

Bimetallic Systems. Part 14.¹ Mixed Iridium(I)–Platinum(II) Acetylide Complexes containing Bridging Ph₂PCH₂PPh₂ Ligands

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Treatment of the cyclo-octene (C₈H₁₄) iridium(I) complex [Ir₂Cl₂(C₈H₁₄)₄] with *trans*-[Pt(C≡CR)₂(dppm-*P*)₂] (R = Ph or *p*-tolyl; dppm = Ph₂PCH₂PPh₂) gave the dark green complexes [(RC≡C)Pt(μ-dppm)₂(μ-C≡CR)IrCl], which reacted with dihydrogen to give the dihydrides [(RC≡C)₂Pt(μ-dppm)₂(μ-H)IrH(Cl)]. [(PhC≡C)Pt(μ-dppm)₂(μ-C≡CPh)IrCl] reacted with CO to give [(PhC≡C)Pt(μ-dppm)₂(μ-C≡CPh)Ir(CO)Cl], more conveniently prepared by treating *trans*-[IrCl(CO)(PPh₃)₂] with *trans*-[Pt(C≡CPh)₂(dppm-*P*)₂]. The *p*-tolylacetylide and methylacetylide analogues were prepared similarly. Treatment of [(RC≡C)Pt(μ-dppm)₂(μ-C≡CR)Ir(CO)Cl] with large anions, e.g. PF₆⁻ or BPh₄⁻, gave the corresponding red cationic species [(RC≡C)Pt(μ-dppm)₂(μ-C≡CR)Ir(CO)]⁺, isolated as PF₆⁻ or BPh₄⁻ 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≡C)Pt(μ-dppm)₂(μ-C≡CR)(μ-H)IrH(CO)]⁺. I.r. and ¹H, ³¹P, and ¹⁹⁵Pt n.m.r. data are given.

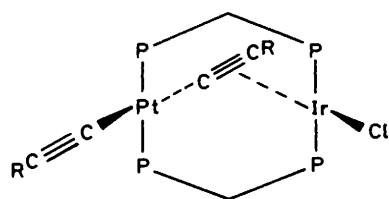
In previous papers in this series we have described systematic syntheses of heterobimetallic complexes containing M¹(μ-dppm)₂M² moieties (M¹, M² are two different metals, dppm = Ph₂PCH₂PPh₂). Although there are many examples of di-platinum²⁻⁶ and di-iridium⁷⁻¹⁰ complexes containing two bridging dppm 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 paper¹² 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 (C₈H₁₄) iridium(I) complex [Ir₂Cl₂(C₈H₁₄)₄] with [Pt(C≡CPh)₂(dppm-*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 di-platinum acetylide complex [Pt₂(C≡CPh)₄(μ-dppm)₂] by ³¹P-¹H n.m.r. spectroscopy. The green mother-liquor gave an olive green solid which we formulate as [(PhC≡C)Pt(μ-dppm)₂(μ-C≡CPh)IrCl] (**1a**) on the basis of (i) elemental analysis (C, H, and Cl) (Table 1); (ii) the ³¹P-¹H n.m.r. spectrum, which showed the characteristic AA'BB' splitting pattern with ¹⁹⁵Pt satellites (see Table 2); (iii) the ¹H and ¹H-³¹P n.m.r. spectra, which showed a single CH₂ resonance,

