na_2S{\cdot}9H_2O$ gives HgS and high yields of the mononuclear complexes *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (3a)—(3c), with R = $C_6H_4Me\text{-}p$, Ph, or Me respectively. More conveniently, when $[Pt(dppm\text{-}PP')_2]Cl_2$ is treated with $Hg(O_2CMe)_2$ + $RC{\equiv}CH$ the platinum–mercury complexes (4a)—(4c) are formed in excellent yields. Preliminary work shows that $[(HOCH_2CH_2C{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (4e) is formed from $[Pt(dppm\text{-}PP')_2]Cl_2$ + $Hg(O_2CMe)_2$ + $HOCH_2CH_2C{\equiv}CH$. Treatment of the complex *trans*-$[Pt(C{\equiv}CPh)_2(dppm\text{-}P)_2]$ (3b) with $HgCl_2$ gives $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (4b). The fluxional monodentate-dppm complexes *trans*-$[Pt(C{\equiv}CR)_2(Ph_2PCH_2PPh_2)_2]$ (3a)—(3c), R = $C_6H_4Me\text{-}p$, Ph, or Me respectively, are oxidised by hydrogen peroxide to give the non-fluxional phosphine oxide complexes *trans*-$[Pt(C{\equiv}CR)_2\{Ph_2PCH_2P({=}O)Ph_2\}_2]$ (5a)—(5c) or quaternised by methyl iodide to give *trans*-$[Pt(C{\equiv}CR)_2(Ph_2PCH_2PMePh_2)_2]I_2$ (6a)—(6c). Complex (6b; R = Ph) is deprotonated by lithium propan-2-oxide probably to give the di-ylide *trans*-$[Pt(C{\equiv}CPh)_2(Ph_2PCH{=}PMePh_2)_2]$ (7) which hydrolyses to *trans*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$. I.r., and ^1H, ^{31}P, and ^{195}Pt n.m.r. data are given.

Bis(diphenylphosphino)methane (dppm) is remarkably versatile in its properties as a ligand. Thus, in addition to stabilising metal–metal bonded species, *e.g.* $[Pd_2Cl_2(\mu\text{-dppm})_2]$ [1] and 'A-frames', *e.g.* $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-CO})]$ [2] it promotes eight-membered ring formation, as in the 'face-to-face' complex *trans,trans*-$[Rh_2Cl_2(\mu\text{-dppm})_2(CO)_2]$ (1) [3,4] and in *cis,cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$ with a 'twist boat' conformation.[5] Four-membered chelate rings are also known, *e.g.* $[PtCl_2(dppm\text{-}PP')]$.

Prior to our work, the only diplatinum eight-membered ring compound containing bridging dppm groups was the complex *cis,cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$, referred to above, which is unstable in hot benzene. By analogy with the eight-membered ring dirhodium complex (1), we reasoned that 'face-to-face' diplatinum complexes of the type *trans,trans*-$[Pt_2X_4(\mu\text{-dppm})_2]$ might be stable provided that the ligands X had a pronounced tendency to be mutually *trans*. Acetylides seemed to be a suitable choice for X since they have a distinct preference to be mutually *trans* in complexes of type $[M(C{\equiv}CR)_2L_2]$ (M = Pt or Pd, R = alkyl or aryl, L = tertiary phosphine).[6–9] Complexes of platinum(II) with *cis*-acetylide groups are known but are reported to be less stable.[10] We therefore treated $[PtCl_2(dppm\text{-}PP')]$ with 2 mol equiv. of lithium *p*-tolylacetylide in benzene–tetrahydrofuran (thf). This gave the desired binuclear 'face-to-face' complex $[Pt_2(C{\equiv}CC_6H_4Me\text{-}p)_4(\mu\text{-dppm})_2]$ (2a) in 88% yield as a yellow crystalline solid (see Experimental section). The elemental analytical and molecular weight data are given in Table 1. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, shown in Figure 1, indicates the presence of a $Pt_2(\mu\text{-dppm})_2$ moiety with chemically equivalent phosphorus atoms. The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum shows a 1 : 8 : 18 : 8 : 1 quintet pattern for the CH_2 group which is what one would expect to be produced from the various isotopomers of platinum. The i.r. spectrum shows a band at 2 105 cm^{-1} due to $\nu(C{\equiv}C)$. This binuclear *p*-tolylacetylide complex (2a) is readily soluble in chlorinated solvents but, after its solution in dichloromethane has stood for a few hours, a rather insoluble crystalline solvate separates. This we formulate as the dichloromethane solvate $[Pt_2(C{\equiv}CC_6H_4Me\text{-}p)_4(\mu\text{-dppm})_2]{\cdot}1.5CH_2Cl_2$ on the basis of microanalysis (C, H, and Cl) and integration of the ^1H n.m.r. spectrum. The binuclear phenylacetylide complex (2b) was made in a similar fashion to (2a) and is much less soluble than (2a).

