# Bimetallic Systems. Part 14.[1] Mixed Iridium(I)–Platinum(II) Acetylide Complexes containing Bridging $Ph_2PCH_2PPh_2$ Ligands

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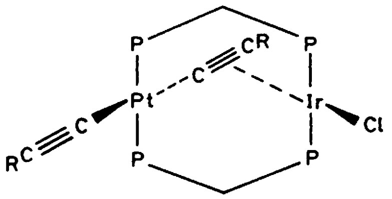
Treatment of the cyclo-octene ($C_8H_{14}$) iridium(I) complex $[Ir_2Cl_2(C_8H_{14})_4]$ with *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (R = Ph or *p*-tolyl; dppm = $Ph_2PCH_2PPh_2$) gave the dark green complexes $[(RC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CR)IrCl]$, which reacted with dihydrogen to give the dihydrides $[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2(\mu\text{-}H)IrH(Cl)]$. $[(PhC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CPh)IrCl]$ reacted with CO to give $[(PhC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CPh)Ir(CO)Cl]$, more conveniently prepared by treating *trans*-$[IrCl(CO)(PPh_3)_2]$ with *trans*-$[Pt(C{\equiv}CPh)_2(dppm\text{-}P)_2]$. The *p*-tolylacetylide and methylacetylide analogues were prepared similarly. Treatment of $[(RC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CR)Ir(CO)Cl]$ with large anions, *e.g.* $PF_6^-$ or $BPh_4^-$, gave the corresponding red cationic species $[(RC{\equiv}C)Pt(\mu\text{-}dppm)(\mu\text{-}C{\equiv}CR)Ir(CO)]^+$, isolated as $PF_6^-$ or $BPh_4^-$ salts. The conversion was reversed by addition of $Cl^-$. These cations (R = Me, Ph, or *p*-tolyl) reacted rapidly with dihydrogen to give the corresponding dihydrides $[(RC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CR)(\mu\text{-}H)IrH(CO)]^+$. I.r. and $^1H$, $^{31}P$, and $^{195}Pt$ n.m.r. data are given.

In previous papers in this series we have described systematic syntheses of heterobimetallic complexes containing $M^1(\mu\text{-}dppm)_2M^2$ moieties ($M^1$, $M^2$ are two different metals, dppm = $Ph_2PCH_2PPh_2$). Although there are many examples of diplatinum[2–6] and di-iridium[7–10] complexes containing two bridging dppm ligands, apart from our preliminary communications,[11] there are no examples of mixed platinum–iridium complexes. In general the methods which have been used to synthesize diplatinum or di-iridium complexes would not be applicable to the systematic synthesis of mixed platinum–iridium bimetallics. However, in a previous paper[12] we have described some mixed platinum–rhodium acetylide complexes and now describe similar work with platinum–iridium acetylides. A preliminary account of some of this work has been published.[11]

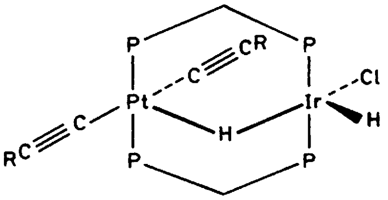
## Results and Discussion

Treatment of the labile cyclo-octene ($C_8H_{14}$) iridium(I) complex $[Ir_2Cl_2(C_8H_{14})_4]$ with $[Pt(C{\equiv}CPh)_2(dppm\text{-}P)_2]$ in warm (*ca.* 65 °C) benzene gave a dark green solution. After this mixture had been stirred for 14 h at *ca.* 20 °C, a dirty-yellow solid had separated which was shown to be mainly the diplatinum acetylide complex $[Pt_2(C{\equiv}CPh)_4(\mu\text{-}dppm)_2]$ by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. The green mother-liquor gave an olive green solid which we formulate as $[(PhC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CPh)IrCl]$ (**1a**) on the basis of (*i*) elemental analysis (C, H, and Cl) (Table 1); (*ii*) the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, which showed the characteristic AA′BB′ splitting pattern with $^{195}Pt$ satellites (see Table 2); (*iii*) the $^1H$ and $^1H\text{-}\{^{31}P\}$ n.m.r. spectra, which showed a single $CH_2$ resonance, *i.e.* $H_e$ and $H_a$ are equivalent (see Table 3); (*iv*) the i.r. spectrum, which had bands at 2 112 and 2 075 $cm^{-1}$ assigned to ν(C≡C) (Table 1); and (*v*) the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum, which showed the expected triplet of triplets pattern due to coupling to two near and two distant $^{31}P$ nuclei (Table 4). We have no strong evidence for the presence of a bridging acetylide group, except for the two i.r. bands due to acetylide stretch and that it is extremely unlikely that the iridium would only be three-co-ordinate. N.m.r. evidence and crystal-structure determination of a related compound $[(MeC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CMe)Rh(CO)]PF_6$ show one acetylide group to be weakly bridging in a σ,η fashion[12] and we formulate complex (**1a**) similarly.

