Bimetallic Systems. Part 16.[1] Formation of Group 6 Metal(0)–Platinum(II) Hydride Complexes, by Ring Opening of *fac*- or *mer*-[M(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (M = Cr, Mo, or W; dppm = Ph$_2$PCH$_2$PPh$_2$). Reactions of [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)]

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The new complexes *fac*- and *mer*-[W(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (dppm = Ph$_2$PCH$_2$PPh$_2$) are described. Treatment of *fac*- or *mer*-[M(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (M = Cr, Mo, or W) with *trans*-[PtH(Cl)(PPh$_3$)$_2$] gave the heterobimetallic complexes [(CO)$_3$M(μ-dppm)$_2$PtH(Cl)] in good yields. Similarly *fac*- or *mer*-[Mo(CO)$_3$(dppm-*PP'*)(dppm-*P*)] reacted with *trans*-[PtH(C≡CPh)(PPh$_3$)$_2$] to give [(CO)$_3$Mo(μ-dppm)$_2$PhH(C≡CPh)], but the corresponding chromium– or tungsten–platinum complexes could not be prepared. Phosphorus-31 and ^{1}H n.m.r., and i.r. spectroscopic data are given and discussed. ^{1}H-{^{31}P} N.m.r. studies at different temperatures showed the complexes of type [(CO)$_3$M(μ-dppm)$_2$PtH(Y)] (M = Cr, Mo, or W, Y = Cl; M = Mo, Y = C≡CPh) to be fluxional, corresponding to inversion of the M(μ-dppm)$_2$Pt ring and exchange of positions of the H and Y ligands: a mechanism for this inversion is suggested. The chloride ligand of [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] was found to be readily substituted by nucleophiles Y (Y = Br, CN, N$_3$, H, or CO) to give new heterobimetallic species. Treatment of [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] with NaBH$_4$ gave a heterobimetallic dihydride with a bridging and a terminal hydride. ^{1}H-{^{31}P} N.m.r. studies showed this dihydride to undergo bridging-to-terminal hydride exchange at +21 °C in solution.

We have shown previously that Group 6 metal(0)–platinum(II) complexes of the type [(RC≡C)Pt(μ-C≡CR)(μ-dppm)$_2$-M(CO)$_3$] (R = alkyl or aryl; M = Cr, Mo, or W; dppm = Ph$_2$PCH$_2$PPh$_2$), can be synthesised by either treating *trans*-[Pt(C≡CR)$_2$(dppm-*P*)$_2$] with a labile W (or Mo) carbonyl derivative or by displacing silver from [(RC≡C)$_2$Pt(μ-dppm)$_2$AgX] (X = Cl or I), using a labile source of the zerovalent Group 6 metal (Cr, Mo, or W) (transmetallation).[2] We have also described the ring-opening reactions of *fac*-[M(CO)$_3$(dppm-*PP'*)(dppm-*P*)] [M = Mo (**1a**) or W (**1b**)] and *mer*-[M(CO)$_3$(dppm-*PP'*)(dppm-*P*)] [M = Cr (**2a**), Mo (**2b**), or W (**2c**)] with labile Rh^I, Ir^I, Cu^I, Ag^I, or Au^I compounds to give heterobinuclear complexes containing the M(μ-dppm)$_2$M' (M' = Rh, Ir, Cu, Ag, or Au) moiety.[3–6] In the present paper we report the systematic synthesis of Group 6 metal–platinum hydride complexes by the latter route, *i.e. via* ring opening of *fac*- or *mer*-[M(CO)$_3$-(dppm-*PP'*)(dppm-*P*)]. Some of the reactions of the heterobimetallic complex [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] will be described. First, however, we report reliable preparations for the Group 6 metal dppm species of types (**1**) and (**2**).

Results and Discussion

We have previously described[3–6] how heterobimetallic complexes, bridged by dppm, may be prepared from the Group 6 metal bis(dppm) species (**1**) or (**2**). In order to develop further this method of synthesis we first required reliable methods of preparing the mononuclear Group 6 metal complexes (**1**) and (**2**).

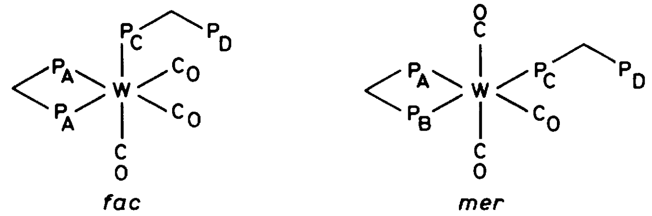
The syntheses of *fac*- and *mer*-[Mo(CO)$_3$(dppm-*PP'*)-(dppm-*P*)] have been previously reported by Graham and Isaacs.[7] Although the method described provided a reliable and convenient means of preparing the *fac* isomer (**1a**), we found the preparation of the *mer* isomer (**2b**), by treating [Mo(CO)$_3$(cht)] (cht = cycloheptatriene) with an excess of dppm in benzene at 20 °C, unreliable. We find that the *mer* isomer (**2b**), however, can be reliably prepared by isomerisation of the *fac* isomer (**1a**), as previously reported[7] (see Experimental section). *mer*-[Cr(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**2a**)[8] and the previously unreported *fac*-[W(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**1b**) were synthesized in good yield, from the corresponding cycloheptatriene complex [M(CO)$_3$(cht)] (M = Cr or W) and dppm in refluxing ethanol.

When a solution of *fac*-[W(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**1b**) was heated in benzene, it gave the corresponding *mer* isomer (**2c**) in 92% yield; preparative details are given in the Experimental section and characterizing data in Table 1.