We also attempted to synthesise the binuclear methylacetylide complex (2c) using similar methods but it was not formed. However, the synthesis of this compound has been claimed and it was reported by Puddephatt and Thomson [11] that the $^{31}P\text{-}\{^1H\}$ spectrum showed broad signals with $^1J(PtP)$ = 2 600 Hz. We suggest that the spectrum they measured was of *trans*-$[Pt(C{\equiv}CMe)_2(dppm\text{-}P)_2]$, which we have made (see below). We have almost certainly observed the binuclear complex (2c) in solution as a by-product of treating $[W(CO)_3(NCMe)_3]$ with $[Pt(C{\equiv}CMe)_2(dppm\text{-}P)_2]$.[12] We have not isolated this binuclear complex but the $^{31}P\text{-}\{^1H\}$ n.m.r. spectral pattern and parameters [$\delta(P) = +1.8$ p.p.m., $^1J(PtP)$ = 2 893, $^3J(PtP) = -66$ Hz (in CD_2Cl_2)] are very similar to those of (2a) and (2b) (Table 2). We have also prepared and characterised two other complexes of type $[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ with R = CH_2CH_2Ph (2d) and with R = $C(Me){=}CH_2$ (2e); details are in the Experimental section and characterisation data in Tables 1—3.

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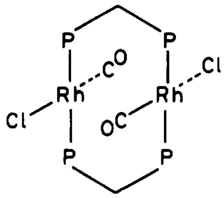
† Part 1 taken as ref. 1.

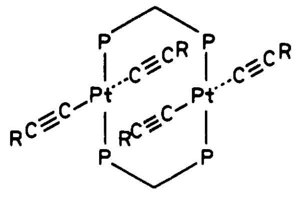
Table 1. Melting points, analytical and molecular weight data

Complex	M.p. (°C) [b]	Analysis (%) [a] C	H	Halogen	M [a]
(2a)	270—273	64.0 (63.8)	4.75 (4.5)		1 580 (1 619)
(2a)·1.5CH$_2$Cl$_2$ [c]	n.d.	59.6 (60.1)	4.05 (4.3)	6.45 (6.1)	
(2b)	285—290	63.7 (63.9)	4.25 (4.15)		
(2d)·0.5CH$_2$Cl$_2$ [c]	218—222	63.55 (63.3)	4.85 (4.75)	1.65 (2.05)	
(2e)·CH$_2$Cl$_2$ [c]	decomp. >200	56.45 (56.7)	4.25 (4.4)	4.25 (4.7)	
(3a)	237—238	68.65 (68.4)	5.05 (4.9)		
(3b)	232—233	68.2 (67.9)	4.75 (4.75)		1 192 (1 167)
(3c)	189—190	64.4 (64.55)	5.0 (4.85)		1 018 (1 042)
(3d)	157—159	68.7 (68.9)	5.2 (5.1)		
(3e)	176—178	65.6 (65.9)	5.2 (5.0)		
(4a)	228—230	55.5 (55.7)	4.05 (4.0)	4.6 (4.85)	
(4b)	216—218	54.85 (55.15)	3.9 (3.8)	4.75 (4.9)	
(4c)·CH$_2$Cl$_2$ [c]	183—185	49.3 (48.95)	3.75 (3.75)	9.6 (10.15)	
(4d)	n.d.	52.7 (52.6)	4.45 (4.25)	5.0 (5.2)	
(5a)	n.d.	66.5 (66.5)	4.95 (4.75)		
(6a)	n.d.	57.7 (56.9)	4.55 (4.35)	17.1 (17.75)	
(6b)	n.d.	55.2 (55.0)	4.2 (4.35)	17.0 (17.1)	
(6c)	n.d.	52.6 (52.55)	4.4 (4.25)	18.95 (19.15)	

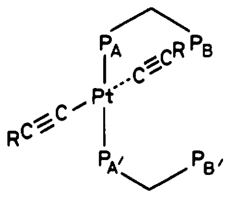
[a] Calculated values are in parentheses. [b] Corrected; all complexes decompose on melting; n.d. = not determined. [c] The presence of CH$_2$Cl$_2$ in these isolated complexes was shown by ^{1}H n.m.r. spectroscopy.



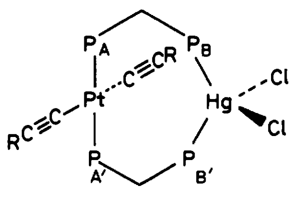
(1)



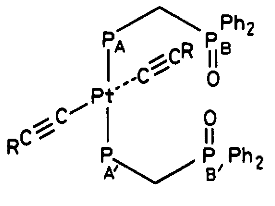
(2a) R = C$_6$H$_4$Me-p
(2b) R = Ph
(2c) R = Me
(2d) R = CH$_2$CH$_2$Ph
(2e) R = C(Me)=CH$_2$



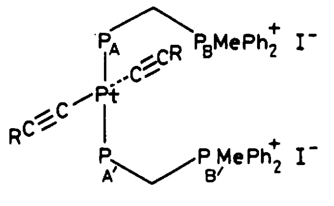
(3a) R = C$_6$H$_4$Me-p
(3b) R = Ph
(3c) R = Me
(3d) R = CH$_2$CH$_2$Ph
(3e) R = C(Me)=CH$_2$



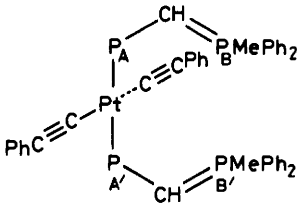
(4a) R = C$_6$H$_4$Me-p
(4b) R = Ph
(4c) R = Me
(4d) R = Pr^n
(4e) R = CH$_2$CH$_2$OH



(5a) R = C$_6$H$_4$Me-p
(5b) R = Ph
(5c) R = Me



(6a) R = C$_6$H$_4$Me-p
(6b) R = Ph
(6c) R = Me



(7)