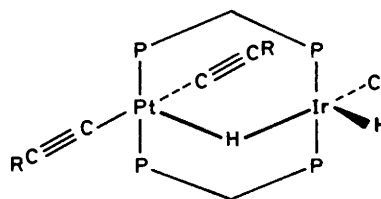
i.e. H_c and H_a are equivalent (see Table 3); (iv) the i.r. spectrum, which had bands at 2 112 and 2 075 cm⁻¹ assigned to ν(C≡C) (Table 1); and (v) the ¹⁹⁵Pt-¹H n.m.r. spectrum, which showed the expected triplet of triplets pattern due to coupling to two near and two distant ³¹P nuclei (Table 4). We 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-coordinate. N.m.r. evidence and crystal-structure determination of a related compound [(MeC≡C)Pt(μ-dppm)₂(μ-C≡CMe)Rh(CO)]PF₆ show one acetylide group to be weakly bridging in a σ,η fashion¹² 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≡C)₂Pt(μ-dppm)₂(μ-H)IrH(Cl)] (**2a**) on the basis of (i) elemental analysis (C, H, and Cl) (Table 1); (ii) the ³¹P-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 ¹⁹⁵Pt-¹H n.m.r. spectrum, which showed the expected triplet of triplets pattern (see Table 4); and (vi) the ¹H and ¹H-³¹P n.m.r. spectra, which are particularly informative in the metal-hydride region (Table 3). In the ¹H-³¹P 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

Complex	Analysis ^a			$\Lambda^b/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	I.r. ^c (cm ⁻¹)			
	C	H	Cl [or F]		$\nu(\text{C}\equiv\text{C})$	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{Ir}-\text{Cl})$	$\nu(\text{Ir}-\text{H})$
(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 ₆ H 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 ₂ Cl 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 CHCl₃.

Table 2. ³¹P-{¹H} N.m.r. data^a

Complex	$\delta(\text{P}_A)$	¹ J(PtP _A)	$\delta(\text{P}_B)$	³ J(PtP _B)	^a N ^b	Solvent
(1a)	+4.7	2 670	+23.4	48	102	C ₆ D 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) ₂ CO
(4b)	+1.3	2 391	+10.0		40	(CD ₃) ₂ CO
(4c)	+0.7	2 338	+5.2		39	(CD ₃) ₂ CO
(4d)	+0.1	2 368	+10.1		39	(CD ₃) ₂ CO
(4e)	-1.0	2 436	+10.3	c	39	(CD ₃) ₂ CO
(5a)	+8.3	2 436	-12.5		66	(CD ₃) ₂ CO
(5b)	+8.2	2 446	-12.6		68	(CD ₃) ₂ CO

^a Spectra (40.25 Hz) measured at ca. +21 °C. Chemical shifts (δ) in p.p.m. (± 0.1) to high frequency of 85% H₃PO₄ 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-{³¹P} N.m.r. data^a

Complex	Methylene ^b			Acetylide			Hydride ^c				Solvent		
	$\delta(\text{H}_e)$	³ J(Pt-H _e)	$\delta(\text{H}_a)$	³ J(Pt-H _a)	² J(H _c -H _a)	$\delta(\text{CH}_3)$	⁴ J(Pt-H) ^d	$\delta(\text{H}_i)$	³ J(Pt-H _i)	$\delta(\text{H}_b)$		¹ J(Pt-H _b)	² J(H _i -H _b)
(1a)	4.58	26.5											
(2a)	4.27	57.2	4.83	19.6	12.9			-19.85	25	-12.5	615	~2	
(3a)	5.20	51.0											
(3b)	5.23	51.3											
(3c)	5.17	50.8				1.26	7.8						
(4a)	3.85	67.0	4.27	—	12.9								
(4b)	4.88	67.0	4.67	—	13.7	2.18, 2.15							
(4d)	4.88	67.2	4.66	—	13.7	2.19, 2.16							
(4d)	4.03	67.0	4.40	—	13.4	2.20, 2.15							
(4e)	4.71	72.6	4.71	2.5	13.4	1.53, ^e 0.94 ^f	17.3, 6.8						
(5a)	4.97	49.0	3.9	18.0	13.7			-9.17	162	-12.48	391	~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
(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
(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
(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

^a Spectra measured at 100 MHz and 21 °C. Chemical shifts (δ) in p.p.m. (± 0.01) to high frequency of SiMe₄, and coupling constants (J) in Hz (± 0.1 Hz). ^b H_e = pseudo-equatorial hydrogen, H_a = pseudo-axial hydrogen. ^c H_i = 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.

