Preparation, Structural Studies, and Some Reactions of New Heterobinuclear Complexes containing Molybdenum, Tungsten, or Manganese and Rhodium or Copper; *X*-Ray Crystal Structures of $[MoRh(CO)(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ and Two Isomers of $[CuW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ †

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Reaction of the anions $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ or $[Mn(CO)_5]^-$ with $[RhCl(PPh_3)_3]$ in tetrahydrofuran produces the formally unsaturated bimetallic complexes $[MRh(CO)(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ [M = Mo (1) or W (2)] or $[MnRh(CO)_2(\mu\text{-}CO)_2(PPh_3)_3]$ (3) respectively. An *X*-ray diffraction study of (1) has established its molecular structure: monoclinic, space group $P2_1/c$, a = 18.102(2), b = 10.407(1), c = 20.736(2) Å, β = 104.99(1)°, and Z = 4. The structure, determined from 5 233 independent intensities, was refined to R = 0.036 (R' = 0.074). It comprises a $Mo(CO)(\eta\text{-}C_5H_5)$ group bonded to $Rh(PPh_3)_2$ with a short Mo–Rh separation 2.588(1) Å and two asymmetric (μ-CO) ligands with Mo–C 1.980(6) and 2.026(5) Å and Rh–C 2.182(6) and 2.092(5) Å; the $Mo(\mu\text{-}CO)_2Rh$ framework has a dihedral angle (Mo–Rh–C/Mo–Rh–C) of 161°. I.r., ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of complexes (1)—(3) are presented and discussed in relation to their structures: formal metal–metal multiple bonds, $Rh\rightleftharpoons M$, are proposed. Complex (1) acts as a catalyst in hydrogenation of cyclohexene and reactions involving the cleavage of M–Rh bonds are described for complexes (1) and (3). Reactions of $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ with $[\{CuCl(PPh_3)\}_4]$ give the bimetallic products $[CuM(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ [M = Mo (4) or W (5)] in relatively low yields. Complex (5) has been obtained in two isomeric crystalline forms, (5a) and (5b), for which *X*-ray crystal structure determinations have been undertaken: (5a), triclinic, space group $P\bar{1}$ (no. 2), a = 12.404(4), b = 11.756(3), c = 14.208(3) Å, α = 101.4(2), β = 79.5(2), γ = 110.3(2)°, and Z = 2; (5b), monoclinic, space group $P2_1/c$ (no. 14), a = 17.991(3), b = 10.098(2), c = 21.608(2) Å, β = 105.66(1)°, with Z = 4. The structures of (5a) and (5b) have been refined to residuals R = 0.058 and 0.034 from 3 997 and 4 009 unique reflections, respectively. Both isomers contain $W(CO)_3(\eta\text{-}C_5H_5)$ groups bonded to $Cu(PPh_3)_2$ units. The carbonyl ligands are essentially terminally bound to W but two CO groups show some semibridging interactions with Cu, especially in structure (5b); Cu–C 2.309(13) and 2.405(13) Å in (5a), 2.260(8) and 2.197(9) Å in (5b). In (5a) the $Cu(PPh_3)_2$ unit occupies the position typical of a ligand to W in a complex with 'four-legged piano stool' geometry [W–Cu 2.721(1) Å; dihedral angle (W–Cu–C/W–Cu–C′) 139.8°]. In (5b) the $W(\mu\text{-}CO)_2Cu$ fragment is almost planar (W–Cu–C/W–Cu–C′ 170.9°) and W–Cu [2.771(1) Å] is longer. The structures and bonding of complexes (4) and (5) are discussed in relation to i.r. and n.m.r. spectral data; in solution, $^{13}C\text{-}\{^1H\}$ n.m.r. spectra support a non-rigid structure for complex (5).

Heterometallic complexes with metal–metal bonds have been the subject of much current research.[1] The possibility that co-operative effects between different metal centres may influence the reactivity of such complexes is of interest and this has encouraged investigations into the use of both bi- and poly-nuclear heterometallic complexes in organic synthesis, especially in homogeneous or heterogeneous catalytic systems.[1,2] The varying strengths and polarities of bonds between dissimilar metals, contained within differing ligand environments, should confer a wide range of reactivity upon an individual metal centre: cleavage of metal–metal bonds may be either homolytic [1,3] or heterolytic.[1,4] Moreover, studies of simpler binuclear derivatives should give an insight into the preparation, structure, and reactivity of larger heterometallic clusters.[1,2a]

Herein we report the characterisation and study of binuclear complexes containing rhodium bonded to molybdenum or tungsten, $[MRh(CO)(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ [M = Mo (1) or W (2)], or manganese, $[MnRh(CO)_4(PPh_3)_3]$ (3), and copper bonded to molybdenum and tungsten, $[CuM(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ [M = Mo (4) or W (5)]. Preliminary reports of certain aspects of this work have appeared.[5] Both Rh and Cu are implicated in a number of catalytic organic reactions [6] and the effects of the earlier transition metals Mo, W, or Mn on the reactivity of these elements is of interest. There have been only a few previous reports of binuclear organometallic complexes containing M–Rh (M = Mo,[7] W,[7b,8] or Mn [9]) and Cu–M (M = Mo [10] or W [10a,c]) bonds.

Results

Rhodium Complexes.—Reactions of Wilkinson's complex $[RhCl(PPh_3)_3]$ with the anions $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) or $[Mn(CO)_5]^-$ in tetrahydrofuran (thf) result in the nucleophilic displacement of the chloro-ligand and the formation of metal–rhodium bonds. In this process one triphenylphosphine ligand is lost from the co-ordination shell of the rhodium atom. The black crystalline products $[MRh(CO)(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ [M = Mo (1) or W (2)] are relatively stable to air in the solid state but somewhat unstable to air in solution. Green, microcrystalline $[MnRh(CO)_4(PPh_3)_3]$ (3) reacts readily with air both in solution and in the solid state.

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† Di-μ-carbonyl-2-carbonyl-2-η-cyclopentadienyl-1,1-bis(triphenylphosphine)rhodium-molybdenum(*Rh–Mo*) and 2,2,2-tricarbonyl-2-η-cyclopentadienyl-1,1-bis(triphenylphosphine)coppertungsten-(*Cu–W*).

Supplementary data available (No. SUP 23926, 85 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical and physical data for complexes (1)—(5)

Complex	Colour	$^{31}P-\{^1H\}$ N.m.r. δ/p.p.m., (*J*/Hz)	$\tilde{\nu}_{max.}$(CO)/cm^{-1}	Analyses/% [a]				
				C	H	P	Mo	Rh,Cu
(1) $[MoRh(CO)_3(PPh_3)_2(\eta-C_5H_5)]$	Black	37.1 (d),	1 873, 1 778, 1 749 [c]	60.9	4.4	7.3	10.7	11.2
		^1J(Rh–P) 170 [b]	1 890, 1 760 [d]	(60.6)	(4.0)	(7.1)	(11.8)	(11.0)
(2) $[WRh(CO)_3(PPh_3)_2(\eta-C_5H_5)]$	Black	30.2 (d),	1 871, 1 770, 1 738 [c]	55.1	3.65	6.4	—	—
		^1J(Rh–P) 174 [b]	1 886, 1 748 [d]	(55.0)	(3.7)	(6.45)	—	—
(3) $[MnRh(CO)_4(PPh_3)_3]$	Green	88.7 (s), 4.13 (d),	1 947, 1 874, 1 776,	66.5	4.7	8.1	—	—
		^1J(Rh–P) 256 [b]	1 771, 1 750 [c]	(65.9)	(4.3)	(8.8)	—	—
			1 955, 1 882, 1 751 [d]					
(4) $[CuMo(CO)_3(PPh_3)_2(\eta-C_5H_5)]$	Yellow	−3.0 (s) [b]	1 896, 1 795, 1 778 [c]	63.3	4.6	7.0	10.3	7.5
			1 914, 1 808, 1 776 [d]	(63.4)	(4.2)	(7.4)	(11.5)	(7.6)
(5a) $[CuW(CO)_3(PPh_3)_2(\eta-C_5H_5)]$	Yellow	−1.5 (s) [e]	1 890, 1 790, 1 769 [c]	56.9	3.9	5.8	—	—
			1 908, 1 803, 1 769 [d]	(57.4)	(3.8)	(6.7)	—	—
(5b) $[CuW(CO)_3(PPh_3)_2(\eta-C_5H_5)]$	Orange-red	−1.5 (s) [e]	1 890, 1 786, 1 731 [d]	56.7	3.6	6.8	—	6.9
			1 908, 1 803, 1 769 [d]	(57.4)	(3.8)	(6.7)	—	(6.9)

[a] Calculated values in parentheses. [b] In C_6D_6. [c] In Nujol. [d] In CH_2Cl_2. [e] In $CDCl_3$.

