Bimetallic Systems. Part 12.[1] Mixed Rhodium(I)–Platinum(II) Acetylide Complexes containing Bridging $Ph_2PCH_2PPh_2$. Crystal Structures of $[(MeC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CMe)Rh(CO)]PF_6$ and of $[ClPt(\mu\text{-dppm})_2\text{-}(\sigma,\eta\text{-}C{\equiv}CMe)Rh(CO)]PF_6$†

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Treatment of $[Pt(C{\equiv}CMe)_2(dppm\text{-}P)_2]$ with $[Rh_2Cl_2(CO)_4]$ gave $[(MeC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CMe)Rh(CO)]Cl$ readily converted into the corresponding PF_6^- salt (**1b**) the crystal structure of which was determined. Other complexes of the type $[(RC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CR)Rh(CO)]Cl$ were made similarly; with R = Ph, *p*-tolyl, CH_2CH_2Ph, or $C(Me){=}CH_2$. The complexes are fluxional with the low-temperature limiting $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum showing non-equivalent pseudo-equatorial and pseudo-axial CH_2 protons, H_e coupled to ^{195}Pt and H_a not. The fluxional process corresponds to interchange of H_e and H_a and interchange of terminal and bridging C≡CR. When heated in toluene for 3 h, $[(RC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CR)Rh(CO)]Cl$ (R = *p*-tolyl or Ph) was converted into $[(RC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CR)RhCl]$. With CO, $[(p\text{-}MeC_6H_4C{\equiv}C)Pt(\mu\text{-dppm})_2\text{-}(\sigma,\eta\text{-}C{\equiv}CC_6H_4Me\text{-}p)RhCl]$ rapidly gave back $[(p\text{-}MeC_6H_4C{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CC_6H_4Me\text{-}p)\text{-}Rh(CO)]Cl$. Treatment of $[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ with $[Rh_2Cl_2(C_8H_{14})_4]$ (C_8H_{14} = cyclo-octene) also gave $[(RC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CR)RhCl]$ (R = *p*-tolyl or Ph) but the complexes were not isolated pure. Treatment of $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ with $[Rh_2Cl_2(CO)_4]$ caused rapid and complete displacement of $HgCl_2$, giving $[(PhC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CPh)Rh(CO)]^+$; similarly treatment of $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$, $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2CuI]$, or $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Au]Cl$ with $[Rh_2Cl_2(CO)_4]$ gave $[(PhC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CPh)Rh(CO)]^+$. Treatment of $[Cl(RC{\equiv}C)Pt(\mu\text{-dppm})_2AgCl]$ with $[Rh_2Cl_2(CO)_4]$ gave $[ClPt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CR)Rh(CO)]^+$ (R = Me, Ph, or *p*-tolyl) isolated as PF_6^- or $AgCl_2^-$ salts. These complexes could also be made in 'one-pot' syntheses, *viz.* successive treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ with AgO_2CMe–$PhC{\equiv}CH$ followed by treatment with $[Rh_2Cl_2(CO)_4]$, without isolation of the intermediate platinum–silver complex. The crystal structures of $[(MeC{\equiv}C)Pt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CMe)Rh(CO)]PF_6$ (**1b**) as the dichloromethane solvate and of $[ClPt(\mu\text{-dppm})_2(\sigma,\eta\text{-}C{\equiv}CMe)Rh(CO)]PF_6$ (**5a**) were determined. Crystals of (**1b**) are orthorhombic, space group *Pbca*, a = 19.212(7), b = 27.364(6), c = 21.468(5) Å, and Z = 8; those of (**5a**) are orthorhombic, space group $Pn2_1a$, a = 43.39(1), b = 25.178(9), c = 10.164(6) Å, and Z = 8. Final R factors were 0.088 for 4 500 and 0.058 for 6 320 observed reflections, respectively. In each complex cation the two metal centres [Pt ··· Rh 3.099(2) for (**1b**) 3.066(2) and 3.086(2) Å for (**5a**)] are bridged by a methylacetylide group σ-bonded to Pt and π-bonded in an unsymmetrical side-on fashion to Rh [mean Rh–CPt 2.24(2), mean Rh–CMe 2.44(2) Å], giving rise to an A-frame structure.

In previous papers in this series we have described systematic syntheses of heterobimetallic complexes generated from platinum(II) acetylides containing unidentate $Ph_2PCH_2PPh_2$ (dppm) of type $[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (R = a variety of alkyl or aryl groups). The heterobimetallic complexes were of type $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2MX_n]$ (M = Hg, Cu, Ag, Au, Cr, Mo, or W; X = a variety of ligands).[2–4] We now report on the synthesis and properties of some platinum–rhodium bis-μ-dppm complexes containing acetylide ligands. Preliminary accounts of some of this work have been published.[5,6]

Results and Discussion

Treatment of a benzene solution of $[Pt(C{\equiv}CMe)_2(dppm\text{-}P)_2]$ with $[Rh_2Cl_2(CO)_4]$ (1 atom Rh per Pt atom) caused rapid evolution of CO and gave a bright orange microcrystalline solid. We assigned the ionic structure $[(MeC{\equiv}C)Pt(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CMe)Rh(CO)]Cl$ to this complex on evidence of elemental analysis, electrical conductivity, and the i.r. and n.m.r. spectra (see below).[5] However, we did not establish the nature of the bridging acetylide group until the crystal structure of the corresponding PF_6 salt was determined (see below): this showed it to be (**1a**) and the PF_6 salt (**1b**) was readily made by treating the chloride salt with NH_4PF_6. Details of the preparation of complexes (**1a**) and (**1b**) are in the Experimental section and elemental analytical data are in Table 1. The i.r. spectrum of (**1a**) (Nujol mull) showed a strong band at 1 980 cm^{-1} assigned to ν(C≡O) and two weak bands, at 2 118 and 2 040 cm^{-1}, assigned to ν(C≡C); the lower-frequency band is presumably due to the bridging acetylide. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (Figure 1) showed deceptively simple triplet patterns

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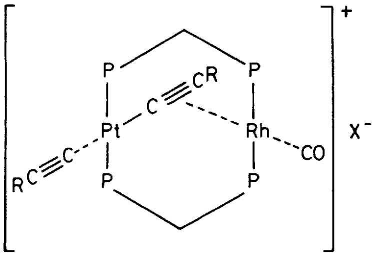
† Bis[μ-bis(diphenylphosphino)methane]-2-carbonyl-μ-[propynyl-C^1-(Pt)$C^{1\text{-}2}$(Rh)]-1-propynylplatinumrhodium hexafluorophosphate and bis[μ-bis(diphenylphosphino)methane]-2-carbonyl-1-chloro-μ-[propynyl-C^1(Pt)$C^{1\text{-}2}$(Rh)]-platinumrhodium hexafluorophosphate.

Supplementary data available (No. SUP 56276, 10 pp.): thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

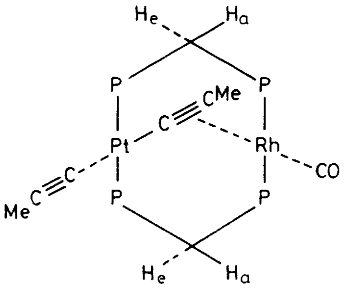
Table 1. Microanalysis, melting point, conductivity, and i.r. data

Complex	M.p.[a]/°C	Analysis (%)[b] C	H	Halogen	Λ^c/Ω^{-1} cm^2 mol^{-1}	I.r. (cm^{-1})[d] ν(C≡C)	ν(CO)
(1a)	115—120	56.7 (56.65)	4.1 (4.2)	3.0 (2.95)	n.d.	2 118, 2 040	1 980
(1b) $\cdot$0.5 CH_2Cl_2	n.d.	50.55 (50.75)	3.75 (3.8)	n.d.		n.d.	n.d.
(1c)	180—182	61.05 (60.9)	4.35 (4.3)	2.7 (2.6)	23	2 108	1 972
(1d)	175—176	60.3 (60.4)	4.15 (4.1)	2.55 (2.65)	78[e]	n.d.	n.d.
(1e)	< 139	51.4 (51.95)	4.7 (4.5)	2.75 (2.55)	19	2 060	1 970
(1f)	190—192	57.9 (58.1)	4.45 (4.3)	3.2 (2.8)	18	2 110, 2 060, 2 015	1 957
(1g)	288—289	56.45 (56.4)	4.0 (4.0)	7.4 (7.75)	n.d.		
(4a)	230—235	61.6 (61.3)	4.5 (4.4)	2.75 (2.65)	6[e]	2 110, 1900	
(5a)	n.d.	49.35 (49.35)	3.6 (3.6)	Cl 3.0 (2.7)	n.d.	2 072	1 988
				F 8.95 (8.7)			
(5b)	n.d.	51.1 (51.5)	3.6 (3.6)	Cl 2.65 (2.6)	n.d.	2 040	1 985
				F 8.7 (8.3)			
(5c) $\cdot$0.25 CH_2Cl_2	n.d.	50.85 (51.25)	3.85 (3.7)	Cl 3.7 (3.7)	n.d.	2 042	1 982
(5e) $\cdot CH_2Cl_2$	n.d.	45.95 (46.1)	3.55 (3.45)	Cl 12.05 (12.35)	n.d.	2 065	1 978
(5f)	n.d.	50.2 (50.6)	3.4 (3.6)	Cl 7.9 (7.5)	n.d.	2 060	1 982

[a] With decomposition, n.d. = not determined. [b] Calculated values in parentheses. [c] 10^{-3} mol dm^{-3} solutions in nitrobenzene at +21 °C, unless stated otherwise. [d] Nujol mulls. Bands due to ν(C≡C) were all weak or very weak in intensity. Bands due to ν(CO) were of high intensity; n.d. = not determined. [e] In acetone.



