# Bimetallic Systems. Part 4.[1] Synthesis and Characterisation of Mixed Copper(I)–, Silver(I)–, or Gold(I)–Platinum(II) Acetylide Complexes containing Bridging $Ph_2PCH_2PPh_2$

**Gary R. Cooper, Alan T. Hutton, C. Richard Langrick, David M. McEwan, Paul G. Pringle, and Bernard L. Shaw** *
*School of Chemistry, University of Leeds, Leeds LS2 9JT*

The bis(monodentate dppm)diacetylide complexes of type *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (dppm = $Ph_2PCH_2PPh_2$; R = Ph, *p*-tolyl, Me, *etc.*) react with silver nitrate or silver hexafluorophosphate to give mixed platinum–silver salts of the type $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2Ag]X$ (X = $NO_3^-$ or $PF_6^-$) or with $[\{AgX(PPh_3)\}_4]$ (X = Cl or I) to give neutral platinum–silver complexes, $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgX]$ (X = Cl or I), in excellent yield. The salts and neutral complexes can be interconverted, *e.g.* the nitrate salt with NaI gives the neutral platinum–silver iodide complex and when the neutral platinum–silver chloride complex $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$ is treated with $[NH_4][PF_6]$ in acetone the corresponding $[PF_6]^-$ salt is formed. A more convenient method of synthesis of the complex $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgX]$ is to treat $[Pt(dppm\text{-}PP')_2]X_2$ (X = Cl or I) with two equivalents of $AgO_2CMe$ + $PhC{\equiv}CH$. Treatment of $[Pt(dppm\text{-}PP')_2]X_2$ with one equivalent of $AgO_2CMe$ + $RC{\equiv}CH$ gives platinum–silver monoacetylides of type $[(RC{\equiv}C)ClPt(\mu\text{-dppm})_2AgCl]$ (R = Ph, *p*-tolyl, Me, $CH_2CH_2Ph$, or $CMe{=}CH_2$). In 'one-pot' reactions $PtCl_2$ (or $K_2[PtCl_4]$) was treated with two equivalents of dppm followed by one equivalent of $AgO_2CMe$ + $PhC{\equiv}CH$ to give the complex $[(PhC{\equiv}C)ClPt(\mu\text{-dppm})_2AgCl]$ in 71% overall yield. This chloro-complex, when treated with LiBr or NaI in dichloromethane–acetone, gave the corresponding bromo- or iodo-complexes $[(PhC{\equiv}C)XPt(\mu\text{-dppm})_2AgX]$ (X = Br or I) in *ca.* 90% yields. Treatment of $[Pt(C{\equiv}CC_6H_4Me\text{-}p)_2(dppm\text{-}P)_2]$ with $[AuCl(PPh_3)]$ gave the platinum–gold complex salt $[(p\text{-}MeC_6H_4C{\equiv}C)_2Pt(\mu\text{-dppm})_2Au]Cl$. Treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ with $Li[Cu(C{\equiv}CPh)_2]$ gives $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2CuCl]$, which in acetone solution + $Na[BPh_4]$ gives the corresponding salt $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Cu][BPh_4]$. All of the complexes were characterised by microanalysis, solution conductivity measurements, i.r. spectroscopy, and particularly $^{31}P\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ n.m.r. spectroscopy. The variable-temperature $^1H\text{-}\{^{31}P\}$ and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the complexes are discussed.

In a previous paper[2] and in preliminary communications[3,4] we have shown that monodentate $Ph_2PCH_2PPh_2$ (dppm) complexes of type *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$, R = alkyl or aryl, react with $HgCl_2$ to give mixed platinum–mercury complexes of the type $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ in excellent yield. Moreover, treatment of the readily prepared $[Pt(dppm\text{-}PP')_2]Cl_2$ with $Hg(O_2CMe)_2$ + $2RC{\equiv}CH$ gave the same mixed platinum–mercury complexes, often in quantitative yield. The mercury could then be displaced, as HgS, by treatment with $Na_2S$, giving *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$. Alternatively, treatment with $[Rh_2Cl_2(CO)_4]$ gave $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]Cl$ and $HgCl_2$, in a transmetallation reaction.[5] In the present paper we describe the extension of this type of chemistry to copper(I), silver(I), or gold(I) (all with $d^{10}$-electron configuration) bridged to platinum(II) acetylides by dppm ligands.