There has been some discussion [13-18] of the electronic spectra of 'face-to-face' dirhodium complexes, *e.g.* complex (1) showed a large low-frequency shift in the charge-transfer band compared to related mononuclear or larger ring binuclear complexes. This effect was ascribed to the closeness of the metal centres and termed 'metal-proximity shift'. We have measured the electronic spectra of the diplatinum complexes (2a) and (2b) which are isoelectronic with (1), and of the mononuclear species (3a) and (3b) for comparison. The spectra for (2a) and (3a) are shown in Figure 2 and the data given in Table 4. It can be seen that there is one charge-transfer band for the mononuclear species (3a) and (3b) in the region expected [10] but that two bands are seen for the binuclear species (2a) and (2b). We propose that this 'splitting' of the

Table 2. $^{31}P-\{^1H\}$ [a] and $^{195}Pt-\{^1H\}$ [b] n.m.r. data

Complex	Temperature (°C) [c]	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_B)$	$^3J(PtP_B)$	$\lvert ^2J(P_AP_B) + {}^4J(P_AP_{B'})\rvert$
(2a) [b]		2.2	2 826		−66	
(2b)		2.3	2 837		−65	
(2c) [d,e]		1.8	2 893		−66	
(2d)		2.8	2 910		−51	
(2e)		1.8	2 849		−54	
(3a)	−30	8.3	2 505	−27.5	78	54
(3b)	−30	8.5	2 516	−27.3	78	54
(3c)	0	9.2	2 600	−27.4	72	64
(3d)	−60	8.4	2 554	−28.3	*f*	59
(3e)	−60	7.7	2 485	−27.6	83	51
(4a)		9.85	2 644	15.7 (5 495) [g]	244	68
(4b)		9.8	2 644	15.2 (5 525) [g]	244	61
(4c) [d]		10.2	2 686	14.8 (5 576) [g]	256	64
(4d)		10.6	2 676	16.7 (5 593) [g]	264	64
(5a) [b]		5.2	2 606	25.8	92	12
(5b)		5.2	2 600	25.6	90	13
(5c)		6.4	2 646	25.8	103	12
(6b)		4.3	2 595	19.2	*ca.* 0	*ca.* 0
(6c)		3.9	2 649	19.6	*ca.* 0	*ca.* 0
trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$		1.2	2 532			

[a] In $CDCl_3$, chemical shifts (δ) in p.p.m. (±0.1 p.p.m.) to high frequency of 85% H_3PO_4; coupling constants (*J*) in Hz (±3 Hz). The designations P_A and P_B do not apply to the symmetrical complexes (2a)—(2c). [b] To high frequency of $\Xi(^{195}Pt) = 21.4$ MHz. Complex (2a), δ(Pt) = −108 p.p.m.; (5a), δ(Pt) = −179 p.p.m. [c] At *ca.* +21 °C unless otherwise stated. [d] In CD_2Cl_2. [e] Not isolated, see Discussion section. [f] Obscured. [g] $^1J(^{199}HgP)$ in parentheses (±3 Hz).

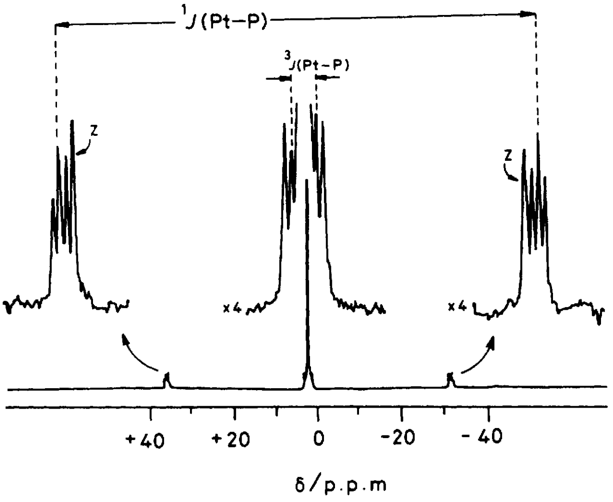


Figure 1. $^{31}P-\{^1H\}$ n.m.r. spectrum (40.25 MHz) of (2a) in $CDCl_3$ at *ca.* +22 °C. The peaks labelled Z are separated by $^1J(PtP) + {}^3J(PtP)$

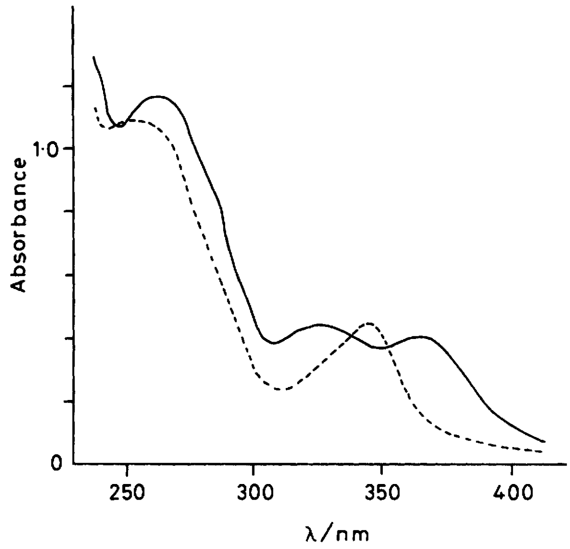


Figure 2. Electronic absorption spectra of (2a) (——) and (3a) (— — —), in dichloromethane solution (2.0 × 10^{-5} mol dm^{-3})

charge-transfer band for the binuclear species (2a) and (2b) is a consequence of the closeness of the metal centres interacting in a manner similar to that proposed for the dirhodium species.

