Some Chemistry of the Heterobimetallic Complexes $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ and $[(OC)_3Mo(\mu\text{-dppm})_2M(CO)_2]PF_6$ (M = Rh or Ir, dppm = $Ph_2PCH_2PPh_2$). Structure of $[(OC)_3Mo(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CMe)Rh(CO)]$ †

Adrian Blagg, Richard Robson, Bernard L. Shaw,* and Mark Thornton-Pett
School of Chemistry, The University of Leeds, Leeds LS2 9JT

The previously described complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ (**1a**) does not readily undergo metathesis, thus when treated with NaI it gave $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)I]$ in only *ca.* 50% yield even after 3 h. However, the salt $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (**2a**) when treated with NH_4Br, NH_4I, NaN_3, or NaCN gave complexes of type $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)X]$ (X = Br, I, N_3, or CN) in good yield. $^{31}P\text{-}\{^1H\}$ N.m.r. evidence suggests that $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Br]$ occurs in two forms, a major form analogous to (**1a**) and a minor form (**3**) which possibly has a semibridging CO. Complex (**1a**) or (**2a**) reacts with $NaBH_4$ to give a hydrido complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)H]$. Treatment of (**2a**) with Li(C≡CR) gave the acetylide complexes $[(OC)_3Mo(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CR)Rh(CO)]$ (R = Me, Ph, or C_6H_4Me-*p*) (**4a**)—(**4c**). Treatment of (**1a**) or (**2a**) with MeCN in the presence of PF_6^- gave the complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(NCMe)]PF_6$. The previously described $[(OC)_3Mo(\mu\text{-dppm})_2Ir(CO)_2]PF_6$ reacts similarly with NCR (R = Me or Ph) to give the analogous nitrile complexes $[(OC)_3Mo(\mu\text{-dppm})_2Ir(CO)(NCR)]PF_6$. Treatment of (**1a**) or (**2a**) with Bu^tNC gives $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(CNBu^t)]^+$. Crystals of the compound $[(OC)_3Mo(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CMe)Rh(CO)]$ are triclinic, space group $P\bar{1}$, with *a* = 1 802.2(3), *b* = 1 303.2(3), *c* = 1 228.2(3) pm, α = 114.77(2), β = 97.52(2), γ = 102.02(2)°, and *Z* = 2; final *R'* factor 0.037 for 6 006 observed reflections. The structure shows that the two metal centres [Mo ··· Rh 312.2(0) pm] are asymmetrically bridged by methylacetylide which forms a σ bond to rhodium and a side-on π bond to molybdenum.

We have described in previous papers the preparation of Group 6 metal–rhodium and -iridium complexes of the types $[(OC)_3M^1(\mu\text{-dppm})_2M^2(CO)Cl]$ and $[(OC)_3M^1(\mu\text{-dppm})_2M^2(CO)_2]PF_6$ (M^1 = Cr, Mo, or W; M^2 = Rh or Ir; dppm = $Ph_2PCH_2PPh_2$). We have also reported preliminary studies which indicate that these complexes react with nucleophiles to give new heterobimetallic species.[1] In the present paper we detail some of the chemistry of three of these complexes, $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ (**1a**), $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (**2a**), and $[(OC)_3Mo(\mu\text{-dppm})_2Ir(CO)_2]PF_6$ (**2b**), chosen because of the relative stability of their μ-dppm framework.[2] Nucleophilic attack is expected to occur primarily at the Rh or Ir followed by the possibility of interaction between the new ligand and the molybdenum atom. The rhodium centre of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ is similar to those of the much studied face-to-face dimer $[Cl(OC)Rh(\mu\text{-dppm})_2Rh(CO)Cl]$,[3] enabling the chemistries of the two species to be compared: the rhodium and iridium centres of the heterobimetallic cations (**2a**) and (**2b**) have no analogue in homobimetallic chemistry.

Results and Discussion

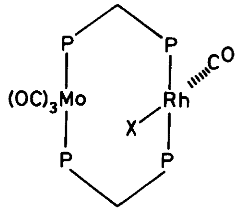
Reactions with Halides and Pseudo-halides.—The neutral complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ (**1a**)[2] is only sparingly soluble in ionizing solvents, and its solubility in chlorinated solvents is also poor. Thus the corresponding bromide and iodide complexes $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)X]$ [X = Br (**1b**) or I (**1c**)] are not readily prepared from the chloro complex (**1a**) by metathesis. For example, treatment of a CH_2Cl_2 solution of (**1a**) with a ten-fold excess of NaI in water, using NMe_4I as a phase-transfer catalyst, gave only a 49% yield of the iodide (**1c**) after 3 h. The bromide (**1b**) and iodide (**1c**) analogues were more conveniently synthesized from $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (**2a**)[2] and an excess of the corresponding halide. Treatment of an acetone solution of cationic complex (**2a**) with a five-fold excess of NH_4Br in methanol gave $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Br]$ in 91% yield after only 15 min, see Experimental section. The iodide complex (**1c**) was prepared, similarly, in 93% yield. These neutral complexes are characterized by $^{31}P\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ n.m.r. spectroscopy, microanalysis, and i.r. spectroscopy (see Tables 1—3).