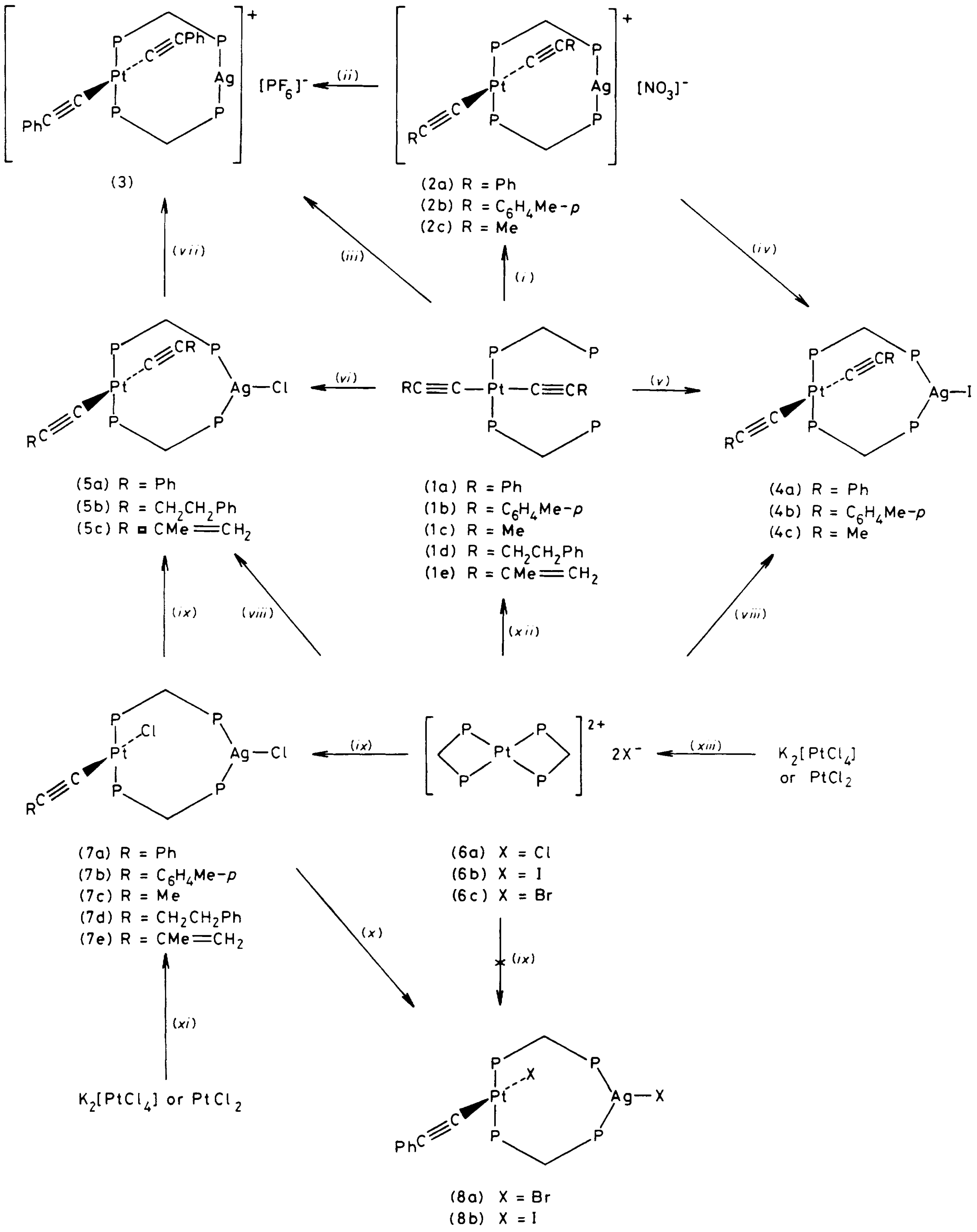
## Results and Discussion

The elements of Group 1B in oxidation state +1 readily form bis(phosphine) complexes. We therefore anticipated that the previously described bis(dppm-*P*) species (1a)—(1e) (Scheme 1) would form heterobinuclear complexes with $Cu^I$, $Ag^I$, or $Au^I$. Most of our work has been with $Ag^I$ and we will describe this first.

*Silver Complexes.*—The routes to the platinum–silver complexes are summarised in Scheme 1. Treatment of the bis(dppm-*P*) species (1a)—(1c) with an aqueous acetone solution of silver(I) nitrate gave the nitrate salts (2a)—(2c). Although (2a)—(2c) were not isolated in pure form, the corresponding $[PF_6]^-$ salt (3) was readily made by addition of $[NH_4][PF_6]$ to (2a) or by treatment of (1a) with silver hexafluorophosphate. When a solution of sodium iodide was added to an acetone solution of the nitrates (2a)—(2c), pale yellow solids formed which were formulated as the platinum–silver iodide complexes (4a)—(4c). The same complexes (4a)—(4c) were made directly from (1a)—(1c) by treatment with the dichloromethane-soluble complex $[\{AgI(PPh_3)\}_4]$. In a similar fashion, the platinum–silver chloride complexes (5a)—(5c) were readily made from (1a), (1d), and (1e) and $[\{AgCl(PPh_3)\}_4]$. All of the platinum–silver complexes (3), (4a)—(4c), and (5a)—(5c) are air-stable, white or yellow, crystalline solids, soluble in chlorinated solvents and can be readily recrystallised from dichloromethane–methanol, in air, without decomposition. Their formulation follows from elemental analysis and conductivity measurements (Table 1), $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (Table 2), and from $^1H\text{-}\{^{31}P\}$ n.m.r. and i.r. spectroscopy (Table 3). Moreover, the structure of (2a) has been confirmed by *X*-ray crystallography.[3]

Conductivity measurements in nitrobenzene indicate that complexes (4a)—(4c) and (5a)—(5c) are neutral but we have found that treatment of (5a) with $[NH_4][PF_6]$ in acetone gave a species with identical $^{31}P\text{-}\{^1H\}$ n.m.r. parameters to the $[PF_6]^-$ salt (3), and, moreover, solutions of (5a)—(5c) in acetone rapidly gave precipitates when treated with $NaBPh_4$, indicating that the halide is readily ionised from silver.

As described above, the mixed platinum–mercury complexes of type $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ were most readily prepared by treating $[Pt(dppm\text{-}PP')_2]Cl_2$ with $Hg(O_2CMe)_2$ + $2RC{\equiv}CH$. We therefore attempted analogous syntheses with $AgO_2CMe$ and found they worked exceedingly well. Thus treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ (6a) with two equivalents of



**Scheme 1.** Synthesis and interconversions of platinum–silver complexes: (*i*) $AgNO_3$ in aqueous acetone; (*ii*) $[NH_4][PF_6]$ in acetone; (*iii*) $Ag[PF_6]$ in acetone; (*iv*) NaI in acetone; (*v*) $[\{AgI(PPh_3)\}_4]$ in dichloromethane; (*vi*) $[\{AgCl(PPh_3)\}_4]$ in dichloromethane; (*vii*) $[NH_4][PF_6]$ in acetone; (*viii*) 2 equiv. $AgO_2CMe$ + $RC{\equiv}CH$ in dichloromethane; (*ix*) 1 equiv. $AgO_2CMe$ + $RC{\equiv}CH$; (*x*) LiBr or NaI in acetone; (*xi*) 'one-pot' reaction, see Experimental section; (*xii*) $Hg(O_2CMe)_2$ + $RC{\equiv}CH$ in dichloromethane followed by $Na_2S$ in ethanol, see ref. 4; (*xiii*) 2 equiv. dppm in ethanol