A benzene solution of complex (**1a**) reacted rapidly with hydrogen to give a dark orange solution. This solution was more air-stable than the solutions of the green starting material and the solid product, which was isolated by evaporation of the solvent under reduced pressure, could be handled in air. We formulate this new complex as $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2(\mu\text{-}H)IrH(Cl)]$ (**2a**) on the basis of (*i*) elemental analysis (C, H, and Cl) (Table 1); (*ii*) the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, which shows the expected AA′BB′ splitting pattern (Table 2); (*iii*) the i.r. spectrum, which has bands at 2 220 $cm^{-1}$ assigned to ν(IrH) and 2 118 $cm^{-1}$ assigned to ν(C≡C); we have not assigned a band to the bridging ν(IrHPt) which would probably appear in the region of 1 600 $cm^{-1}$; (*iv*) the non-electrical conductivity of its acetone solutions; (*v*) the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum, which showed the expected triplet of triplets pattern (see Table 4); and (*vi*) the $^1H$ and $^1H\text{-}\{^{31}P\}$ n.m.r. spectra, which are particularly informative in the metal–hydride region (Table 3). In the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum, a doublet resonance at δ −12.5 p.p.m. [$^2J(HH)$ *ca.* 2 Hz] was



(**1a**) R = Ph
(**1b**) R = *p*-tolyl



(**2a**) R = Ph
(**2b**) R = *p*-tolyl

**Table 1.** Microanalytical (%), i.r., and conductivity data

| | Analysis[a] | | | | I.r.[c] (cm$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|
| Complex | C | H | Cl [or F] | $\Lambda$[b]/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ | ν(C≡C) | ν(C≡O) | ν(Ir–Cl) | ν(Ir–H) |
| **(1a)** | 56.85 (56.8) | 3.9 (3.9) | 2.5 (2.55) | n.d. | 2 112, 2 075 | | | |
| **(2a)** | 56.65 (56.8) | 4.1 (4.05) | 2.7 (2.55) | 3 | 2 118 | | | 2 220 |
| **(3a)** | 56.35 (56.6) | 4.0 (3.85) | 2.35 (2.5) | 7 | 2 102 | 2 025 | 250 | |
| **(3b)** | 57.35 (57.15) | 4.2 (4.05) | 2.3 (2.45) | 6 | 2 105 | 2 035 | 254 | |
| **(3c)**·$0.5C_6H_6$ | 54.2 (53.9) | 4.05 (4.0) | | n.d. | 2 135 | 2 035 | 253 | |
| **(4a)** | 64.45 (64.15) | 4.5 (4.25) | | n.d. | 2 125 | 1 970 | | |
| **(4b)** | 64.4 (64.45) | 4.5 (4.55) | | n.d. | 2 110 | 1 960 | | |
| **(4d)** | 53.45 (53.15) | 3.8 (3.75) | [7.1 (7.3)] | n.d. | 2 125 | 1 960 | | |
| **(4d)**[d] | | | | | 2 130 | 1 975 | | |
| **(4e)**·$0.25CH_2Cl_2$ | 48.05 (48.15) | 3.75 (3.55) | [7.8 (8.0)] | n.d. | 2 045 | 1 955 | | |
| **(5b)**[d] | | | | | 2 155 | 2 080 | | 2 125 |
| **(6a)**[d] | | | | | 2 150 | 2 075 | | |

[a] Calculated values in parentheses. [b] For $10^{-3}$ mol dm$^{-3}$ solutions in nitrobenzene at +20 °C, n.d. = not determined. [c] As Nujol mulls, unless otherwise stated. [d] In ethanol-free $CHCl_3$.

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

| Complex | δ($P_A$) | $^1J(PtP_A)$ | δ($P_B$) | $^3J(PtP_B)$ | '$N$'[b] | Solvent |
|---|---|---|---|---|---|---|
| **(1a)** | +4.7 | 2 670 | +23.4 | 48 | 102 | $C_6D_6$ |
| **(1b)** | +3.7 | 2 627 | +19.8 | 44 | 95 | $CDCl_3$ |
| **(2a)** | +7.3 | 2 541 | −3.4 | *c* | 63 | $CDCl_3$ |
| **(2b)** | +7.1 | 2 551 | −3.4 | *c* | 64 | $CDCl_3$ |
| **(3a)** | −0.7 | 3 051 | −28.5 | 139 | 93 | $CDCl_3$ |
| **(3b)** | −0.5 | 3 058 | −28.5 | 142 | 95 | $CDCl_3$ |
| **(3c)** | +0.5 | 3 142 | −29.9 | 144 | 95 | $CDCl_3$ |
| **(4a)** | +1.0 | 2 882 | +10.1 | | 34 | $(CD_3)_2CO$ |
| **(4b)** | +1.3 | 2 391 | +10.0 | | 40 | $(CD_3)_2CO$ |
| **(4c)** | +0.7 | 2 338 | +5.2 | | 39 | $(CD_3)_2CO$ |
| **(4d)** | +0.1 | 2 368 | +10.1 | | 39 | $(CD_3)_2CO$ |
| **(4e)** | −1.0 | 2 436 | +10.3 | *c* | 39 | $(CD_3)_2CO$ |
| **(5a)** | +8.3 | 2 436 | −12.5 | | 66 | $(CD_3)_2CO$ |
| **(5b)** | +8.2 | 2 446 | −12.6 | | 68 | $(CD_3)_2CO$ |

[a] Spectra (40.25 Hz) measured at *ca.* +21 °C. Chemical shifts (δ) 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 iridium. [b] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [c] Not resolved but less than 20 Hz.