The i.r. spectra of complexes (1)—(3) all exhibit ν(CO) bands typical of both terminal and bridging (< 1 800 cm^{-1}) carbonyl ligands (see Table 1). The spectra of (1) and (2) correlate so closely that these complexes must be isostructural, containing one terminal and two bridging CO groups. From its i.r. spectrum complex (3) appears to contain a minimum of two terminal CO groups and, probably, two bridging CO groups (at least in the solid state), the latter in similar environments to those of (1) and (2). The ^1H n.m.r. spectra of complexes (1)—(3) confirm the presence of $\eta-C_5H_5$ and PPh_3 ligands. The $^{31}P-\{^1H\}$ n.m.r. spectra of (1) and (2) at room temperature (r.t.) in $[^2H_6]$benzene are assignable to two, apparently equivalent $^{31}PPh_3$ groups co-ordinated to ^{103}Rh ($I = \frac{1}{2}$, doublet resonance) and in (2) these PPh_3 ligands remain equivalent at −65 °C in $CDCl_3$; with reference to the structure determined by *X*-ray diffraction (see below), this equivalence may arise from an exchange process. The $^{31}P-\{^1H\}$ n.m.r. spectrum of complex (3) is assignable to one $^{31}PPh_3$ (singlet resonance) presumably attached to Mn and two equivalent $^{31}PPh_3$ groups bonded to ^{103}Rh (doublet resonance); in this case, as for complexes (1) and (2), exchange processes cannot be ruled out.

Crystals of (1), suitable for *X*-ray analysis, were obtained from dichloromethane–hexane mixtures and the crystallographically determined structure is illustrated in Figure 1 with appropriate numbering. The results of this *X*-ray study are summarised in Tables 2 and 3: the $\eta-C_5H_5$ ring takes up one of two possible sites in the ratios 0.74 : 0.26 and the former is shown in Figure 1. The bonding between $\eta-C_5H_5$ and Mo is typical, as is the interaction between the two PPh_3 groups and Rh, although it should be noted that these ligands are in magnetically inequivalent positions which is inconsistent with the $^{31}P-\{^1H\}$ n.m.r. spectrum in solution if such a static structure persists. The carbonyl group C(1)–O(1) is terminal to Mo and, although slightly bent [174.7(5)°], the long Rh–C(1) distance [2.919(10) Å] precludes any significant bridging character. {However, it may be noted that semi-bridging CO groups in $[Mo_2(\mu-C_2R_2)(CO)_4(\eta-C_5H_5)_2]$ [R = H, Et, or Ph) have Mo–C distances in the range 2.826—2.902 Å.[11]}

The carbonyl groups C(2)–O(2) and C(3)–O(3) are clearly bridging but there is asymmetry in this bonding; some asymmetry is to be expected in this heteronuclear complex since even the homonuclear derivatives $[Rh_2(\mu-CO)_2(PR_3)_4]$ (R = Ph[12] or OPr^i [13]) have distinctly asymmetric bridges. The bond lengths Rh–C(2) [2.182(6) Å] and Rh–C(3) [2.092(5) Å] are slightly larger than in the homonuclear dirhodium complexes (1.956—2.054 Å) and the longer value approaches the distance assigned to semibridging CO groups in $[CrRh(\mu-CO)_2(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)]$ [*i.e.* 2.200(7) Å][14] and in related MnRh species.[9b] The Mo–C(2) and Mo–C(3) bond lengths [1.980(6) and 2.026(5) Å, respectively] do differ significantly but are close to values for a CO bridging system involving Mo atoms.[15–17] The angles Mo–C(2)–O(2), Mo–C(3)–O(3), Rh–C(2)–O(2), and Rh–C(3)–O(3) [164.7(5), 159.4(4), 118.6(5), and 122.7(4)°, respectively] indicate that C(2)–O(2) and C(3)–O(3) are more close to linearity with respect to Mo. The $Rh(\mu-CO)_2Mo$ framework possesses a 'butterfly' configuration with the Rh–C–Mo interplanar dihedral angle of 161°; this is related to the geometry of the homonuclear complexes $[Rh_2(\mu-CO)_2(PR_3)_4]$ although significantly smaller dihedral angles are found in these complexes [132.8(5) (R = Ph)[12] and 140.8(6)° (R = OPr^i)].[13]

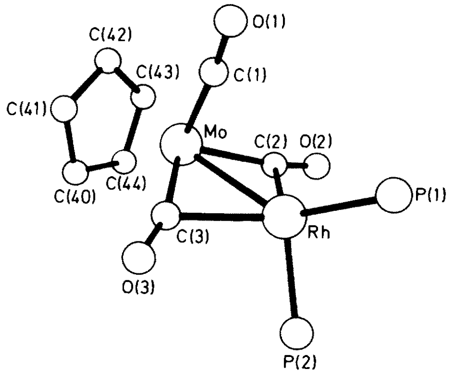


Figure 1. *X*-Ray crystal structure of complex (1)

The Mo–Rh bond [2.588(1) Å] is shorter than expected for a single-bond distance: comparable single Mo–Mo bonds are in the range 2.98—3.23 Å,[11,18] triple Mo≡Mo bonds in molybdenum(I) organometallics are 2.448(1)[16] and 2.594(1) Å,[17] single Rh–Rh bonds in rhodium(0) derivatives are in the range 2.63—2.78 Å,[12,13,19] and in $[MoRh(\mu-PMe_2)_2(CO)_4(\eta-C_5Me_5)]$ the Rh–Mo distance is 2.9212(7) Å.[7a] From these data an estimated Rh^0–Mo^I bond length is 2.8—3.0 Å and this supports some multiple-bond character for Mo–Rh in complex (1).

In toluene solution at ambient temperature and under atmospheric pressure of dihydrogen, complex (1) acts as a catalyst for hydrogenation of cyclohexene to cyclohexane but