	R	X
(1a)	Me	Cl
(1b)	Me	PF_6
(1c)	*p*-tolyl	Cl
(1d)	Ph	Cl
(1e)	CH_2CH_2Ph	Cl
(1f)	C(Me)=CH_2	Cl
(1g)	*p*-tolyl	PF_6



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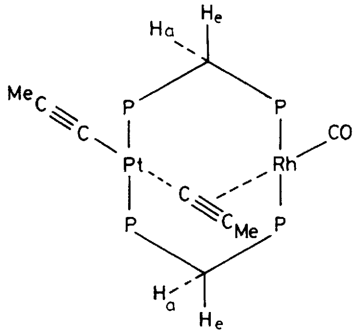


(3)

for the AA′BB′X spin system with satellites due to coupling by ^{195}Pt (data in Table 2).

The ^{1}H-{^{31}P} n.m.r. pattern showed that the molecule was fluxional. At +20 °C the resonances for both CH_2 and CH_3 were broad singlets. When the solution was cooled these resonances split and sharpened until, at or below −35 °C, the signals corresponded to the static structure **(1a)** (data in Table 3). One of the CH_3 resonances showed satellites due to coupling with ^{195}Pt, $^4J(PtC{\equiv}CCH_3)$ = 16 Hz, but the other (at δ = 0.8 p.p.m.) showed no resolved coupling to ^{195}Pt; it was, however, broad ($w_{\frac{1}{2}}$ *ca.* 8 Hz) possibly due to coupling to both ^{195}Pt and ^{103}Rh and we assign it to the bridging acetylide (Table 3). The CH_2 resonance had a central AB pattern with the hydrogen absorbing at low frequency being strongly coupled to ^{195}Pt, $^3J(^{195}PtPCH_2)$ = 73 Hz, whilst the other showed no coupling. We assign the ^{195}Pt-coupled hydrogen to $H_{equatorial}$ (H_e), see structure **(2)**, and the uncoupled hydrogen to H_{axial} (H_a). We have discussed this phenomenon previously for platinum–tungsten complexes of the type [(RC≡C)Pt(μ-dppm)$_2$(μ-C≡CR)W(CO)$_3$][4] and explained it in terms of torsion angles, as in the well known effect of torsion angles on $^3J(H\text{–}C\text{–}C\text{–}H)$ in organic compounds. We interpret the effect of temperature on the collapse of the H_e and H_a resonances and the merging of the two CH_3 resonances in terms of the fluxional process **(2)** $\rightleftharpoons$ **(3)**. The corresponding *p*-tolyl- **(1c)**, phenyl- **(1d)**, 2-phenylethyl- **(1e)**, and propenyl-acetylide **(1f)** complexes were made and characterized in a similar fashion to **(1a)**: see Experimental section and Tables 1—3. They showed a similar fluxional behaviour, as evidenced by the ^{1}H-{^{31}P} n.m.r. spectra at different temperatures (Table 3). The ^{195}Pt-{^{1}H} n.m.r. spectrum of complex **(1c)** is shown in Figure 2 and shows a rhodium–platinum coupling, *J*(PtRh), of 63 Hz.

When the orange complex **(1c)** was heated in toluene for 3 h it was converted into a red-brown product, which we formulate as the neutral complex **(4a)**. This formulation is based on: (*i*) elemental analysis (Table 1); (*ii*) the ^{31}P-{^{1}H} n.m.r. spectrum, which was of the AA′BB′X type with satellites due to ^{195}Pt coupling; (*iii*) the ^{1}H-{^{31}P} n.m.r. spectrum which, at 20 °C, showed two sharp resonances for the CH_3 groups and an AB pattern for the PCH_2P groups (Table 3): this indicated that there was no fluxionality in the complex suggesting a stronger acetylide–rhodium interaction than in **(1c)**; (*iv*) the i.r. spectrum which showed a band at 2 110 cm^{-1}, assigned to terminal C≡C, a

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

Complex	δ(P_A)	$^1J(PtP_A)$	δ(P_B)	$^1J(RhP_B)$	N[b]	Solvent
(1a)	+0.3	2 450	+21.1	115	42	$CDCl_3$
(1c)	+0.9	2 404	+20.4	112	40	$CDCl_3$
(1d)	+0.9	2 390	+20.40	112	41	$CDCl_3$
(1e)	+0.5	2 446	+20.5	112	39	$CDCl_3$
(1f)	+0.9	2 402	+20.4	112	42	$CDCl_3$
(4a)	−3.3	2 758	+10.3	134	17	$CDCl_3$
(4b)	−3.4	2 736	+10.5	132	19	$CDCl_3$
(5a)	+0.7	2 382	19.9	114	34	CD_2Cl_2
(5b)	+1.1	2 358	19.5	112	32	CD_2Cl_2
(5c)	+1.3	2 358	19.9	110	32	CD_2Cl_2

[a] Spectra (40.25 MHz) 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 rhodium. [b] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$.

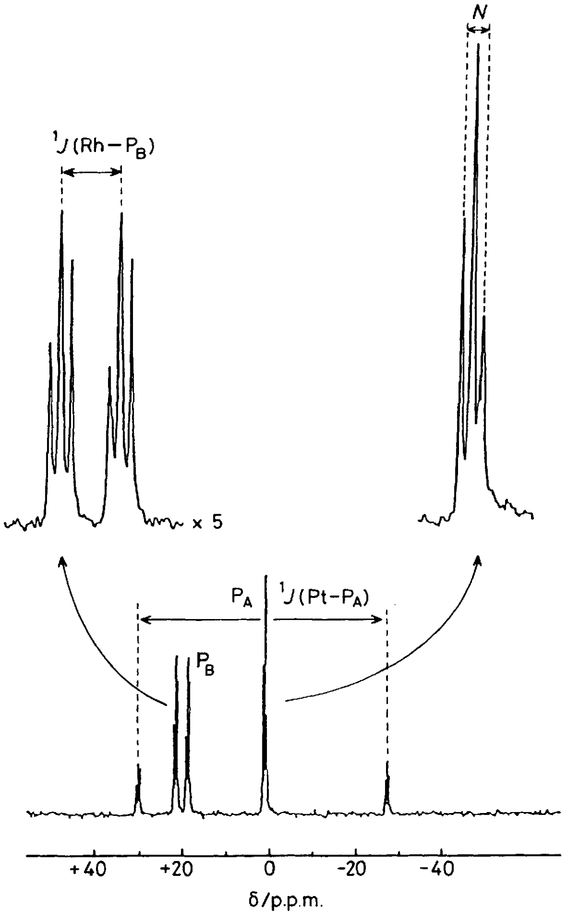


Figure 1. $^{31}P-\{^1H\}$ N.m.r. spectrum (40.25 MHz) of [(MeC≡C)Pt(μ-dppm)$_2$(σ,η-C≡CMe)Rh(CO)]Cl (**1a**) in CD_2Cl_2 at *ca.* 21 °C

weak band at 1 900 cm^{-1} tentatively assigned to bridging C≡C, and a weak band at 294 cm^{-1} assigned to ν(Rh–Cl); there was no band due to ν(CO) of the starting material; and (*v*) the complex was non-conducting in acetone solution. When [Pt(C≡CC$_6$H$_4$-Me-*p*)$_2$(dppm-*P*)$_2$] was added to a benzene solution of the labile cyclo-octene complex [$Rh_2Cl_2(C_8H_{14})_4$] the $^{31}P-\{^1H\}$ n.m.r. spectrum of the resulting dark red solution showed the presence of the platinum–rhodium complex (**4a**): the phenylacetylide analogue (**4b**) was shown to form similarly. However, in both cases, the solutions contained other homobinuclear and mononuclear species and (**4a**) or (**4b**) were not prepared pure by this method. The deep red complex (**4a**) is air sensitive, particularly in solution, and it reacts rapidly with CO in benzene solution to give the orange cationic complex (**1c**). When a benzene solution of (**4a**) was treated with SO_2 it rapidly gave a mixture of two platinum–rhodium bimetallic complexes, containing Pt(μ-dppm)$_2$Rh moieties [$^{31}P-\{^1H\}$ n.m.r. evidence] which we have not characterized.