The 40.25-MHz $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Br]$ (**1b**) at +20 °C shows a broad, poorly separated, simplified AA′BB′ splitting pattern. At high field (161 MHz) the resonances are broad and poorly defined [see Figure 1(*i*)] suggesting that two (or more) species are in rapid dynamic equilibrium. The 161-MHz $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum at −50 °C is well defined, showing two new heterobimetallic species in the ratio of *ca.* 17:1 [see Figure 1(*ii*)]. It is possible that rapid interconversion of these species on the n.m.r. time-scale, at ambient temperatures, leads to the observed broadening of the $^{31}P\text{-}\{^1H\}$ n.m.r. resonances: additionally, CO ligands might be scrambling between Mo and Rh at ambient temperatures. The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Br]$ shows a broad singlet for the PCH_2P protons at +20 °C which sharpens to an AB pattern at −30 °C. This AB pattern is assigned to the methylene protons of the major isomer; no resonance(s) attributable to the PCH_2P hydrogens of the minor species was(were) observed, presumably due to lack of intensity. The i.r. spectrum shows four carbonyl stretching bands, the lowest frequency of which indicates that the major isomer has no bridging carbonyl and we therefore suggest it has structure (**1b**). The structure of the minor isomer is uncertain: it may

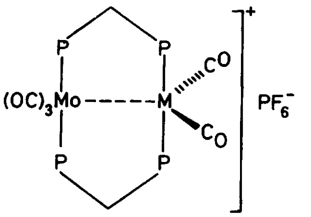
---

† Bis[μ-bis(diphenylphosphino)methane]-1,2,2,2-tetracarbonyl-μ-propynyl-C^1(Mo,Rh)C^2(Mo)-1-rhodium-2-molybdenum.

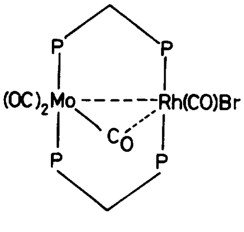
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.



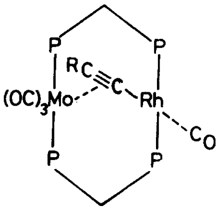
X
(**1a**) Cl
(**1b**) Br
(**1c**) I
(**1d**) N_3
(**1e**) CN
(**1f**) H



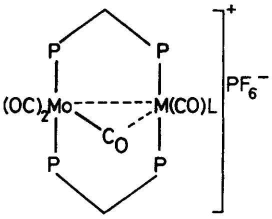
M
(**2a**) Rh
(**2b**) Ir



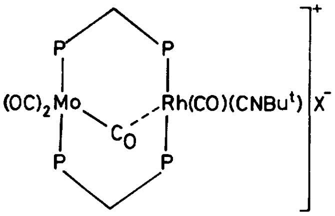
(**3**)



R
(**4a**) Me
(**4b**) Ph
(**4c**) C_6H_4Me-*p*



L M
(**5a**) NCMe Ph
(**5b**) NCMe Ir
(**5c**) NCPh Ir



(**6**) X = Cl

have the semibridging carbonyl structure (**3**) by analogy with the previously characterized complex [(OC)$_3$Cr(μ-dppm)$_2$Rh(CO)Cl].[2,*]

The 40.25-MHz ^{31}P-{^{1}H} n.m.r. spectrum of [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)I] shows a sharp, simplified AA'BB' splitting pattern at 20 °C characteristic of a single heterobinuclear species. We tentatively assign this species the structure (**1c**). Interestingly, treatment of [Rh$_2$(CO)$_2$Cl$_2$(μ-dppm)$_2$] with a five-fold excess of halide salt (NaBr or KI) gives the μ-carbonyl species [Rh$_2$(CO)(μ-CO)X(μ-dppm)$_2$]X rather than the corresponding face-to-face complexes [Rh$_2$(CO)$_2$X$_2$(μ-dppm)$_2$] (X = Br or I):[4] [Rh$_2$(CO)(μ-CO)Br(μ-dppm)$_2$]Br subsequently rearranges in solution to give the 'A-frame' complex [Rh$_2$(μ-CO)Br$_2$(μ-dppm)$_2$].[4] It is thought that the bulkier bromide and iodide ligands make the face-to-face structure [Rh$_2$(CO)$_2$X$_2$(μ-dppm)$_2$], where X = Br or I, unstable. Clearly this is not the case for our heterobimetallic species (**1b**) and (**1c**).