Table 2. Fractional co-ordinates with standard deviations for complex (1)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	0.220 20(2)	0.506 26(3)	0.153 85(2)	C(23)	0.220 59(23)	0.828 2(3)	0.223 26(15)
Mo(1)	0.107 39(2)	0.355 23(4)	0.100 49(2)	C(24)	0.210 60(23)	0.959 1(3)	0.232 67(15)
P(1)	0.237 40(7)	0.572 02(10)	0.259 67(6)	C(25)	0.193 60(23)	1.002 1(3)	0.290 92(15)
P(2)	0.319 97(6)	0.604 00(11)	0.121 20(6)	C(26)	0.186 59(23)	0.914 2(3)	0.339 75(15)
C(1)	0.142 2(3)	0.404 1(5)	0.022 8(3)	C(27)	0.196 58(23)	0.783 2(3)	0.330 34(15)
O(1)	0.157 8(3)	0.429 7(5)	−0.026 68(22)	C(22)	0.213 58(23)	0.740 2(3)	0.272 09(15)
C(2)	0.097 7(3)	0.541 2(6)	0.116 7(3)	C(29)	0.358 26(20)	0.626 6(3)	0.374 56(16)
O(2)	0.074 4(3)	0.647 2(4)	0.119 41(25)	C(30)	0.429 35(20)	0.602 3(3)	0.418 59(16)
C(3)	0.212 6(3)	0.305 9(4)	0.156 67(24)	C(31)	0.473 47(20)	0.499 1(3)	0.407 10(6)
O(3)	0.263 47(22)	0.240 9(3)	0.185 56(23)	C(32)	0.446 50(20)	0.420 3(3)	0.351 56(16)
C(5)	0.332 82(17)	0.874 5(3)	0.101 18(17)	C(33)	0.375 41(20)	0.444 7(3)	0.307 53(16)
C(6)	0.304 66(17)	0.991 5(3)	0.072 07(17)	C(28)	0.331 29(20)	0.547 9(3)	0.319 03(16)
C(7)	0.234 19(17)	0.996 1(3)	0.024 71(17)	C(35)	0.201 84(23)	0.381 7(3)	0.342 10(19)
C(8)	0.191 88(17)	0.883 8(3)	0.006 45(17)	C(36)	0.152 08(23)	0.306 2(3)	0.367 32(19)
C(9)	0.220 05(17)	0.766 8(3)	0.035 55(17)	C(37)	0.073 73(23)	0.331 4(3)	0.348 79(19)
C(4)	0.290 52(17)	0.762 2(3)	0.082 92(17)	C(38)	0.045 15(23)	0.432 1(3)	0.305 04(19)
C(11)	0.342 86(25)	0.381 3(3)	0.053 17(18)	C(39)	0.094 91(23)	0.507 6(3)	0.279 82(19)
C(12)	0.364 21(25)	0.312 3(3)	0.003 22(18)	C(34)	0.173 26(23)	0.482 4(3)	0.298 35(19)
C(13)	0.385 57(25)	0.377 2(3)	−0.047 98(18)	C(40)	−0.010 0(4)	0.311 3(7)	0.118 8(5)
C(14)	0.385 58(25)	0.511 3(3)	−0.049 21(18)	C(41)	0.038 3(4)	0.206 7(7)	0.146 3(5)
C(15)	0.364 24(25)	0.580 3(3)	0.000 74(18)	C(42)	0.059 0(4)	0.142 4(7)	0.092 3(5)
C(10)	0.342 88(25)	0.515 3(3)	0.051 94(18)	C(43)	0.023 4(4)	0.207 2(7)	0.032 8(5)
C(17)	0.479 24(19)	0.567 7(3)	0.168 72(16)	C(44)	−0.019 3(4)	0.311 6(7)	0.048 7(5)
C(18)	0.549 71(19)	0.583 0(3)	0.215 21(16)	C(40′)	−0.026 0(8)	0.320 9(12)	0.081 7(12)
C(19)	0.555 76(19)	0.662 9(3)	0.270 69(16)	C(41′)	0.010 2(8)	0.254 7(12)	0.141 3(12)
C(20)	0.491 34(19)	0.725 7(3)	0.279 68(16)	C(42′)	0.056 9(8)	0.156 8(12)	0.124 9(12)
C(21)	0.420 86(19)	0.710 3(3)	0.233 19(16)	C(43′)	0.049 5(8)	0.162 6(12)	0.055 1(12)
C(16)	0.414 81(19)	0.631 3(3)	0.177 71(16)	C(44′)	−0.001 8(8)	0.264 0(12)	0.028 4(12)

Table 3. Selected internuclear geometrical parameters (distances in Å, angles in °) for the central atoms in $[MoRh(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1)

Mo–Rh	2.588(1)	Rh–C(2)	2.182(6)	C(1)–Mo–Rh	78.8(2)	O(3)–C(3)–Mo	159.4(4)
Mo–C(1)	1.943(6)	Rh–C(3)	2.092(5)	C(2)–Mo–Rh	55.2(2)	O(2)–C(2)–Rh	118.6(5)
Mo–C(2)	1.980(6)	P(1)–C(22)	1.837(3)	C(3)–Mo–Rh	52.2(1)	O(3)–C(3)–Rh	122.7(4)
Mo–C(3)	2.026(5)	P(1)–C(28)	1.840(3)	C(2)–Mo–C(1)	87.0(2)	Mo–C(2)–Rh	76.7(2)
Mo–C(40)	2.300(7)	P(1)–C(34)	1.829(4)	C(3)–Mo–C(1)	94.8(2)	Mo–C(3)–Rh	77.9(2)
Mo–C(41)	2.338(9)	P(2)–C(4)	1.845(3)	C(3)–Mo–C(2)	105.2(2)	C(22)–P(1)–Rh	116.7(1)
Mo–C(42)	2.372(7)	P(2)–C(10)	1.842(3)	P(1)–Rh–Mo	119.9(0)	C(28)–P(1)–Rh	118.9(1)
Mo–C(43)	2.356(7)	P(2)–C(16)	1.833(4)	P(2)–Rh–Mo	136.8(0)	C(34)–P(1)–Rh(1)	109.3(2)
Mo–C(44)	2.311(8)	C(1)–O(1)	1.163(7)	P(2)–Rh–P(1)	103.3(0)	C(28)–P(1)–C(22)	104.3(2)
Rh–P(1)	2.242(1)	C(2)–O(2)	1.188(7)	C(2)–Rh–Mo	48.1(2)	C(34)–P(1)–C(22)	103.1(2)
Rh–P(2)	2.321(1)	C(3)–O(3)	1.174(6)	C(3)–Rh–Mo	49.9(1)	C(34)–P(1)–C(28)	102.6(2)
				C(2)–Rh–P(1)	99.5(2)	C(4)–P(2)–Rh	110.9(1)
				C(2)–Rh–P(2)	128.4(2)	C(10)–P(2)–Rh	110.9(1)
				C(3)–Rh–P(1)	105.7(1)	C(16)–P(2)–Rh	123.5(1)
				C(3)–Rh–P(2)	120.4(1)	C(10)–P(2)–C(4)	102.1(2)
				C(3)–Rh–C(2)	96.2(2)	C(16)–P(2)–C(4)	104.8(2)
				O(1)–C(1)–Mo	174.7(5)	C(16)–P(2)–C(10)	102.3(2)
				O(2)–C(2)–Mo	164.7(5)		

at a rate significantly slower than $[RhCl(PPh_3)_3]$.[20] The active catalytic species in this hydrogenation has not been established and it is possible that it is not the bimetallic complex (1) itself.

The Mo–Rh bond of (1) is photolytically cleaved (medium-pressure mercury lamp, Pyrex filter) at −70 °C and in the presence of nitrosodurene (1,2,4,5-tetramethyl-3-nitrosobenzene) the species $[Mo(CO)_n(NOC_6Me_4H)(\eta\text{-}C_5H_5)]$ ($n \leqslant 3$)[3b,21] may be identified as a product by e.s.r. spectroscopy. A second signal (a multiplet of at least 12 lines) is also observed in the e.s.r. spectrum and this may arise from a rhodium species trapped by nitrosodurene; possible paramagnetic species which would give signals consistent with the observed spectrum are $[Rh(CO)_n(NOC_6Me_4H)(PPh_3)_2]$ $[A_{iso}(^{31}P^1) \approx \frac{1}{2}A_{iso}(^{31}P^2) \approx \frac{1}{2}A_{iso}(^{14}N) \approx \frac{1}{4}A_{iso}(^{103}Rh) \approx 0.78$ mT] or $[Rh(CO)_n(NOC_6Me_4H)(PPh_3)]$ $[A_{iso}(^{31}P) \approx \frac{1}{2}A_{iso}(^{14}N) \approx \frac{1}{6}A_{iso}(^{103}Rh) \approx 0.78$ mT]. No e.s.r. evidence for comparable paramagnetic species was obtained from the analogous tungsten complex (2) although prolonged photolysis of this complex caused decomposition.