Treatment of *fac*- or *mer*-[M(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (M = Cr, Mo, or W) with substitution-labile compounds of a second metal has been a convenient and high yielding route to heterobimetallic complexes of the Group 6 metals with Rh^I, Ir^I, Cu^I, Ag^I, and Au^I. Likewise we found that treatment of *fac*-[Mo(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**1a**) with the labile Pt^{II} derivative *trans*-[PtH(Cl)(PPh$_3$)$_2$], in boiling benzene, gives the maroon molybdenum–platinum complex [(CO)$_3$-Mo(μ-dppm)$_2$PtH(Cl)] (**3a**) in 71% yield. *mer*-[Mo(CO)$_3$-(dppm-*PP'*)(dppm-*P*)] (**2b**) reacts with *trans*-[PtH(Cl)(PPh$_3$)$_2$] under similar conditions, to give an identical product. The analogous Cr–Pt (**3b**) and W–Pt (**3c**) complexes were similarly prepared (see Scheme 1). The *fac*- or *mer*-molybdenum species, (**1a**) or (**2b**), were found to react with *trans*-[PtH(C≡CPh)-(PPh$_3$)$_2$], in boiling benzene, to give the orange-red complex [(CO)$_3$Mo(μ-dppm)$_2$PtH(C≡CPh)] (**3d**). However, attempts to prepare similarly the analogous Cr and W complexes [(CO)$_3$M(μ-dppm)$_2$PtH(C≡CPh)] (M = Cr or W) were unsuccessful with no heterobimetallic products being observed by ^{31}P-{^{1}H} n.m.r. spectroscopy. The above heterobinuclear complexes were formulated as (**3a**)—(**3d**) on the basis of microanalysis (Table 2), ^{31}P-{^{1}H} n.m.r. and i.r. spectroscopy (Table 3), and ^{1}H-{^{31}P} and ^{1}H n.m.r. spectroscopy (Table 4).

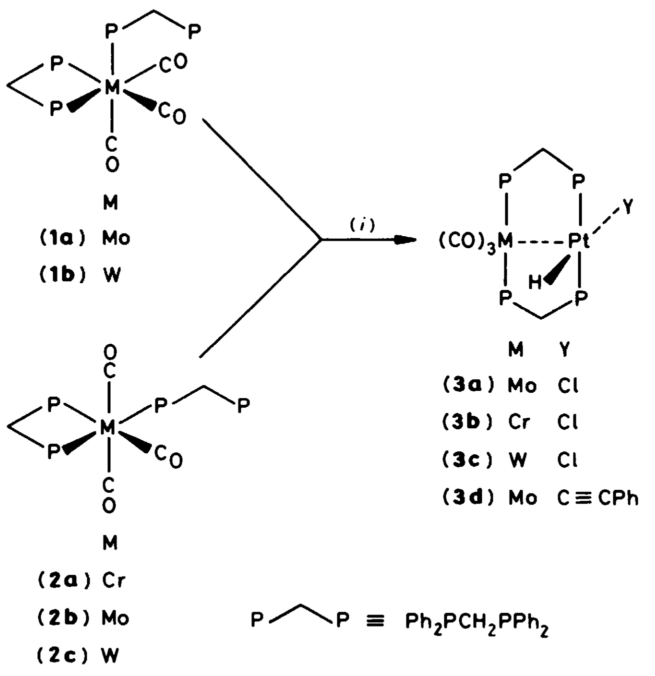
The ^{31}P-{^{1}H} n.m.r. spectra of complexes (**3a**)—(**3d**) all show a simplified AA'XX' (or AA'BB') splitting pattern with ^{195}Pt satellites, characteristic of a *trans,trans*-M(μ-dppm)$_2$Pt moiety. The i.r. spectra of species (**3a**)—(**3d**) show ν(CO) bands typical

Table 1. I.r.,[a] ^{31}P-{^{1}H} n.m.r. and ^{1}H{^{31}P} n.m.r. data for the complexes *fac*- or *mer*-[W(CO)$_3$(dppm-*PP'*)(dppm-*P*)]



						Methylene protons	
Complex	ν(CO)/cm^{-1}	δ(P)[b]/p.p.m.	Assign-ment[c]	J(W–P)[d]/Hz	J(P–P)[e]/Hz	Mono-dentate (δ/p.p.m.)	Chelate (δ/p.p.m.)
(**1b**) *fac*-[W(CO)$_3$(dppm-*PP'*)(dppm-*P*)]	1 931s,	−26.3 (d)	D	N.o.	32 (C-D)	2.71	4.92, 4.37[f]
	1 844s,	11.5 (dt)	C	N.o.	32, 22 (A-C)		
	1 829s	−21.0 (d)	A	195	22		
(**2c**) *mer*-[W(CO)$_3$(dppm-*PP'*)(dppm-*P*)]	1 953s,	−25.0 (d)	D	45	62 (C-D)	3.19	4.99
	1 863 (sh),	21.4 (ddd)	C	301	62, 23 (A-C), 67 (B-C)		
	1 852s br	−23.7 (dd)	A	182	23, 29 (A-B)		
		−11.0 (dd)	B	248	67, 29		

[a] Spectra recorded as Nujol mulls. [b] Spectrum of (**1b**) recorded at 40.25 MHz, spectrum of (**2c**) recorded at 161 MHz; d = doublet, t = triplet. [c] A = P$_A$ *etc.* [d] N.o. = Not observed. [e] C-D = ^2J(P$_C$–P$_D$) *etc.* [f] AB spin system, J(H–H) 15 Hz.



Scheme 1. (*i*) *trans*-[PtH(Y)(PPh$_3$)$_2$] (Y = Cl, M = Cr, Mo, or W; Y = C≡CPh, M = Mo) in benzene

of terminal carbonyl groups, with a ν(C≡C) band at 2 118 cm^{-1} being observed for the phenylacetylide complex (**3d**). The far-i.r. spectra of the chloro complexes (**3a**)—(**3c**) show a ν(Pt–Cl) band at *ca.* 300 cm^{-1}, indicative of a terminal chloride. No bands attributable to ν(Pt–H) are observed in the i.r. spectra of (**3a**)—(**3d**), presumably due to lack of intensity: ν(Pt–H) bands are commonly found to be of low intensity in complexes of this type.