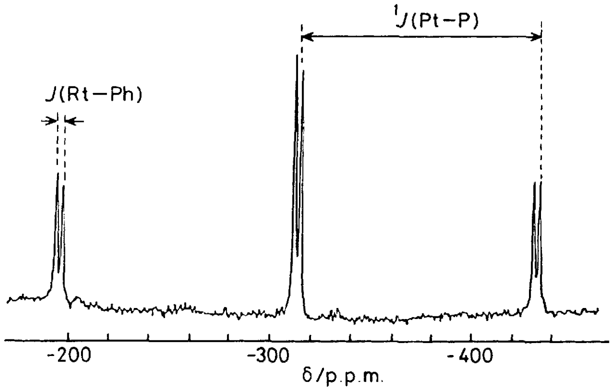
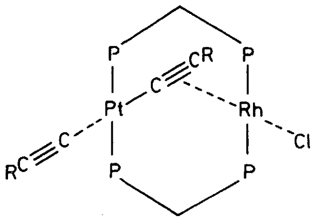


Figure 2. $^{195}Pt-\{^1H\}$ N.m.r. spectrum of [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-C≡CC$_6$H$_4$Me-*p*)Rh(CO)]Cl (**1c**) at 19.175 MHz



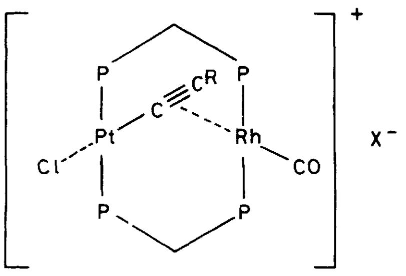
(4a) R = *p*-tolyl
(4b) R = Ph

In a $^{31}P-\{^1H\}$ n.m.r. experiment, the cationic *p*-tolylacetylide complex (**1c**) was heated in a small amount of toluene–deuteriotoluene at 110 °C (0.4 g complex in 10 cm^3 solvent). After 3 h, species were formed which had very complicated $^{31}P-\{^1H\}$ n.m.r. spectra. They might be clusters but after prolonged heating (14 h) the platinum–rhodium complex (**4a**) was essentially the only product in solution. Hence, what appears at first sight to be a simple nucleophilic displacement of CO by Cl is more complicated than this.

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

Complex	θ_c/°C	$\delta(H_e)$	$^{3}J(PtH_e)$	$\delta(H_a)$[b]	$^{2}J(H_eH_a)$	$\delta(CH_3)$	Solvent
(1a)	−35	3.81	73	4.4	12.5	1.54,[c] 0.80[d]	$CDCl_3$
(1c)	−50	3.67	76	4.4	12.0	2.15, 2.11	CD_2Cl_2
(1d)	−20	3.61	75	4.5	12.5		$CDCl_3$
(1e)[e]	−50	3.62	74	4.03	11.5		CD_2Cl_2
(1f)[f]	−50	3.65	77	not resolved		1.34	$CDCl_3$
(4a)	+21	2.85	69	3.76	13.1	2.20, 2.17	$CDCl_3$
(5a)	+21	3.51	*ca.* 89	4.29	13.1	0.96[g]	CD_2Cl_2
(5b)	+21	3.68	*ca.* 87	4.28	13.4	—	CD_2Cl_2
(5c)	+21	3.46	*ca.* 88	4.28	13.2	2.21	CD_2Cl_2

[a] Spectra measured at 100 MHz. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$ and coupling constants (*J*) in Hz (±0.1). [b] In each case $^{3}J(PtH_a)$ was not resolved but was less than 8 Hz. [c] $^{4}J(PtCH_3)$ = 16 Hz (terminal $C{\equiv}CCH_3$). [d] Broad signal, $w_{\frac{1}{2}}$ 8 Hz, possibly due to both Rh–H and Pt–H coupling. [e] $\delta(CH_2CH_2)$ *ca.* 2.2 p.p.m., broad. [f] $\delta(C{=}CH_2)$ 4.65 and 4.39. [g] $^{4}J(PtCH_3)$ = 16 Hz, $^{4}J(RhCH_3)$ = 1.2 Hz.



	R	X
(5a)	Me	PF_6
(5b)	Ph	PF_6
(5c)	*p*-tolyl	PF_6
(5d)	Ph	$AgCl_2$
(5e)	Me	$AgCl_2$
(5f)	*p*-tolyl	$AgCl_2$

Synthesis or Formation of Platinum–Rhodium Complexes by Transmetallation.—Treatment of the previously described and readily made platinum–mercury complex $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2HgCl_2]$[2] with $[Rh_2Cl_2(CO)_4]$ in $CDCl_3$ caused immediate and complete conversion into $[(PhC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}\eta\text{-}C{\equiv}CPh)Rh(CO)]^+$, as evidenced by the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the solution. We also isolated $[(PhC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}\eta\text{-}C{\equiv}CPh)Rh(CO)]Cl$ in 71% overall yields in a 'one-pot' synthesis from $[Pt(dppm\text{-}PP')_2]Cl_2$, *viz.* treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ with $Hg(O_2CMe)_2$–$PhC{\equiv}CH$ in dichloromethane {which, as shown previously, caused complete conversion into $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2HgCl_2]$},[2] followed by addition of $[Rh_2Cl_2(CO)_4]$ and isolation (see Experimental section). The yield, as evidenced by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy on the reaction solution, was virtually 100% and the lower yield of pure material isolated in the preparative experiment (71%) is mainly a reflection of the small scale on which the reaction was carried out.

We have similarly prepared $[(PhC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CPh)Rh(CO)]^+$ by displacing other d^{10} metals *viz.* Ag^I, Cu^I, or Au^I from their known complexes. Treatment of the previously described and readily made platinum–silver complex $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$[2] with the equivalent amount of $[Rh_2Cl_2(CO)_4]$, in dichloromethane at 20 °C, caused immediate precipitation of silver chloride and the formation of the desired platinum–rhodium complex **(1d)**, characterized by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy: no other phosphorus-containing product was produced, *i.e.* the conversion appeared to be essentially quantitative, although the product was not isolated. Similar treatment of $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2CuI]$ or $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Au]Cl$ in dichloromethane solution with $[Rh_2Cl_2(CO)_4]$ caused complete displacement of the d^{10} metal with formation of the platinum–rhodium complex **(1d)**.

We have shown previously that treatment of $[Pt(dppm\text{-}PP')_2]Cl_2$ with AgO_2CMe–$RC{\equiv}CH$, using a 1:1 mol ratio of the silver and platinum complexes, gave platinum–silver monoacetylide complexes $[(RC{\equiv}C)ClPt(\mu\text{-}dppm)_2AgCl]$ in excellent yields.[3] It was clearly of interest to see if one could displace the silver by rhodium(I) in such complexes by transmetallation.

When an acetone suspension of $[Cl(MeC{\equiv}C)Pt(\mu\text{-}dppm)_2AgCl]$ was treated with the equivalent amount of $[Rh_2Cl_2(CO)_4]$ there was immediate formation of an orange solution. $^{31}P-\{^{1}H\}$ N.m.r. studies established the formation of a platinum–rhodium complex cation, $[ClPt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CMe)Rh(CO)]^+$, but the silver stayed in solution, almost certainly as the counter ion $[AgCl_2]^-$. Addition of an excess of NH_4PF_6 caused immediate precipitation of AgCl and the salt $[ClPt(\mu\text{-}dppm)_2(\sigma,\eta\text{-}C{\equiv}CMe)Rh(CO)]PF_6$ was readily isolated. The crystal structure has been determined and shown to be **(5a)** (see below). Characterizing data include elemental analyses (C, H, Cl, and F) (Table 1) and the $^{31}P-\{^{1}H\}$ n.m.r. spectrum (data in Table 2), typical of a complex containing a $Pt(\mu\text{-}dppm)_2Rh$ moiety. The $^{1}H-\{^{31}P\}$ n.m.r. spectrum (100 MHz, data in Table 3) showed that the PCH_2P protons are non-equivalent at room temperature, in contrast with **(1b)**; one of them (H_e) shows coupling to ^{195}Pt (89 Hz) and even to ^{103}Rh (1.5 Hz) whilst the other (H_a) does not show detectable coupling to ^{195}Pt or ^{103}Rh. The same couplings were observed at 360 MHz at which frequency the AB quartet for the PCH_2P protons was better separated. In the i.r. spectrum there were bands at 2 072 ν(C≡C), 1 988 ν(C≡O), 842 ν(P–F), and 320 cm^{-1} ν(Pt–Cl).

Similar treatment of $[Cl(PhC{\equiv}C)Pt(\mu\text{-}dppm)_2AgCl]$ with $[Rh_2Cl_2(CO)_4]$, followed by NH_4PF_6, gave the corresponding phenylacetylide complex **(5b)** (83% yield); details in the Experimental section, characterizing data in Tables 1—3. The *p*-tolylacetylide analogue **(5c)** was prepared similarly.