Photolysis of complex (3) at −40 °C in the presence of nitrosodurene forms $[Mn(CO)_n(NOC_6Me_4H)(PPh_3)]$ ($n \leqslant 4$)[3b] and, in the presence of O_2 in CH_2Cl_2 at −70 °C, the unstable dioxygen species $[Mn(O_2)(CO)_n(PPh_3)]$ [$g_{iso} = 2.020$, $A_{iso}(^{55}Mn) = 1.53$ mT, and $A_{iso}(^{31}P) \approx 0.76$ mT] identical to the species obtained from $[Mn_2(CO)_8(PPh_3)_2]$.[22] In solution at ambient temperature, complex (3) is fairly unstable, especially on exposure to traces of air, and Mn–Rh bond cleavage occurs. One product isolated from this decomposition is a yellow crystalline rhodium(I) derivative of stoicheiometric formula $[Rh(CO)(PPh_3)_2]$ (6) having ν(CO) at 1 966 cm^{-1} (i.r. in Nujol); species (6) probably corresponds to [{Rh(CO)-

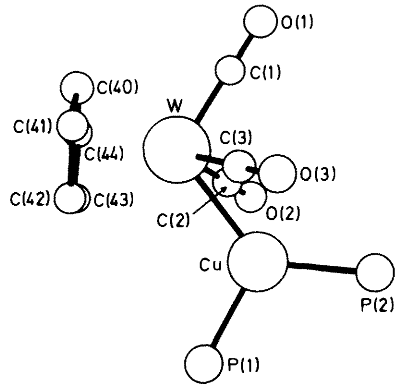


Figure 2. *X*-Ray crystal structure of complex (5a)

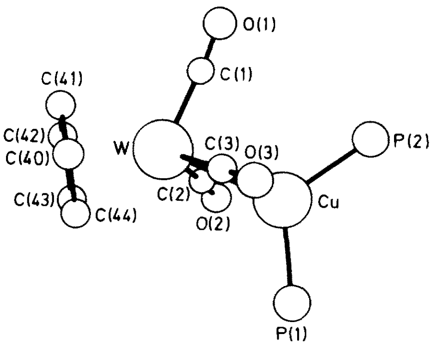


Figure 3. *X*-Ray crystal structure of complex (5b)

$(PPh_3)_2\}_2]$ first described by Wilkinson and co-workers,[23] but the alternative *ortho*-metallated structure $[Rh\{PPh_2(C_6H_4\text{-}2)\}(CO)(PPh_3)]$ has not been conclusively ruled out. Another decomposition product is an orange solid possessing a complex set of bands in its i.r. spectrum between 1 976 and 1 900 cm^{-1}, typical of $\nu(CO)$ vibrations, and this may be a triphenylphosphine-substituted manganese carbonyl cluster.

Copper Complexes.—The tetramer $[\{CuCl(PPh_3)\}_4]$ reacts with the anions $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) in thf to form the bimetallic complexes $[CuM(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ [M = Mo (4) or W (5)] in relatively low yields. These crystalline products are accompanied by considerable amounts of yellow, carbonyl-containing material which is insoluble in CH_2Cl_2 but, as yet, is incompletely characterised. Both (4) and (5) form air-stable solids but are unstable to air in solution. Complex (4) has been obtained in only one crystalline form as yellow needles; however, complex (5) can be crystallized from CH_2Cl_2–hexane mixtures in two different forms, often in admixture, yellow needles (5a) or red-orange plates (5b).

I.r. spectra in the solid state or in solution of (4) and (5) exhibit one band typical of a terminal CO group and two bands of lower frequencies, probably assignable to bridging CO groups. The i.r. spectrum of the yellow form (5a) bears a close resemblance to that of (4), but although both (5a) and (5b) give identical i.r. spectra in solution, the bridging $\nu(CO)$ vibrations of (5b) in the solid state are distinctly lower than those of (5a) (see Table 1). Proton n.m.r. spectra of complexes (4) and (5) show resonances of $\eta\text{-}C_5H_5$ and PPh_3 groups; broadened, singlet resonances in the $^{1}P\text{-}\{^{1}H\}$ n.m.r. spectra support the presence of apparently equivalent PPh_3 ligands but the chemical shifts are only slightly to low field of unco-ordinated triphenylphosphine. In the $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum of (5) at temperatures > -71 °C, *all* the CO ligands appear equivalent ($\delta = -220.8$ in toluene-10% C_6D_6 at -71 °C) so that the molecule must be non-rigid. Also, it should be noted that species (5a) and (5b) are indistinguishable in solution by i.r. or n.m.r. spectroscopy.

Crystals of (5a) and (5b) have been subjected to *X*-ray analysis and the crystallographically determined structures are depicted in Figures 2 and 3, respectively. The results of these *X*-ray studies are given in Tables 4—7. The $\eta\text{-}C_5H_5\text{-}W$ interactions are typical but in both (5a) and (5b) the rings are disordered between two or more sites, respectively, and the sites of major occupancy are illustrated in the Figures. The $Cu\text{-}PPh_3$ bonds of both (5a) and (5b) resemble those of related copper(I) phosphine complexes.[24]

All the CO ligands in complexes (5a) and (5b) approach linear co-ordination to the W atoms (W–C–O angles $>170°$) and must be considered as being essentially terminally bound to this metal atom having typical W–C and C–O bond lengths (see Tables 5 and 7).[25] However, in both (5a) and (5b) the C atoms of two of these CO ligands are relatively close to the Cu atom; in (5a) these Cu–C distances are 2.309(13) and 2.405(13) Å; in (5b) the related distances are distinctly shorter [2.197(9) and 2.260(8) Å] and, in this structure at least, there must be a significant bonding interaction between these CO groups [C(2)–O(2) and C(3)–O(3)] and Cu. Note that in related, reported heterobimetallic compounds containing W or Mo the separations between all carbonyl C atoms and the second metal atom are considerably greater, *e.g.* $[\{Me_2N(CH_2)_3\}ZnW(CO)_3(\eta\text{-}C_5H_5)]$ (Zn–C > 2.55 Å),[26] $[Zn\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and $[(Et_2O)ClZnMo(CO)_3(\eta\text{-}C_5H_5)]$ [Zn–C > 2.522(6) Å],[27] $[Ga\{W(CO)_3(\eta\text{-}C_5H_5)\}_3]$ and $[Me_2GaW(CO)_3(\eta\text{-}C_5H_5)]$ (Ga–C > 2.50 Å),[28] and $[(Ph_3P)AuW(CO)_3(\eta\text{-}C_5H_5)]$ [Au–C > 2.51(5) Å].[29] Moreover the bond distances between the bridging acetylide ligands and the Cu atom of a $Cu(PMe_3)_2$ unit in $[\{Cu(C{\equiv}CPh)(PMe_3)\}_4]$ [30] are comparable to Cu–C distances in (5b). Thus, the evidence supports the presence of semibridging carbonyl groups in complex (5b). Recently the first dicopper(I) complexes with single symmetrical bridging carbonyl groups have been characterised[31] and in $[Cu_2(diamine)_2(\mu\text{-}PhCO_2)(\mu\text{-}CO)]^+$ the Cu–C bonds (1.860—1.882 Å) are considerably shorter than in (5b) which contains a formal Cu^0 atom. A normal Cu^I–C(*sp*) single bond length has been estimated to be 2.05 Å.[32]

The W–Cu bonds in (5a) and (5b) are relatively long, being greater than W–Au,[29] W–Ga,[28] and W–Zn [26] bond lengths in the bimetallic complexes mentioned above. This suggests a relatively weak metal–metal interaction. Interestingly the W–Cu bond in (5a) [2.721(1) Å] is shorter than in (5b) [2.771(1) Å]. Also, the W–Cu bond in (5a) lies outside the three CO groups and occupies a position equivalent to a unidentate ligand in a 3 : 4 'four-legged piano stool,' arrangement around tungsten whereas in complex (5b) the W–Cu bond is almost in the plane of the semibridging CO groups [interplanar angles: W–Cu–C(2)/W–Cu–C(3) 170.9 (5b) and 139.8° (5a)]. This structural difference resembles that of ligand X in the complexes $[Fe(CO)_3(\eta^3\text{-}C_3H_5)X]$; when X = $Au(PPh_3)$ the Au atom is located between CO groups [*cf.* (5b)] but when X = Br it occupies a pseudo-octahedral co-ordination position around Fe.[33]

Discussion

Both rhodium and copper form structurally related hetero-binuclear complexes $[(\eta\text{-}C_5H_5)(OC)M(\mu\text{-}CO)_2M'(PPh_3)_2]$ (M = Mo or W; M′ = Rh or Cu) in which a formal metal–metal bond is present and two carbonyl groups are, to some extent, bridging. There are, however, two extra valence-shell

Table 4. Fractional co-ordinates with standard deviations for complex (5a)