The ^{1}H-{^{31}P} n.m.r. spectra of (**3a**)—(**3d**) all show a single PCH_2P resonance with ^{195}Pt satellites at +21 °C, and a hydride resonance strongly coupled to ^{195}Pt [^1J(PtH) = *ca.* 1 100 Hz]. With the exception of the W–Pt complex (**3c**) all show weak coupling of the CH_2 resonance to hydride. The large values of ^1J(Pt–H) for (**3a**)—(**3d**) suggest that the hydrides are terminal on platinum.[9] In support of this, ^{1}H n.m.r. spectroscopic studies, with selective ^{31}P decoupling, on complexes (**3a**), (**3b**), and (**3d**), all show the hydride resonance to be coupled to the phosphorus atoms bound to Pt(P$_B$), and not observably coupled to the phosphorus atoms bound to the Group 6 metal (P$_A$) (coupling to both P$_A$ and P$_B$ would be expected if the hydride were bridging).

The ^{1}H-{^{31}P} n.m.r. spectra of the W–Pt complex (**3c**) at +21 and −90 °C, show coupling of the hydride resonance to ^{183}W [J(W–H) *ca.* 29 Hz], see Figure 1. We suggest that this coupling is due to strong ^2J interaction between tungsten and hydride (terminal on platinum), through a dative metal–metal bond, *i.e.* W←Pt–H coupling. The ^2J(W–H) coupling constants for the dative-bonded complexes [(η-C$_5$H$_5$)$_2$H$_2$MW(CO)$_5$] (M = Mo or W) have been found to be approximately 19 Hz,[10] whereas the ^1J(W–H) values for bridging hydrides have been measured to be *ca.* 42 Hz in the complexes [(CO)$_5$M(μ-H)W(CO)$_5$]$^-$ (M = Cr, Mo, or W).[11] The J(W–H) coupling constant for complex (**3c**) is intermediate between these two values. A ^{1}H-{^{31}P(selective)} n.m.r. study of complex (**3c**) was prevented by the closeness of the ^{31}P resonances. However, the ^{1}H n.m.r. spectrum at +21 °C shows a triplet for the central hydride resonance, indicating that the hydride is terminal: a multiplet (due to coupling to all four phosphorus atoms) is expected if the hydride is bridging. The intense colours of complexes (**3a**)—(**3c**), both in the solid and in solution, suggest the presence of a strong metal–metal interaction.

The pseudo-axial, H$_{ax}$, and pseudo-equatorial, H$_{eq}$, CH$_2$ protons of complexes of the type [(CO)$_3$M(μ-dppm)$_2$PtH(Y)] (Y = Cl, M = Cr, Mo, or W; Y = C≡CPh, M = Mo) are chemically inequivalent in the static structure. However, the ^{1}H-{^{31}P} n.m.r. spectra of these complexes all show a single CH_2 resonance, at +21 °C, rather than an AB pattern. A variable-temperature 360-MHz ^{1}H-{^{31}P} n.m.r. spectroscopic study of complex (**3c**) shows that the CH_2 protons are equivalent above −50 °C. Below this temperature, however, two

Table 2. Colours, yields, and microanalytical[a] data for $[(CO)_3M(\mu\text{-dppm})_2PtH(Y)]$ **(3a)**—**(3d)** and **(4a)**—**(4d)** and $[(CO)_3Mo(\mu\text{-dppm})_2PtH(CO)]PF_6$ **(4e)**

Complex	M	Y	Colour	Yield (%)	Analysis(%) C	H	Other
(3a)·$0.5C_6H_6$	Mo	Cl	Maroon	87	54.85 (55.15)	3.95 (3.95)	Cl, 2.6 (2.9)
(3b)·$0.5C_6H_6$	Cr	Cl	Grey-green	72	57.25 (57.2)	4.15 (4.1)	Cl, 3.2 (3.0)
(3c)	W	Cl	Grey-maroon	47	50.2 (50.2)	3.55 (3.6)	Cl, 2.8 (2.8)
(3d)	Mo	C≡CPh	Orange	71	58.45 (58.8)	4.0 (4.05)	
(4a)·$0.5CH_2Cl_2$	Mo	Br	Red-pink	70	50.35 (50.7)	3.6 (3.65)	*b*
(4b)	Mo	CN	Red	73	55.35 (55.4)	3.95 (3.9)	N, 1.25 (1.2)
(4c)	Mo	N_3	Red	81	53.55 (53.6)	3.9 (3.8)	N, 3.2 (3.5)
(4d)	Mo	H	Orange	85	55.35 (55.55)	4.0 (4.05)	
(4e)			Orange	72	51.45 (51.6)	3.65 (3.7)	F, 8.15 (8.2)

[a] Calculated values in parentheses. [b] Titre of $Hg(NO_3)_2$ solution 1.00 cm³ (calc. 0.99 cm³).

Table 3. $^{31}P\text{-}\{^1H\}$ N.m.r.[a] and i.r.[b] data for $[(CO)_3M(\mu\text{-dppm})_2PtH(Y)]$ and $[(CO)_3Mo(\mu\text{-dppm})_2PtH(CO)]PF_6$ **(4e)**