We discovered that the binuclear μ-dppm complexes (2a) or (2b), when treated with more dppm (two moles per mole of binuclear complex) in benzene or dichloromethane, were converted essentially quantitatively into the mononuclear monodentate dppm complexes, *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$, (3a) and (3b), respectively. The conversion is reversible since on boiling a toluene solution of (3b) the binuclear complex (2b) is precipitated in 60% yield. The formulation is based on (*i*) elemental analysis (C and H) and molecular weight determination (Table 1); (*ii*) i.r. spectroscopy, $\nu(C{\equiv}C) = 2\,105\ cm^{-1}$; (*iii*) $^{31}P-\{^1H\}$ n.m.r. spectroscopy; at room temperature the spectrum of (3b) showed two broad resonances, one of which had satellites due to platinum-195 but not other fine structure. At −20 °C the spectrum showed two well defined ' virtual triplet ' resonances, one of these resonances had associated satellites, due to platinum-195 coupling, with a large value (2 516 Hz) for *J*(PtP), clearly a one-bond coupling, and the other resonance showed a much smaller value for *J*(PtP) (78 Hz), which we attribute to a three-bond coupling. The value of 2 516 Hz for ^1J(PtP) and the ' virtual triplet ' patterns of the resonances indicates a *trans* arrangement of the dppm ligands. We interpret this variable-temperature behaviour as rapid ' end over end ' exchange, *viz.* $Ph_2PCH_2P^*Ph_2Pt \rightleftharpoons Ph_2P^*\text{-}CH_2PPh_2Pt$ at room temperature which is effectively stopped

Table 3. Hydrogen-1 and ^{1}H-{^{31}P} n.m.r. data [a] and values of ν(C≡C) [b]

Complex	ν(C≡C)/cm^{-1}	Temperature (°C)	δ(CH_2) [c]	^3J(PtCH_2)	^2J(PCH_2)	Other data [d]
(2a)	2 105	+22	4.64	34.7	4.7	δ(CH_3) 2.19
(2b)	2 105	+22	4.7	34.5	n.r.[d]	
(2d)	2 112	+22	4.57	34.4	4.4	δ(CH_2CH_2) 2.2 br
(2e)	2 110 2 080	+22	4.6	34.0	n.r.[d]	δ(CH_3) 1.33 δ(C=CH_2) 4.3—4.6
(3a)	2 105	+22	3.80 (13)			δ(CH_3) 2.21 (2.5)
		−20	3.83 (5)	18.1		
(3b)	2 105	+22	3.81 (17)			
		−28	3.86 (7)	17.8		
(3c)	2 125	+22	3.78 (8)	22.0		δ(CH_3) 1.31 ^4J(PtCH_3) = 14.9 Hz
(3d)	2 125	+22	3.76 (5)	23		δ(CH_2CH_2) 1.8—2.3
		−30	3.76 (10)	n.r.		
(3e)	2 105 2 075	+22	3.71 (25)			δ(C=CH_2) 4.3—4.5m
		−30	3.68 (16)	~20		δ(CH_3) 1.3
(4b)	2 114 2 102	+22	4.33	30.5		^3J(HgCH_2) = 68.3 Hz
(4c)		+22	4.2	30.5		^3J(HgCH_2) = 66.7 Hz, δ(CH_3) 1.19 ^4J(PtCH_3) = 14.9 Hz

[a] Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) to high frequency of SiMe$_4$; coupling constant (J) in Hz (±0.5 Hz). Measured in CDCl$_3$. [b] Nujol mulls. [c] Widths at half height ($w_{\frac{1}{2}}$/Hz) shown in parentheses. [d] n.r. = Not resolved, br = broad, m = multiplet.

Table 4. Electronic spectral data (400—250 nm)

Complex	$\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1})
(2a)	370 (20 100), 330 (22 700), 266 (59 400)
(2b)	378 (23 600), 335 (24 700), 275 (65 100)
(3a)	348 (20 600), 260 (54 000)
(3b)	345 (19 800), 260 (52 000)

at −20 °C. The ^{31}P-{^{1}H} n.m.r. spectra of (3b) at +24 and −30 °C were reproduced in our preliminary publication.[19] The room temperature ^{1}H- and ^{1}H-{^{31}P} n.m.r. spectra of (3b) showed a broad CH$_2$ resonance at δ 3.81 p.p.m. ($w_{\frac{1}{2}}$ *ca.* 17 Hz) which remained quite broad ($w_{\frac{1}{2}}$ *ca.* 7 Hz) at −30 °C although coupling to platinum-195 was observed (Table 2). The resonances were too complex to analyse fully. We also prepared these monodentate-dppm diacetylide complexes by treating [PtCl$_2$(dppm-*PP'*)] with two moles of LiC≡CR in the presence of one mole of dppm. This method gave yields of 52% (3a) and 58% (3b). We also synthesised three new complexes of the type [Pt(C≡CR)$_2$(dppm-*P*)$_2$] by this method, namely (3c) 35%, (3d) 49%, and (3e) 44% (characterising data in Tables 1—3). We found, however, that treatment of the salt [Pt(dppm-*PP'*)$_2$]Cl$_2$ with two moles of lithium phenylacetylide in thf gave a rather low yield of the monodentate-dppm complex (3b), the main product being the insoluble material [Pt(Ph$_2$PCHPPh$_2$)$_2$] formed by deprotonation.[20] We also found that the monodentate-dppm complex (3b) was formed when [PtCl$_2$(dppm-*PP'*)] was treated with an excess (five-fold) of LiC≡CPh in thf–benzene. In this reaction two platinum-containing species were formed. One of these, which was soluble in water, gave a precipitate with tetra-n-butylammonium chloride which was characterised as [NBu$^n_4$]$_2$[Pt(C≡CPh)$_4$] by microanalysis and by comparison of the i.r. spectrum with that reported for [Pt(C≡CPh)$_4$]$^{2-}$.[21] The other product was (3b), isolated in a yield of 50%, based on dppm.