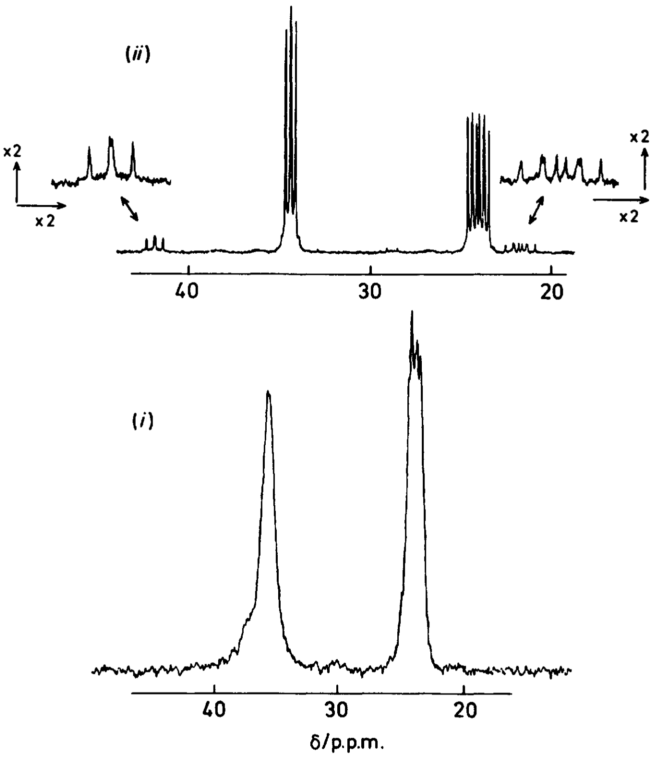


Figure 1. 161-MHz ^{31}P-{^{1}H} N.m.r. spectra of [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)Br] at (*i*) +20 °C and (*ii*) −50 °C

Attack on the rhodium centre of [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)$_2$]PF$_6$ by pseudo-halides also leads to elimination of CO and formation of neutral species. For example, treatment of an acetone solution of the Mo–Rh cation (**2a**) with NaN$_3$ in methanol gave an azido complex of formula [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)N$_3$] (**1d**) in 89% yield. The cyanide complex [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)CN] (**1e**) was similarly prepared in 67% yield.

Reactions with Hydride.—When 1.2 mol equivalents of NaBH$_4$ in methanol were added to a solution/suspension of [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)Cl] (**1a**) in CH$_2$Cl$_2$, under a N$_2$ atmosphere, a dark red solution formed with rapid evolution of gas. ^{31}P-{^{1}H} N.m.r. spectroscopy showed this solution to contain two heterobinuclear species in the ratio of *ca.* 2:1. The major species was the unchanged starting material (**1a**), whereas the minor species was the new heterobimetallic hydrido complex [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)H] (**1f**). The hydrido complex could not be isolated pure by this method of preparation despite repeated attempts, but was readily obtained by treatment of [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)$_2$]PF$_6$ with a slight excess of NaBH$_4$ in acetone solution, see Experimental section. The ^{1}H-{^{31}P} n.m.r. spectrum of (**1f**) showed a singlet at 3.69 p.p.m. assigned to the CH$_2$ protons, and a hydride resonance at −11.4 p.p.m. split into a doublet by ^{103}Rh. However, no ν(Rh–H) absorption was observed in the i.r. spectrum, presumably due to lack of intensity. When [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)$_2$]PF$_6$ was reduced with NaBD$_4$ we could not observe a band due to ν(Rh–D).

Treatment of [Rh$_2$(CO)$_2$Cl$_2$(μ-dppm)$_2$] with NaBH$_4$ in ethanol does not give a hydrido complex, instead a purple air-sensitive rhodium(0) species [Rh$_2$(CO)$_2$(μ-dppm)$_2$] is formed.[5]

---

[*] It is possible that in some of the compounds of type (**1**) the X group bridges Mo and Rh. In the case of X = Cl, *i.e.* (**1a**), we have suggested that a bridging chlorine is unlikely since the PCH$_2$P protons are equivalent in the ^{1}H-{^{31}P} n.m.r. spectrum at room temperature and we thought this showed that Mo···Cl interaction was at best weak. However, we cannot exclude the possibility completely for X = other groups or atoms. With compound (**4a**) (see below), for which the crystal structure shows that the methylacetylide group is bridging, the PCH$_2$P methylene protons are non-equivalent (see Table 3).

Table 1. Microanalytical[a] and conductivity data in nitrobenzene at 20 °C

	Complex		Analyses		
	M	X	C	H	Other(s)
(1b)	Rh	Br	56.0 (55.9)	3.85 (3.8)	Br 6.95 (6.9)
(1c)	Rh	I	53.85 (53.75)	3.6 (3.7)	I 10.8 (10.5)
(1d)	Rh	N_3	57.6 (57.8)	3.9 (3.95)	N 3.65 (3.75)
(1e)	Rh	CN	59.5 (59.7)	3.95 (4.0)	N 1.51 (1.3)
(1f)	Rh	H	59.85 (60.0)	4.1 (4.2)	
(4a)·$0.25CH_2Cl_2$	Rh	C≡CMe	60.0 (60.3)	4.05 (4.2)	Cl 1.85 (1.55)
(4b)·thf	Rh	C≡CPh	63.3 (63.25)	4.45 (4.6)	
(4c)·thf	Rh	$C≡CC_6H_4Me$-*p*	63.65 (63.5)	4.5 (4.7)	
(5a)	Rh	NCMe[b]	51.95 (53.15)	3.6 (3.75)	N 0.9 (1.10)
(5b)	Ir	NCMe	48.3 (49.6)	3.3 (3.5)	N 0.9 (1.0)
(5c)	Ir	NCPh	53.35 (53.75)	3.6 (3.6)	N 1.7 (1.85)
(6)	Rh	$CNBu^t$[c]	58.0 (59.15)	4.9 (4.45)	N 1.85 (1.15) Cl 2.8 (2.95)