Complex	M	Y	Solvent	$\delta(P_A)$/ p.p.m.	$\delta(P_B)$/ p.p.m.	$^1J(Pt\text{–}P_B)$/ Hz	N^c/Hz	$\nu(CO)/cm^{-1}$	$\nu(Pt\text{–}H)/cm^{-1}$	Others (ν/cm^{-1})
(3a)	Mo	Cl	CD_2Cl_2	37.3	15.8	2 544	98	1 966m, 1 866s br, 1 833s br	N.o.	ν(Pt–Cl) 302
(3b)	Cr	Cl	CD_2Cl_2	64.4	17.4	2 567	100	1 946m, 1 846vs br	N.o.	ν(Pt–Cl) 300
(3c)	W	Cl	CD_2Cl_2	17.4[d]	15.4[e]	2 516[e]	99[e]	1 961m, 1 855s, 1 830s	N.o.	ν(Pt–Cl) 303
(3d)	Mo	C≡CPh	$CDCl_3$	40.7	12.8	2 544	93	1 973m, 1 870s br, 1 838 (sh)	N.o.	ν(C≡C) 2 118
(4a)	Mo	Br	CD_2Cl_2	37.2	15.0	2 515	96	1 969m, 1 866s br, 1 832s br	N.o.	ν(Pt–Br) N.o.
(4b)	Mo	CN	CD_2Cl_2	39.5	12.0	2 422	95	1 962m, 1 859s, 1 832s br	N.o.	ν(C≡N) 2 128
(4c)	Mo	N_3	CD_2Cl_2	38.5	15.7	2 732	84	1 968m, 1 858s br, 1 792s br	2 116w br	$\nu(N_3)$ 2 036s
(4d)	Mo	H	CD_2Cl_2	44.2	20.9	2 818	100	1 961m, 1 863s br, 1 792s br	2 034w br	
(4e)			$(CD_3)_2CO$	41.0	24.5	2 666	104	2 024s, 1 987s, 1 872s, 1 849s	2 104w	

[a] Spectrum recorded at 40.25 MHz unless otherwise stated. [b] Nujol mulls; N.o. = not observed. [c] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$ [d] Approximate value determined from 161-MHz spectrum. [e] Values determined from ^{195}Pt satellites, coupling to ^{183}W not resolved.

Table 4. Hydrogen-1 and $^1H\text{-}\{^{31}P\}$ n.m.r. data[a] for $[(CO)_3M(\mu\text{-dppm})_2PtH(Y)]$ and $[(CO)_3Mo(\mu\text{-dppm})_2PtH(CO)]PF_6$ **(4e)**

Complex	M	Y	θ_c/°C	$\delta(CH_2)$/p.p.m.	δ(H)/p.p.m.	$^3J(Pt\text{–}CH_2)$/ Hz	$^1J(Pt\text{–}H)$/Hz	$^2J(P_B\text{–}H)$/Hz	Other(*J*/Hz)	Solvent
(3a)	Mo	Cl	+21	3.76	−17.6	54	1 125	14	$^4J(CH_2\text{–}H) \sim 1$	CD_2Cl_2
(3b)	Cr	Cl	+21	3.67	−21.2	51	1 096	11	$^4J(CH_2\text{–}H) \sim 1$	CD_2Cl_2
(3c)	W	Cl	+21	3.95	−16.2	51	1 102	12	*J*(W–H) 29	CD_2Cl_2
			−90	[b]4.73 (H_{eq}),	−16.5	$J(Pt\text{–}H_{eq})$	1 115		*J*(W–H) 30	CD_2Cl_2
				3.31 (H_{ax})		*ca.* 77			$J(H_{ax}\text{–}H_{eq})$ 11	
(3d)	Mo	C≡CPh	+21	3.99	−11.4	44	686	13	$^4J(CH_2\text{–}H) \sim 2$	CD_2Cl_2
(4a)	Mo	Br	+21	3.76	−16.1	54	1 172	13		CD_2Cl_2
(4b)	Mo	CN	+21	3.94	−12.7	46	753	14		CD_2Cl_2
(4c)	Mo	N_3	+21	3.68	−18.7	47	1 073	14		CD_2Cl_2
(4d)	Mo	H	+21	3.92	−1.23,	39	1 004,	N.r.		CD_2Cl_2
					−7.84 (H_μ)		$J(Pt\text{–}H_\mu)$ 685	N.r.		
			−30		−1.22,		999,	12		
					−7.86 (H_μ)		$J(Pt\text{–}H_\mu)$ 683	$J(P_B\text{–}H_\mu)$ 11[c]	$^2J(H\text{–}H_\mu)$ 18	CD_2Cl_2
(4e)			+21	3.90	−2.96	28	1 591	9		$(CD_3)_2CO$

[a] Spectra recorded at 100 MHz unless otherwise stated; N.r. = not resolved. [b] Spectrum recorded at 360 MHz, H_{ax} and H_{eq} are pseudo-axial and pseudo-equatorial CH_2 protons. [c] $^1J(P_A\text{–}H_\mu)$ coupling not fully resolved.

distinct methylene resonances are observed (see Figure 1) with the $J(H_{ax}\text{–}H_{eq})$ coupling being fully resolved at −90 °C: similar fluxional behaviour has been observed for the diplatinum cation $[Pt_2H_2Cl(\mu\text{-dppm})_2]^+$, where high-field (400 MHz) ¹H n.m.r. spectroscopy has shown the CH_2 protons to be equivalent down to −16 °C, the limiting low-temperature spectrum being obtained at −77 °C. Puddephatt and co-workers[12] have proposed a mechanism to account for the equivalence of the CH_2 protons which involves a linear H–Pt–H–Pt–Cl intermediate. We suggest that the CH_2 hydrogens of the complexes $[(CO)_3M(\mu\text{-dppm})_2PtH(Y)]$ may be rendered equivalent by a similar process. This process, shown in Scheme 2, involves the initial formation of a μ-hydrido intermediate, which can invert through the $\overline{\text{MPCPPtPCP}}$ ring *via* a linear M–H–Pt–Y transient.*

The Mo–Pt complex **(3a)** is an air-stable maroon solid which is soluble in chlorinated solvents, but only sparingly

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* One of the referees favours formulating complexes **(3a)**—**(3d)** and **(4a)**—**(4c)** with a bridging or semi-bridging hydrogen ligand. Highly asymmetrically bridged structures cannot be ruled out but we consider that the weight of the evidence indicates that for **(3a)**—**(3d)**, **(4a)**—**(4c)**, and **(4e)** the hydride ligand is essentially terminally bonded to platinum.