**Table 3.** $^1H-\{^{31}P\}$[a] N.m.r. data

| | Methylene[b] | | | | | Acetylide | | Hydride[c] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Complex | δ($H_e$) | $^3J(Pt-H_e)$ | δ($H_a$) | $^3J(Pt-H_a)$ | $^2J(H_eH_a)$ | δ($CH_3$) | $^4J(Pt-H)$[d] | δ($H_t$) | $^3J(Pt-H_t)$ | δ($H_b$) | $^1J(Pt-H_b)$ | $^2J(H_t-H_b)$ | $^4J(H_e-H_b)$ | Solvent |
| **(1a)** | 4.58 | 26.5 | | | | | | | | | | | | $CDCl_3$ |
| **(2a)** | 4.27 | 57.2 | 4.83 | 19.6 | 12.9 | | | −19.85 | 25 | −12.5 | 615 | ~2 | | $CDCl_3$ |
| **(3a)** | 5.20 | 51.0 | | | | | | | | | | | | $CDCl_3$ |
| **(3b)** | 5.23 | 51.3 | | | | | | | | | | | | $CDCl_3$ |
| **(3c)** | 5.17 | 50.8 | | | | 1.26 | 7.8 | | | | | | | $CD_2Cl_2$ |
| **(4a)** | 3.85 | 67.0 | 4.27 | — | 12.9 | | | | | | | | | $CDCl_3$ |
| **(4b)** | 4.88 | 67.0 | 4.67 | — | 13.7 | 2.18, 2.15 | | | | | | | | $(CD_3)_2CO$ |
| **(4d)** | 4.88 | 67.2 | 4.66 | — | 13.7 | 2.19, 2.16 | | | | | | | | $(CD_3)_2CO$ |
| **(4d)** | 4.03 | 67.0 | 4.40 | — | 13.4 | 2.20, 2.15 | | | | | | | | $CD_2Cl_2$ |
| **(4e)** | 4.71 | 72.6 | 4.71 | 2.5 | 13.4 | 1.53,[e] 0.94[f] | 17.3, 6.8 | | | | | | | $(CD_3)_2CO$ |
| **(5a)** | 4.97 | 49.0 | 3.9 | 18.0 | 13.7 | | | −9.17 | 162 | −12.48 | 391 | ~3 | | $CDCl_3$ |
| **(5b)** | 5.99 | 60.1 | 4.65 | 6.6 | 13.9 | 2.17, 2.06 | | −7.6 | 44.7 | −13.2 | 524 | 4.4 | 3.0 | $(CD_3)_2CO$ |
| **(5b)** | 5.14 | 50.9 | 4.13 | 14.6 | 13.2 | 2.25, 2.10 | | −8.97 | 14.7 | −12.5 | 409 | 3.7 | 2.2 | $CDCl_3$ |
| **(5b)** | 5.16 | 50.3 | 4.05 | 14.4 | 13.9 | 2.22, 2.09 | | −8.5 | 115 | −12.8 | 442 | 3.7 | 2.4 | $CD_2Cl_2$ |
| **(5c)** | 5.71 | 52.8 | 4.57 | 13.9 | 13.7 | 1.16,[e] 1.54[f] | 20.0, n.r. | −7.8 | 35.9 | −13.5 | 454 | 3.6 | 2.4 | $(CD_3)_2CO$ |

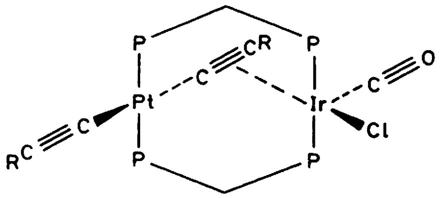
[a] Spectra measured at 100 MHz and 21 °C. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$, and coupling constants ($J$) in Hz (±0.1 Hz). [b] $H_e$ = pseudo-equatorial hydrogen, $H_a$ = pseudo-axial hydrogen. [c] $H_t$ = terminal (Ir-bonded hydride), $H_b$ = bridging hydride. [d] Only observed in methylacetylide complexes; n.r. = not resolved. [e] Assigned to terminal acetylide on platinum. [f] Assigned to bridging acetylide.

strongly coupled to $^{195}Pt$ [$^1J(PtH)$ 615 Hz] and was assigned to the bridging hydride. Similar values of $^1J(PtH)$ have been observed for the bridging hydrides in $[Pt_2H_2(\mu-H)(\mu-dppm)_2]^+$ [$^1J(PtH)$ = 540 Hz][13] and in $[(Et_3P)(C_6H_5)Pt(\mu-H)_2IrH(PEt_3)_2]^+$ [$^1J(PtH)$ = 671 Hz].[14] The resonance of the terminal hydride in (**2a**) appears at δ −19.85 p.p.m. with $^2J(HH)$ *ca.* 2 and $^3J(PtH)$ 25 Hz. The occurrence of only one band due to ν(C≡C) in the i.r. spectrum suggests the absence of a strongly bridging acetylide and we formulate complex (**2a**) as shown, with an acetylide group blocking a co-ordination site of

**Table 4.** $^{195}$Pt-{$^1$H} N.m.r. data

| Complex | δ(Pt)[a] | $^1J$(PtP$_A$)[b] | $^3J$(PtP$_B$)[b] | Solvent |
|---|---|---|---|---|
| (**1a**) | +146 | 2 489 | 44 | $CDCl_3$ |
| (**2a**) | −399 | 2 566 | <*ca.* 20 | $CDCl_3$ |
| (**3a**) | −306 | 2 668 | 124 | $CDCl_3$ |
| (**4a**) | −270 | 2 385 | <*ca.* 20 | $(CD_3)_2CO$ |
| (**5b**) | −294 | 2 434 | <*ca.* 20 | $(CD_3)_2CO$ |

[a] To high frequency of Ξ $^{195}$Pt 21.4 MHz, error ±0.5 p.p.m. [b] Error ±10 Hz.