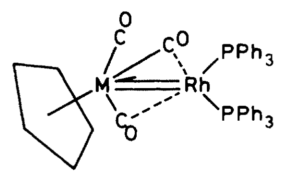
Atom	*x*	*y*	*y*	Atom	*x*	*y*	*z*
W(1)	0.472 66(5)	0.015 07(5)	0.260 53(4)	C(23)	0.790 8(6)	0.125 6(8)	0.040 3(7)
Cu(1)	0.619 40(12)	0.244 17(12)	0.237 36(11)	C(24)	0.831 2(6)	0.073 2(8)	−0.050 0(7)
P(1)	0.812 7(3)	0.269 7(3)	0.220 8(3)	C(25)	0.949 9(6)	0.098 3(8)	−0.077 8(7)
P(2)	0.583 9(3)	0.422 6(3)	0.235 29(24)	C(26)	1.028 4(6)	0.175 8(8)	−0.015 2(7)
C(3)	0.476 3(11)	0.088 1(11)	0.147 5(10)	C(27)	0.988 0(6)	0.228 2(8)	0.075 2(7)
O(3)	0.474 3(9)	0.121 8(9)	0.077 2(7)	C(22)	0.869 3(6)	0.203 1(8)	0.102 9(7)
C(1)	0.313 7(14)	0.009 9(12)	0.288 5(11)	C(29)	0.928 1(7)	0.137 6(8)	0.291 2(6)
O(1)	0.214 2(9)	0.003 0(10)	0.306 6(8)	C(30)	0.950 2(7)	0.088 8(8)	0.364 7(6)
C(2)	0.501 7(11)	0.149 1(12)	0.364 0(10)	C(31)	0.891 6(7)	0.102 4(8)	0.457 6(6)
O(2)	0.511 2(9)	0.222 4(10)	0.435 7(8)	C(32)	0.811 0(7)	0.164 9(8)	0.477 1(6)
C(5)	0.348 9(7)	0.309 9(6)	0.250 5(6)	C(33)	0.789 0(7)	0.213 8(8)	0.403 5(6)
C(6)	0.232 3(7)	0.299 9(6)	0.276 1(6)	C(28)	0.847 5(7)	0.200 1(8)	0.310 6(6)
C(7)	0.201 3(7)	0.402 6(6)	0.321 7(6)	C(35)	0.939 9(10)	0.491 5(10)	0.326 4(7)
C(8)	0.287 0(7)	0.515 2(6)	0.341 5(6)	C(36)	1.007 8(10)	0.614 8(10)	0.337 1(7)
C(9)	0.403 6(7)	0.525 2(6)	0.315 9(6)	C(37)	1.047 0(10)	0.676 3(10)	0.256 6(7)
C(4)	0.434 5(7)	0.422 5(6)	0.270 4(6)	C(38)	1.018 4(10)	0.614 5(10)	0.165 5(7)
C(11)	0.599 0(7)	0.573 4(7)	0.099 1(6)	C(39)	0.950 6(10)	0.491 1(10)	0.154 8(7)
C(12)	0.637 1(7)	0.612 8(7)	0.008 8(6)	C(34)	0.911 3(10)	0.429 6(10)	0.235 3(7)
C(13)	0.697 8(7)	0.551 0(7)	−0.063 1(6)	C(40)	0.417 0(11)	−0.194 4(17)	0.259 6(19)
C(14)	0.720 4(7)	0.449 8(7)	−0.044 7(6)	C(41)	0.488 9(11)	−0.136 1(17)	0.334 1(19)
C(15)	0.682 4(7)	0.410 4(7)	0.045 6(6)	C(42)	0.602 0(11)	−0.077 6(17)	0.290 1(19)
C(10)	0.621 7(7)	0.472 2(7)	0.117 4(6)	C(43)	0.600 1(11)	−0.099 7(17)	0.188 4(19)
C(17)	0.640 2(8)	0.550 0(7)	0.413 5(6)	C(44)	0.485 7(11)	−0.171 9(17)	0.169 6(19)
C(18)	0.694 0(8)	0.650 4(7)	0.478 8(6)	C(40′)	0.455 8(20)	−0.166 6(24)	0.318 1(19)
C(19)	0.772 4(8)	0.756 1(7)	0.445 0(6)	C(41′)	0.572 7(20)	−0.089 8(24)	0.321 0(19)
C(20)	0.796 9(8)	0.761 2(7)	0.345 8(6)	C(42′)	0.624 3(20)	−0.076 4(24)	0.224 3(19)
C(21)	0.743 1(8)	0.660 8(7)	0.280 5(6)	C(43′)	0.539 4(20)	−0.144 8(24)	0.161 8(19)
C(16)	0.664 7(8)	0.555 2(7)	0.314 4(6)	C(44′)	0.435 2(20)	0.200 6(24)	0.219 8(19)

Table 5. Selected internuclear geometrical parameters (distances in Å, angles in °) for the central atoms of $[CuW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ (5a)

W–Cu	2.721(1)	Cu–C(2)	2.309(13)	C(1)–W–Cu	112.1(4)	O(3)–C(3)–W	174.5(11)
W–C(1)	1.922(16)	Cu–C(3)	2.405(13)	C(2)–W–Cu	56.6(4)	O(2)–C(2)–Cu	108.4(9)
W–C(2)	1.913(15)	P(1)–C(22)	1.829(10)	C(3)–W–Cu	59.3(4)	O(3)–C(3)–Cu	108.6(9)
W–C(3)	1.952(13)	P(1)–C(28)	1.828(9)	C(2)–W–C(1)	86.0(6)	Cu–C(2)–W	79.7(5)
W–C(40)	2.313(17)	P(1)–C(34)	1.848(11)	C(1)–W–C(3)	85.4(6)	Cu–C(3)–W	76.5(4)
W–C(41)	2.313(20)	P(2)–C(4)	1.829(8)	C(2)–W–C(3)	105.0(5)	C(22)–P(1)–Cu	114.4(3)
W–C(42)	2.362(19)	P(2)–C(10)	1.809(8)	P(1)–Cu–W	116.2(1)	C(28)–P(1)–Cu	111.7(3)
W–C(43)	2.391(20)	P(2)–C(16)	1.824(9)	P(2)–Cu–W	131.2(1)	C(34)–P(1)–Cu	116.3(4)
W–C(44)	2.362(22)	C(1)–O(1)	1.190(16)	P(1)–Cu–P(2)	112.6(1)	C(28)–P(1)–C(22)	105.9(4)
Cu–P(1)	2.285(3)	C(2)–O(2)	1.192(15)	C(2)–Cu–W	43.8(4)	C(34)–P(1)–C(22)	103.3(4)
Cu–P(2)	2.295(3)	C(3)–O(3)	1.153(14)	C(3)–Cu–W	44.2(3)	C(34)–P(1)–C(28)	104.1(4)
				C(2)–Cu–P(1)	118.2(3)	C(4)–P(2)–Cu	117.1(3)
				C(3)–Cu–P(1)	126.7(3)	C(10)–P(2)–Cu	113.2(3)
				C(2)–Cu–P	109.3(3)	C(16)–P(2)–Cu	114.7(3)
				C(3)–Cu–P(2)	104.6(3)	C(10)–P(2)–C(4)	103.7(4)
				C(3)–Cu–C(3)	81.2(5)	C(16)–P(2)–C(4)	102.7(4)
				O(1)–C(1)–W	177.8(11)	C(16)–P(2)–C(10)	103.7(4)
				O(2)–C(2)–W	171.9(11)		

electrons in the copper species and this fact is reflected in some obvious dissimilarities in structures when M′ = Rh or Cu.

The Mo–Rh bond in complex (1) is short and lies between the three CO ligands. The two μ-CO groups, as noted previously, are not totally symmetrically positioned between the two metal atoms; the bond angles and distances suggest that C(2)–O(2) and C(3)–O(3) approach terminal bonding configurations with respect to Mo and are semibridging to Rh [see structure (A)]. Although the number of electrons involved in these carbonyl-bridge bonds is not completely clear the co-ordination geometry does not support the presence of strong '4-electron' (μ-σ:η^2) carbonyl bridges,[34] so that it may be assumed that the CO groups are essentially two-electron donors. Hence, if a single Mo–Rh bond is present both Mo and Rh are formally in 16-electron environments.