We found that treatment of $[Cl(RC{\equiv}C)Pt(\mu\text{-}dppm)_2AgCl]$ (R = Me, Ph, or *p*-tolyl) with $[Rh_2Cl_2(CO)_4]$ gave salts in high yield which had identical ^{31}P or ^{1}H n.m.r. parameters to the PF_6^- salts **(5a)**—**(5c)** and appeared to have $[AgCl_2]^-$ as the counter ion. We formulate them therefore as **(5d)**—**(5f)**. Preparative details are in the Experimental section and elemental analytical data (C, H, and Cl only) in Table 1. Moreover, treatment of these salts in acetone with an excess of NH_4PF_6 converted them into the corresponding PF_6 salts **(5a)**—**(5c)** in good (*ca.* 70%) yield, with precipitation of silver chloride.

Table 4. Selected interatomic distances (Å) and angles (°) for complexes (**1b**) and (**5a**) with estimated standard deviations (e.s.d.s) in parentheses

		(**5a**)	
	(**1b**)	Molecule A	Molecule B
Pt • • • Rh	3.099(2)	3.066(2)	3.086(2)
P(1) • • • P(2)	3.10(1)	3.08(1)	3.09(1)
P(3) • • • P(4)	3.09(1)	3.06(1)	3.10(1)
Pt–P(1)	2.296(6)	2.354(7)	2.355(6)
Pt–P(3)	2.317(6)	2.273(6)	2.266(7)
Pt–C(4)	2.01(2)	1.95(2)	1.94(2)
C(4)–C(5)	1.16(2)	1.21(3)	1.23(3)
C(5)–Me(1)	1.58(3)	1.48(4)	1.51(4)
Pt–C(6)	1.96(2)	—	—
C(6)–C(7)	1.13(3)	—	—
C(7)–Me(2)	1.53(5)	—	—
Pt–Cl	—	2.379(7)	2.327(7)
Rh–P(2)	2.322(6)	2.327(7)	2.325(7)
Rh–P(4)	2.301(6)	2.313(7)	2.316(7)
Rh–C(4)	2.22(2)	2.22(2)	2.29(2)
Rh–C(5)	2.40(2)	2.46(3)	2.46(2)
Rh–C(3)	1.76(2)	1.79(4)	1.80(3)
C(3)–O	1.19(2)	1.17(4)	1.13(4)
P–CH$_2$	1.85(2)—1.88(2)	1.80(2)—1.86(2)	1.84(2)—1.87(2)
P–C$_6$H$_5$	1.79(1)—1.86(1)	1.79(2)—1.84(2)	1.77(1)—1.85(2)
P–F	1.43(4)—1.60(4)	1.54(2)—1.58(2)	1.51(2)—1.59(2)
C(8)–Cl(1)	1.50(5)	—	—
C(8)–Cl(2)	1.69(6)	—	—
P(1)–Pt–P(3)	177.4(2)	177.2(2)	173.7(2)
P(1)–Pt–C(4)	88.1(6)	87.8(6)	84.9(6)
P(3)–Pt–C(4)	90.5(6)	89.4(6)	89.5(6)
C(4)–Pt–C(6)	172.7(8)	—	—
P(1)–Pt–C(6)	90.6(6)	—	—
P(3)–Pt–C(6)	90.5(6)	—	—
C(4)–Pt–Cl	—	175.7(6)	171.8(6)
P(1)–Pt–Cl	—	89.5(2)	91.4(2)
P(3)–Pt–Cl	—	93.4(2)	93.8(2)
Rh • • • Pt–Cl	—	137.2(2)	139.5(2)
Rh • • • Pt–C(6)	141.4(6)	—	—
Rh • • • Pt–P(1)	90.9(2)	88.1(1)	88.6(1)
Rh • • • Pt–P(3)	89.7(1)	89.8(2)	89.6(1)
Rh • • • Pt–C(4)	45.8(5)	46.1(6)	47.8(6)
Pt–C(4)–C(5)	178(2)	177(2)	176(2)
Pt–C(4)–Rh	94.0(7)	94.5(9)	93.2(8)
C(4)–C(5)–Me(1)	172(2)	166(3)	165(2)
C(4)–C(5)–Rh	67(1)	64(2)	67(1)
Pt–C(6)–C(7)	175(2)	—	—
C(6)–C(7)–Me(2)	177(3)	—	—
P(2)–Rh–P(4)	175.0(2)	169.7(2)	168.2(2)
P(2)–Rh–C(3)	93.2(7)	92(1)	93(1)
P(4)–Rh–C(3)	90.4(7)	93(1)	94(1)
Pt • • • Rh–P(2)	89.1(1)	92.2(2)	91.5(2)
Pt • • • Rh–P(4)	89.9(1)	90.0(2)	90.5(2)
Pt • • • Rh–C(4)	40.3(5)	39.4(5)	39.0(5)
Pt • • • Rh–C(5)	69.0(5)	68.6(6)	68.6(5)
Pt • • • Rh–C(3)	144.0(7)	138(1)	134(1)
C(4)–Rh–P(2)	88.1(5)	87.4(6)	88.2(5)
C(4)–Rh–P(4)	88.0(5)	87.8(6)	86.1(5)
C(5)–Rh–P(2)	88.2(6)	83.2(6)	85.0(6)
C(5)–Rh–P(4)	86.9(6)	88.2(6)	84.9(6)
C(4)–Rh–C(3)	175.5(8)	177(1)	172(1)
C(5)–Rh–C(3)	147.0(8)	154(1)	158(1)
Rh–C(3)–O	177(2)	178(4)	176(3)
P(1)–C(1)–P(2)	112(1)	115(1)	112(1)
P(3)–C(2)–P(4)	112(1)	113(1)	114(1)
M–P–CH$_2$	112.1(7)—114.5(7)	112.2(8)—113.9(8)	112.0(7)—114.7(7)
F–P–F (*trans*)	161(2)—177(2)	176(1)—178(1)	171(1)—178(1)
F–P–F (*cis*)	78(2)—110(2)	85(1)—94(1)	84(1)—95(1)
Cl(1)–C(8)–Cl(2)	110(4)	—	—

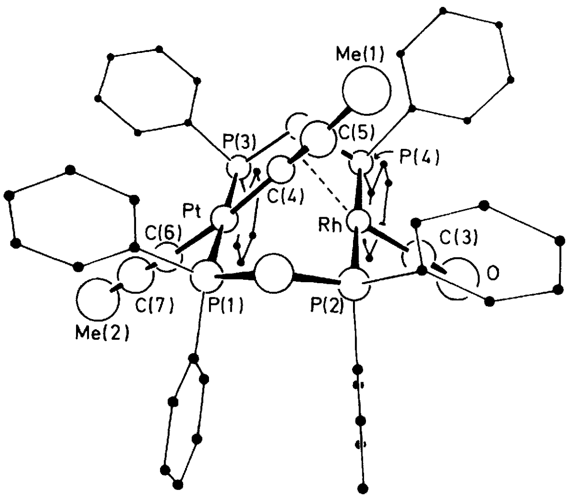


Figure 3. Molecular structure of the $[(\mathrm{MeC{\equiv}C})\mathrm{Pt}(\mu\text{-dppm})_2(\sigma,\eta\text{-C{\equiv}CMe})\mathrm{Rh(CO)}]^+$ cation of (**1b**) showing the principal atomic numbering. Atoms are represented by spheres of arbitrary size

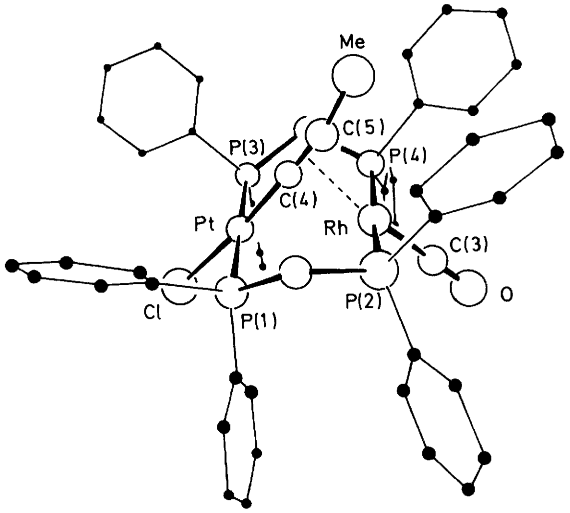
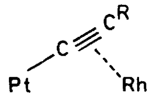


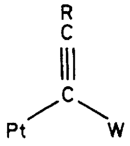
Figure 4. Molecular structure of the $[\mathrm{ClPt}(\mu\text{-dppm})_2(\mu,\eta\text{-C{\equiv}CMe})\mathrm{Rh(CO)}]^+$ cation of (**5a**) showing the principal atomic numbering. Atoms are represented by spheres of arbitrary size and only cation A is depicted

Crystal Structures of $[(\mathrm{MeC{\equiv}C})\mathrm{Pt}(\mu\text{-dppm})_2(\sigma,\eta\text{-C{\equiv}CMe})\mathrm{Rh(CO)}]\mathrm{PF}_6$ (**1b**) *and* $[\mathrm{ClPt}(\mu\text{-dppm})_2(\sigma,\eta\text{-C{\equiv}CMe})\mathrm{Rh(CO)}]\mathrm{PF}_6$ (**5a**).—The salt (**1b**) crystallized with one cation, one anion, and one molecule of dichloromethane in the asymmetric unit. The asymmetric unit in crystals of (**5a**) comprises two virtually identical cations and two anions and thus the parameters are given in duplicate. There are no unusually short contacts between the cations, anions, or solvent molecule in either structure. The geometry of the PF_6^- anions is as expected (see Table 4) but less well defined in the case of (**1b**), where the fluorine atoms undergo very high thermal vibrations, suggesting that they may be involved in some kind of disorder or that refinement with anisotropic thermal parameters would have been desirable. The $\mathrm{CH_2Cl_2}$ solvent molecule in (**1b**) also exhibits large thermal vibrations but is adequately defined (see Table 4).