As described above, the highly basic acetylide, lithium phenylacetylide, preferentially deprotonated [Pt(dppm-*PP'*)$_2$]$^{2+}$ to give [Pt(Ph$_2$PCHPPh$_2$)$_2$] and the yield of (3b) was low. We reasoned that a much less basic acetylide, such as Hg(C≡CR)$_2$ might introduce acetylide groups onto platinum without causing deprotonation. We thus treated [Pt(dppm-*PP'*)$_2$]Cl$_2$ with 1 mol equiv. of Hg(C≡CC$_6$H$_4$Me-*p*)$_2$ in warm ethanol and discovered the remarkable conversion to the mixed platinum–mercury complex (4a), similarly for the PhC≡C analogue (4b). Conversions were complete in a few minutes and the isolated yields of pure products (4a) or (4b) were *ca.* 90%. Moreover, ^{31}P-{^{1}H} n.m.r. studies of these reactions in CH$_2$Cl$_2$–CD$_2$Cl$_2$ solution showed that they were stoicheiometric and no other phosphorus-containing product could be detected. The products are identical to those formed by treating *trans*-[Pt(C≡CR)$_2$(dppm-*P*)$_2$] (R = C$_6$H$_4$Me-*p* or Ph) with mercury(II) chloride in thf–benzene. These eight-membered ring platinum–mercury complexes (4a) and (4b) were characterised by elemental analysis (Table 1) and by i.r. spectroscopy; *e.g.* for (4b), ν(C≡C) = 2 102 and 2 114 cm^{-1} and ν(Hg–Cl) = 234 cm^{-1} (Nujol mull). The ^{31}P-{^{1}H} n.m.r. spectra are particularly well defined and informative because of couplings to both platinum-195 ($I = \frac{1}{2}$, 33.8% abundant) and mercury-199 ($I = \frac{1}{2}$, 16.9% abundant) and the presence of several 'virtual triplet' patterns caused by the various isotopomers and the large values of ^2J(P$_A$P$_{A'}$) and possibly also of ^2J(P$_B$P$_{B'}$) (see Table 2 for data). The ^{31}P-{^{1}H} n.m.r. spectrum of (4a) was reproduced in our preliminary communication on this work.[22] The ^{1}H and ^{1}H-{^{31}P} n.m.r. spectra showed equivalent CH$_2$ protons even at −50 °C: couplings to mercury-199 as well as platinum-195 were well resolved (data in Table 3). These platinum–mercury complexes (4a) and (4b) are non-conducting in nitrobenzene solution.

We then found that we could readily remove the mercury (as the sulphide) from the platinum–mercury complexes (4a) or (4b) by treatment with sodium sulphide. After removal of the mercury sulphide the monodentate-dppm complexes (3a) or (3b) were readily isolated from the mother-liquor, in excellent yield and purity (see Experimental section). This is a convenient method of synthesis and we find it works equally well for the synthesis of mixed platinum–mercury binuclear complexes with aliphatic acetylide groups such as the methylacetylide (4c) or n-propylacetylide (4d). Preliminary ^{31}P-{^{1}H} n.m.r. studies showed that when [Pt(dppm-*PP'*)$_2$]Cl$_2$ was treated with [Hg(C≡CMe)$_2$] or [Hg(C≡CPr^n)$_2$] in CD$_2$Cl$_2$ solution above −30 °C, (4c) or (4d) were formed by what appeared to be stoicheiometric reactions. On a preparative scale (4c) and (4d) were isolated in 89.5 and 74% yields respectively. Moreover, when the methylacetylide complex (4c) was treated with sodium sulphide the complex $[Pt(C\equiv CMe)_2(dppm\text{-}P)_2]$ was isolated in 73% yield. These preparations required the prior synthesis of $Hg(C\equiv CR)_2$ and we tried to devise more convenient syntheses by forming the mercury acetylides *in situ* from the readily available mercury(II) acetate and the aryl- or alkyl-acetylene. We thus treated $[Pt(dppm\text{-}PP')_2]Cl_2$ with $Hg(O_2CMe)_2 + PhC\equiv CH$ in CD_2Cl_2 and found that conversion to the required $[(PhC\equiv C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (4b) appeared to be quantitative by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (4b) is particularly well defined and even small amounts of phosphorus-containing impurities (*i.e.* 1% of total) would probably have been detectable, but none was. On a preparative scale pure (4b) was prepared in 88% isolated yield by this method. Similarly, the methylacetylide complex (4c) was prepared in 82% isolated yield. In some preliminary $^{31}P\text{-}\{^1H\}$ n.m.r. experiments we have attempted to synthesise a complex of type (4) with $R = CH_2CH_2OH$. Treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ with $Hg(O_2CMe)_2 + HC\equiv CCH_2CH_2OH$ in warm CD_2Cl_2 gave a species with the characteristic $^{31}P\text{-}\{^1H\}$ n.m.r. pattern expected for the compound (4e), namely, $\delta(P_A) = 12.7$ p.p.m., $^1J(PtP_A) = 2\,576$ Hz; $\delta(P_B) = 20.3$ p.p.m., $^1J(HgP_B) = 5\,454$ Hz; $|^2J(P_AP_B) + {}^4J(P_AP_{B'})| = 59$ Hz, but we did not isolate the product in a pure state. Recently in a detailed study, mercury acetylides, $Hg(C\equiv CR)_2$, have been used to convert complexes of type $[PtCl_2(CO)(PR'_3)]$ into $[Pt(C\equiv CR)_2(CO)(PR'_3)]$.[23]