**Table 1.** Microanalysis, melting point, and conductivity data

| Complex | M.p.[a]/°C | Analysis (%)[b] C | H | Halogen | $\Lambda$[c]/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ |
|---|---|---|---|---|---|
| (3) | 235—240 | 56.1 (55.85) | 3.9 (3.85) | F 7.95 (8.05) | 131[d] |
| (4a) | 195—203 | 56.4 (56.6) | 3.9 (3.9) | I 9.3 (9.1) | 2 |
| (4b) | 220—222 | 56.85 (57.15) | 4.1 (4.1) | I 9.1 (8.9) | |
| (4c)·$CH_2Cl_2$[e] | 240—242 | 50.45 (50.3) | 3.85 (3.85) | I 9.55 (9.35) | |
| (5a) | >180 | 59.95 (60.55) | 4.15 (4.15) | Cl 3.2 (2.7) | |
| (5b) | 212—215 | 61.6 (61.6) | 4.7 (4.6) | Cl 2.3 (2.6) | 0.3 |
| (5c) | 213—217 | 58.0 (58.2) | 4.6 (4.4) | Cl 2.6 (2.9) | 0 |
| (7a) | 199—203 | 56.15 (56.0) | 4.2 (4.0) | Cl 5.95 (5.7) | 2 |
| (7b) | 173—177 | 55.95 (56.3) | 4.2 (4.1) | Cl 5.9 (5.6) | 2 |
| (7c) | 202—206 | 53.4 (53.9) | 4.05 (4.0) | Cl 5.9 (6.0) | 3 |
| (7d) | 179—183 | 56.35 (56.7) | 4.25 (4.2) | Cl 5.7 (5.6) | |
| (7e) | 169—172 | 54.85 (54.7) | 4.35 (4.1) | Cl 5.8 (5.9) | |
| (8a)·$Me_2CO$ | 168—171 | 53.4 (52.7) | 3.5 (4.0) | Br 11.1 (11.5) | 4 |
| (8b) | >158 | 49.3 (48.8) | 3.15 (3.5) | I 17.55 (17.8) | |
| (9) | 278—280 | 57.1 (57.25) | 4.1 (4.1) | Cl 2.8 (2.5) | 25 |
| (11)·0.25$CH_2Cl_2$ | >135 | 61.75 (61.7) | 4.3 (4.25) | Cl 3.85 (4.15) | 9 |
| (12) | 165—167 | 70.05 (69.8) | 4.75 (4.8) | | 24 |

[a] With decomposition. [b] Calculated values in parentheses. [c] $10^{-3}$ mol dm$^{-3}$ solutions in nitrobenzene at +20 °C. [d] In acetone. [e] Cl analysis: 5.2 (5.5%).

**Table 2.** $^{31}P-\{^1H\}$ N.m.r. data[a]

| Complex | $\delta(P_A)$ p.p.m. | $^1J(PtP_A)$ Hz | $\delta(P_B)$ p.p.m. | $^1J(^{109}AgP_B)$ Hz | $^1J(^{107}AgP_B)$ Hz | $^3J(PtP_B)$ Hz | $N$[b] Hz | $\theta_c$/°C |
|---|---|---|---|---|---|---|---|---|
| (3)[c] | +12.7 | 2 546 | −4.2 | 486[d] | | 98 | 78 | −50 |
| (4a) | +13.3 | 2 534 | −11.7 | 422 | 364 | 166 | 93 | −50 |
| (4b)[e] | +13.2 | 2 538 | −12.0 | 422 | 364 | 166 | 95 | −50 |
| (4c) | +12.7 | 2 607 | −12.8 | 420 | 364 | 162 | 115 | −50 |
| (5a)[e] | +12.4 | 2 540 | −10.7 | 464 | 401 | 170 | 93 | −50 |
| (5b) | +11.8 | 2 612 | −11.8 | 457 | 396 | 165 | 93 | −50 |
| (5c) | +12.0 | 2 563 | −11.5 | 461 | 400 | 161 | 90 | −50 |
| (7a) | +15.5 | 2 586 | −11.1 | 458 | 394 | 112 | 90 | 21 |
| (7b) | +15.4 | 2 590 | −11.2 | 457 | 393 | 115 | 93 | 21 |
| (7c) | +14.8 | 2 622 | −11.5 | 454 | 391 | *f* | 93 | 21 |
| (7d) | +14.8 | 2 595 | −11.1 | 461 | 398 | 132 | 90 | −10 |
| (7e) | +15.3 | 2 598 | −11.4 | 459 | 393 | 102 | 90 | 21 |
| (8a) | +14.4 | 2 544 | −11.0 | 442 | 386 | 130 | 90 | 21 |
| (8b) | +13.2 | 2 581 | −12.5 | 420 | 355 | *f* | 95 | 21 |
| (9) | +9.7 | 2 600 | +31.5 | | | 147 | 51 | 21 |
| (10) | +12.7 | 2 578 | +30.6 | | | 118 | 49 | 21 |
| (11) | +12.4 | 2 580 | −18.6 | | | *f* | 81 | 21 |
| (12) | +13.2 | 2 454 | −6.6 | | | *f* | 68 | 21 |

[a] Spectra (40.25 MHz) measured in $CDCl_3$ unless stated otherwise; chemical shifts ($\delta$) in p.p.m. (±0.1) to high frequency of 85% $H_3PO_4$ and coupling constants ($J$) in Hz (±3). $P_A$ is bonded to platinum and $P_B$ to copper, silver, or gold. [b] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [c] The data for this complex were given incorrectly in ref. 3. [d] Individual $^{109}$Ag and $^{107}$Ag couplings not resolved. [e] In $CD_2Cl_2$. [f] Not resolved.

$AgO_2CMe$ + PhC≡CH in boiling dichloromethane gave the platinum–silver chloride complex [$(PhC\equiv C)_2Pt(\mu\text{-dppm})_2AgCl$] (5a) in high (71%) yield; similarly with the iodide salt (6b).

The $^{31}P-\{^1H\}$ n.m.r. spectra of the platinum–silver complexes (3)—(5) are very characteristic (see Figure 1). They are all second-order AA′BB′ spin systems with further couplings to $^{195}$Pt, $^{109}$Ag, or $^{107}$Ag (see Table 2). At ambient temperatures the resonance for $P_B$ (the phosphorus bonded to silver) consists of two broad humps with little resolved fine structure, but at −40 °C fine structure is clearly resolved and the individual values of $^1J(^{107}AgP_B)$, $^1J(^{109}AgP_B)$, and $^3J(PtP_B)$ can be determined (Figure 1 and Table 2). Note that the ratios $^1J(^{109}AgP)/^1J(^{107}AgP)$ are all *ca.* 1.15, the same as the ratio of the gyromagnetic ratios of the respective isotopes. The fluxionality observed is probably due to phosphine exchange at silver(I) which is common in mononuclear silver(I) phosphine complexes.[6] It has been found that, in general, the values of $^1J(^{107}AgP)$ for neutral three-co-ordinate silver(I) complexes of type [$(R_3P)_2AgX$] fall in the range 380—470 Hz, whereas for cationic two-co-ordinate silver(I) complexes of type [$(R_3P)_2Ag]^+X^-$, $^1J(^{107}AgP)$ is greater than *ca.* 470 Hz.[6] Clearly our $^1J(AgP)$ values are consistent with the structures we propose (see Table 2). The values of $^1J(PtP_A)$ are consistent with a *trans* configuration of dppm ligands at platinum.