(A)

The 16-electron state is not exceptional for Rh^{I} (formally Rh^{0} here) but is unusual for Mo in low oxidation states. Both metals could achieve formal 18-electron environments if a triple bond Mo$\equiv$Rh exists, as proposed for $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[16] but if this was true a shorter Mo–Rh distance might have been expected. A likely alternative explana-

Table 6. Fractional co-ordinates with standard deviations for complex (5b)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	0.891 22(1)	0.643 36(2)	0.408 96(1)	C(23)	0.658 3(3)	0.627 5(4)	0.454 93(20)
Cu(1)	0.772 10(4)	0.483 19(7)	0.340 60(3)	C(24)	0.639 5(3)	0.694 8(4)	0.505 01(20)
P(1)	0.769 49(8)	0.420 65(15)	0.237 32(7)	C(25)	0.618 7(3)	0.623 9(4)	0.553 22(20)
P(2)	0.677 84(8)	0.404 09(15)	0.385 38(7)	C(26)	0.616 8(3)	0.485 9(4)	0.551 34(20)
C(1)	0.859 3(4)	0.600 1(6)	0.485 7(3)	C(27)	0.635 7(3)	0.418 6(4)	0.501 26(20)
O(1)	0.845 5(4)	0.574 2(6)	0.533 4(3)	C(22)	0.654 6(3)	0.489 4(4)	0.453 05(20)
C(2)	0.898 3(3)	0.453 8(7)	0.391 7(3)	C(29)	0.662 43(19)	0.124 2(4)	0.398 18(19)
O(2)	0.913 1(3)	0.343 7(5)	0.384 1(3)	C(30)	0.689 71(19)	0.001 6(4)	0.424 48(19)
C(3)	0.787 7(4)	0.696 4(6)	0.359 9(3)	C(31)	0.760 67(19)	−0.007 0(4)	0.470 74(19)
O(3)	0.729 2(3)	0.744 4(4)	0.331 79(24)	C(32)	0.804 34(19)	0.107 0(4)	0.490 70(19)
C(5)	0.807 8(3)	0.196 0(4)	0.173 74(17)	C(33)	0.777 06(19)	0.229 6(4)	0.464 40(19)
C(6)	0.813 6(3)	0.059 7(4)	0.165 53(17)	C(28)	0.706 10(19)	0.238 2(4)	0.418 14(19)
C(7)	0.799 0(3)	−0.027 7(4)	0.210 84(17)	C(35)	0.574 10(21)	0.311 0(4)	0.273 35(19)
C(8)	0.778 5(3)	0.021 1(4)	0.264 37(17)	C(36)	0.502 65(21)	0.303 1(4)	0.227 70(19)
C(9)	0.772 7(3)	0.157 4(4)	0.272 58(17)	C(37)	0.438 87(21)	0.369 0(4)	0.238 00(19)
C(4)	0.787 3(3)	0.244 8(4)	0.227 27(17)	C(38)	0.446 54(21)	0.442 8(4)	0.293 95(19)
C(11)	0.817 1(3)	0.599 2(5)	0.155 09(23)	C(39)	0.517 99(21)	0.450 7(4)	0.339 61(19)
C(12)	0.873 0(3)	0.669 1(5)	0.134 54(23)	C(34)	0.581 77(21)	0.384 8(4)	0.329 31(19)
C(13)	0.951 2(3)	0.645 5(5)	0.162 99(23)	C(40)	0.938 3(4)	0.856 8(6)	0.399 4(7)
C(14)	0.973 5(3)	0.551 9(5)	0.212 00(23)	C(41)	0.978 2(4)	0.807 0(6)	0.460 8(7)
C(15)	0.917 7(3)	0.482 0(5)	0.232 56(23)	C(42)	1.021 5(4)	0.694 6(6)	0.451 5(7)
C(10)	0.839 5(3)	0.505 6(5)	0.204 10(23)	C(43)	1.008 3(4)	0.675 0(6)	0.384 4(7)
C(17)	0.647 16(24)	0.372 6(4)	0.121 17(20)	C(44)	0.956 9(4)	0.775 2(6)	0.352 1(7)
C(18)	0.575 60(24)	0.401 4(4)	0.082 65(20)	C(40′)	0.953 3(15)	0.850 2(20)	0.436 0(17)
C(19)	0.533 31(24)	0.510 4(4)	0.093 75(20)	C(41′)	1.004 4(15)	0.750 2(20)	0.468 9(17)
C(20)	0.562 57(24)	0.590 6(4)	0.147 36(20)	C(42′)	1.025 6(15)	0.670 5(20)	0.422 3(17)
C(21)	0.634 13(24)	0.561 8(4)	0.189 88(20)	C(43′)	0.987 6(15)	0.721 2(20)	0.360 5(17)
C(16)	0.676 43(24)	0.452 9(4)	0.178 78(20)	C(44′)	0.942 9(15)	0.832 2(20)	0.369 0(17)

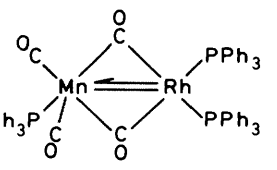
Table 7. Selected internuclear geometrical parameters (distances in Å, angles in °) for the central atoms of $[CuW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ (5b)

W–Cu	2.771(1)	Cu–C(2)	2.260(8)	C(1)–W–Cu	87.7(3)	O(3)–C(3)–W	171.4(7)
W–C(1)	1.945(10)	Cu–C(3)	2.197(9)	C(2)–W–Cu	53.8(2)	O(2)–C(2)–Cu	107.1(7)
W–C(2)	1.960(10)	P(1)–C(4)	1.828(6)	C(3)–W–Cu	52.0(2)	O(3)–C(3)–Cu	104.9(6)
W–C(3)	1.952(10)	P(1)–C(10)	1.823(7)	C(2)–W–C(1)	89.5(4)	Cu–C(2)–W	81.7(3)
W–C(40)	2.345(10)	P(1)–C(16)	1.834(6)	C(3)–W–C(1)	93.8(4)	Cu–C(3)–W	83.6(4)
W–C(41)	2.343(14)	P(2)–C(22)	1.826(6)	C(3)–W–C(2)	105.4(3)	C(4)–P(1)–Cu	115.0(2)
W–C(42)	2.332(12)	P(2)–C(28)	1.836(5)	P(1)–Cu–W	119.1(1)	C(10)–P(1)–Cu	114.6(3)
W–C(43)	2.329(13)	P(2)–C(34)	1.833(6)	P(2)–Cu–W	121.9(1)	C(16)–P(1)–Cu	113.2(2)
W–C(44)	2.337(15)	C(1)–O(1)	1.153(11)	P(2)–Cu–P(1)	119.0(1)	C(10)–P(1)–C(4)	104.4(3)
Cu–P(1)	2.307(2)	C(2)–O(2)	1.166(11)	C(2)–Cu–W	44.4(3)	C(16)–P(1)–C(4)	104.3(3)
Cu–P(2)	2.310(2)	C(3)–O(3)	1.168(10)	C(3)–Cu–W	44.4(3)	C(16)–P(1)–C(10)	104.1(3)
				C(2)–Cu–P(1)	101.1(3)	C(22)–P(2)–Cu	120.6(2)
				C(2)–Cu–P(2)	120.3(3)	C(28)–P(2)–Cu	108.6(2)
				C(3)–Cu–P(1)	114.8(2)	C(34)–P(2)–Cu	115.3(2)
				C(3)–Cu–P(2)	109.3(2)	C(28)–P(2)–C(22)	102.6(3)
				C(3)–Cu–C(2)	88.6(4)	C(34)–P(2)–C(22)	102.4(3)
				O(1)–C(1)–W	175.4(9)	C(34)–P(2)–C(28)	105.7(3)
				O(2)–C(2)–W	170.9(8)		

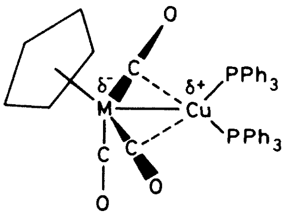
tion, which provides an 18-electron environment for Mo, is an additional dative interaction Rh→Mo giving a formal metal–metal double bond (A); this is more consistent with the observed Mo–Rh bond length. The ability of metals such as Rh to act as Lewis bases is well documented [35] and single dative interactions between metals have been proposed for a number of bimetallic complexes.[9b,14,36] The dative component of the double bond, probably of π symmetry, may also involve a contribution from orbitals of the bridging CO groups so that this may not be a simple, direct metal–metal interaction. In this context it should be noted that the simple concept of single or multiple metal–metal bonds in complexes with bridging ligands, such as $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ or $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, respectively, is not supported by theoretical models or even by some experimental *X*-ray studies.[37] Recent extended-Hückel molecular-orbital calculations on complexes with formal dative M→M′ bonds and bridging μ-CO groups indicate the absence of direct M–M′ interaction.[38] Molecular-orbital calculations on complex (1) and related species are in progress. It is notable that the complex $[\{WIr(CO)_5(\eta\text{-}C_5H_5)\}_2]$ which is isoelectronic with (1) forms a saturated tetranuclear cluster rather than the formally unsaturated binuclear structure of (1).[39]

It can be assumed from the spectral data that complex (2) has a very similar structure to that of (1). The fact that both PPh_3 groups in (1) and (2) appear equivalent in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra probably arises from a fluxional process taking place in solution. By analogy, it is probable that complex (3) has the structure and bonding depicted in (B); this is consistent with $^{31}P\text{-}\{^1H\}$ n.m.r. and i.r. spectra.