The heterobimetallic cations are depicted in Figures 3 and 4 while Table 4 summarizes the results of the *X*-ray diffraction measurements. In each structure the metal centres are linked by two *trans*-dppm bridges to give an eight-membered $\mathrm{PtP_4C_2Rh}$ ring in the 'boat' conformation. The Pt $\cdots$ Rh distance (*ca.* 3.1 Å) is substantially longer than that generally accepted for a Pt–Rh bond (2.6—2.8 Å)[7-9] and no significant metal–metal interaction is proposed. Instead, the square-planar co-ordination about the rhodium atom is completed by interaction with the methylacetylide group which is σ-bonded to Pt and which bridges the metals to form an unsymmetrical side-on π bond to Rh. The square-planar co-ordination geometry about each metal centre therefore results in an 'A-frame' type of structure (see Figures 3 and 4), with the methylene linkages of the dppm groups folded towards the apex of the 'A-frame,' as is commonly observed in these systems.[4,10] This allows the bulky phenyl rings to avoid unfavourable contacts with the bridging entity.



(**6**)



(**7**)

The acetylenic carbon to rhodium distances [Rh–C(4) and Rh–C(5) 2.24 and 2.44 Å respectively] are significantly longer than Rh–C distances found in mononuclear or binuclear rhodium–acetylene compounds (usually 2.02—2.13 Å)[11,12] and indicate, at most, weak rhodium–acetylene interaction. However, our observation of magnetic coupling of the methyl-group protons to ^{103}Rh in the ^{1}H-{^{1}P} spectrum of complex (**5a**) (see above) is evidence for some bonding interaction between the rhodium and the acetylene. The errors are such that one cannot draw definite conclusions about the C≡C bond lengths, although the values of 1.16(2) and 1.13(3) Å for (**1b**) do not seem to be greater than the accepted values for unco-ordinated (free) acetylenes.[13,14] The deviations from linearity of the η^2-bridging PtC≡CMe groups towards *cis*-bent configurations are small (Table 4) but nevertheless evident for (**5a**), *e.g.* the values of C(4)–C(5)–Me(1) for (**5a**) are 14(3) and 15(2)°, but barely evident for (**1b**) [8(2)°]. Thus the evidence from the crystal structure determinations is that the rhodium–acetylene interactions are weak.

The present structures, containing an unsymmetrical μ-η^2 bridge (σ,η bridge) [as in (**6**)], provide an interesting contrast to the (unsymmetrically) μ-σ-bridged structure (**7**) recently reported by us in the *X*-ray analysis of $[(p\text{-MeC}_6\mathrm{H_4C{\equiv}C})\mathrm{Pt}(\mu\text{-dppm})_2(\mu\text{-C{\equiv}CC}_6\mathrm{H_4Me}\text{-}p)\mathrm{W(CO)_3}]$,[4] where the C≡C vector of the bridging alkynyl group is perpendicular to the $\mathrm{PtP_4W}$ plane, *i.e.* with no π interaction of the C≡C acetylenic linkage with the tungsten atom. The factors controlling the particular mode of bonding in each case, *viz.* σ,η or μ-η^2 (**6**) *vs.* μ-σ (**7**), are not readily apparent, but as the steric requirements around the metals are similar we presume electronic factors play a role but cannot suggest what these are. Interestingly, the metal–metal distances in both types of complex are very similar, as are the C≡C distances. It is also not obvious, in the molecular structure of complex (**5a**), why the acetylide group, rather than the chloride, bridges the metal centres. We note a significant difference in the Pt–P bond lengths in the structure of (**5a**) but are unable to offer an explanation. The remaining parameters, summarized in Table 4, are unremarkable.

Experimental

General methods were the same as those described in previous papers from this laboratory.[15]

Table 5. Fractional atomic co-ordinates for complex (**1b**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.225 93(4)	0.510 09(3)	0.598 59(4)	C(44)	0.208 0(8)	0.676 6(6)	0.287 3(7)
Rh	0.233 08(7)	0.506 42(5)	0.454 45(7)	C(45)	0.173 6(8)	0.680 6(6)	0.344 3(7)
P(1)	0.272 3(3)	0.587 4(2)	0.598 9(3)	C(46)	0.196 0(8)	0.653 3(6)	0.395 3(7)
P(2)	0.283 1(3)	0.583 7(2)	0.454 8(3)	C(51)	0.110 7(7)	0.427 9(6)	0.660 4(6)
P(3)	0.174 1(3)	0.433 6(2)	0.599 2(2)	C(52)	0.055 3(7)	0.395 1(6)	0.656 4(6)
P(4)	0.174 2(3)	0.433 2(2)	0.455 2(2)	C(53)	0.007 3(7)	0.391 9(6)	0.705 0(6)
C(1)	0.257 3(11)	0.620 7(8)	0.523 7(10)	C(54)	0.014 7(7)	0.421 4(6)	0.757 5(6)
C(2)	0.122 7(10)	0.422 0(8)	0.526 4(9)	C(55)	0.070 1(7)	0.454 2(6)	0.761 5(6)
C(3)	0.283 7(11)	0.486 5(9)	0.390 7(10)	C(56)	0.118 1(7)	0.457 5(6)	0.712 9(6)
O	0.318 7(9)	0.471 6(6)	0.349 3(8)	C(61)	0.227 8(7)	0.378 9(5)	0.606 3(7)
C(4)	0.162 2(9)	0.531 7(7)	0.529 8(9)	C(62)	0.298 6(7)	0.383 1(5)	0.619 6(7)
C(5)	0.126 5(11)	0.543 4(9)	0.488 8(10)	C(63)	0.339 3(7)	0.341 2(5)	0.625 7(7)
Me(1)	0.074 7(15)	0.565 7(12)	0.438 8(14)	C(64)	0.309 2(7)	0.295 1(5)	0.618 6(7)
C(6)	0.280 1(10)	0.493 1(8)	0.673 1(9)	C(65)	0.238 4(7)	0.290 9(5)	0.605 4(7)
C(7)	0.306 9(14)	0.481 7(10)	0.717 9(13)	C(66)	0.197 7(7)	0.332 9(5)	0.599 2(7)
Me(2)	0.347 0(26)	0.467 0(18)	0.776 4(22)	C(71)	0.226 2(7)	0.376 5(5)	0.446 0(7)
C(11)	0.225 4(8)	0.623 7(6)	0.654 8(7)	C(72)	0.297 8(7)	0.376 8(5)	0.456 8(7)
C(12)	0.167 3(8)	0.651 9(6)	0.639 4(7)	C(73)	0.335 8(7)	0.333 5(5)	0.452 7(7)
C(13)	0.131 7(8)	0.677 4(6)	0.685 8(7)	C(74)	0.302 1(7)	0.289 8(5)	0.437 8(7)
C(14)	0.154 2(8)	0.674 7(6)	0.747 5(7)	C(75)	0.230 5(7)	0.289 6(5)	0.427 0(7)
C(15)	0.212 3(8)	0.646 6(6)	0.762 8(7)	C(76)	0.192 6(7)	0.332 9(5)	0.431 1(7)
C(16)	0.247 9(8)	0.621 1(6)	0.716 5(7)	C(81)	0.104 9(7)	0.431 1(6)	0.395 0(6)
C(21)	0.363 2(6)	0.597 0(7)	0.613 5(7)	C(82)	0.035 0(7)	0.439 8(6)	0.408 7(6)
C(22)	0.409 9(6)	0.558 0(7)	0.616 4(7)	C(83)	−0.014 9(7)	0.436 9(6)	0.361 6(6)
C(23)	0.480 8(6)	0.566 9(7)	0.625 1(7)	C(84)	0.005 1(7)	0.425 4(6)	0.300 9(6)
C(24)	0.504 9(6)	0.614 8(7)	0.630 9(7)	C(85)	0.075 0(7)	0.416 8(6)	0.287 2(6)
C(25)	0.458 2(6)	0.653 8(7)	0.628 0(7)	C(86)	0.124 9(7)	0.419 6(6)	0.334 3(6)
C(26)	0.387 4(6)	0.644 9(7)	0.619 3(7)	P(5)	0.484 7(4)	0.213 1(3)	0.500 1(4)
C(31)	0.377 5(5)	0.588 9(6)	0.450 9(7)	F(1)	0.555 9(17)	0.241 0(12)	0.497 1(13)
C(32)	0.418 8(5)	0.547 1(6)	0.454 9(7)	F(2)	0.410 8(12)	0.187 7(9)	0.502 9(10)
C(33)	0.491 1(5)	0.551 2(6)	0.453 9(7)	F(3)	0.460 2(12)	0.252 9(9)	0.459 1(10)
C(34)	0.522 2(5)	0.597 1(6)	0.449 0(7)	F(4)	0.511 1(21)	0.183 6(17)	0.554 6(19)
C(35)	0.480 9(5)	0.639 0(6)	0.445 1(7)	F(5)	0.526 6(18)	0.179 9(14)	0.465 2(14)
C(36)	0.408 5(5)	0.634 9(6)	0.446 0(7)	F(6)	0.459 8(20)	0.249 3(15)	0.554 0(19)
C(41)	0.253 0(8)	0.622 0(6)	0.389 4(7)	C(8)	0.062 0(33)	0.242 0(21)	0.307 9(24)
C(42)	0.287 4(8)	0.618 0(6)	0.332 4(7)	Cl(1)	0.001 1(14)	0.232 1(9)	0.266 2(16)
C(43)	0.264 9(8)	0.645 3(6)	0.281 4(7)	Cl(2)	0.128 5(17)	0.265 1(11)	0.265 9(14)