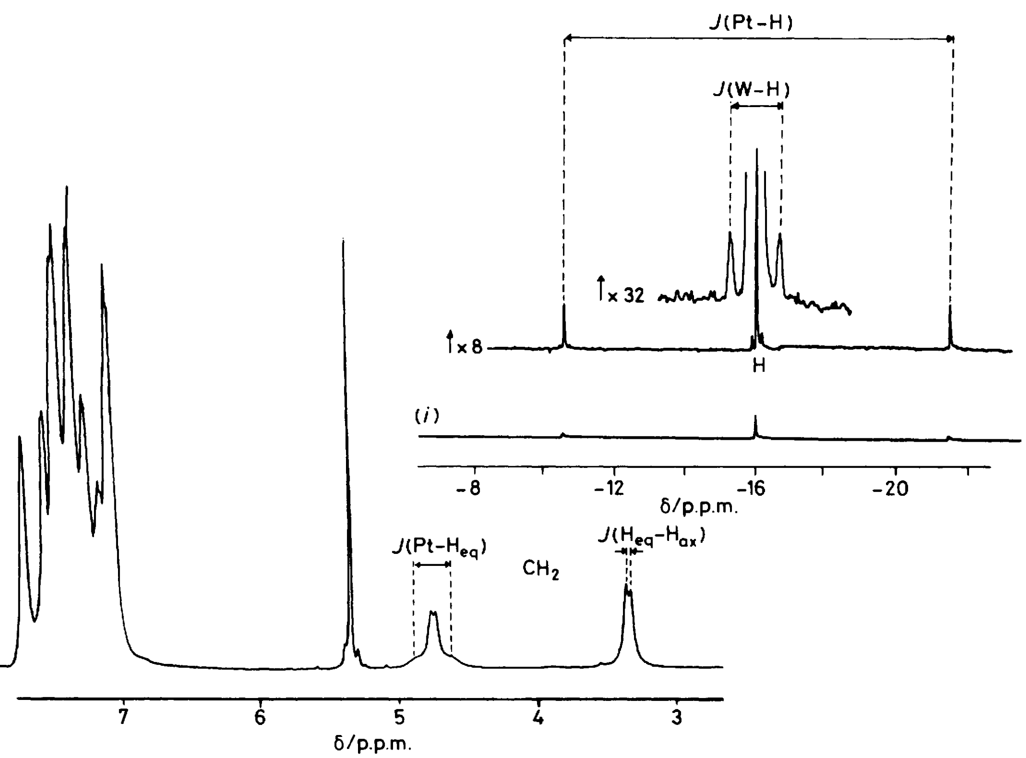


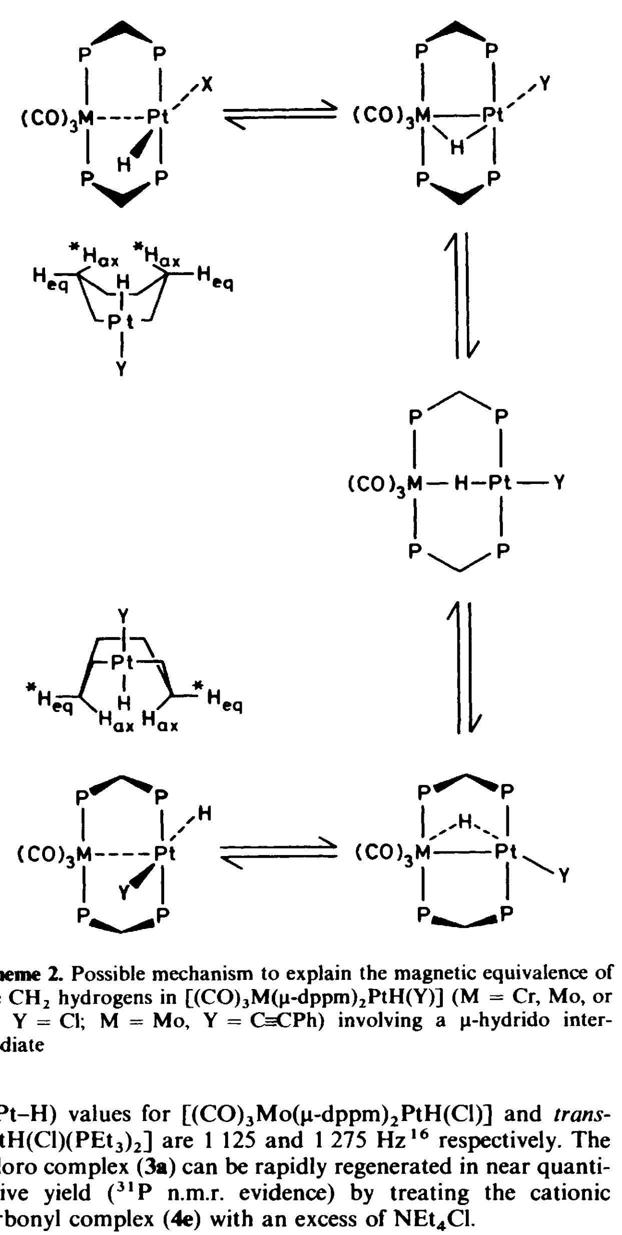
Figure 1. $^1H\text{-}\{^{31}P\}$ N.m.r. spectra of $[(OC)_3W(\mu\text{-dppm})_2PtH(Cl)]$ (**3c**) in CD_2Cl_2: (*i*) at +21 °C and 100 MHz in the hydride region and (*ii*) at −90 °C and 360 MHz, showing the PCH_2P resonances

soluble in ionising solvents such as acetone or methanol. $[(CO)_3Mo(\mu\text{-dppm})_2PtH(Cl)]$ (**3a**) is moderately stable in solution in air; no appreciable decomposition is observed after one day in CH_2Cl_2 at +20 °C ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence). It does not undergo H–D exchange with D_2O, in the presence of a catalytic amount of HCl, over a period of 4 h (i.r. evidence). In contrast, the chloride ligand is quite labile and can be readily substituted by halides, pseudo-halides, and other nucleophiles, see Scheme 3. Thus treatment of a dichloromethane solution of the chloro complex (**3a**) with a ten-fold excess of NaBr in H_2O, in the presence of NMe_4Br as a phase-transfer catalyst, gave $[(CO)_3Mo(\mu\text{-dppm})_2PtH(Br)]$ (**4a**) in 70% yield. The pseudo-halide complexes $[(CO)_3Mo(\mu\text{-dppm})_2PtH(Y)]$ [Y = CN (**4b**) or N_3 (**4c**)] are prepared similarly. Further details are given in the Experimental section and characterizing spectroscopic and microanalytical data in the Tables.