The copper complex (5) exists in two structural forms in the solid state. The relatively long Cu–W distances in both (5a)



(B)



(C)

and (5b) are indicative of weak metal–metal interactions rather than a multiple bond as in (1); these interactions may involve significant polarity of the type $\overset{\delta-}{\mathrm{W}}\text{–}\overset{\delta+}{\mathrm{Cu}}$. In complex (5a) the Cu atom adopts the position of typical ligands in a 'four-legged piano stool' geometry about W but in (5b) the W–Cu bond is longer and virtually in the plane containing the two bridging CO ligands. In both (5a) and (5b) all CO ligands approach a terminal bonding configuration with W, giving this metal an 18-electron environment. In complex (5b) the ligands C(2)–O(2) and C(3)–O(3) are semibridging to Cu; the electron distribution in this bridging interaction is, again, not clear but, if the $\overset{\delta-}{\mathrm{W}}\text{–}\overset{\delta+}{\mathrm{Cu}}$ bond is polar [see (C)], this may involve some donation of electrons to Cu to remove the electron deficiency of the formally 14-electron copper(I) atom. In (5a) the two groups C(2)–O(2) and C(3)–O(3) are not so closely associated with the Cu atom but could still be considered to interact weakly in a semibridging manner; the Cu–W bond is shorter and possibly less polar. The fact that complex (5) exists in two different forms in the solid state, which on spectroscopic evidence become indistinguishable in solution, indicates that structures (5a) and (5b) are of comparable energy. Structural interchange involving variation in polar metal–metal bonds may be an important feature in the chemistry of heterometallic complexes.

In solution the rhodium complexes (1)—(3) undergo homolytic bond fission on u.v. photolysis in the presence of spin-trapping agents such as nitrosodurene and dioxygen [equation (i)]. The manganese complex (3) readily undergoes

$$\mathrm{L}_m\mathrm{M}(\mu\text{-CO})_2\mathrm{Rh(PPh_3)_2} \xrightarrow{h\nu} \mathrm{L}_m\dot{\mathrm{M}}(\mathrm{CO})_n + \dot{\mathrm{R}}\mathrm{h(CO)}_n(\mathrm{PPh_3})_2 \; (n \leqslant 2) \qquad \text{(i)}$$

Mn–Rh bond cleavage thermally at r.t., one product being $[\{\mathrm{Rh(CO)(PPh_3)_2}\}_x]$. The ability of complex (1) to act as a catalyst for hydrogenation is of interest; these co-ordinatively unsaturated complexes including a low-oxidation-state rhodium centre possess several features of potential catalytic activity and this aspect of their chemistry is being investigated.

The non-rigidity of the copper complexes (4) and (5) in solution may arise from a heterolytic rather than homolytic fission of the polarised $\overset{\delta+}{\mathrm{Cu}}\text{–}\overset{\delta-}{\mathrm{W}}$ bond and their chemical reactivity may also be related to such a process.

Experimental

All reactions were carried out using Schlenk-type apparatus under an atmosphere of dry, dioxygen-free dinitrogen or under vacuum. All solvents were deoxygenated and dried before use by distillation from $\mathrm{CaH_2}$, sodium-benzophenone, or $\mathrm{P_4O_{10}}$ for hydrocarbons, ethers, or dichloromethane, respectively.

N.m.r. spectra were recorded on a JEOL MH 100-MHz spectrometer (^{1}H) or a Bruker WP 200 SY spectrometer (^{31}P-{^{1}H} and ^{13}C-{^{1}H}) and positive chemical shifts (δ/p.p.m.) are to high frequency of internal $\mathrm{SiMe_4}$ (^{1}H and ^{13}C) or external 85% $\mathrm{H_3PO_4}$ (^{31}P). I.r. spectra were recorded on a Perkin-Elmer 580 instrument and e.s.r. spectra on a JEOL PE1-X *X*-band spectrometer. The conditions for photolytic experiments in the e.s.r. cavity have been previously described.[22] Elemental analyses (Table 1) were performed by Butterworth Laboratories, Teddington. The starting materials $[\mathrm{RhCl(PPh_3)_3}]$,[20] $[\{\mathrm{CuCl(PPh_3)}\}_4]$,[40] and the sodium salts $\mathrm{Na[M(CO)_3(\eta\text{-}C_5H_5)]}$ [41] (M = Mo or W) or $\mathrm{Na[Mn(CO)_5]}$,[41] in thf solutions, were prepared by literature methods.

Preparation of $[\mathrm{MoRh(CO)(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (1).—A solution of $\mathrm{Na[Mo(CO)_3(\eta\text{-}C_5H_5)]}$ (0.38 mmol) in thf (1.5 cm^3) was added to $[\mathrm{RhCl(PPh_3)_3}]$ (0.31 g, 0.34 mmol) and the mixture stirred at r.t. for 30 min. Water (20 cm^3) was added over 1—2 min to give a black solid and cloudy white solution. The liquid was removed by filtration and the solid washed well with water before drying under high vacuum. Recrystallisation by dissolving in $\mathrm{CH_2Cl_2}$ (15 cm^3), filtering, and adding hexane (50 cm^3) followed by concentration to *ca.* 50 cm^3 gave black microcrystals of complex (1) which were washed with hexane and dried *in vacuo* (yield 0.19 g, 64%). Proton n.m.r. ($\mathrm{CDCl_3}$): δ *ca.* 7.3 (m, $\mathrm{PPh_3}$) and 5.20 (s, $\mathrm{C_5H_5}$).

Preparation of $[\mathrm{WRh(CO)(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (2).—As in the synthesis of (1), $\mathrm{Na[W(CO)_3(\eta\text{-}C_5H_5)]}$ (0.28 mmol) in thf (1.1 cm^3) and $[\mathrm{RhCl(PPh_3)_3}]$ (0.22 g, 0.24 mmol) after stirring for 1 h gave a black solid which was obtained as a black microcrystalline product (2) on recrystallisation from $\mathrm{CH_2Cl_2\text{–}Et_2O}$ (yield 0.13 g, 85%). Proton n.m.r. ($\mathrm{CDCl_3}$): δ *ca.* 7.3 (m, $\mathrm{PPh_3}$) and 5.24 (s, $\mathrm{C_5H_5}$).

Preparation of $[\mathrm{MnRh(CO)_4(PPh_3)_3}]$ (3).—A solution of $\mathrm{Na[Mn(CO)_5]}$ (0.23 mmol) in thf (4.5 cm^3) was added to $[\mathrm{RhCl(PPh_3)_3}]$ (0.20 g, 0.22 mmol) and the mixture stirred for 5 min at r.t. to form a dark green solution. The solvent was removed under vacuum and the soluble product extracted with $\mathrm{CH_2Cl_2}$ (5 cm^3). After filtration and addition of hexane (50 cm^3) to the filtrate, complex (3) was obtained as a dark green microcrystalline powder which was washed with hexane and dried *in vacuo* (yield 0.11 g, 48%).