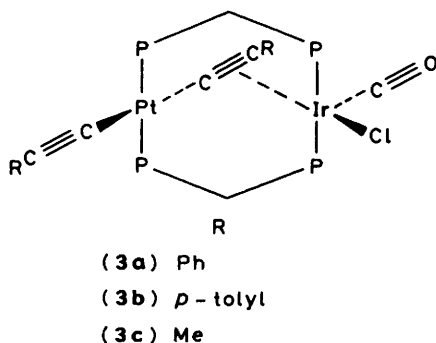
strongly coupled to ¹⁹⁵Pt [¹J(PtH) 615 Hz] and was assigned to the bridging hydride. Similar values of ¹J(PtH) have been observed for the bridging hydrides in [Pt₂H₂(μ-H)(μ-dppm)₂]⁺ [¹J(PtH) = 540 Hz]¹³ and in [(Et₃P)(C₆H₅)Pt(μ-H)₂IrH(PEt₃)₂]⁺ [¹J(PtH) = 671 Hz].¹⁴ The resonance of the

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 $\nu(\text{C}\equiv\text{C})$ 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 - $\{^1\text{H}\}$ N.m.r. data

Complex	$\delta(\text{Pt})^a$	$^1J(\text{PtP}_A)^b$	$^3J(\text{PtP}_B)^b$	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	$(\text{CD}_3)_2\text{CO}$
(5b)	-294	2 434	< ca. 20	$(\text{CD}_3)_2\text{CO}$

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



Ir and possibly interacting weakly with it. The small value of $^2J(\text{HH})$ 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 $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2(\mu\text{-H})\text{IrH}(\text{Cl})]$ (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 - $\{^1\text{H}\}$ n.m.r. spectra (see Table 2).

The electronic structures of the complexes $[(\text{RC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2(\mu\text{-H})\text{IrH}(\text{Cl})]$ are intriguing. The large value of $^1J(\text{PtH})$ 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 - $\{^1\text{H}\}$ n.m.r. spectroscopy as $[(\text{PhC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{Ir}(\text{CO})\text{Cl}]$. 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*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ with $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2]$ 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 $[(\text{PhC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{Ir}(\text{CO})\text{Cl}]$ was isolated in over 80% yield. The formulation follows from (i) elemental analysis (C, H, and Cl) (Table 1); (ii) the ^{31}P - $\{^1\text{H}\}$ 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 $\nu(\text{CO})$ band at $2\,025\text{ cm}^{-1}$ and a band at $2\,102\text{ cm}^{-1}$ assigned to $\nu(\text{C}\equiv\text{C})$; (v) the ^1H - $\{^{31}\text{P}\}$ 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 - $\{^1\text{H}\}$ 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 $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)\text{Rh}(\text{CO})\text{Cl}]$ by heating the complex in toluene, a similar treatment of $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)\text{Ir}(\text{CO})\text{Cl}]$ (3b) gave a mixture of products, none of which appeared to be binuclear (as evidenced by ^{31}P - $\{^1\text{H}\}$ n.m.r. spectroscopy).

The i.r. spectra of the neutral platinum-iridium complexes (3a)–(3c) all show a band in the region of $2\,025\text{ cm}^{-1}$, assigned to $\nu(\text{CO})$, and a band in the region of 250 cm^{-1} , assigned to $\nu(\text{IrCl})$. These are unusual frequencies for iridium(I) chloro-carbonyl complexes, e.g. for *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, $\nu(\text{CO})$ is at $1\,961\text{ cm}^{-1}$ and $\nu(\text{IrCl})$ is at 310 cm^{-1} .¹⁵ The low frequency of the $\nu(\text{IrCl})$ band in $[(\text{PhC}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CPh})\text{Ir}(\text{CO})\text{Cl}]$ (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 $\text{C}\equiv\text{CPh}$ with iridium as depicted in (3a); similarly for (3b) and (3c). However, ^1H - $\{^{31}\text{P}\}$ 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 $\text{P}_2\text{Ir}(\text{CO})\text{Cl}$ 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 $[(\text{PhC}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CPh})\text{Ir}(\text{CO})\text{Cl}]$ (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 - $\{^1\text{H}\}$ 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 $\delta(\text{P}_B)$ for the phosphorus bound to iridium, relative to the neutral starting material.