Treatment of a dichloromethane solution of $[(CO)_3Mo(\mu\text{-dppm})_2PtH(Cl)]$ with $NaBH_4$, followed by methanol, gave an orange compound in 85% yield, formulated as $[(CO)_3Mo(\mu\text{-dppm})_2Pt(H)_2]$ (**4d**) (characterizing data are in the Tables). The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum at +21 °C shows a single sharp CH_2 resonance with ^{195}Pt satellites and two broad hydride resonances at −1.23 and −7.84 p.p.m., see Figure 2. Both hydride resonances are coupled to ^{195}Pt, but no hydride–hydride coupling is resolved at this temperature. At −30 °C, however, the hydride–hydride coupling is well resolved, a doublet with ^{195}Pt satellites being observed for each hydride resonance (see Figure 2). The high-frequency hydride, H_a, is strongly coupled to ^{195}Pt indicating that it is terminal on platinum, whereas the low-frequency hydride, H_b, is more weakly coupled to ^{195}Pt suggesting that it may be bridging. Puddephatt and co-workers[13,14] have previously found that, for diplatinum complexes which contain both bridging H_μ, and terminal, H_t, hydrides, $^1J(Pt\text{–}H_\mu)$ values are considerably lower than those of $^1J(Pt\text{–}H_t)$. For example, the $^1J(Pt\text{–}H_\mu)$ and $^1J(Pt\text{–}H_t)$ coupling constants for the complex $[Pt_2H(Me)(\mu\text{-}H)(\mu\text{-dppm})_2]SbF_6$ are 540 and 1 135 Hz respectively.[14] Hence the $^1H\text{-}\{^{31}P\}$ n.m.r. data for complex (**4d**) are consistent with a structure containing both bridging and terminal hydrides. Furthermore, the $^1H\text{-}\{^{31}P(\text{selective})\}$ n.m.r. spectra of (**4d**) at −30 °C, shown in Figure 2, show H_a to be terminal on platinum and H_b to be bridging; H_a being coupled only to the phosphorus atoms bound to platinum (P_B) whereas H_b is coupled to all four phosphorus atoms, although the $J(P_A\text{–}H_\mu)$ coupling is poorly defined.

The broadening of the hydride resonances at +21 °C suggests that the bridging and terminal hydrides are exchanging at ambient temperature. A similar process has been observed for the diplatinum cation $[PtH_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$.[12,13] The temperature at which the hydride resonances coalesce could not be determined as the dihydride species (**4d**) is insoluble in aromatic hydrocarbons and decomposes in chlorinated solvents at elevated temperatures. At −30 °C, the hydride–hydride coupling is well defined, indicating that the terminal-to-bridging ligand exchange has ceased. However, the CH_2 protons remain equivalent at this temperature, indicating that a second fluxional process may also operate. We suggest that this process involves inversion of the hydride bridge through the MoPCPPtPCP ring, akin to the process shown in Scheme 2. A similar process has been proposed by Puddephatt and co-workers[12,13] to explain the fluxional behaviour of $[PtH_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$.

We found that $[(CO)_3Mo(\mu\text{-dppm})_2PtH(Cl)]$ reacts with CO, in the presence of $TlPF_6$, to give an orange cationic carbonyl complex and a white precipitate of TlCl. We formulate this cationic complex as $[(CO)_3Mo(\mu\text{-(dppm)}_2PtH(CO)]PF_6$ (**4e**), see Tables 2—4 for characterising data. The hydride resonance is very strongly coupled to ^{195}Pt [$J(Pt\text{–}H)$ = 1 591 Hz] in the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum, especially since $J(Pt\text{–}H)$ is only 967 Hz for *trans*-$[PtH(CO)(PEt_3)_2]ClO_4$.[15] By comparison the



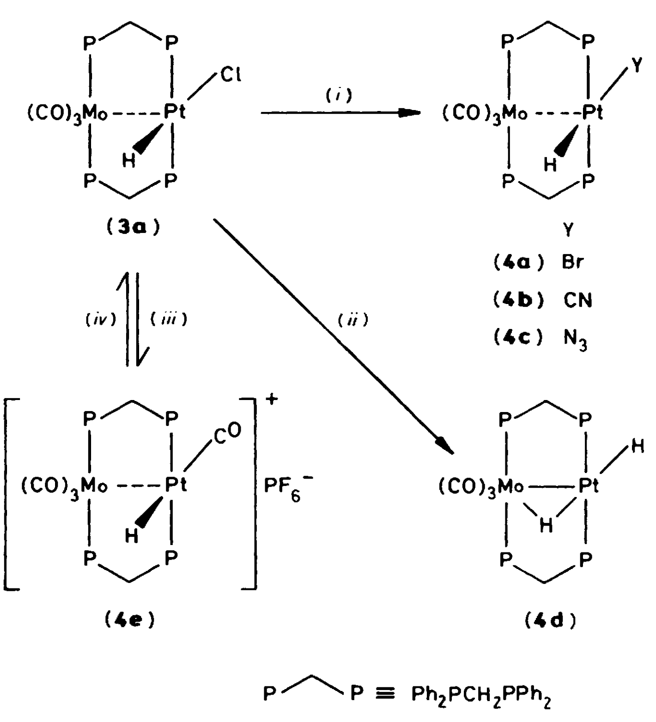
Scheme 2. Possible mechanism to explain the magnetic equivalence of the CH$_2$ hydrogens in [(CO)$_3$M(μ-dppm)$_2$PtH(Y)] (M = Cr, Mo, or W, Y = Cl; M = Mo, Y = C≡CPh) involving a μ-hydrido intermediate

J(Pt–H) values for [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] and *trans*-[PtH(Cl)(PEt$_3$)$_2$] are 1 125 and 1 275 Hz[16] respectively. The chloro complex (**3a**) can be rapidly regenerated in near quantitative yield (^{31}P n.m.r. evidence) by treating the cationic carbonyl complex (**4e**) with an excess of NEt$_4$Cl.