R

(**3a**) Ph

(**3b**) *p*-tolyl

(**3c**) Me

Ir and possibly interacting weakly with it. The small value of $^2J$(HH) supports a *cis* arrangement of the two hydride ligands.

The analogous complexes $[(p\text{-MeC}_6\text{H}_4\text{C}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CC}_6\text{H}_4\text{Me-}p)\text{IrCl}]$ (**1b**) and $[(p\text{-MeC}_6\text{H}_4\text{C}{\equiv}\text{C})_2\text{Pt}(\mu\text{-dppm})_2(\mu\text{-H})\text{IrH(Cl)}]$ (**2b**) here prepared in a similar fashion to complexes (**1a**) and (**2a**). However, the *p*-tolylacetylide complexes were not obtained in pure form because of the difficulty in separating them from the soluble by-product $[\text{Pt}_2(\text{C}{\equiv}\text{CC}_6\text{H}_4\text{Me-}p)_4(\mu\text{-dppm})_2]$, but they have been observed and characterised by their $^{31}$P-{$^1$H} n.m.r. spectra (see Table 2).

The electronic structures of the complexes $[(\text{RC}{\equiv}\text{C})_2\text{Pt}(\mu\text{-dppm})_2(\mu\text{-H})\text{IrH(Cl)}]$ are intriguing. The large value of $^1J$(PtH) for the bridging hydride suggests that it is almost symmetrically bonded to the two metals. This would give odd-electron counts for each of the metals. We may invoke a three-centred, two-electron Pt–H–Ir bonding scheme which would then give even electron counts for both metals: 18 for platinum and 16 for iridium.

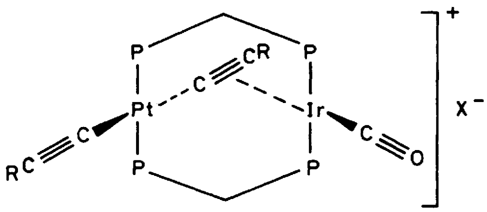
Complex $[(\text{PhC}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CPh})\text{IrCl}]$ (**1a**) reacts with carbon monoxide to give a single yellow species, which was characterized by $^{31}$P-{$^1$H} n.m.r. spectroscopy as $[(\text{PhC}{\equiv}\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{Ir(CO)Cl}]$. However, we did not isolate this complex from the reaction since we found a more convenient route to its preparation. Thus, treatment of the readily available iridium(I) complex *trans*-$[\text{IrCl(CO)(PPh}_3)_2]$ with $[\text{Pt(C}{\equiv}\text{CPh)}_2(\text{dppm-}P)_2]$ in boiling benzene gave, after 2 min, a deep purple solution which paled to orange after *ca.* 1 h and paled further to yellow after 1.5 h. From this yellow solution, the yellow, neutral complex $[(\text{PhC}{\equiv}\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{Ir(CO)Cl}]$ was isolated in over 80% yield. The formulation follows from (*i*) elemental analysis (C, H, and Cl) (Table 1); (*ii*) the $^{31}$P-{$^1$H} n.m.r. spectrum, which showed the characteristic AA′BB′ splitting pattern with $^{195}$Pt satellites (see Table 2); (*iii*) the non-electrical conductivity of its acetone solutions; (*iv*) the i.r. spectrum, which showed a terminal ν(CO) band at 2 025 cm$^{-1}$ and a band at 2 102 cm$^{-1}$ assigned to ν(C≡C); (*v*) the $^1$H-{$^{31}$P} n.m.r. spectrum, which showed a singlet resonance at δ 5.20 p.p.m. with $^{195}$Pt satellites (see Table 3); and (*vi*) the $^{195}$Pt-{$^1$H} n.m.r. spectrum, which showed the expected triplet of triplets pattern due to coupling to two near and two distant $^{31}$P nuclei (see Table 4). We suggest that there is a weak interaction between one of the acetylides and the iridium, for the reasons discussed below, and therefore suggest structure (**3a**) for the complex. The *p*-tolylacetylide (**3b**) and methylacetylide (**3c**) analogues were prepared similarly and fully characterized (see Tables). These complexes differ from their rhodium analogues in that they are non-electrolytes in nitrobenzene or acetone. The structural difference between the bis(acetylide)platinum–rhodium and bis(acetylide)platinum–iridium complexes is reflected in their chemistries. For instance, whereas carbon monoxide can be eliminated from the complex $[(p\text{-MeC}_6\text{H}_4\text{C}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CC}_6\text{H}_4\text{Me-}p)\text{Rh(CO)Cl}]$ by heating the complex in toluene, a similar treatment of $[(p\text{-MeC}_6\text{H}_4\text{C}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CC}_6\text{H}_4\text{Me-}p)\text{Ir(CO)Cl}]$ (**3b**) gave a mixture of products, none of which appeared to be binuclear (as evidenced by $^{31}$P-{$^1$H} n.m.r. spectroscopy).