We have isolated these cations $[(\text{RC}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CR})\text{Ir}(\text{CO})]^+$ as BPh_4^- [R = Ph (4a), $\text{C}_6\text{H}_4\text{Me-}p$ (4b), or Me (4c)] or PF_6^- salts [R = $\text{C}_6\text{H}_4\text{Me-}p$ (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 measurement in acetone, which was typical of a 1:1 electrolyte; (iii) the ^{31}P - $\{^1\text{H}\}$ 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 $\nu(\text{IrCl})$ in the starting complex (3a) and a new $\nu(\text{CO})$ band at $1\,970\text{ cm}^{-1}$; and (v) the ^1H and ^1H - $\{^{31}\text{P}\}$ n.m.r. spectra, which showed an AB pattern for the CH_2 resonances, the lower frequency signal, due to pseudo-equatorial 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 ^1H n.m.r. spectrum the methyls of the two *p*-

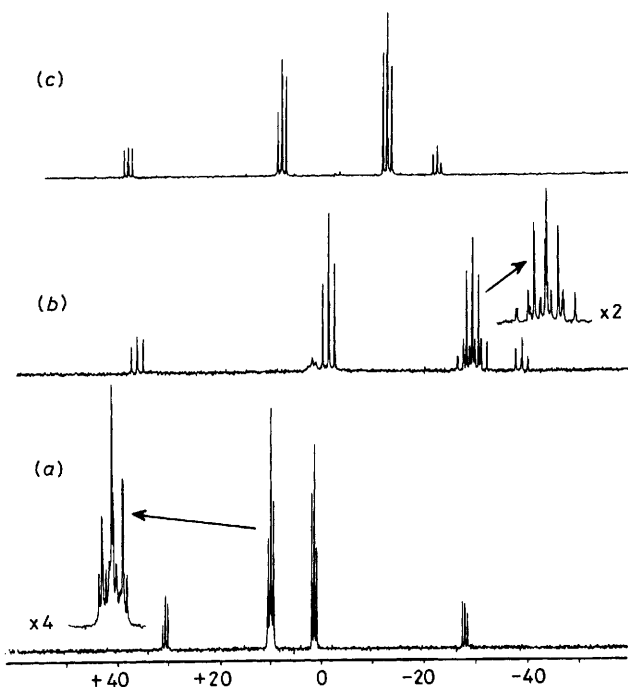
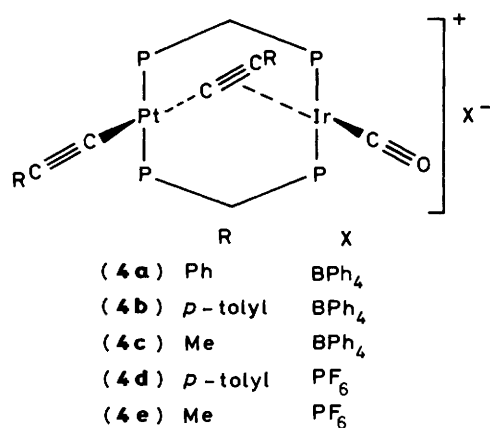