The $^1H-\{^{31}P\}$ n.m.r. spectra are also useful diagnostically since the $CH_2$ resonance of the μ-dppm ligands shows coupling to $^{195}$Pt, and both $\delta(CH_2)$ and $^3J(PtH)$ are sensitive to the environment (see Table 3). Occasionally coupling to silver was also observed and Figure 2 shows a particularly well defined $^1H-\{^{31}P\}$ n.m.r. spectrum of the methylacetylide complex (4c). Not only is coupling of the $CH_2$ to $^{195}$Pt and Ag resolved but coupling of the $CH_3$ of the acetylide to $^{195}$Pt is also resolved. Only one $CH_2$ resonance is observed for the bis(acetylide)

**Table 3.** Proton n.m.r.[a] and i.r. data

| Complex | $\delta(PCH_2P)$ p.p.m. | $^3J(PtPCH_2)$ Hz | $^3J(AgPCH_2)$ Hz | $^2J(HH)$ Hz | Other $^1H$ resonances | $\nu(C\equiv C)$[b] cm$^{-1}$ | $\nu(Pt-Cl)$[c] cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| (3) | 4.13 | 34.4 | 3.2 | | | 2 105 | |
| (4a) | 4.09 | 36.0 | | | | 2 105 | |
| (4b) | 4.06 | 36.8 | | | $\delta(CH_3)$ 2.22 | 2 105 | |
| (4c) | 3.94 | 36.0 | 2.1 | | $\delta(CH_3)$ 1.30, $^4J(PtH)$ 15.0 | 2 120 | |
| (5a) | 4.05 | 37.6 | | | | 2 105 | |
| (5b) | 3.93 | 38.0 | | | $\delta(CH_2)$ 2.15 (br); | 2 120 | |
| (5c) | 4.02 | 37.0 | | | $\delta(CH_3)$ 1.31; $\delta(=CH_2)$ 4.70, 4.36 | 2 110, 2 080 | |
| (7a)[d] | 4.19, 3.70 | *e* | | 13 | | 2 120 | 315 |
| (7b)[d] | 4.12, 3.70 | *e* | *ca.* 3[f] | 13 | $\delta(CH_3)$ 2.22 | 2 120 | 314 |
| (7c)[d] | 4.06, 3.55 | 60.0[f] | *ca.* 3[f] | 12 | $\delta(CH_3)$ 1.21, $^4J(PtH)$ 22.0 | 2 144 | 312 |
| (7d)[d] | 4.02, 3.65 | *e* | | 15 | $\delta(CH_2)$ 1.8—2.3 | 2 140 | 313 |
| (7e)[d] | 4.21, 3.53 | *e* | *ca.* 3[f] | 13 | $\delta(CH_3)$ 1.19; $\delta(=CH_2)$ 4.55, 4.16 | 2 102 | 317 |
| (8a) | 4.02 | 33.2 | | | | 2 120 | |
| (8b) | 4.09 | 35.9 | | | | 2 109 | |
| (9) | 4.66 | 36.6 | | | $\delta(CH_3)$ 2.22 | 2 105 | |
| (11) | 3.91 | 35.6 | | | | 2 110 | |
| (12) | 3.82 | 33.0 | | | | 2 130 | |

[a] Spectra (100 MHz) measured in $CDCl_3$ at +21 °C unless otherwise stated. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$ and coupling constants ($J$) in Hz (±0.1 Hz). [b] KBr disc. [c] Nujol mull. [d] At −40 °C. [e] Coupling to $^{195}Pt$ not resolved. [f] Coupling to the lower-frequency signal only (equatorial hydrogen, see text).

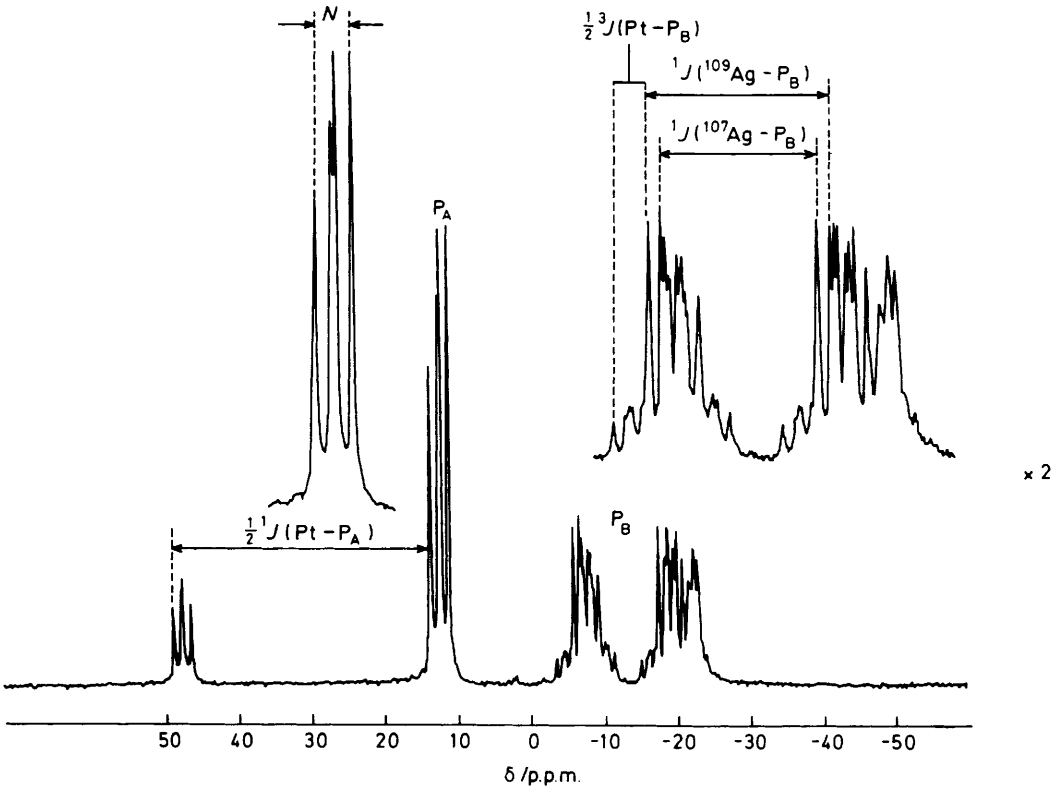


**Figure 1.** $^{31}P-\{^1H\}$ N.m.r. spectrum (40.25 MHz) of $[(PhCH_2CH_2C\equiv C)_2Pt(\mu\text{-dppm})_2AgCl]$ (5b) at −50 °C in $CDCl_3$