Preparations.—[(PhC≡C)Pt(μ-dppm)$_2$(σ,η-C≡CPh)Rh(CO)]Cl (**1d**). The complex [Rh$_2$Cl$_2$(CO)$_4$] (0.075 g, 0.195 mmol) was added to a solution of *trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] (0.460 g, 0.39 mmol) in deoxygenated benzene (25 cm^3). Immediately, there was effervescence and an orange solution formed; after 15 s an orange solid began to separate. The mixture was allowed to stand for 3 h and the required product filtered off, washed with benzene, and dried *in vacuo*. Yield 0.462 g, 89%. Complexes (**1a**), (**1c**), (**1e**), and (**1f**) were prepared similarly in yields of 92, 96, 88, and 95% respectively.

[(PhCH$_2$CH$_2$C≡C)Pt(μ-dppm)$_2$(μ-σ,η-C≡CCH$_2$CH$_2$Ph)-Rh(CO)]Cl (**1e**) *using trans*-[RhCl(CO)(AsPh$_3$)$_2$]. A solution of *trans*-[RhCl(CO)(AsPh$_3$)$_2$] (0.51 g, 0.65 mmol) in benzene (6 cm^3) was added to a solution of [Pt(C≡CCH$_2$CH$_2$Ph)$_2$-(dppm-*P*)$_2$] (0.70 g, 0.64 mmol) in warm benzene (10 cm^3). The solution immediately turned red and, after cooling the solution to *ca.* 20 °C, the required product separated and was recovered as before. Yield 0.68 g, 76%. Complex (**1f**) was made similarly in 77% yield.

[(MeC≡C)Pt(μ-dppm)$_2$(μ-σ,η-C≡CMe)Rh(CO)]PF$_6$ (**1b**). A solution of NH$_4$PF$_6$ (0.10 g, 0.61 mmol) in ethanol (10 cm^3) was filtered into a solution of complex (**1a**) (0.080 g, 0.07 mmol) in ethanol (10 cm^3). The solvent was allowed to evaporate slowly to give the required product as deep orange rhombs. Yield 0.080 g, 92 %. Complex (**1g**) was made similarly in 91% yield.

[(*p*-MeC$_6$H$_4$C≡C)Pt(μ-dppm)$_2$(μ-σ,η-C≡CC$_6$H$_4$Me-*p*)-RhCl] (**4a**). A suspension of complex (**1c**) (0.180 g, 0.132 mmol) in toluene (20 cm^3) was heated under reflux in argon for 3 h, to give a dark red, air-sensitive, solution. The solvent was removed under reduced pressure and the residue triturated with n-pentane. This gave the required product as dark red microcrystals. Yield 0.16 g, 91%.

Transmetallations.—Complex (**1d**) *in a 'one-pot' synthesis* via *the mercury–platinum complex.* Phenylacetylene (32 μl, 0.29 mmol) was added to a slurry of mercury(II) acetate (46 mg, 0.145 mmol) in dichloromethane (5 cm^3). A solution of [Pt(dppm-*PP*′)$_2$]Cl$_2$ (100 mg, 0.097 mmol) in dichloromethane (5 cm^3) was then added. The resultant solution was put aside for 10 min before a solution of [Rh$_2$Cl$_2$(CO)$_4$] (18.8 mg, 0.048 mmol) in dichloromethane (*ca.* 1 cm^3) was added. The resultant red solution was evaporated under reduced pressure and the residue recrystallized from dichloromethane–benzene to give the required product (yield 93 mg, 71%), identified by its ^{31}P-{^{1}H} n.m.r. spectrum.

[ClPt(μ-dppm)$_2$(μ-σ,η-C≡CPh)Rh(CO)]PF$_6$ (**5b**) *from the platinum–silver complex.* A solution of [Rh$_2$Cl$_2$(CO)$_4$] (39.7 mg, 0.102 mmol) in acetone (5 cm^3) was added at room temperature with stirring to a suspension of [Cl(PhC≡C)Pt(μ-dppm)$_2$AgCl] (254 mg, 0.204 mmol) in acetone (30 cm^3). A deep yellow-orange solution formed. After 10 min a solution of NH$_4$PF$_6$ (330 mg, 2.04 mmol) in acetone (5 cm^3) was added. An immediate white precipitate of silver chloride formed (the flask was protected from light). After a further 30 min the AgCl was