The heterobinuclear cation [(CO)$_3$Mo(μ-dppm)$_2$PtH(CNBu^t)]$^+$ is not formed on treatment of [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] with one mole equivalent of CNBu^t. Instead, a platinum homobinuclear species is the major product, together with a number of unidentified Mo–dppm species (^{31}P-{^{1}H} n.m.r. evidence). Decomposition of this heterobinuclear framework also occurred on treatment of (**3a**) with SO$_2$, in the presence of NaBPh$_4$. In contrast the chloro complex (**3a**) appears to be inert in the presence of buta-1,3-diene and NaBPh$_4$, with no reaction being observed by ^{31}P-{^{1}H} n.m.r. spectroscopy after 24 h at 20 °C.

Experimental

General methods were as previously described in recent papers from this laboratory.[17] The complex *fac*-[W(CO)$_3$(dppm-*PP′*)(dppm-*P*)] was prepared from [W(CO)$_3$(cht)] (cht = cycloheptatriene) and dppm in 77% yield (m.p. 202—204 °C) in a similar manner to the reported synthesis of the *mer*-Cr complex (**2a**)[8] (Found: C, 61.35; H, 4.5. Calc. for C$_{53}$H$_{44}$O$_3$P$_4$W: C, 61.4; H, 4.3%). Other characterising data are given in Table 1.



Scheme 3. Some reactions of [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] (**3a**). (*i*) Y$^-$ (Y = Br, CN, or N$_3$) in H$_2$O stirred with (**3a**) in dichloromethane in the presence of NMe$_4$$^+$; (*ii*) NaBH$_4$ in dichloromethane–methanol; (*iii*) CO, TlPF$_6$; (*iv*) NEt$_4$Cl

Preparations.—*mer*-[W(CO)$_3$(dppm-*PP′*)(dppm-*P*)]·0.25CH$_2$Cl$_2$ *from* *fac*-[W(CO)$_3$(dppm-*PP′*)(dppm-*P*)]. A solution of *fac*-[W(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (1.00 g, 0.96 mmol) was refluxed in benzene (50 cm^3), under dinitrogen, for 46 h. The yellow solution was evaporated to dryness under reduced pressure and the resultant residue recrystallised from CH$_2$Cl$_2$–MeOH. The required product formed yellow plates. Yield: 0.92 g (92%), m.p. 205—207 °C (Found: 60.5; H, 4.5; Cl, 1.55. Calc. for C$_{53.25}$H$_{44.5}$Cl$_{0.5}$O$_3$P$_4$W: C, 60.45; H, 4.25; Cl, 1.65%). Other characterising data are given in Table 1.

mer-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)] was similarly prepared from the *fac*-Mo complex (**2b**): reflux for 10 h was required for complete isomerisation.

[(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] (**3a**). *trans*-[PtH(Cl)(PPh$_3$)$_2$] (0.16 g, 0.21 mmol) was added to a solution of *fac*-[M(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (0.20 g, 0.21 mmol) in hot benzene (10 cm^3) under dinitrogen. The mixture was refluxed for 5 min and allowed to cool. The burgundy solution was evaporated to dryness under reduced pressure. Trituration of the residue, with diethyl ether, gave the required product as a maroon solid. Yield: 0.22 g (71%).

The complex [(CO)$_3$Mo(μ-dppm)$_2$PtH(C≡CCPh)] (**3d**) was prepared similarly, from *trans*-[PtH(C≡CPh)(PPh$_3$)$_2$] and *fac*-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)]. The Cr–Pt complex (**3b**) was prepared similarly, from *trans*-[PtH(Cl)(PPh$_3$)$_2$] and *mer*-[Cr(CO)$_3$(dppm-*PP′*)(dppm-*P*)], except that the required product was precipitated from the cooled reaction mixture with diethyl ether. When [(CO)$_3$W(μ-dppm)$_2$PtH(Cl)] (**3c**) was prepared in a similar manner to [(CO)$_3$Cr(μ-dppm)$_2$PtH(Cl)] (**3b**), the isolated product was found to be impure. A pure sample of (**3c**) was obtained on recrystallisation from CHCl$_3$–MeOH.

[(CO)$_3$Mo(μ-dppm)$_2$PtH(Br)] (**4a**). A mixture of [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] (**3a**) (0.200 g, 0.16 mmol) in dichloromethane (5 cm^3) and NaBr (0.20 g, 1.9 mmol) in water (5 cm^3)