Figure 1. $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. spectra (40.25 MHz) of some platinum-iridium complexes. (a) $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)\text{Ir}(\text{CO})]\text{PF}_6$ (**4d**) in $(\text{CD}_3)_2\text{CO}$. (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) $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)(\mu\text{-H})\text{IrH}(\text{CO})]\text{PF}_6$ (**5b**) prepared by bubbling H_2 through a solution of (**4d**) in $(\text{CD}_3)_2\text{CO}$ for 30 s

tolylacetylide groups were non-equivalent. The $^{31}\text{P}\{-^1\text{H}\}$ 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 $^1\text{H}\{-^{31}\text{P}\}$ 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, $^4J(\text{PtC}\equiv\text{CCH}_3) = 17.3$ 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 , $^4J(\text{PtC}\equiv\text{CCH}_3) = 6.8$ Hz, and is assigned to the bridging methylacetylide group. In the ^1H n.m.r. spectrum, the CH_3 resonance at δ 1.53 p.p.m. is coupled to only two P nuclei

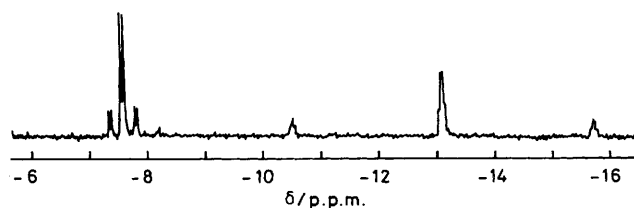


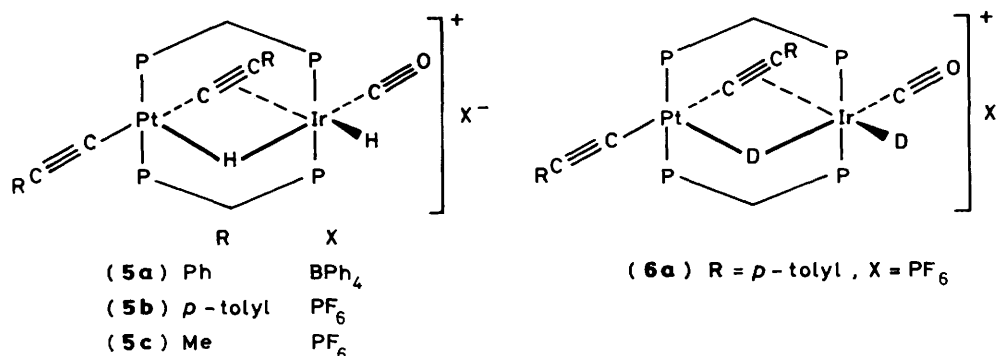
Figure 2. ^1H N.m.r. spectrum in the hydride region of $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)(\mu\text{-H})\text{IrH}(\text{CO})]\text{PF}_6$ (**5b**), prepared by bubbling H_2 through a solution of (**4d**) in $(\text{CD}_3)_2\text{CO}$ for 30 s

$[^5J(\text{PPtC}\equiv\text{CCH}_3) = 2.0$ 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 $\mu\text{-C}\equiv\text{CCH}_3$ group should render the CH_2 hydrogens non-equivalent, however, they have the same chemical shift, but because one of them (H_a) is strongly coupled to ^{195}Pt and the other (H_b) is weakly coupled to Pt the satellites form two AB patterns from which the data given in Table 3 were calculated.