The i.r. spectra of the neutral platinum–iridium complexes (**3a**)—(**3c**) all show a band in the region of 2 025 cm$^{-1}$, assigned to ν(CO), and a band in the region of 250 cm$^{-1}$, assigned to ν(IrCl). These are unusual frequencies for iridium(I) chlorocarbonyl complexes, *e.g.* for *trans*-$[\text{IrCl(CO)(PPh}_3)_2]$, ν(CO) is at 1 961 cm$^{-1}$ and ν(IrCl) is at 310 cm$^{-1}$.[15] The low frequency of the ν(IrCl) band in $[(\text{PhC}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CPh})\text{Ir(CO)Cl}]$ (**3a**) indicates a weakening of this bond. We suggest that this weakening is brought about by the non-linearity of the Cl–Ir–C≡O moiety and by some interaction of C≡CPh with iridium as depicted in (**3a**); similarly for (**3b**) and (**3c**). However, $^1$H-{$^{31}$P} n.m.r. spectroscopy of (**3a**)—(**3c**) shows that in all three cases the $CH_2$ protons are equivalent and for the di-*p*-tolylacetylide complex (**3b**) and dimethylacetylide complex (**3c**) both methyl groups are equivalent (Table 3). These results show that some rapid rate process interchanges the positions of Cl and CO. We do not know what this process is: perhaps a *cis*-planar $\text{P}_2\text{Ir(CO)Cl}$ moiety is involved as an intermediate allowing the Cl and CO to switch from one side to the other side of the plane formed by the four P atoms. Even at −80 °C the process is rapid, *e.g.* for (**3b**) the *p*-tolyl methyls give only one sharp singlet and although the $CH_2$ resonance is broadened it is still not resolved into an AB quartet; similarly for the methylacetylide complex (**3c**).

Although acetone solutions of $[(\text{PhC}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CPh})\text{Ir(CO)Cl}]$ (**3a**) are essentially non-conducting the addition of large, non-co-ordinating anions such as $PF_6^-$, $BPh_4^-$, or $BF_4^-$ gave deep red solutions. The $^{31}$P-{$^1$H} n.m.r. spectra of these red solutions are all very similar (except for the $PF_6^-$ resonances) and show a large shift to high frequency of *ca.* 38 p.p.m. in δ(P$_B$) for the phosphorus bound to iridium, relative to the neutral starting material.

We have isolated these cations $[(\text{RC}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CR})\text{Ir(CO)}]^+$ as $BPh_4^-$ [R = Ph (**4a**), $C_6H_4$Me-*p* (**4b**), or Me (**4c**)] or $PF_6^-$ salts [R = $C_6H_4$Me-*p* (**4d**) or Me (**4e**)] (elemental analytical and spectroscopic data in the Tables). Thus for the complex prepared by treating (**3a**) with $NaBPh_4$ we assign to it structure (**4a**) based on (*i*) elemental analysis (C and H); (*ii*) a conductivity mesurement in acetone, which was typical of a 1 : 1 electrolyte; (*iii*) the $^{31}$P-{$^1$H} n.m.r. spectrum (see Table 2); (*iv*) the i.r. spectrum, which showed the absence of the band at 254 cm$^{-1}$ assigned to ν(IrCl) in the starting complex (**3a**) and a new ν(CO) band at 1 970 cm$^{-1}$; and (*v*) the $^1$H and $^1$H-{$^{31}$P} n.m.r. spectra, which showed an AB pattern for the $CH_2$ resonances, the lower frequency signal, due to pseudo-equational hydrogen (H$_e$) being strongly coupled to $^{195}$Pt and the higher frequency signal (H$_a$), weakly coupled to $^{195}$Pt.

We have prepared and studied in some detail the bis(*p*-tolylacetylide) complex (**4d**). This red salt was made by treating the neutral complex (**3b**) with $NH_4PF_6$ in acetone (see Experimental section for details and Tables 1—3 for characterizing data). In the $^1$H n.m.r. spectrum the methyls of the two *p*-



| | R | X |
|---|---|---|
| (**4a**) | Ph | BPh$_4$ |
| (**4b**) | *p*-tolyl | BPh$_4$ |
| (**4c**) | Me | BPh$_4$ |
| (**4d**) | *p*-tolyl | PF$_6$ |
| (**4e**) | Me | PF$_6$ |