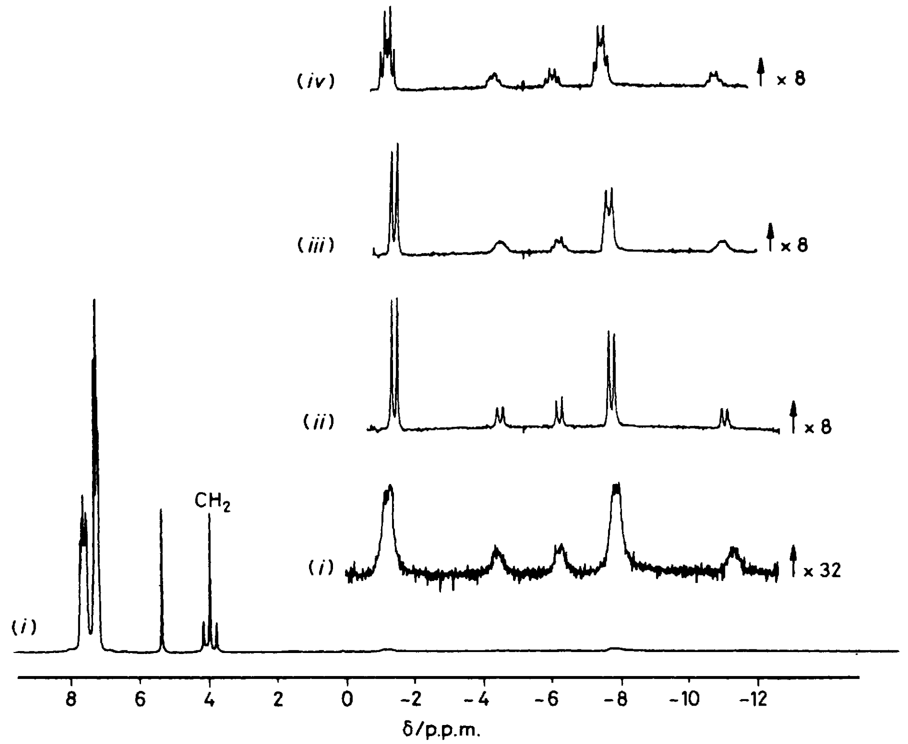


Figure 2. Proton n.m.r. spectra of [(CO)$_3$Mo(μ-dppm)$_2$(μ-H)PtH] (**4d**) at 100 MHz in CD$_2$Cl$_2$: (*i*) at +21 °C with complete decoupling of ^{31}P, (*ii*) at −30 °C with complete decoupling of ^{31}P, (*iii*) at −30 °C with selective decoupling of ^{31}P$_B$, *i.e.* irradiation at 20.9 p.p.m., and (*iv*) at −30 °C with selective decoupling of ^{31}P$_A$, *i.e.* irradiation at 44.2 p.p.m. (see Table 3)

was stirred, in the presence of NMe$_4$Br (0.010 g, 0.06 mmol) as a phase-transfer catalyst, for 4 h. The aqueous layer was separated from the dichloromethane layer and discarded. The maroon dichloromethane layer was evaporated to dryness under reduced pressure, and the resultant residue recrystallised from CH$_2$Cl$_2$–MeOH to give the required product as a red-pink solid. Yield: 0.145 g (70%).

[(CO)$_3$Mo(μ-dppm)$_2$PtH(CN)] (**4b**) and [(CO)$_3$Mo(μ-dppm)$_2$PtH(N$_3$)] (**4c**) were prepared similarly.

[(CO)$_3$Mo(μ-dppm)$_2$(μ-H)PtH] (**4d**). NaBH$_4$ (0.015 g, 0.39 mmol) was added to a stirred solution of [(CO)$_3$Mo(μ-dppm)$_2$-PtH(Cl)] (**3a**) (0.200 g, 0.16 mmol) in dichloromethane (8 cm^3) followed by methanol (3 cm^3). Effervescence was observed and the solution became orange within 5 min. A further portion of methanol (*ca.* 5 cm^3) was added, and the solution concentrated until the required product was deposited as an orange solid. Yield: 0.159 g (85%).

[(CO)$_3$Mo(μ-dppm)$_2$PtH(CO)]PF$_6$ (**4e**). A solution of TlPF$_6$ (0.045 g, 0.13 mmol) in acetone (1 cm^3) was added to a carbon monoxide-saturated solution of [(CO)$_3$Mo(μ-dppm)$_2$PtH(Cl)] (**3a**) (0.150 g, 0.12 mmol) in dichloromethane (10 cm^3). Carbon monoxide was bubbled into the solution for a further 5 min, during which time a white precipitate of TlCl formed. The yellow-orange solution was filtered into CO-saturated benzene and the mixture evaporated by passing CO into it. The required product was deposited as orange microcrystals as the dichloromethane evaporated. Yield: 0.124 g (72%).

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References

1 Part 15, S. W. Carr and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1986, 1815.
2 D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 859.
3 A. Blagg, A. T. Hutton, P. G. Pringle, and B. L. Shaw, *Inorg. Chim. Acta*, 1983, **76**, L265.
4 A. Blagg, A. T. Hutton, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 1815.
5 A. Blagg, G. R. Cooper, P. G. Pringle, R. Robson, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1984, 933.
6 A. Blagg, A. T. Hutton, B. L. Shaw, and M. Thornton-Pett, *Inorg. Chim. Acta*, 1985, **100**, L33.
7 W. A. G. Graham and E. E. Isaacs, *Inorg. Chem.*, 1975, **14**, 2560.
8 A. Blagg, T. Boddington, S. W. Carr, G. R. Cooper, I. D. Dobson, J. B. Gill, D. C. Goodall, B. L. Shaw, and N. Taylor, *J. Chem. Soc., Dalton Trans.*, 1985, 1213.
9 U. Belluco, 'Organometallic and Coordination Chemistry of Platinum,' Academic press, London, New York, 1974.
10 B. Deubzer and H. D. Kaesz, *J. Am. Chem. Soc.*, 1968, **90**, 3276.
11 R. G. Hayter, *J. Am. Chem. Soc.*, 1966, **88**, 4376.
12 K. A. Azam, M. P. Brown, M. C. Grossel, R. H. Hill, R. P. Moulding, C. D. Nelson, R. J. Puddephatt, and K. R. Seddon, *J. Am. Chem. Soc.*, 1983, **105**, 5642.
13 M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1978, 516.
14 K. A. Azam and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1396.
15 M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1968, 3074.
16 J. Powell and B. L. Shaw, *J. Chem. Soc.*, 1965, 3879.
17 H. D. Empall, E. M. Hyde, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 1690.

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