In the bis(methylacetylide) complex $[(\text{MeC}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CMe})\text{Rh}(\text{CO})]\text{PF}_6$ the terminal $\text{MeC}\equiv\text{C}$ hydrogens are more strongly coupled to Pt than are the bridging $\text{MeC}\equiv\text{C}$ hydrogens.¹² In the i.r. spectra of complexes (**4**) bands due to $\nu(\text{C}\equiv\text{C})$ are very low in intensity and often cannot be observed: the bridging acetylide may absorb at very low frequencies. A band due to $\nu(\text{C}\equiv\text{C})$ might be obscured by the much more intense band due to $\nu(\text{C}\equiv\text{O})$. 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**) \rightarrow (**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 $^{31}\text{P}\{-^1\text{H}\}$ 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 $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)\text{Ir}(\text{CO})]\text{PF}_6$ (**4d**) a pale yellow solution formed within 20 s. $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. spectroscopy showed that conversion to a single heterobimetallic species was complete, see Figure 1, the $^1\text{H}\{-^{31}\text{P}\}$ 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, $^1J(\text{Pt-H}) = 524$ 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, $^3J(\text{Pt-H}) = 44.7$ Hz, being assigned as a terminal hydride on iridium. The very small value of the hydride-hydride coupling $^2J(\text{H-Ir-H}) = 4.4$ 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 $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)(\mu\text{-H})\text{IrH}(\text{CO})]\text{PF}_6$ (**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 $\nu(\text{CO})$ is at 1975 vs cm^{-1} , with dihydrogen very rapidly gave the dihydride (**5b**), for which $\nu(\text{CO})$ is at 2080 vs cm^{-1} and $\nu(\text{Ir-H})$ at 2125 vs 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



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 $^{31}\text{P}\{-^1\text{H}\}$ 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 $^{31}\text{P}\{-^1\text{H}\}$ 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 hetero-bimetallic complexes containing Pt(μ -dppm)₂Ir moieties were produced [$^{31}\text{P}\{-^1\text{H}\}$ n.m.r. evidence]. None of the complexes was isolated or identified although $^1\text{H}\{-^{31}\text{P}\}$ 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 [Ir₂Cl₂(C₈H₁₄)₄] (0.133 g, 0.15 mmol) in benzene (20 cm³). 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 $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy to be mainly [Pt₂(C≡CPh)₄(μ -dppm)₂]}. Light petroleum (b.p. 100–120 °C, 20 cm³) 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*-MeC₆H₄C≡C)Pt(μ -dppm)₂(μ -C≡CC₆H₄-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)₂Pt(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 [Ir₂Cl₂(C₈H₁₄)₄] (0.133 g, 0.15 mmol) in benzene (20 cm³). 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 [Pt₂(C≡CPh)₄(μ -dppm)₂]}. The volume was reduced to *ca.* 5 cm³ 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)(PPh₃)₂] (0.25 g, 0.32 mmol) in deoxygenated benzene (20 cm³) 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 cm³) 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 micro-analytical 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)]-BPh₄ (4a).—A solution of NaBPh₄ (0.10 g, 0.29 mmol) in acetone (10 cm³) was filtered into a suspension of [(PhC≡C)₂Pt(μ -dppm)₂Ir(CO)Cl] (0.35 g, 0.25 mmol) in acetone (10 cm³) 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*-MeC₆H₄C≡C)Pt(μ -dppm)₂(μ -C≡CC₆H₄-Me-*p*)Ir(CO)]PF₆ (4d).—(a) A solution of NH₄PF₆ (0.022 g, 0.135 mmol) in acetone (5 cm³) was added to a stirred suspension of [(*p*-MeC₆H₄C≡C)₂Pt(μ -dppm)₂Ir(CO)Cl] (0.171 g, 0.118 mmol) in acetone (15 cm³) 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 cm³) to yield an orange powder which was

filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.155 g (84%).

(b) $[\text{Pt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)_2(\text{dppm-}P)_2]$ (2.27 g, 1.9 mmol) was added to a solution of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ (1.48 g, 1.90 mmol) in degassed benzene (100 cm³). 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 cm³), and to this solution was added NH_4PF_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 $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)(\mu\text{-H})\text{IrH}(\text{CO})]\text{PF}_6$ (**5b**).— $[(p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{Me-}p)\text{Ir}(\text{CO})]\text{PF}_6$ (**4d**) (0.025 g, 0.016 mmol) was dissolved in [²H₆]acetone (0.4 cm³) 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 ³¹P-{¹H} or ¹H-{³¹P} n.m.r. spectra were recorded.

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

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