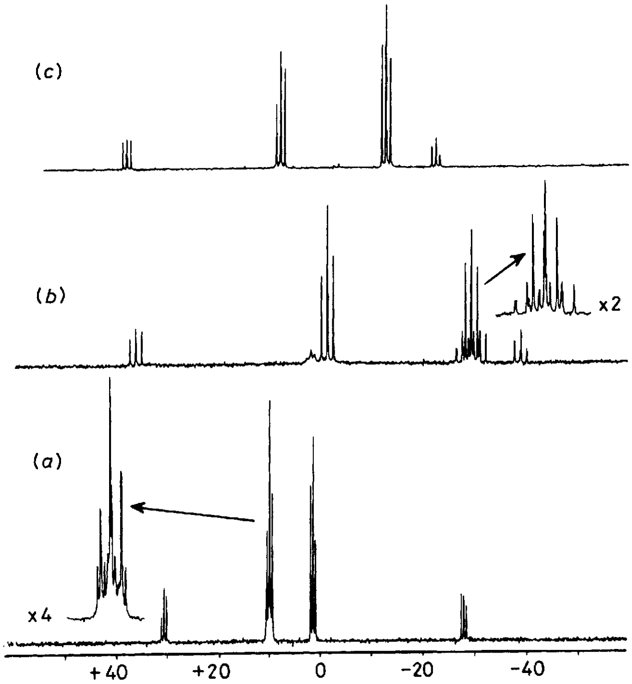


**Figure 1.** $^{31}$P-{$^1$H} N.m.r. spectra (40.25 MHz) of some platinum–iridium complexes. (*a*) [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)Ir(CO)]PF$_6$ (**4d**) in (CD$_3$)$_2$CO. (*b*) Spectrum obtained by treating a solution of (**4d**) with an excess (*ca.* 10 fold) of LiCl. The product is identified as the neutral complex (**3b**), the spectrum being virtually identical with that of an authentic sample. (*c*) [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)(μ-H)IrH(CO)]PF$_6$ (**5b**) prepared by bubbling H$_2$ through a solution of (**4d**) in (CD$_3$)$_2$CO for 30 s

tolylacetylide groups were non-equivalent. The $^{31}$P-{$^1$H} n.m.r. spectrum of (**4d**), excluding the resonance due to PF$_6^-$, is shown in Figure 1.

Complex (**4e**) was prepared and characterized, see Experimental section for details and Tables for characterizing data. The $^1$H-{$^{31}$P} n.m.r. spectrum shows the two methylacetylide groups to be non-equivalent, both giving singlets with satellites due to $^{195}$Pt coupling. The signal at δ 1.53 p.p.m. shows the larger coupling to platinum, $^4J(Pt\text{C}\equiv\text{C}CH_3)$ = 17.3 Hz, and is assigned to the terminal acetylide whilst the signal at δ 0.94 p.p.m. showed a much smaller coupling to $^{195}$Pt, $^4J(Pt\text{C}\equiv\text{C}CH_3)$ = 6.8 Hz, and is assigned to the bridging methylacetylide group. In the $^1$H n.m.r. spectrum, the CH$_3$ resonance at δ 1.53 p.p.m. is coupled to only two P nuclei [$^5J(P\text{PtC}\equiv\text{C}CH_3)$ = 2.0 Hz], clearly the Pt-bonded P nuclei, whilst the CH$_3$ resonance at 0.94 p.p.m. gives a broad singlet resonance ($w_{\frac{1}{2}} \sim$ 3 Hz) which we suggest is because of coupling to all four P nuclei. The presence of a μ-C≡CCH$_3$ group should render the CH$_2$ hydrogens non-equivalent, however, they have the same chemical shift, but because one of them (H$_e$) is strongly coupled to $^{195}$Pt and the other (H$_a$) is weakly coupled to Pt the satellites form two AB patterns from which the data given in Table 3 were calculated.

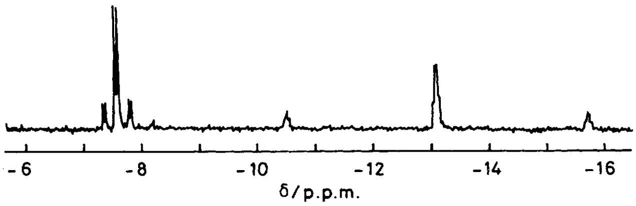
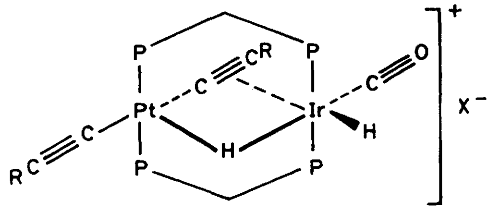


**Figure 2.** $^1$H N.m.r. spectrum in the hydride region of [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)(μ-H)IrH(CO)]PF$_6$ (**5b**), prepared by bubbling H$_2$ through a solution of (**4d**) in (CD$_3$)$_2$CO for 30 s