[a] Calculated values in parentheses. [b] $\Lambda = 26\ \Omega^{-1}\ cm^2\ mol^{-1}$. [c] $\Lambda = 20\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Table 2. $^{31}P-\{^1H\}$ N.m.r. and i.r. data

	$^{31}P-\{^1H\}$ N.m.r.[a]				I.r. (cm^{-1})[b]	
Complex	$\delta(P_A)$	$\delta(P_B)$	$^1J(Rh-P_B)$	N[c]/Hz	ν(CO)	Others
(3)[d,e]	[f] 41.7	21.6	113	145	1 977s, 1 952s,br, 1 852s,br, 1 798s,br	
(1b)	[g] 34.2	23.9	109	87		
(1c)	[e] 31.3	23.3	103	102	1 976 (sh), 1 951vs,br, 1 863s,br, 1 786s,br	
(1d)	38.7	23.6	123	59	1 974s, 1 942s,br, 1 838s,br, 1 808s,br	$\nu(N_3)$ 2 080s
(1e)	42.6	26.7	117	145	1 985s,br, 1 939s,br, 1 805s,vbr[h]	ν(CN) 2 100w
(1f)	43.6	26.0	122	124	1 983s,br, 1 946s,br, 1 842vs,br, 1 825 (sh)[h]	
(4a)	36.0	25.5	124	76	1 987s, 1 926s, 1 824s, 1 800s,br	ν(C≡C) 2 024w
(4b)	[e] 36.0	25.0	112	82	1 975 (sh), 1 942s,br, 1 846s,br, 1 813s,br	
(4c)	36.0	25.2	115	83	1 974m, 1 939s,br, 1 851s, 1 822s,br	
(5a)	43.1	22.4	110	112	[i] 1 986vs,vbr, 1 836s,vbr, 1 789s,vbr [i] 2 016 (sh), 1 995vs,br, 1 834s,br, 1 794s,br, 1 744m[h]	
(5b)	44.2	14.6		115	[i] 2 000s, 1 983vs,br, 1 790s,br[h]	
(5c)	43.5	15.2		116	[i] 1 994s, 1 958s, 1 783s, 1 768s	
(6)	42.1	24.5	115	135	1 961s,vbr, 1 785s,vbr	ν(CN) 2 134s,br

[a] Spectra recorded at 40.25 MHz and +20 °C in CD_2Cl_2, unless otherwise stated; 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 bound to Mo, P_B to rhodium or iridium. [b] Spectra recorded for Nujol mulls unless otherwise stated. [c] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [d] Spectrum recorded at 162 MHz and −50 °C. [e] In $CDCl_3$. [f] Minor species. [g] Major species. [h] In CH_2Cl_2 solution. [i] ν(CO) or ν(CN).

In contrast, treatment of the mononuclear species $[Rh(CO)Cl(PPh_3)_2]$ with $NaBH_4$ in ethanol, in the presence of PPh_3, gives the rhodium(I) hydrido complex $[Rh(CO)H(PPh_3)_3]$;[6] thus the rhodium centres of the Mo–Rh complexes **(1a)** and **(2a)** react in a similar fashion to give mononuclear species when treated with $NaBH_4$, rather than as the dirhodium species $[Rh_2(CO)_2Cl_2(\mu\text{-dppm})_2]$.

Reactions with Acetylides.—Treatment of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ with 1 mol equivalent of Li(C≡CR) (R = Me, Ph, or C_6H_4Me-*p*) in tetrahydrofuran (thf) gave, after rapid evolution of gas, heterobimetallic complexes of composition $[MoRh(CO)_4(C≡CR)(\mu\text{-dppm})_2]$. The structure of the methylacetylide complex was established as **(4a)** by *X*-ray diffraction (see below) and the phenylacetylide and *p*-tolylacetylide are assigned analogous structures **(4b)** and **(4c)** respectively. The $^1H-\{^{31}P\}$ n.m.r. spectra of $[MoRh(CO)_4(C≡CR)(\mu\text{-dppm})_2]$ all showed an AB pattern for the PCH_2P protons, at 20 °C, with coupling of the lower-frequency methylene resonance (assigned to the pseudo-equatorial hydrogens H_e) to ^{103}Rh. The higher-frequency CH_2 resonance (assigned to the pseudo-axial hydrogens H_a) was not observably coupled to ^{103}Rh: this feature is associated with Karplus-type behaviour of the $^3J(Rh-H)$ couplings, *i.e.* a transoid arrangement Rh–P–C–H_e gives the observable coupling. A weak band at 2 024 cm^{-1}, attributed to ν(C≡C), was observed in the i.r. spectrum of the methylacetylide complex **(4a)** whereas the i.r. spectra of the phenylacetylide **(4b)** and *p*-tolylacetylide **(4c)** complexes showed no such absorption. The low frequency of the ν(C≡C) band of **(4a)** suggested that the methylacetylide group was in a bridging mode. By analogy, the phenylacetylide and *p*-tolylacetylide groups of **(4b)** and **(4c)** are also bridging, their ν(C≡C) absorptions being masked by ν(C≡O) bands. The μ-C≡CR group might act either as a two-electron donor, forming a three-centre two-electron bond, as in $[(p\text{-}MeC_6H_4C≡C)Pt(\mu\text{-}C≡CC_6H_4Me\text{-}p)(\mu\text{-dppm})_2W(CO)_3]$,[7] or as a four-electron donor, forming a σ,π-bridging bond as in $[ClPt(\mu\text{-}C≡CMe)(\mu\text{-dppm})_2Rh(CO)]PF_6$.[8] Because of these uncertainties the *X*-ray crystal structure of the methylacetylide complex **(4a)** was determined.