Two characteristic reactions of tertiary phosphines are their oxidation to phosphine oxides and their quaternisation with an alkyl halide such as methyl iodide. The free tertiary phosphines of the dppm complexes (3a)—(3c) showed both of these reactions. Thus they reacted rapidly with hydrogen peroxide to give the complexes *trans*-$[Pt(C\equiv CR)_2\{Ph_2PCH_2P(=O)Ph_2\}_2]$ (5a)—(5c) which are not fluxional (see Experimental section for details and Tables 1 and 2 for characterising data). The monodentate-dppm complexes (3a)—(3c) also reacted with methyl iodide in benzene to give the diquaternised species (6a)—(6c), *trans*-$[Pt(C\equiv CR)_2(Ph_2PCH_2PMePh_2)_2]I_2$ (see Experimental section and Tables 1 and 2). A characteristic reaction of quarternary phosphonium salts is the deprotonation of the carbon atom in α-position to the quaternised phosphorus to give ylides.[24] We find that treatment of the diquaternary salt (6b) with sodium propan-2-oxide gives a species whose ^{31}P n.m.r. parameters are consistent with the formation of a bis(ylide) complex (7), *viz.* (in thf solution) $\delta(P_A) = +0.9$ p.p.m., $^1J(PtP_A) = 2\,549$ Hz; $\delta(P_B) = +30.3$ p.p.m., $^3J(PtP_B) \approx 0$ Hz. Work-up of the reaction mixture involved addition of water and gave *trans*-$[Pt(C\equiv CPh)_2(PMe_2Ph)_2]$. Thus, water has cleaved the $P^+\text{–}C^-$ bonds, a known reaction of organophosphorus ylides.[25]

Experimental

The general techniques and apparatus used were the same as in other recent papers from this laboratory.[26]

Preparation of $[Pt_2(C\equiv CPh)_4(\mu\text{-dppm})_2]$ (2b).—A solution of lithium phenylacetylide was prepared from $PhC\equiv CH$ (0.11 g, 1.1 mmol) in thf (10 cm^3) and n-butyl-lithium (0.65 cm^3, 1.55 mol dm^{-3}, 1.0 mmol) in hexane at 0 °C. $[PtCl_2(dppm\text{-}PP')]$ (0.325 g, 0.5 mmol) and benzene (25 cm^3) were added and the mixture stirred for 1 h and then heated under reflux for 14 h. The yellow product was then filtered off, washed successively with benzene, water, and methanol and dried. Yield 0.34 g (87%). It formed yellow microcrystals of a dichloromethane solvate from dichloromethane.

$[Pt_2(C\equiv CC_6H_4Me\text{-}p)_4(\mu\text{-dppm})_2]$ (2a) was made similarly except that owing to its greater solubility some of it remained dissolved in the benzene–thf mother-liquors. A further quantity was isolated by removing the solvent under reduced pressure and triturating the residue with methanol. Total yield 88%. It formed a solvate from dichloromethane (see Table 1).

Complex (2d) was made in a similar manner to (2a). It formed yellow microprisms of a CH_2Cl_2 solvate from CH_2Cl_2—Et_2O. Yield 21%.

Complex (2e) was made and purified similarly. It formed a CH_2Cl_2 solvate. Yield 43%.

Preparation of trans-$[Pt(C\equiv CPh)_2(dppm\text{-}P)_2]$ (3b) *from* (2b).—Bis(diphenylphosphino)methane (0.64 g, 1.66 mmol) was added to a suspension of the binuclear complex (1.00 g, 0.64 mmol) in CH_2Cl_2 (100 cm^3). The mixture was stirred for 3 h at *ca.* 20 °C; the solvent was then evaporated under reduced pressure and the residue recrystallised from benzene–methanol. This gave pure (3b) as yellow prisms. Yield 1.40 g (94%).

The *p*-tolylacetylide analogue (3a) was made similarly in 96% yield. Benzene may be used instead of dichloromethane but then the conversion takes *ca.* 24 h.

Preparation of trans-$[Pt(C\equiv CPh)_2(dppm\text{-}P)_2]$ (3b) *from* $[PtCl_2(dppm\text{-}PP')]$.—A solution of $LiC\equiv CPh$ was prepared from $PhC\equiv CH$ (0.64 g, 6.3 mmol) in thf (30 cm^3) and $LiBu^n$ in hexane (4.0 cm^3, 1.55 mol dm^{-3}, 6.2 mmol). $[PtCl_2(dppm\text{-}PP')]$ (2.02 g, 3.1 mmol) and dppm (1.19 g, 3.1 mmol) were then added with benzene (10 cm^3). The resultant mixture was heated under reflux for 1.5 h, allowed to cool and then stirred for 14 h at *ca.* 20 °C. The solvent was then evaporated under reduced pressure and the residue recrystallised from benzene–methanol to give the required product. Yield 2.10 g (58%).