platinum-silver complexes (3)—(5) even at −75 °C in $CD_2Cl_2$, although for almost any static structure of the $Pt(\mu\text{-dppm})_2Ag$ ring there would be two distinct environments for the $CH_2$ protons, pseudo-axial and pseudo-equatorial. We propose that rapid 'ring flipping' equilibrates the two resonances, even at −75 °C. Rapid ring flipping in bis(μ-dppm) complexes has been previously noted by us and by others.[3,7]

Since the diacetylide complexes of type $[(RC\equiv C)_2Pt(\mu\text{-dppm})_2AgCl]$ were so readily prepared from $[Pt(dppm\text{-}PP')_2]Cl_2$ and $2AgO_2CMe + 2RC\equiv CH$ (see Scheme 1), we attempted to make monoacetylides in a similar manner. We therefore treated $[Pt(dppm\text{-}PP')_2]Cl_2$ with one equivalent of $AgO_2CMe$ and a slight excess of $RC\equiv CH$ in acetone and obtained 52—87% yields of complexes of type $[(RC\equiv C)ClPt(\mu\text{-dppm})_2AgCl]$ (7a)—(7e) [R = Ph, *p*-tolyl, Me, $CH_2CH_2Ph$, or $CMe=CH_2$]; see Scheme 1, Experimental section, and

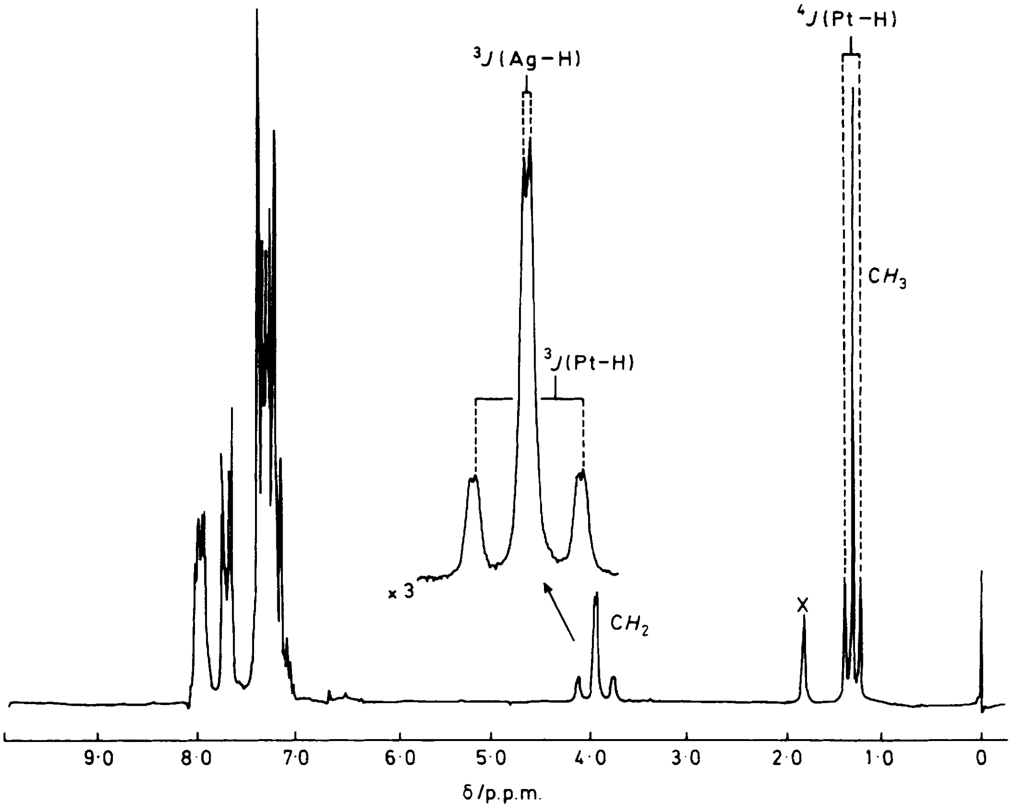
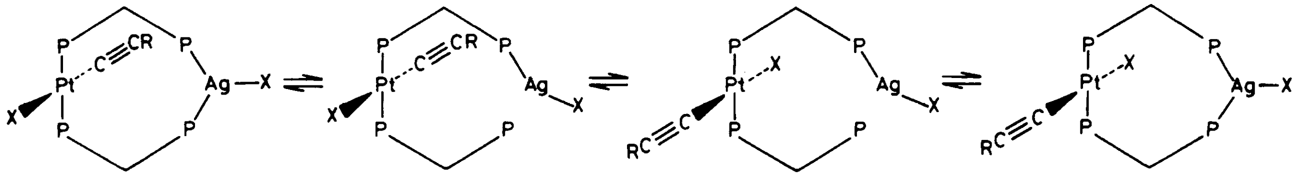


**Figure 2.** $^1$H-{$^{31}$P} N.m.r. spectrum (100 MHz) in the range δ 0—10 of [$(MeC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgI$] (4c) at 21 °C in $CDCl_3$. The resonance marked X is due to water in the solvent



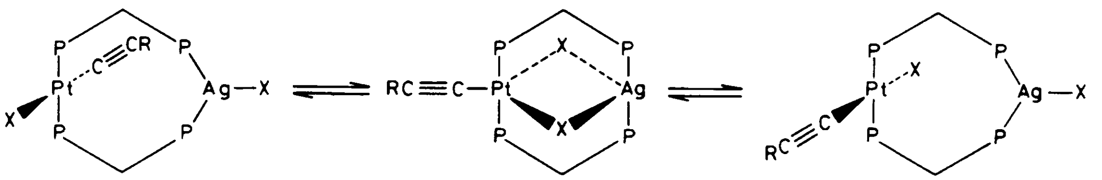
**Scheme 2.** Possible mechanism to explain the magnetic equivalence of the $CH_2$ hydrogens in [$(PhC{\equiv}C)XPt(\mu\text{-dppm})_2AgX$] (X = Cl, Br, or I) involving reversible silver–phosphorus bond fission

Tables for characterising data. We did not establish whether a C≡CR or a Cl group is bridging Pt with Ag.