Crystal Structure of $[(OC)_3Mo(\mu\text{-dppm})_2(\mu\text{-}C≡CMe)Rh(CO)]$ **(4a)**.—The complex **(4a)** crystallized from CH_2Cl_2–MeOH as orange needles. The molecular structure is shown in

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

Complex	θ_C/°C	Methylene resonances	Other resonances
(1b)	20	3.48	
	−30	4.06, 3.19, J(HH) 13	
(1a)	20	4.19, 3.52, J(HH) 13	
(1d)	−30	3.49, 3.40, J(HH) 14	
(1e)	20	2.83	
(1f)	20[b]	3.69	δ(H) −11.4, J(RhH) 22
(4a)	20	δ(H_a) 3.63, δ(H_e) 2.82, ^3J(RhH_e) 2, J(H_aH_a) 12	δ(CH_3) 1.26
(4b)	20	δ(H_a) 3.82, δ(H_e) 2.84, ^3J(RhH_e) 2, J(H_aH_e) 12	
(4c)	20	[b]δ(H_a) 3.78, δ(H_e) 2.94, ^3J(RhH_e) *ca.* 2, J(H_aH_e) 12	δ(CH_3) 2.23
(5a)	20	[b]δ(H_a) 3.23, δ(H_e) 3.41, ^3J(RhH_e) 1, J(H_aH_e) 14	δ(CH_3) 1.21
(5b)	20	[b]3.38, 3.10, J(HH) 14	δ(CH_3) 1.24
(6)	20	[b]3.00	δ(CH_3) 0.37

[a] Spectra (100 MHz) measured in $CDCl_3$, unless otherwise stated; chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz(±0.3). H_a and H_e are defined in the text.
[b] Spectrum measured in CD_2Cl_2.

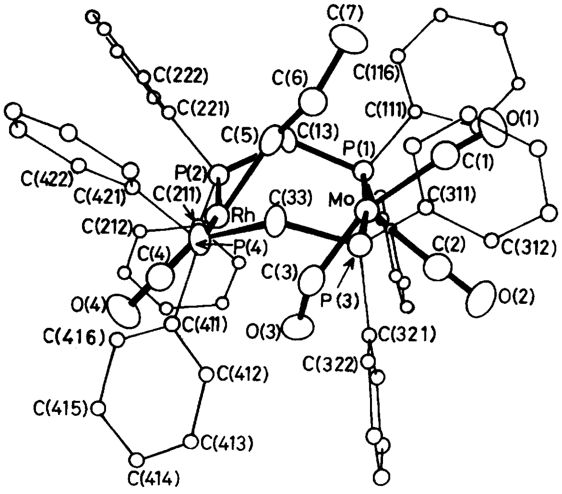


Figure 2. Molecular structure of $[(OC)_3Mo(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CMe})Rh(CO)]$ (**4a**), showing the principal atomic numbering

Table 4. Selected interatomic distances (pm) and angles (°) for complex (**4a**) with estimated standard deviations (e.s.d.s) in parentheses

Mo···Rh	312.2(0)	Rh–P	230.9(3)*
Mo–P	245.5(3)*	Rh–C(5)	201.6(5)
Mo–C(5)	248.4(6)	Rh–C(4)	186.4(5)
Mo–C(6)	261.6(8)	Rh–C(3)	250.0(7)
Mo–C(1)	200.0(5)	C(5)–C(6)	121.8(5)
Mo–C(2)	192.7(7)	C(1)–O(1)	115.1(5)
Mo–C(3)	206.8(5)	C(2)–O(2)	117.5(7)
		C(3)–O(3)	116.9(6)
		C(4)–O(4)	114.3(5)

C(4)–Rh–C(5)	172.0(2)	Rh–C(5)–C(6)	162.7(2)
C(2)–Mo–C(5)	175.3(1)	Mo–C(3)–O(3)	160.1(3)
C(1)–Mo–C(3)	162.7(2)	C(7)–C(6)–C(5)	164.4(5)
		Mo–C(1)–O(1)	174.3(4)

* Average value.