Complexes (3a) (52%), (3c) (35%), (3d) (49%), and (3e) (44%) were made similarly.

Action of $LiC\equiv CPh$ *on* $[Pt(dppm\text{-}PP')_2]Cl_2$.—A solution of $LiC\equiv CPh$, made from $PhC\equiv CH$ (0.15 g, 1.47 mmol) in thf (10 cm^3) and $LiBu^n$ (0.83 cm^3, 1.55 mol dm^{-3}, 1.3 mmol) in hexane was added dropwise to a suspension of $[Pt(dppm\text{-}PP')_2]Cl_2$ (0.42 g, 0.65 mmol) in thf (10 cm^3). The yellow solid which formed was filtered off, washed with thf and dried. Its i.r. spectrum showed it to be $[Pt(Ph_2PCHPPh_2)_2]$. Yield 0.05 g (8% based in Pt). The yellow mother-liquors were evaporated to dryness and methanol added. This gave (3d) (0.265 g, 35% based on Pt).

Action of an Excess of $LiC\equiv CPh$ *on* $[PtCl_2(dppm\text{-}PP')]$.—$[PtCl_2(dppm\text{-}PP')]$ (1.00 g, 1.54 mmol) and benzene (10 cm^3) were added to a solution of $LiC\equiv CPh$, prepared from $PhC\equiv CH$ (1.02 g, 10 mmol) in thf (10 cm^3) and $LiBu^n$ (6.3 cm^3, 1.55 mol dm^{-3}, 10 mmol) in hexane. The resultant mixture was heated under reflux for 1 h, cooled and water (10 cm^3) added to the residue. The remaining solid was recrystallised from benzene–methanol to give pure (3b). Yield 0.55 g (31% based on Pt). The aqueous mother-liquors were treated with a solution of tetra-n-butylammonium chloride (1.50 g, 5.4 mmol) in water (5 cm^3). This gave a precipitate of $[NBu^n{}_4]_2[Pt(C\equiv CPh)_4]$ (Found: C, 70.7; H, 8.45; N, 2.65. $C_{64}H_{92}N_2Pt$ requires C, 70.9; H, 8.55; N, 2.6%). I.r. spectrum (Nujol mull), $\nu(C\equiv C)$ 2 100 cm^{-1}.

Preparation of $[(PhC\equiv C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (4b) *from* $[Pt(dppm\text{-}PP')_2]Cl_2$ *and* $Hg(C\equiv CPh)_2$.—A solution of the platinum salt (0.25 g, 0.24 mmol) in ethanol (5 cm^3) was treated with a solution of $Hg(C\equiv CPh)_2$ (0.193 g, 0.48 mmol) in hot ethanol (10 cm^3, *ca.* 60 °C). A pale yellow solid formed after a few seconds. The mixture was put aside for 30 min and the yellow solid was isolated and identified as the pure required product (4b). Yield 0.31 g (90%).

Complexes (4a) (89%), (4c) (89.5%), and (4d) (74%) were prepared and isolated similarly; (4c) as a CH_2Cl_2 solvate (from CH_2Cl_2–ethanol).

Preparation of $[(PhC\equiv C)_2Pt(\mu\text{-}dppm)_2HgCl_2]$ (4b) *from* $[Pt(dppm\text{-}PP')_2]Cl_2$, $Hg(O_2CMe)_2$, *and* $PhC\equiv CH$.—Phenylacetylene (0.038 g, 0.37 mmol) was added to a solution of mercury(II) acetate (0.0624 g, 0.20 mmol) in ethanol (5 cm^3) and the resultant solution added to a solution of the platinum salt (0.20 g, 0.19 mmol) in ethanol (5 cm^3). The mixture was then heated under reflux for 15 min, cooled and evaporated to dryness under reduced pressure. The residue was extracted into dichloromethane, which was then filtered and evaporated to low bulk. This gave (4b) as yellow microcrystals (0.181 g) and a further quantity (0.038 g) of (4b) was precipitated by adding light petroleum (b.p. 40—60 °C) to the mother-liquor. Total yield 88%. The product was pure as shown by the characteristic $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum and by elemental analysis (Found: C, 55.15; H, 3.8; Cl, 4.7. Calc. for $C_{66}H_{54}Cl_2HgP_2Pt$: C, 55.15; H, 3.8; Cl, 4.95%).

Preparation of $[(MeC\equiv C)_2Pt(\mu\text{-}dppm)_2HgCl_2]$ (4c) *using* $Hg(O_2CMe)_2$.—Methylacetylene (60 cm^3 of the gas) was slowly bubbled into a solution of mercury(II) acetate (0.0624 g, 0.196 mmol) in ethanol–methanol (5 : 6 v/v, 5.5 cm^3) at *ca.* 5 °C. A solution of $[Pt(dppm\text{-}PP')_2]Cl_2$ (0.200 g, 0.193 mmol) in dichloromethane (8 cm^3) was then added. The mixture was then put aside at 20 °C for 2 d after which it was allowed to evaporate to low bulk slowly in air. This gave yellow microcrystals (0.222 g), shown by elemental analysis and n.m.r. spectroscopy to be the pure dichloromethane solvate $[(MeC\equiv C)_2Pt(\mu\text{-}dppm)_2HgCl_2]\cdot CH_2Cl_2$. Yield 82%.