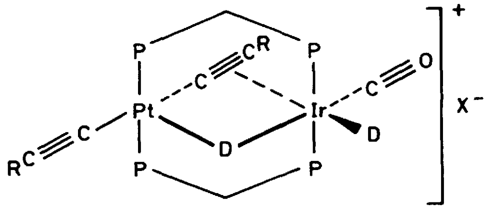
In the bis(methylacetylide) complex [(MeC≡C)Pt(μ-dppm)$_2$(μ-C≡CMe)Rh(CO)]PF$_6$ the terminal MeC≡C hydrogens are more strongly coupled to Pt than are the bridging MeC≡C hydrogens.[12] In the i.r. spectra of complexes (**4**) bands due to ν(C≡C) are very low in intensity and often cannot be observed: the bridging acetylide may absorb at very low frequencies. A band due to ν(C≡C) might be obscured by the much more intense band due to ν(C≡O). The effect of large anions on the conversion of the neutral species (**3**) to cationic species (**4**) is remarkable. It is probably an ion-pairing effect, pulling the equilibrium over in favour of compounds (**4**). The conversion, (**3**) ⟶ (**4**), is reversible and on treating an acetone solution of the salt (**4d**) with a large excess of lithium chloride conversion to the neutral chloro-complex (**3b**) was completed within minutes, see Figure 1. The $^{31}$P-{$^1$H} n.m.r. pattern of the product solution was essentially identical to that of a solution of pure (**3b**). When hydrogen was bubbled through a red acetone solution of the salt [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)Ir(CO)]PF$_6$ (**4d**) a pale yellow solution formed within 20 s. $^{31}$P-{$^1$H} N.m.r. spectroscopy showed that conversion to a single heterobimetallic species was complete, see Figure 1, the $^1$H-{$^{31}$P} n.m.r. spectrum clearly showing the formation of a dihydride species, see Figure 2. The upfield hydride resonance (at −13.2 p.p.m.) was strongly coupled to platinum, $^1J$(Pt–H) = 524 Hz, and hence we assign this as bridging the two metals, the other hydride resonance (at −7.6 p.p.m.) having only a weak coupling to platinum, $^3J$(Pt–H) = 44.7 Hz, being assigned as a terminal hydride on iridium. The very small value of the hydride–hydride coupling $^2J$(H–Ir–H) = 4.4 Hz indicates a mutual *cis* arrangement of the two hydride ligands. The two methylacetylide groups are non-equivalent and we suggest that one is bridging and the other terminal.

A small coupling was also observed between the bridging hydride and the pseudo-equatorial methylene protons on the dppm ligand. We formulate this species as [(*p*-MeC$_6$H$_4$C≡C)-Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)(μ-H)IrH(CO)]PF$_6$ (**5b**).

We have demonstrated the reversibility of the uptake of dihydrogen by (**4d**) to give (**5b**) using solution i.r. spectroscopy. Treatment of an ethanol-free chloroform solution of complex (**4d**), for which ν(CO) is at 1 975vs cm$^{-1}$, with dihydrogen very rapidly gave the dihydride (**5b**), for which ν(CO) is at 2 080s cm$^{-1}$ and ν(Ir–H) at 2 125m cm$^{-1}$. We confirmed these assignments by using dideuterium in place of dihydrogen, giving the analogous complex (**6a**). The presence of the dihydride was also



| | R | X |
|---|---|---|
| (**5a**) | Ph | $BPh_4$ |
| (**5b**) | *p*-tolyl | $PF_6$ |
| (**5c**) | Me | $PF_6$ |



(**6a**) R = *p*-tolyl, X = $PF_6$

confirmed by n.m.r. spectroscopy (data in Table 3). We found that the dihydrogen was only lost quite slowly from the dihydride (**5b**). Thus when dinitrogen was bubbled through its chloroform solution for 15 min there was a slight deepening in colour but i.r. or $^{31}P-\{^1H\}$ n.m.r. spectroscopy showed that the dihydride was essentially unchanged. However, after bubbling dinitrogen through the solution for 5 h a deep red solution of the iridium(I) salt (**4d**), characterized by its $^{31}P-\{^1H\}$ n.m.r. spectrum (see Figure 1) was obtained. This result shows that the equilibrium (**5b**) $\rightleftharpoons$ (**4d**) greatly favours the dihydride (**5b**). When an acetone solution of (**5b**) was exposed to the air for 4 d it had reverted back to (**4d**), essentially completely.

When acetone solutions of (**5b**) were exposed to a dihydrogen atmosphere for several days or weeks mixtures of new heterobimetallic complexes containing Pt(μ-dppm)$_2$Ir moieties were produced [$^{31}P-\{^1H\}$ n.m.r. evidence]. None of the complexes was isolated or identified although $^1H-\{^{31}P\}$ n.m.r. spectroscopy showed that some of them were hydrides.

## Experimental

General methods were the same as those described in previous papers from this laboratory.[1]

*Preparation of* [(PhC≡C)Pt(μ-dppm)$_2$(μ-C≡CPh)IrCl] (**1a**).—*trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] (0.335 g, 0.29 mmol) was added to a solution of [$Ir_2Cl_2(C_8H_{14})_4$] (0.133 g, 0.15 mmol) in benzene (20 cm$^3$). The mixture was stirred and warmed gently (hot water-bath *ca.* 65 °C) under nitrogen for 5 min to give an intense green solution. The mixture was stirred for 14 h at room temperature. The green solution was filtered (under nitrogen) free of the yellow-brown precipitate {which was shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to be mainly [Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$]}. Light petroleum (b.p. 100—120 °C, 20 cm$^3$) was added and nitrogen briskly bubbled through the solution to evaporate the solvent. After 30 min the green solid was filtered off rapidly in air, washed with n-pentane and sucked dry for 1 min. Yield 0.252 g (62%). The product was stored at −30 °C under argon.

The complex [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)IrCl] (**1b**) was prepared in a similar fashion but, due to the solubility of the binuclear platinum acetylide impurity, could not be obtained in pure form and was used *in situ*.