Figure 2 and the relevant interatomic distances and angles are given in Table 4. The acetylide is σ-bonded to rhodium and forms an unsymmetrical side-on π bond to molybdenum. This bridging mode is analogous to that of the weakly bridging methylacetylide group in $[ClPt(\mu\text{-C}\equiv\text{CMe})(\mu\text{-dppm})_2Rh(CO)]PF_6$. The geometry about the molybdenum is approximately octahedral with the μ-acetylide group occupying the sixth co-ordination site. By accepting two electrons from the π system of the acetylide group the molybdenum(0) centre achieves the stable eighteen-electron configuration. The Rh^I has approximately square-planar geometry and a sixteen-electron count. Interestingly, the C≡C group is bent slightly towards the molybdenum centre to facilitate interaction, whereas the methyl group of (C≡CMe) is bent away from the Mo atom; this reduces steric interaction with the pseudo-equatorial phenyl rings. The Mo···Rh separation [312.2(0) pm] is considerably longer than previously determined Mo–Rh bond lengths, *viz.* 259—296 pm,[9,10] ruling out any significant metal–metal interaction. Another interesting feature of the structure is the bent molybdenum carbonyl group Mo–C(3)–O(3), *i.e.* the carbonyl might be semibridging. However, the rhodium–carbonyl carbon separation [250.0(7) pm] is longer than previously determined for semibridging carbonyls to rhodium (217—242 pm),[11] indicating that if an interaction is present at all it is only weak. Thus the distortion of the Mo–C(3)–O(3) bond angle from 180° may be just a crystal-packing effect.

Reactions with Small Molecules.—No reaction was observed (by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy) after 30 min of refluxing a CH_2Cl_2 solution of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ with MeCN. However, when this mixture was heated in the presence of $NaPF_6$ a new heterobimetallic species was formed in under 20 min. The new acetonitrile-containing species could not be isolated pure by this method despite repeated attempts. The complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ also reacted with hot MeCN to give the same heterobinuclear species (^{31}P-$\{^1H\}$ n.m.r. evidence), as an orange-brown microcrystalline solid. The orange-brown product was assigned the formula $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(NCMe)]PF_6$ (**5a**) on the basis of ^{31}P-$\{^1H\}$ and ^1H-$\{^{31}P\}$ spectroscopy, a conductivity measurement, and i.r. spectroscopy (a satisfactory microanalysis was not obtained presumably because of partial MeCN loss). Similarly, treatment of $[(OC)_3Mo(\mu\text{-dppm})_2Ir(CO)_2]PF_6$ with RCN (R = Me or Ph) under reflux gave nitrile complexes of formula $[(OC)_3Mo(\mu\text{-dppm})_2Ir(CO)(NCR)]PF_6$ [R = Me (**5b**) or Ph (**5c**)]. The ^1H-$\{^{31}P\}$ n.m.r. spectra (20 °C) of (**5a**) and (**5b**) showed an AB pattern for the PCH_2P protons, and a singlet assigned to the methyl hydrogens of co-ordinated acetonitrile. In addition, coupling of the high-frequency CH_2 resonance (assigned to H_e) to ^{103}Rh was observed in the case of (**5a**). The i.r. spectra of the nitrile complexes (**5a**)—(**5c**) all showed low-frequency carbonyl stretching bands (< 1 790 cm^{-1}) suggesting the presence of bridging and/or semibridging carbonyls. We thus assign structures (**5a**)—(**5c**) to these complexes.

Treatment of the acetonitrile complex (**5a**) or (**5b**) with an excess of a chloride salt, $NEt_3(CH_2Ph)Cl$, gave the corresponding neutral species $[(OC)_3Mo(\mu\text{-dppm})_2M(CO)Cl]$ (M = Rh or Ir) in near-quantitative yield (^{31}P-$\{^1H\}$ n.m.r. evidence). In contrast, ^{31}P-$\{^1H\}$ n.m.r. spectroscopy showed none of the hoped-for $[(OC)_3Mo(\mu\text{-dppm})_2M(CO)_2]PF_6$ (M = Rh or Ir) to be formed after 1 h of bubbling carbon monoxide into a CH_2Cl_2 solution of (**5a**) or (**5b**).

The complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ reacted with 1 mol equivalent of Bu^tNC in CH_2Cl_2 to give a dark orange product, formulated as $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(CNBu^t)]Cl$ (**6**). The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum (20 °C) showed a singlet for the PCH_2P protons at 3.00 p.p.m., and a singlet at 0.37 p.p.m. assigned to the methyl hydrogens of co-ordinated $CNBu^t$. The i.r. spectrum (in CH_2Cl_2 solution) showed a broad band at 2 139 cm^{-1} assigned to $\nu(C{\equiv}N)$ of terminal $CNBu^t$ and two very broad carbonyl bands at 1 971 and 1 786 cm^{-1}. These carbonyl bands are attributed to two CO groups each, with the lower-frequency absorption being indicative of a semibridging mode.

Experimental

General methods were as previously described in recent papers from this laboratory.[12]

Preparations.—$[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Br]$ (**1b**). A solution of ammonium bromide (0.068 g, 0.69 mmol) in methanol (5 cm^3) was added to a solution of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (0.15 g, 0.12 mmol) in acetone (5 cm^3) with stirring. The solution became orange-red, immediately, and the required product was deposited over 15 min as deep orange microcrystals. Yield 0.120 g (91%).

The complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)I]$ (**1c**) was prepared similarly as red-orange crystals in 93% yield, or alternatively by metathesis from $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ in 49% yield. The azide (**1d**) and cyanide (**1e**) complexes were prepared, in a similar manner to (**1b**) using a slight excess of the pseudo-halide, as orange crystals in 89 and 67% yields, respectively.