Table 6. Fractional atomic co-ordinates for complex (**5a**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule A				Molecule B			
Pt	0.201 25(2)	0*	0.139 92(9)	Pt	−0.042 36(2)	−0.424 96(5)	0.110 62(8)
Rh	0.263 04(4)	−0.018 84(8)	0.278 56(17)	Rh	0.019 61(4)	−0.400 84(9)	0.247 20(19)
Cl	0.154 9(2)	0.047 3(2)	0.182 7(7)	Cl	−0.088 7(1)	−0.468 1(2)	0.153 4(6)
P(1)	0.222 6(1)	0.077 5(2)	0.047 6(6)	P(1)	−0.061 7(1)	−0.344 6(2)	0.195 8(6)
P(2)	0.285 9(1)	0.052 7(2)	0.171 3(6)	P(2)	0.000 3(1)	−0.322 3(2)	0.334 8(6)
P(3)	0.182 9(1)	−0.076 9(2)	0.226 8(6)	P(3)	−0.020 7(1)	−0.496 7(2)	0.012 8(4)
P(4)	0.245 0(1)	−0.099 1(2)	0.357 7(6)	P(4)	0.043 4(1)	−0.467 7(2)	0.127 9(6)
C(1)	0.264 6(3)	0.074 7(8)	0.026 3(18)	C(1)	−0.031 7(4)	−0.294 1(8)	0.236 7(19)
C(2)	0.212 5(4)	−0.125 5(9)	0.257 9(22)	C(2)	0.021 1(3)	−0.487 1(7)	−0.017 9(18)
C(3)	0.280 7(7)	−0.002 0(16)	0.431 9(36)	C(3)	0.036 5(6)	−0.421 5(13)	0.400 9(29)
O	0.292 4(4)	0.007 7(9)	0.533 2(24)	O	0.048 9(6)	−0.434 3(11)	0.492 9(27)
C(4)	0.239 1(4)	−0.036 8(7)	0.091 2(20)	C(4)	−0.007 0(3)	−0.382 5(7)	0.058 0(19)
C(5)	0.262 8(6)	−0.057 9(9)	0.056 3(27)	C(5)	0.015 6(4)	−0.354 9(9)	0.033 7(24)
Me	0.286 8(7)	−0.091 2(14)	−0.006 2(36)	Me	0.038 8(6)	−0.317 7(11)	−0.028 3(27)
C(11)	0.209 2(2)	0.088 6(6)	−0.119 6(12)	C(11)	−0.085 1(2)	−0.311 8(6)	0.078 2(12)
C(12)	0.177 5(2)	0.091 5(6)	−0.140 4(12)	C(12)	−0.108 6(2)	−0.340 6(6)	0.018 0(12)
C(13)	0.166 0(2)	0.099 7(6)	−0.267 0(12)	C(13)	−0.127 7(2)	−0.316 2(6)	−0.074 3(12)
C(14)	0.186 3(2)	0.104 9(6)	−0.372 8(12)	C(14)	−0.123 3(2)	−0.262 9(6)	−0.106 3(12)
C(15)	0.218 0(2)	0.102 0(6)	−0.352 0(12)	C(15)	−0.099 7(2)	−0.234 0(6)	−0.046 1(12)
C(16)	0.229 5(2)	0.093 8(6)	−0.225 4(12)	C(16)	−0.080 6(2)	−0.258 4(6)	0.046 1(12)
C(21)	0.215 9(2)	0.139 6(4)	0.132 1(13)	C(21)	−0.085 3(2)	−0.346 3(6)	0.345 5(12)
C(22)	0.208 1(2)	0.139 4(4)	0.265 2(13)	C(22)	−0.101 4(2)	−0.300 4(6)	0.380 0(12)
C(23)	0.204 3(2)	0.187 3(4)	0.332 3(13)	C(23)	−0.118 8(2)	−0.299 3(6)	0.495 2(12)
C(24)	0.208 3(2)	0.235 4(4)	0.266 3(13)	C(24)	−0.120 2(2)	−0.344 0(6)	0.575 9(12)
C(25)	0.216 1(2)	0.235 6(4)	0.133 1(13)	C(25)	−0.104 1(2)	−0.389 9(6)	0.541 4(12)
C(26)	0.219 9(2)	0.187 7(4)	0.066 0(13)	C(26)	−0.086 6(2)	−0.391 0(6)	0.426 2(12)
C(31)	0.321 8(2)	0.031 9(6)	0.099 6(19)	C(31)	0.028 6(3)	−0.267 6(6)	0.320 0(18)
C(32)	0.339 5(2)	−0.001 0(6)	0.179 8(19)	C(32)	0.020 6(3)	−0.214 9(6)	0.295 2(18)
C(33)	0.367 5(2)	−0.021 2(6)	0.133 7(19)	C(33)	0.043 5(3)	−0.176 2(6)	0.285 0(18)
C(34)	0.377 7(2)	−0.008 4(6)	0.007 4(19)	C(34)	0.074 4(3)	−0.190 2(6)	0.299 6(18)
C(35)	0.359 9(2)	0.024 6(6)	−0.072 8(19)	C(35)	0.082 4(3)	−0.242 9(6)	0.324 4(18)
C(36)	0.331 9(2)	0.044 7(6)	−0.026 7(19)	C(36)	0.059 5(3)	−0.281 6(6)	0.334 6(18)
C(41)	0.293 9(3)	0.114 0(6)	0.255 8(16)	C(41)	−0.013 7(2)	−0.318 7(6)	0.503 5(12)
C(42)	0.278 8(3)	0.125 0(6)	0.373 8(16)	C(42)	−0.018 3(2)	−0.365 7(6)	0.573 2(12)
C(43)	0.284 0(3)	0.173 1(6)	0.438 4(16)	C(43)	−0.030 4(2)	−0.364 1(6)	0.700 2(12)
C(44)	0.304 4(3)	0.210 1(6)	0.384 9(16)	C(44)	−0.038 0(2)	−0.315 5(6)	0.757 5(12)
C(45)	0.319 6(3)	0.199 0(6)	0.267 0(16)	C(45)	−0.033 4(2)	−0.268 4(6)	0.687 7(12)
C(46)	0.314 3(3)	0.151 0(6)	0.202 4(16)	C(46)	−0.021 2(2)	−0.270 0(6)	0.560 7(12)
C(51)	0.156 7(2)	−0.110 5(6)	0.110 6(13)	C(51)	−0.035 4(2)	−0.507 7(6)	−0.153 7(12)
C(52)	0.134 4(2)	−0.080 3(6)	0.045 8(13)	C(52)	−0.067 3(2)	−0.508 9(6)	−0.169 0(12)
C(53)	0.112 7(2)	−0.105 1(6)	−0.034 6(13)	C(53)	−0.080 1(2)	−0.517 3(6)	−0.293 2(12)
C(54)	0.113 3(2)	−0.160 2(6)	−0.050 3(13)	C(54)	−0.061 0(2)	−0.524 4(6)	−0.402 1(12)
C(55)	0.135 6(2)	−0.190 4(6)	0.014 4(13)	C(55)	−0.029 0(2)	−0.523 2(6)	−0.386 7(12)
C(56)	0.157 3(2)	−0.165 6(6)	0.094 9(13)	C(56)	−0.016 2(2)	−0.514 8(6)	−0.262 5(12)
C(61)	0.160 9(2)	−0.072 4(6)	0.378 6(12)	C(61)	−0.025 0(2)	−0.559 1(4)	0.098 2(14)
C(62)	0.146 5(2)	−0.118 3(6)	0.424 7(12)	C(62)	−0.037 2(2)	−0.562 6(4)	0.224 8(14)
C(63)	0.130 4(2)	−0.117 3(6)	0.543 5(12)	C(63)	−0.039 2(2)	−0.611 8(4)	0.287 4(14)
C(64)	0.128 7(2)	−0.070 4(6)	0.616 2(12)	C(64)	−0.028 9(2)	−0.657 5(4)	0.223 4(14)
C(65)	0.143 1(2)	−0.024 5(6)	0.570 0(12)	C(65)	−0.016 7(2)	−0.654 0(4)	0.096 7(14)
C(66)	0.159 2(2)	−0.025 5(6)	0.451 2(12)	C(66)	−0.014 7(2)	−0.604 8(4)	0.034 1(14)
C(71)	0.276 1(2)	−0.148 1(6)	0.334 1(17)	C(71)	0.078 0(2)	−0.439 3(6)	0.055 1(18)
C(72)	0.270 5(2)	−0.197 3(6)	0.275 6(17)	C(72)	0.098 3(2)	−0.413 9(6)	0.141 0(18)
C(73)	0.294 6(2)	−0.233 2(6)	0.257 6(17)	C(73)	0.125 1(2)	−0.390 3(6)	0.092 7(18)
C(74)	0.324 3(2)	−0.219 9(6)	0.298 0(17)	C(74)	0.131 7(2)	−0.392 2(6)	−0.041 5(18)
C(75)	0.330 0(2)	−0.170 7(6)	0.356 4(17)	C(75)	0.111 4(2)	−0.417 7(6)	−0.127 5(18)
C(76)	0.305 9(2)	−0.134 8(6)	0.374 5(17)	C(76)	0.084 6(2)	−0.441 3(6)	−0.079 2(18)
C(81)	0.231 3(2)	−0.105 1(6)	0.523 6(12)	C(81)	0.056 7(3)	−0.527 3(6)	0.207 1(18)
C(82)	0.225 2(2)	−0.060 1(6)	0.599 4(12)	C(82)	0.039 1(3)	−0.547 4(6)	0.310 7(18)
C(83)	0.214 8(2)	−0.065 7(6)	0.728 5(12)	C(83)	0.047 6(3)	−0.595 0(6)	0.371 1(18)
C(84)	0.210 5(2)	−0.116 2(6)	0.781 9(12)	C(84)	0.073 6(3)	−0.622 5(6)	0.327 9(18)
C(85)	0.216 7(2)	−0.161 2(6)	0.706 1(12)	C(85)	0.091 1(3)	−0.602 4(6)	0.224 3(18)
C(86)	0.227 1(2)	−0.155 6(6)	0.577 0(12)	C(86)	0.082 7(3)	−0.554 9(6)	0.163 9(18)
P(5)	0.185 9(2)	−0.294 3(2)	0.319 9(7)	P(5)	0.437 5(2)	−0.126 3(2)	0.251 3(7)
F(1)	0.177 4(4)	−0.237 2(8)	0.373 5(20)	F(1)	0.406 9(4)	−0.141 1(8)	0.312 0(20)
F(2)	0.194 1(4)	−0.349 4(8)	0.263 6(20)	F(2)	0.469 4(4)	−0.111 7(9)	0.197 7(23)
F(3)	0.161 5(3)	−0.320 7(7)	0.413 9(18)	F(3)	0.441 1(3)	−0.180 4(7)	0.174 3(19)
F(4)	0.209 5(3)	−0.263 4(7)	0.229 3(18)	F(4)	0.438 7(4)	−0.070 8(9)	0.314 5(24)
F(5)	0.210 6(3)	−0.301 6(7)	0.429 2(18)	F(5)	0.455 4(4)	−0.151 5(8)	0.373 0(20)
F(6)	0.161 4(3)	−0.289 2(7)	0.206 6(18)	F(6)	0.420 9(3)	−0.101 0(6)	0.132 5(17)

* Co-ordinate fixed.

filtered off and the filtrate was evaporated under reduced pressure and the product isolated. It formed bright orange microcrystals from CH_2Cl_2–light petroleum (b.p. 60—80 °C). Yield 235 mg, 83%. The methylacetylide (**5a**) and *p*-tolylacetylide (**5c**) analogues were made similarly in yields of 81 and 74%, respectively.