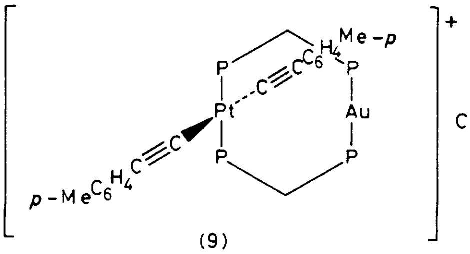
In most cases (see Table 2) the $^{31}$P-{$^1$H} n.m.r. spectra of the monoacetylides (7a)—(7e) show clearly resolved coupling of $P_B$ to each of $^{107}$Ag and $^{109}$Ag at room temperature, in contrast to the corresponding diacetylides (5a)—(5c), which show broad resonances due to $P_B$ at room temperature but resolved coupling at −40 °C. At room temperature, however, the $^1$H-{$^{31}$P} n.m.r. spectra of the monoacetylides (7a)—(7e) generally show only a broad hump in the methylene region and it is necessary to cool to −40 °C to freeze out the non-equivalence of the dppm $CH_2$ hydrogens (see Table 3). Only one of the complexes showed sufficient resolution at −40 °C to enable definite assignment of coupling to platinum: the proton resonating at lower δ shows strong coupling to platinum and we assign this as the pseudo-equatorial proton $H_e$, with a torsion angle (Pt–P–C–$H_e$) of *ca.* 180°; the pseudo-axial proton $H_a$ resonating at higher δ showed no detectable coupling to platinum and would have a torsion angle (Pt–P–C–$H_a$) of *ca.* 60°. This assumes a Karplus-type behaviour [8] for these three-bond couplings which we have discussed previously.[9] In several of these complexes $H_e$ was also coupled to silver (Table 3), but no coupling of $H_a$ to silver was observed, and the same Karplus-type behaviour holds for the Ag–P–C–H couplings.

Treatment of [$Pt(dppm\text{-}PP')_2]X_2$, (6b) or (6c), with $AgO_2CMe$ + PhC≡CH in the same fashion as above gave only the corresponding diacetylide complexes [$(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgX$] (X = I or Br). However, the bromo- (8a) or iodo- (8b) complex can readily be made by treatment of the chloro-complex (7a) with lithium bromide or sodium iodide respectively (Scheme 1). The chloride in (7a) can also be replaced by $PhC{\equiv}C^-$ to give (5a) by treatment with $AgO_2CMe$ + PhC≡CH.

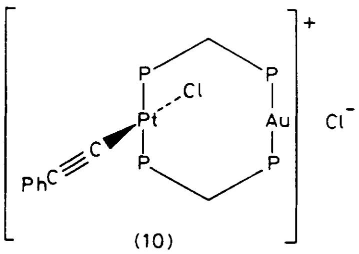
The $^1$H-{$^{31}$P} resonances for the $PCH_2P$ protons of the bromo- (8a) and iodo- (8b) complexes are singlets, with $^{195}$Pt satellites, at ambient temperature. At −80 °C in $CD_2Cl_2$ they are very broad but still not resolved into the expected AB pattern. We find that the fluxional process which equilibrates the $CH_2$ protons in (7a)—(7e) and (8a) and (8b) is not dependent on the concentration of the complexes (*i.e.* the pattern is independent of concentration) and hence is probably intramolecular. Phosphine exchange at Ag may equilibrate the protons by the mechanism shown in Scheme 2. High-



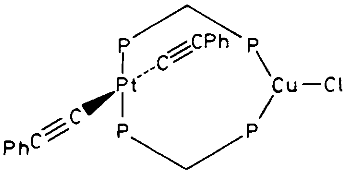
**Scheme 3.** Possible mechanism to explain the magnetic equivalence of the $CH_2$ hydrogens in [(PhC≡C)XPt(μ-dppm)$_2$AgX] (X = Cl, Br, or I) involving intramolecular halogen exchange



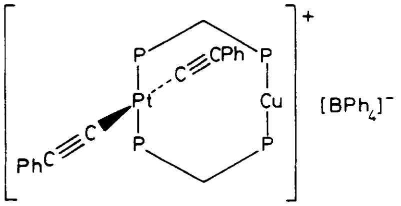
(9)



(10)



(11)



(12)

temperature (+55 °C) $^{31}$P-{$^1$H} n.m.r. studies show that exchange is more rapid in the bromo- and iodo-complexes (8a) and (8b) than in the chloro-complex (7a) and hence this would explain the more rapid $^1$H-fluxionality of the bromo- and iodo-complexes.

Another mechanism, consistent with the fluxional n.m.r. behaviour, is by halogen exchange between the metals as shown in Scheme 3. A similar intramolecular halogen exchange has recently been reported for [Pt$_2$H$_2$Cl(μ-dppm)$_2$]$^+$.[10]

*Copper or Gold Complexes.*—We have also made some platinum–gold and platinum–copper complexes analogous to the platinum–silver complexes discussed above. Treatment of the bis(dppm-*P*) species (1b) with [AuCl(PPh$_3$)] in dichloromethane readily gave the salt (9) in high (95%) yield. This complex has been fully characterised (Tables 1—3). It is probable that many analogous platinum–gold complexes could be similarly made, but we have not attempted to do this. The platinum–gold complex is ionic with two-co-ordinate gold: gold(I) has a greater tendency to be two-co-ordinate than silver(I).[11]

Treatment of the salt [Pt(dppm-*PP'*)$_2$]Cl$_2$ (6a) with one equivalent of [{Au(C≡CPh)}$_n$] in CDCl$_3$ gave a single platinum-gold species (from $^{31}$P-{$^1$H} n.m.r. evidence, see Table 3 for data) to which we tentatively assign structure (10) although we have not isolated this species.