$[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)H]$ (**1f**). Sodium tetrahydroborate (0.008 g, 0.21 mmol) was added to a stirred solution of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (0.200 g, 0.15 mmol) in acetone (6 cm^3). A gas was immediately evolved and the solution became deep red. The reaction mixture was stirred for a few minutes, then methanol was added to precipitate the required product as red microcrystals. Yield 0.123 g (75%).

$[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(C{\equiv}CMe)]$ (**4a**). n-Butyl-lithium (1.55 mol dm^{-3}, 0.155 mmol) in hexane (0.10 cm^3) was added with stirring to cooled (0 °C), dry thf (6 cm^3) into which an excess of methylacetylene [80 cm^3 at 20 °C, 1 atm (101 325 Pa); 3.6 mmol] had been bubbled. The mixture was stirred at 0 °C for 5 min, then allowed to warm to room temperature over 15 min. The complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (0.200 g, 0.15 mmol) was then added followed by dry thf (4 cm^3). The mixture was stirred for 50 min, then evaporated to dryness under reduced pressure. The orange residue was recrystallized from CH_2Cl_2–MeOH yielding the required product as orange crystals. Yield 0.093 g (55%).

$[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(C{\equiv}CPh)]$ (**4b**). n-Butyl-lithium (1.55 mol dm^{-3}, 0.155 mmol) in hexane (0.10 cm^3) was added with stirring to a cool (0 °C) solution of phenylacetylene (0.047 g, 0.46 mmol) in dry thf (5 cm^3). The mixture was stirred at 0 °C for 10 min then allowed to warm to room temperature over 15 min. The complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (0.200 g, 0.15 mmol) was then added. A gas was immediately evolved and the solution became red. The reaction mixture was stirred for a further 30 min then filtered. Methanol was added to the filtrate to precipitate out the required product as orange microcrystals. Yield 0.149 g (79%). The complex $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(C{\equiv}CC_6H_4Me\text{-}p)]$ (**4c**) was prepared similarly in 79% yield.

Table 5. Atom co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
Mo	2 367.4(2)	1 663.4(2)	−1 071.2(3)
Rh	2 884.6(2)	3 170.5(2)	1 802.3(2)
P(1)	3 533(1)	971(1)	−997(1)
P(2)	3 946(1)	2 458(1)	1 946(1)
P(3)	1 704(1)	2 359(1)	−914(1)
P(4)	1 734(1)	3 666(1)	1 982(1)
C(1)	1 726(2)	95(3)	−2 458(4)
O(1)	1 367(2)	−767(3)	−3 322(3)
C(2)	2 463(2)	1 955(3)	−2 468(3)
O(2)	2 490(2)	2 077(3)	−3 358(3)
C(3)	3 111(2)	3 366(3)	−76(3)
O(3)	3 534(2)	4 276(2)	138(2)
C(4)	3 472(2)	4 721(3)	2 900(3)
O(4)	3 827(2)	5 673(2)	3 578(3)
C(5)	2 245(2)	1 460(3)	825(3)
C(6)	1 899(2)	441(3)	72(4)
C(7)	1 488(3)	−848(4)	−541(4)
C(111)	3 388(2)	−612(2)	−2 002(3)
C(112)	3 202(2)	−965(2)	−3 269(2)
C(113)	3 053(2)	−2 150(2)	−4 114(2)
C(114)	3 090(2)	−2 983(2)	−3 691(1)
C(115)	3 276(2)	−2 631(2)	−2 424(2)
C(116)	3 426(2)	−1 445(2)	−1 580(2)
C(121)	4 395(1)	1 563(2)	−1 449(2)
C(122)	4 418(1)	2 463(2)	−1 788(2)
C(123)	5 082(1)	2 922(2)	−2 099(2)
C(124)	5 722(1)	2 481(2)	−2 071(2)
C(125)	5 699(1)	1 581(2)	−1 731(2)
C(126)	5 035(1)	1 122(2)	−1 420(2)
C(13)	3 960(2)	1 150(3)	552(3)
C(211)	4 885(1)	3 570(2)	2 390(2)
C(212)	5 258(1)	4 279(2)	3 640(2)
C(213)	5 918(1)	5 235(2)	3 999(2)
C(214)	6 205(1)	5 483(2)	3 107(2)
C(215)	5 832(1)	4 774(2)	1 857(2)
C(216)	5 172(1)	3 818(2)	1 498(2)
C(221)	4 036(1)	1 882(2)	3 071(2)
C(222)	3 383(1)	1 571(2)	3 488(2)
C(223)	3 436(1)	1 102(2)	4 319(2)
C(224)	4 141(1)	943(2)	4 732(2)
C(225)	4 795(1)	1 254(2)	4 315(2)
C(226)	4 742(1)	1 724(2)	3 484(2)
C(311)	274(1)	1 286(2)	−1 988(2)
C(312)	77(1)	1 221(2)	−3 157(2)
C(313)	−605(1)	389(2)	−4 017(2)
C(314)	−1 089(1)	−379(2)	−3 708(2)
C(315)	−892(1)	−313(2)	−2 539(2)
C(316)	−210(1)	519(2)	−1 679(2)
C(321)	1 171(1)	3 655(2)	−1 166(2)
C(322)	500(1)	4 030(2)	−1 125(2)
C(323)	484(1)	5 026(2)	−1 281(2)
C(324)	1 138(1)	5 647(2)	−1 478(2)
C(325)	1 809(1)	5 272(2)	−1 518(2)
C(326)	1 826(1)	4 276(2)	−1 362(2)
C(33)	931(2)	2 739(3)	579(3)
C(411)	1 756(1)	5 201(2)	2 336(2)
C(412)	2 145(1)	5 717(2)	1 728(2)
C(413)	2 146(1)	6 855(2)	1 936(2)
C(414)	1 758(1)	7 477(2)	2 781(2)
C(415)	1 368(1)	6 961(2)	3 419(2)
C(416)	1 367(1)	5 823(2)	3 211(2)
C(421)	1 308(1)	3 454(2)	3 173(2)
C(422)	1 820(1)	3 616(2)	4 226(2)
C(423)	1 530(1)	3 552(2)	5 202(2)
C(424)	728(1)	3 326(2)	5 124(2)
C(425)	217(1)	3 165(2)	4 071(2)
C(426)	507(1)	3 229(2)	3 095(2)