[ClPt(μ-dppm)$_2$(μ-σ,η-C≡CPh)Rh(CO)][AgCl$_2$] (**5d**) *from the platinum–silver complex.* A solution of [Rh$_2$Cl$_2$(CO)$_4$] (86 mg, 0.221 mmol) in acetone (20 cm^3) was added to a stirred suspension of [Cl(PhC≡C)Pt(μ-dppm)$_2$AgCl] (550 mg, 0.442 mmol) in acetone (40 cm^3). The mixture became clear as the platinum–silver complex dissolved. After 40 min the acetone was evaporated under reduced pressure, the residue taken up in dichloromethane, and the required product precipitated by adding light petroleum (b.p. 60—80 °C). Bright yellow-orange microcrystals. Yield 437 mg, 78%. The methylacetylide (**5e**) and *p*-tolylacetylide (**5f**) analogues were made similarly in yields of 56 and 49%, respectively.

Conversion of [ClPt(μ-dppm)$_2$(μ-σ,η-C≡CC$_6$H$_4$Me-*p*)Rh(CO)][AgCl$_2$] (**5f**) *into the corresponding* PF$_6$ *Salt* (**5c**).—A solution of the salt (**5f**) (56 mg) in acetone (10 cm^3) was treated with a solution of NH_4PF_6 (71 mg) in acetone (*ca.* 10 cm^3). There was an immediate white precipitate of silver chloride. The required product was isolated by evaporation of the mother-liquors and extraction into dichloromethane. Yield 39 mg. The product was shown to be identical to an authentic sample of the PF$_6$ salt, prepared as above, by i.r. spectroscopy.

Conversion of [Pt(dppm-*PP'*)]$_2$Cl$_2$ *into* [ClPt (μ-dppm)$_2$(μ-σ,η-C≡CPh)Rh(CO)][AgCl$_2$] (**5d**) *in a 'One-pot' Synthesis* via *the Silver Complex.*—A slurry was prepared from AgO$_2$CMe (62.6 mg, 0.387 mmol) and PhC≡CH (42 μl) in acetone (10 cm^3); this was then added to a suspension of [Pt(dppm-*PP'*)$_2$]Cl$_2$ (400 mg, 0.387 mmol) in acetone (20 cm^3) at 0 °C. The resultant mixture was stirred at 0 °C for 40 min and then allowed to warm to *ca.* 20 °C. A solution of [Rh$_2$Cl$_2$(CO)$_4$] (75.2 mg, 0.193 mmol) in acetone (10 cm^3) was added. A deep red solution formed immediately. The mixture was stirred at *ca.* 20 °C for a further 1 h, filtered, and the product isolated by evaporation, extraction into dichloromethane, and recrystallization from dichloromethane–light petroleum (b.p. 60—80 °C). Yield 110 mg, 31%. It was shown to be the required compound (**5d**) by its ^{31}P-{^{1}H} n.m.r. spectrum; a very small amount of [PtCl$_2$(dppm-*PP'*)] was present as contaminant.

Crystallography.—Crystal data for [(MeC≡C)Pt(μ-dppm)$_2$(μ-σ,η-C≡CMe)Rh(CO)]PF$_6$·CH$_2$Cl$_2$ (**1b**). C$_{57}$H$_{50}$F$_6$OP$_5$PtRh·CH$_2$Cl$_2$, $M = 1\,402.8$, orthorhombic, $a = 19.212(7)$, $b = 27.364(6)$, $c = 21.468(5)$ Å, $U = 11\,286(5)$ Å^3, space group *Pbca* (no. 61), $Z = 8$, $D_c = 1.65$ g cm^{-3}, $F(000) = 5\,552$, graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 30.83 cm^{-1}. Yellow-orange tablets from dichloromethane–ethanol (3 : 1). Crystal dimensions (distance to faces from centre): 0.345 (001, 00$\bar{1}$), 0.090 (010, 0$\bar{1}$0), 0.138 (110, $\bar{1}\bar{1}$0), 0.120 (1$\bar{1}$0), 0.105 ($\bar{2}$30) mm.

Crystal data for [ClPt(μ-dppm)$_2$(μ-σ,η-C≡CMe)Rh(CO)]PF$_6$ (**5a**). C$_{54}$H$_{47}$ClF$_6$OP$_5$PtRh, $M = 1\,314.3$, orthorhombic, $a = 43.39(1)$, $b = 25.178(9)$, $c = 10.164(6)$ Å, $U = 11\,104(8)$ Å^3, space group $Pn2_1a$ ($a\bar{c}b$ setting of $Pna2_1$, no. 33), $Z = 8$, $D_c = 1.57$ g cm^{-3}, $F(000) = 5\,184$, graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 30.81 cm^{-1}. Yellow-orange broken cuboidal fragments by slow diffusion of diethyl ether into a dichloromethane solution of the complex salt. Crystal dimensions *ca.* 0.30 × 0.35 × 0.30 mm.

Structure determinations. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections having $36 < 2\theta < 44°$ for complex (**1b**) or $26 < 2\theta < 39°$ for (**5a**). Intensities of all independent reflections (h,k,l, $4 < 2\theta < 45°$) were measured on a Syntex $P2_1$ diffractometer in the ω—2θ scan mode using scan speeds between 2 and 29° min^{-1}, and with the scans running from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$ for (**1b**) or from 0.8° below $K_{\alpha1}$ to 0.8° above $K_{\alpha2}$ for (**5a**). The structure analysis for complex (**1b**) used the 4 500 reflections having $I > 2.5\sigma(I)$, leaving 1 609 reflections as 'unobserved;' that for (**5a**) used 6 320 reflections having $I > 2\sigma(I)$, leaving 904 'unobserved' reflections. Corrections were applied for Lorentz and polarization factors; absorption effects were corrected numerically for (**1b**) (maximum, minimum transmission factors for full data set = 0.62, 0.47),[16] and by an empirical method for (**5a**) (maximum, minimum absorption corrections for full data set = 1.13, 0.79).[17]

Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement [in two blocks for (**5a**)] with anisotropic thermal parameters for Pt, Rh, P, and Cl atoms, using the SHELX program system.[16] All phenyl rings were refined as rigid groups with idealized D_{6h} geometry, the C atoms having individual isotropic thermal parameters and C–C distances of 1.395 Å, No H atoms were included in the final refinements, which converged at $R = 0.088$, $R' = (\Sigma w\Delta F^2/\Sigma wF_o^{\,2})^{\frac{1}{2}} = 0.095$ for complex (**1b**) and $R = 0.058$, $R' = 0.056$ for (**5a**), employing the weighting scheme $w = 1/(\sigma^2F_o + gF_o^{\,2})$. The final values of g [0.0011 for (**1b**), 0.0005 for (**5a**)] were chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o. Refinement of the alternative enantiomorphic specification for (**5a**) gave significantly larger R factors, so the original structure was retained. The final difference maps showed no unusual features. Possible disorder in the PF$_6^-$ anion of (**1b**) was noted, but a better model was not apparent. Complex neutral-atom scattering factors were calculated from the analytical approximation and coefficients given in ref. 18. The final atomic co-ordinates for each structure are given in Tables 5 and 6.

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References

1 Part 11, A. T. Hutton, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 1677.

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

3 G. R. Cooper, A. T. Hutton, C. R. Langrick, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 855.

4 A. Blagg, A. T. Hutton, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 1815.

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

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

7 A. Fumagalli, S. Martinengo, P. Chini, A. Albinati, S. Bruckner, and B. T. Heaton, *J. Chem. Soc., Chem. Commun.*, 1978, 195.

8 M. Green, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1309, 1321.

9 M. Green, J. A. K. Howard, G. N. Pain, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 1327.

10 See, for example, M. Cowie and T. G. Southern, *Inorg. Chem.*, 1982, **21**, 246.

11 J. H. Barlow, G. R. Clark, M. G. Curl, M. E. Howden, R. D. W. Kemmitt, and D. R. Russell, *J. Organomet. Chem.*, 1978, **144**, C47.

12 M. A. Bennett, R. N. Johnson, G. B. Robertson, T. W. Turney, and P. O. Whimp, *Inorg. Chem.*, 1976, **15**, 97.

13 L. H. Sutton, ed., 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' *Special Publ.*, The Chemical Society, London, 1958, no. 11; 1965, no. 18 (Supplement).

14 R. Nast, *Coord. Chem. Rev.*, 1982, **47**, 89.

15 J. A. Iggo and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 1009.

16 G. M. Sheldrick, SHELX 76 Program System, University of Cambridge, 1976.

17 N. Walker and D. Stuart, *Acta Crystallogr., Sect A*, 1983, **39**, 158.

18 'International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

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