*Preparation of* [(PhC≡C)$_2$Pt(μ-dppm)$_2$(μ-H)IrH(Cl)] (**2a**).—*trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] (0.335 g, 0.29 mmol) was added to a solution of [$Ir_2Cl_2(C_8H_{14})_4$] (0.133 g, 0.15 mmol) in benzene (20 cm$^3$). The mixture was stirred and warmed gently (to *ca.* 65 °C) under nitrogen for 5 min to give an intense green solution. The apparatus was then evacuated and filled with hydrogen; this was repeated five times to ensure that the nitrogen was completely displaced by hydrogen. The solution changed from green to brown and was stirred for a further 14 h. The resulting orange-brown solution was filtered (in air) to remove some undissolved material {shown to be the binuclear acetylide complex [Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$]}. The volume was reduced to *ca.* 5 cm$^3$ and the product precipitated with cyclohexane. It was filtered off (in air) and dried *in vacuo*. Yield 0.24 g (59%). The product was stored at −30 °C under argon.

The complex (**2b**) was prepared similarly but not obtained in pure form due to the difficulty in separating the binuclear platinum acetylide impurity.

*Preparation of* [(PhC≡C)Pt(μ-dppm)$_2$(μ-C≡CPh)Ir(CO)Cl] (**3a**).—A solution of *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0.25 g, 0.32 mmol) in deoxygenated benzene (20 cm$^3$) was treated with *trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] (0.374 g, 0.32 mmol) and the mixture heated under reflux. An intense purple solution formed after *ca.* 2 min which gradually paled to orange and then yellow. After 1.5 h the yellow solution was allowed to cool. The solvent was removed under reduced pressure and diethyl ether (20 cm$^3$) added to the residue. The yellow solid was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.38 g (84%). The product thus obtained gave satisfactory microanalytical results; it could be recrystallised from dichloromethane–cyclohexane.

The *p*-tolylacetylide analogue (**3b**) was prepared in a similar fashion in 82% yield. The methylacetylide analogue (**3c**) was also prepared in a similar fashion but was not obtained in pure form.

*Preparation of* [(PhC≡C)Pt(μ-dppm)$_2$(μ-C≡CPh)Ir(CO)]BPh$_4$ (**4a**).—A solution of NaBPh$_4$ (0.10 g, 0.29 mmol) in acetone (10 cm$^3$) was filtered into a suspension of [(PhC≡C)$_2$Pt(μ-dppm)$_2$Ir(CO)Cl] (0.35 g, 0.25 mmol) in acetone (10 cm$^3$) and the mixture was warmed (to *ca.* 50 °C) and swirled for 2 min to give a cloudy red-orange solution. This suspension was filtered and the solvent removed from the filtrate under reduced pressure. The residue was triturated with methanol and the red-orange solid filtered off, washed with cold methanol, and dried *in vacuo*. Yield 0.403 g (95%).

The *p*-tolylacetylide and methylacetylide analogues, (**4b**) and (**4c**) were prepared in a similar fashion in 92 and 64% yields, respectively.

*Preparation of* [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)Ir(CO)]PF$_6$ (**4d**).—(*a*) A solution of NH$_4$PF$_6$ (0.022 g, 0.135 mmol) in acetone (5 cm$^3$) was added to a stirred suspension of [(*p*-MeC$_6$H$_4$C≡C)$_2$Pt(μ-dppm)$_2$Ir(CO)Cl] (0.171 g, 0.118 mmol) in acetone (15 cm$^3$) to give a cloudy orange solution within 10 s. After stirring for 5 min, the mixture was filtered, and the solvent evaporated from the filtrate under reduced pressure. The orange residue was triturated with diethyl ether (10 cm$^3$) to yield an orange powder which was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.155 g (84%).

(*b*) [Pt(C$\equiv$CC$_6$H$_4$Me-*p*)$_2$(dppm-*P*)$_2$] (2.27 g, 1.9 mmol) was added to a solution of [Ir(CO)Cl(PPh$_3$)$_2$] (1.48 g, 1.90 mmol) in degassed benzene (100 cm$^3$). The mixture was refluxed under nitrogen for 1 h, before cooling and removing the solvent under reduced pressure. The residue was redissolved in acetone (50 cm$^3$), and to this solution was added NH$_4$PF$_6$ (0.30 g, 1.84 mmol) to give an orange solution which after stirring for 5 min was filtered; the solvent was then evaporated from the filtrate under reduced pressure, to give an orange residue which was recrystallised from dichloromethane–benzene giving red crystals. Yield 2.20 g, (75%).

The methylacetylide analogue (**4e**) was prepared in a similar fashion in 47% yield.

*Preparation of* [(*p*-MeC$_6$H$_4$C$\equiv$C)Pt($\mu$-dppm)$_2$($\mu$-C$\equiv$CC$_6$H$_4$Me-*p*)($\mu$-H)IrH(CO)]PF$_6$ (**5b**).—[(*p*-MeC$_6$H$_4$C$\equiv$C)Pt($\mu$-dppm)$_2$($\mu$-C$\equiv$CC$_6$H$_4$Me-*p*)Ir(CO)]PF$_6$ (**4d**) (0.025 g, 0.016 mmol) was dissolved in [$^2$H$_6$]acetone (0.4 cm$^3$) in a 5-mm n.m.r. tube. Hydrogen was bubbled through the solution using a drawn out Pasteur-pipette until a pale yellow colouration was observed, whereupon the $^{31}$P-{$^1$H} or $^1$H-{$^{31}$P} n.m.r. spectra were recorded.

Species (**5a**) was generated in a similar manner.

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