$[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(NCMe)]PF_6$ (**5a**). A solution of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ (0.200 g, 0.15 mmol) in MeCN (10 cm^3, 190 mmol) was refluxed under dinitrogen for 5 min. The reaction mixture was allowed to cool then reduced in volume under reduced pressure. Diethyl ether was added to precipitate the required product as orange-brown microcrystals. Yield 0.167 g (84%).

The Mo–Ir acetonitrile (**5b**) and benzonitrile (**5c**) complexes were prepared similarly, in 85 and 81% yields, respectively.

$[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)(CNBu^t)]Cl$ (**6**). A solution of $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ (0.200 g, 0.18 mmol) in CH_2Cl_2 (10 cm^3) was treated with Bu^{t}NC (0.66 mol dm^{-3}, 0.2 mmol) in CH_2Cl_2 (0.3 cm^3). The reaction mixture was stirred for 20 min then reduced in volume under reduced pressure. Hexane was then added to precipitate the required product as a dark orange solid. Yield 0.200 g (94%).

Crystallographic Studies.—Unit-cell and intensity data were obtained using a Syntex $P2_1$ diffractometer operating in the ω—2θ scan mode using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm) following a procedure described elsewhere in detail.[13] The data set was corrected for absorption once the structure had been solved.[14] The structure was solved *via* standard heavy-atom techniques and refined by blocked full-matrix least-squares refinement using the SHELX program system.[15] All non-hydrogen atoms were assigned anisotropic thermal parameters with the phenyl rings treated as rigid bodies with idealized hexagonal symmetry (C–C 139.5 pm). All hydrogen atoms were included in calculated positions (C–H 108 pm) and were assigned an overall isotropic thermal parameter for each methyl, methylene, or phenyl group. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement in order to obtain a flat analysis of variance with increasing $\sin\theta$ and $[F/F_{max.}]^{\frac{1}{2}}$.

Crystal data. $C_{57}H_{47}MoO_4P_4Rh$, M = 1 118.74, triclinic, a = 1 802.2(3), b = 1 303.2(3), c = 1 228.2(3) pm, α = 114.77(2), β = 97.52(2), γ = 102.02(2)°, U = 2.483 nm^3, space group $P\bar{1}$, Z = 2, D_c = 1.496 g cm^{-3}, μ(Mo-K_α) = 6.74 cm^{-1}, $F(000)$ = 1 136.

Data collection. Scans running from 1° below K_{α_1} to 1° above K_{α_2}, scan speeds 2.0—29.3° min^{-1}, $4.0 \leqslant 2\theta \leqslant 45.0°$. 6 349 Unique data, 6 006 observed [$I > 2.0\sigma(I)$], T = 290 K.

Structure refinement. Number of parameters = 539, weighting factor g = 0.0005, R = 0.0301, R' = 0.0371. The final atomic co-ordinates and their standard deviations are listed in Table 5.

Acknowledgements

We thank the S.E.R.C. for support and Johnson Matthey Ltd. for the loan of rare metal salts.

References

1 A. Blagg, G. R. Cooper, P. G. Pringle, R. Robson, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1984, 933.

2 A. Blagg, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1987, 1495.

3 A. R. Sanger, *J. Chem. Soc., Chem. Commun.*, 1975, 893.

4 M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 2500.

5 R. Eisenberg, C. P. Kubiak, and C. Woodcock, *Inorg. Chem.*, 1982, **21**, 2119.

6 D. Evans, P. S. Hallman, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 1967, 305.

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

8 A. T. Hutton, C. R. Langrick, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 2121.

9 L. Carlton, W. E. Lindsell, K. J. McCullough, and P. N. Preston, *J. Chem. Soc., Chem. Commun.*, 1982, 1001.

10 R. G. Finke, G. Gaughan, J. H. Noordik, and C. Pierpont, *Organometallics*, 1983, **2**, 1481.

11 M. L. Aldridge, M. Green, J. A. K. Howard, G. N. Pain, S. J. Porter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1333.

12 S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.

13 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.

14 N. Walker and R. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

15 G. M. Sheldrick, SHELX 76, Program System for *X*-Ray Structure Determination, University of Cambridge, 1976.

Received 14*th November* 1986; *Paper* 6/2202