Treatment of [Pt(dppm-*PP'*)$_2$]Cl$_2$ with Li[Cu(C≡CPh)$_2$] in tetrahydrofuran gave the yellow platinum–copper complex [(PhC≡C)$_2$Pt(μ-dppm)$_2$CuCl] (11): the structure follows from elemental analysis, $^{31}$P-{$^1$H} and $^1$H-{$^{31}$P} n.m.r., and i.r. spectroscopy (Tables 1—3). Complex (11) gives a weakly conducting solution in nitrobenzene (Table 1) and addition of Na[BPh$_4$] in acetone to a dichloromethane solution led to the isolation of a species to which we assign structure (12) on the basis of elemental analysis (Table 1) and the $^{31}$P-{$^1$H} and $^1$H-{$^{31}$P} n.m.r. spectra; the n.m.r. spectroscopic data for (12) are quite different from those of (11). The structure of the copper complex (12) is analogous to the silver complex (3) and the gold complex (9).

We have found that the platinum–copper, –silver, and –gold complexes described above react with [Rh$_2$Cl$_2$(CO)$_4$] rapidly to give the mixed platinum–rhodium complexes described previously. These and other transmetallation reactions will be reported in subsequent papers.

## Experimental

General methods were the same as those described in previous papers from this laboratory.[12]

*Preparations.*—[(PhC≡C)$_2$Pt(μ-dppm)$_2$AgI] (4a) *from* AgNO$_3$–NaI. A solution of silver(I) nitrate (0.034 g, 0.20 mmol) in water (0.1 cm$^3$) was diluted with acetone (5 cm$^3$) and added to a solution of *trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] (0.232 g, 0.20 mmol) in dichloromethane (10 cm$^3$) to give a yellow solution. The solvent was then removed under reduced pressure to give a dirty yellow solid which was redissolved in acetone (10 cm$^3$). The resulting solution was filtered and then treated with a solution of sodium iodide (0.20 g, 1.33 mmol) in acetone (10 cm$^3$). The yellow crystalline solid which formed was filtered off, washed with aqueous sodium iodide, water, and methanol, and dried *in vacuo*. Yield 0.25 g (89%). The complexes [(*p*-MeC$_6$H$_4$C≡C)$_2$Pt(μ-dppm)$_2$AgI] (4b) and [(MeC≡C)$_2$Pt(μ-dppm)$_2$AgI]·CH$_2$Cl$_2$ (4c) were made similarly in 83 and 72% yields, respectively.

(4a) *from* [{AgI(PPh$_3$)}$_4$]. A solution of [{AgI(PPh$_3$)}$_4$] (0.125 g, 0.063 mmol) in dichloromethane (5 cm$^3$) was added to a solution of *trans*-$[Pt(C{\equiv}CPh)_2(dppm\text{-}P)_2]$ (0.29 g, 0.25 mmol) in dichloromethane (10 $cm^3$), and the mixture was boiled gently to give a yellow solution. The solvent was then removed under reduced pressure and the residue triturated with diethyl ether to give the yellow product which was collected and dried *in vacuo*. Yield 0.25 g (89%). The complexes (4b) and (4c) were made similarly in 98 and 82% yields, respectively.

$[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ (5a) *from* $[Pt(dppm\text{-}PP')_2]Cl_2$ (6a). A mixture of $AgO_2CMe$ (0.068 g, 0.41 mmol) and $PhC{\equiv}CH$ (0.042 g, 0.42 mmol) was warmed in dichloromethane (5 $cm^3$) to give a pale yellow solution. To this solution was added a solution of $[Pt(dppm\text{-}PP')_2]Cl_2$ (0.200 g, 0.19 mmol) in dichloromethane (10 $cm^3$) and the mixture was boiled under reflux for 30 min. The solution was then filtered and reduced to 1 $cm^3$; the product was precipitated by adding a large volume of diethyl ether (35 $cm^3$), collected and dried. Yield 0.187 g (71%). The complex $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgI]$ (4a) was made similarly from $[Pt(dppm\text{-}PP')_2]I_2$ (6b) and a slight excess of $PhC{\equiv}CH + AgO_2CMe$ in 73% yield.

$[(PhCH_2CH_2C{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ (5b) *from* $[\{AgCl(PPh_3)\}_4]$. The complex $[\{AgCl(PPh_3)\}_4]$ (0.34 g, 0.21 mmol) was added to a solution of *trans*-$[Pt(C{\equiv}CCH_2CH_2Ph)_2(dppm\text{-}P)_2]$ (1.00 g, 0.82 mmol) in dichloromethane (20 $cm^3$). When all the solids had dissolved (*ca.* 5 min) a large volume of diethyl ether (100 $cm^3$) was added and the solution was reduced in volume to *ca.* 30 $cm^3$. More diethyl ether (50 $cm^3$) was then added and the mixture again reduced to *ca.* 30 $cm^3$. The white product was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.99 g (89%). The complex $[(CH_2{=}CMeC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ (5c) was made similarly in 89% yield.

$[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Ag][PF_6]$ (3). This complex has been made in two ways.

(*i*) A solution of $Ag[PF_6]$ (0.043 g, 0.17 mmol) in acetone (2 $cm^3$) was added to a suspension of *trans*-$[Pt(C{\equiv}CPh)_2(dppm\text{-}P)_2]$ (0.20 g, 0.17 mmol) in acetone (10 $cm^3$) and the mixture warmed gently (to *ca.* 50 °C) for 5 min to give a yellow solution. The solvent was removed under reduced pressure and the residue taken up in ethanol (10 $cm^3$). This yellow solution was filtered, acetone (10 $cm^3$) was added, and the mixture set aside for 3 d. The yellow needles which had formed were filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.11 g (46%).

(*ii*) A solution of silver nitrate (0.17 g, 0.10 mmol) in water (0.1 $cm^3$) was diluted with acetone (5 $cm^3$) and added to a solution of $[Pt(C{\equiv}CPh)_2(dppm\text{-}P)_2]$ (0.116 g, 0.10 mmol) in dichloromethane (10 $cm^3$). The solvent was then removed under reduced pressure and the residue was dissolved in ethanol (10 $cm^3$) to give a yellow solution which was filtered into a solution of $[NH_4][PF_6]$ (0.10 g, 0.61 mmol) in ethanol (10 $cm^3$). The volume was then reduced to 5 $cm^3$ and the solution set aside for 2 d. The yellow product was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.075 g (53%).