Action of trans-$[Pt(C\equiv CC_6H_4Me\text{-}p)_2(dppm\text{-}P)_2]$ (3a) *on* $HgCl_2$.—A solution of $HgCl_2$ (0.045 g, 0.17 mmol) in thf (1 cm^3) was added to a solution of (3a) (0.20 g, 0.17 mmol) in benzene (20 cm^3). A deep yellow oily precipitate formed rapidly but gradually dissolved when the mixture was warmed and a much paler, fine precipitate formed. The pale yellow suspension was decanted from the small amount of deep yellow solid. The deep yellow solid was dissolved in thf (2 cm^3) and re-added to the benzene suspension. After 30 min the product was filtered off, washed with benzene and n-pentane. It was identified as (4a) by $^{31}P\text{-}\{^1H\}$ n.m.r. and i.r. spectroscopy. Yield 0.22 g (88%).

The phenylethynyl analogue (4b) was made similarly. Yield 85%.

Preparation of $[Pt(C\equiv CPh)_2(dppm\text{-}P)_2]$ *from* $[Pt(dppm\text{-}PP')_2]Cl_2$ *and* $Hg(C\equiv CPh)_2$.—A solution of $Hg(C\equiv CPh)_2$ (0.21 g, 0.30 mmol) in hot ethanol (10 cm^3, *ca.* 60 °C) was added to a solution of $[Pt(dppm\text{-}PP')_2]Cl_2$ (0.25 g, 0.24 mmol) in ethanol (5 cm^3). The ethanolic mother-liquors were decanted from the yellow precipitate, which was then dissolved in dichloromethane (20 cm^3). A solution of $Na_2S\cdot 9H_2O$ (0.058 g, 0.24 mmol) in ethanol (8 cm^3) was added and the resultant precipitate of mercury(II) sulphide filtered off. The required product was isolated by evaporation and recrystallisation of the residue from benzene–methanol. Yield 0.22 g (80%).

Complex (3a) was made similarly in 78% yield.

Preparation of $[Pt(C\equiv CMe)_2(dppm\text{-}P)_2]$ (3c) *from* $[(MeC\equiv C)_2Pt(\mu\text{-}dppm)_2HgCl_2]\cdot CH_2Cl_2$ (4c).—To a solution of the platinum–mercury compound (4c) (0.250 g, 0.19 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of $Na_2S\cdot 9H_2O$ (0.050 g, 21 mmol) in ethanol (8 cm^3). The black precipitate was filtered off and the required product was isolated from the mother-liquors, as above. Yield 0.144 g (72.5%).

Conversion of trans-$[Pt(C\equiv CPh)_2(Ph_2PCH_2PMePh_2)_2]I_2$ (6b) *into trans*-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$.—A suspension of (6b) (0.18 g, 0.124 mmol) in thf (15 cm^3) was treated with sodium propan-2-oxide in propan-2-ol (1.5 cm^3, 0.18 mol dm^{-3}, 0.27 mmol) and the mixture was stirred for 5 min. A further portion of sodium propan-2-oxide (1.0 cm^3, 0.18 mmol) was then added and the mixture warmed to give a pale yellow homogeneous solution. After 2 h the solvent was removed under reduced pressure and water (5 cm^3) added to the residue to give a pale yellow solid. Yield 0.095 g (96%). The product was recrystallised from CH_2Cl_2–ethanol and characterised by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (in $CDCl_3$), $\delta(P)$ +1.2 p.p.m., $^1J(PtP)$ = 2 532 Hz; by ^1H n.m.r. spectroscopy, $\delta(CH_3)$ 2.42 p.p.m., $^3J(PtCH_3)$ = 33.4 Hz, $|^2J(PH) + {}^4J(PH)|$ = 7.3 Hz; by i.r. spectroscopy, $\nu(C\equiv C)$ 2 105 cm^{-1} (Nujol); and by microanalysis (Found: C, 63.5; H, 4.5. Calc. for $C_{40}H_{36}P_2Pt$: C, 63.25; H, 4.55%).

Preparation of the Bis(phosphine oxide) Complexes (5a)—(5c).—Hydrogen peroxide (0.2 cm^3, 100 vol.) in acetone (5 cm^3) was added to a solution of *trans*-$[Pt(C\equiv CC_6H_4Me\text{-}p)_2(dppm\text{-}P)_2]$ (0.1 g) in benzene (15 cm^3). The mixture was set aside for 14 h. Isolation then gave the required dioxide (5b) as pale yellow microcrystals from benzene. Yield 0.080 g (78%).

Complexes (5a) and (5c) were made similarly in 62% and 45% yields respectively, and characterised by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (see Table 2) and i.r. spectroscopy: $\nu(C\equiv C)$ 2 100 cm^{-1} for (5a) and (5b).

Quaternisation of trans-$[Pt(C\equiv CPh)_2(dppm\text{-}P)_2]$ *with Methyl Iodide*.—A solution of (3b) (0.116 g, 0.1 mmol) and methyl iodide (0.05 g, 0.35 mmol) in benzene (8 cm^3) was put aside for 20 h. The required dimethiodide salt (6b) was isolated by filtration. Yield 0.12 g (90%). Complexes (6a) and (6c) were prepared similarly in 85 and 87% yields respectively and characterised by microanalysis (see Table 1).

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