$[(RC{\equiv}C)ClPt(\mu\text{-}dppm)_2AgCl]$ (7a)—(7e). A suspension of $[Pt(dppm\text{-}PP')_2]Cl_2$ (0.4 mmol) in acetone (20 $cm^3$) was treated with a suspension of silver acetate (0.4 mmol) and $RC{\equiv}CH$ (0.4 mmol or excess) in acetone (10 $cm^3$). The mixture was stirred for 3 h at room temperature to obtain a clear yellow solution or pale yellow precipitate. The volume of acetone was decreased to 10 $cm^3$ under reduced pressure and the product was filtered off, washed with cold acetone, and recrystallised from dichloromethane–acetone. For R = Me (b.p. −23 °C) or $CMe{=}CH_2$ (b.p. 32 °C) the acetylene (excess) was bubbled through or added to a suspension of silver acetate (0.4 mmol) in acetone (25 $cm^3$) at −5 °C before adding $[Pt(dppm\text{-}PP')_2]Cl_2$ (0.4 mmol) as a powder. The mixture was stirred for 3 h and then allowed to warm up slowly to room temperature; the products were then isolated as before. In all cases a little (<10%) $[PtCl_2(dppm\text{-}PP')]$ was formed which was removed by the recrystallisation; using dichloromethane as the reaction solvent resulted in larger quantities of $[PtCl_2(dppm\text{-}PP')]$ even at 0 °C. The yields were: 80%, R = Ph; 87%, R = *p*-tolyl; 77%, R = Me; 52%, R = $CH_2CH_2Ph$; 63%, R = $CMe{=}CH_2$.

$[(PhC{\equiv}C)ClPt(\mu\text{-}dppm)_2AgCl]$ (7a) *from* $PtCl_2$. In this 'one-pot' preparation, $PtCl_2$ (0.50 g, 1.88 mmol) and dppm (1.45 g, 3.76 mmol) were suspended in acetone (100 $cm^3$) and boiled under reflux (nitrogen atmosphere) with stirring. After 5 h the pale yellow suspension was cooled to room temperature and treated with a suspension of silver acetate (0.314 g, 1.88 mmol) and $PhC{\equiv}CH$ (0.192 g, 0.206 $cm^3$; 1.88 mmol) in acetone (20 $cm^3$). The yellow colour immediately deepened and after stirring at room temperature for 3 h the desired product was filtered off and washed with cold acetone (yield 1.92 g, 82%). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed this material to contain *ca.* 5% $[PtCl_2(dppm\text{-}PP')]$. Recrystallisation from dichloromethane–acetone gave the pure compound (yield 1.66 g, 71% based on $PtCl_2$).

$[(PhC{\equiv}C)XPt(\mu\text{-}dppm)_2AgX]$ (8; X = Br or I). A solution of complex (7a) (0.42 g, 0.34 mmol) in dichloromethane (5 $cm^3$) and acetone (15 $cm^3$) was treated with a solution of LiBr or NaI (0.74 mmol) in acetone (10 $cm^3$) and stirred at room temperature for 2 h. After reducing the volume to 20 $cm^3$ the pale yellow (8a; X = Br) or yellow (8b; X = I) solids were filtered off, washed with water and cold acetone, and recrystallised from dichloromethane–acetone. Yields *ca.* 90%.

$[(p\text{-}MeC_6H_4C{\equiv}C)_2Pt(\mu\text{-}dppm)_2Au]Cl$ (9). A solution of $[AuCl(PPh_3)]$ (0.084 g, 0.17 mmol) in dichloromethane (5 $cm^3$) was added to a solution of *trans*-$[Pt(C{\equiv}CC_6H_4Me\text{-}p)_2(dppm\text{-}P)_2]$ (0.20 g, 0.17 mmol) in dichloromethane (10 $cm^3$) to give a deep yellow solution. The volume was then reduced to *ca.* 1 $cm^3$ and diethyl ether (10 $cm^3$) added to precipitate the product which was collected and dried *in vacuo*. Yield 0.23 g (95%).

$[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2CuCl]$ (11) *and* $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Cu][BPh_4]$ (12). The complex $[\{Cu(C{\equiv}CPh)\}_n]$ (0.069 g, 0.42 equivalents) was added at −7 °C to a solution of $PhC{\equiv}CLi$ in dry tetrahydrofuran made from n-butyl-lithium in hexane (0.43 mmol) and $PhC{\equiv}CH$ (46 µl, 0.42 mmol). The mixture was stirred at <0 °C for 2 h to give a pale yellow solution of $Li[Cu(C{\equiv}CPh)_2]$. To this was added $[Pt(dppm\text{-}PP')_2]Cl_2$ (0.435 g, 0.42 mmol) at −7 °C and the mixture was stirred for a further 1 h at 0 °C and then allowed to warm to room temperature. The solvent was then removed under reduced pressure and the glassy residue triturated with diethyl ether to give a bright yellow powder. The solid was taken up in dichloromethane and the pale yellow solution filtered. This solution was reduced to dryness to give $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2CuCl]$ (11), yield 0.284 g (53%). Treatment of a dichloromethane solution of (11) with $Na[BPh_4]$ (excess) in acetone gave $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Cu][BPh_4]$ in quantitative yield (0.309 g).

## Acknowledgements

We thank the S.E.R.C. and University of Leeds for support and Johnson Matthey PLC for a generous loan of platinum salts.

## References

1 Part 3, P. G. Pringle and B. L. Shaw, preceding paper.

2 C. R. Langrick, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 2487.

3 W. S. McDonald, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 861.

4 D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 1240.

5 G. R. Cooper, A. T. Hutton, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *Inorg. Chim. Acta*, 1983, **76**, L267.

6 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1972, **94**, 6386.

7 C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2267.

8 M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2870.

9 D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 859.

10 M. C. Grossel, R. P. Moulding, and K. R. Seddon, *J. Organomet. Chem.*, 1983, **247**, C32.

11 R. J. Puddephatt, 'The Chemistry of Gold,' Elsevier, Amsterdam, 1978.

12 H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 1690.

*Received 29th July* 1983; *Paper* 3/1323