On attempted recrystallisation of complex (3) from $\mathrm{CH_2Cl_2}$, unless great care is taken, some decomposition occurs. On admission of air to a solution of (3) in $\mathrm{CH_2Cl_2}$ the products obtained include: (*a*) yellow crystals, $[\{\mathrm{Rh(CO)(PPh_3)_2}\}_n]$ (6) (Found: C, 68.6; H, 4.1. Calc.: C, 67.8; 4.6%), ν(CO) (Nujol) at 1 965 cm^{-1}; (*b*) orange crystals (Found: C, 66.6; H, 3.9%), ν(CO) (Nujol) at 1 977s, 1 952s, 1 933s, 1 913m, and 1 900m cm^{-1}.

Catalytic Hydrogenation of Cyclohexene using Complex (1).—The hydrogenation was carried out in a closed three-necked flask, fitted with an adjustable manometer filled with diethyl phthalate. The flask with catalyst [complex (1), 0.006 g, 6.8 × 10^{-6} mol] and deoxygenated toluene (9 cm^3) was flushed with hydrogen and the mixture stirred to ensure complete dissolution of catalyst prior to addition of cyclohexene by syringe (1 cm^3, 0.01 mol). The mixture was stirred at constant speed at r.t.; uptake of H_2 was measured at intervals. Samples of reaction solution were analysed using a Hewlett-Packard 4880A series gas chromatograph fitted with a 50-m column of 3% SE54. The ratio of [cyclohexane]/[catalyst] after 5 d was 140 : 1 and the hydrogenation was still continuing.

Preparation of $[\mathrm{CuMo(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (4).—A solution of $\mathrm{Na[Mo(CO)_3(\eta\text{-}C_5H_5)]}$ (0.53 mmol) in thf (2 cm^3) was added to $[\{\mathrm{CuCl(PPh_3)}\}_4]$ (0.184 g, 0.13 mmol) and the mixture stirred at r.t. for 40 min. The solution was evaporated to dryness under vacuum. The solid was extracted with $\mathrm{CH_2Cl_2}$ (5 cm^3) and the resulting solution filtered, concentrated (*ca.* 2 cm^3), and after careful addition of hexane (10 cm^3) afforded yellow crystals of complex (4) on standing. These were collected, washed with hexane, and dried (yield 0.113 g, 52% based on $\mathrm{PPh_3}$). Proton n.m.r. ($\mathrm{C_6D_6}$): δ *ca.* 7.5, 7.0 (br, $\mathrm{PPh_3}$) and 4.87 (s, $\mathrm{C_5H_5}$). The considerable amount of yellow solid remaining after extraction with $\mathrm{CH_2Cl_2}$ exhibited ν(CO) bands (Nujol) in the region 1 935—1 735 cm^{-1}.

Preparation of $[\mathrm{CuW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (5).— As in the synthesis of (4), $\mathrm{Na[W(CO)_3(\eta\text{-}C_5H_5)]}$ (0.25—0.31 mmol) in thf (2 cm^3) and $[\{\mathrm{CuCl(PPh_3)}\}_4]$ (0.075—0.096 g, 0.06—0.08 mmol) were stirred for periods from 10 min to 2 h and then evaporated to dryness. Extraction with $\mathrm{CH_2Cl_2}$ (5 cm^3) and crystallisation over 1—3 d, after careful addition of hexane, gave yellow crystals of complex (5a) or/and orange-red crystals of complex (5b) which were collected, washed with hexane, and dried. It was often possible to separate crystals of (5a) and (5b) by hand. Maximum yields: (5a) 0.028 g, 28%; (5b) 0.032 g, 26%. Proton n.m.r. ($\mathrm{CDCl_3}$): δ 7.4 (br, $\mathrm{PPh_3}$) and 5.27 (s, $\mathrm{C_5H_5}$). Longer reaction times (2 h) appear to favour formation of (5b) and a short time (10 min) produced (5a), but these observations may have resulted from slight variation in the crystallisation procedures. Much yellow solid, insoluble in $\mathrm{CH_2Cl_2}$, was also obtained and this had a complex, variable pattern of ν(CO) bands (Nujol) in the region 2 040—1 750 cm^{-1}.

X-*Ray Crystal Structure Determinations of* $[\mathrm{MoRh(CO)(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (1) *and* $[\mathrm{CuW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (5a) *and* (5b).—*Collection and reduction of diffraction data.* A small dark purple crystal of (1) (dimensions *ca.* 0.27 × 0.40 × 0.43 mm), recrystallised by slow evaporation from $\mathrm{CH_2Cl_2}$–hexane, was mounted on a glass fibre. After preliminary Weissenberg photography, the crystal was transferred to an Enraf–Nonius CAD4 diffractometer for data collection. The cell dimensions were determined by least-squares refinement of the setting angles ($15 > \theta > 16°$) of 25 centred reflections. The ω—2θ scanning technique with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\ 69$ Å) was used to record the intensity data at room temperature for the quadrant of reciprocal space ($+h$, $+k$, $+l$) in the range $2 < 2\theta < 50°$. Analysis of the intensities of two reflections, measured at intervals of 1 h, indicated no significant crystal decay. The raw intensity data were corrected for Lorentz and polarisation effects but not for absorption. Of the 6 560 unique intensities measured, 5 233 with $I > \sigma(I)$ were used in subsequent structure solution and refinement.

Crystal data for (1). $\mathrm{C_{44}H_{35}MoO_3P_2Rh}$, $M = 872.56$, monoclinic, space group $P2_1/c$ (no. 14), $a = 18.102(2)$, $b = 10.407(1)$, $c = 20.736(2)$ Å, $\beta = 104.99(1)°$, $U = 3\ 773.4$ Å^3, $D_m = 1.55$ g cm^{-3}, $Z = 4$, $D_c = 1.53$ g cm^{-3}, $F(000) = 1\ 760$, μ(Mo-K_α) = 7.97 cm^{-1}.

A yellow crystal of (5a) (dimensions *ca.* 0.2 × 0.2 × 0.4 mm) mounted on a glass fibre along the needle axis was used for data collection. The experimental procedure was similar to that for (1). The cell parameters were derived from 25 well centred reflections in the range $14 < \theta < 15°$. The data, collected over the region ($+h$, $\pm k$, $\pm l$) in the range $2 < 2\theta < 50°$, yielded 6 578 intensities of which 3 997 with $I > \sigma(I)$ were used in structural solution and refinement. No significant crystal decay was observed for (5a). Lorentz, polarisation, and absorption corrections were applied to the raw intensity data.

Crystal data for (5a). Yellow needles, $\mathrm{C_{44}H_{35}CuO_3P_2W}$, $M = 921.1$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.404(4)$, $b = 11.756(3)$, $c = 14.208(3)$ Å, $\alpha = 101.4(2)$, $\beta = 79.5(2)$, $\gamma = 110.3(2)°$, $U = 1\ 890.3$ Å^3, $D_m = 1.63$ g cm^{-3}, $Z = 2$, $D_c = 1.62$ g cm^{-3}, $F(000) = 912$, μ(Mo-K_α) = 39.05 cm^{-1}.

A crystalline fragment of (5b) of dimensions *ca.* 0.40 × 0.40 × 0.15 mm was cut from a large plate and mounted on a glass fibre. The experimental procedure was similar to that described above. The intensity data were collected in the quadrant ($\pm h$, $+k$, $+l$) within the limits $2 < 2\theta < 44°$. Of the 4 586 data measured, 4 009 with $I > \theta(I)$ were used in subsequent structural solution and refinement. As for (5a), no crystal decay was observed and absorption corrections were applied.

Crystal data for (5b). Orange-red plates, $\mathrm{C_{44}H_{35}CuO_3P_2W}$, $M = 921.1$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.991(3)$, $b = 10.098(2)$, $c = 21.608(2)$ Å, $\beta = 105.66(1)°$, $U = 3\ 779.7$ Å^3, $D_m = 1.63$ g cm^{-3}, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $F(000) = 1\ 824$, μ(Mo-K_α) = 39.05 cm^{-1}.

Solution and refinement of the structures. All three structures were solved by conventional heavy-atom methods (Patterson and Fourier difference) and refined by full-matrix least-squares methods.[42] The non-hydrogen atoms except the cyclopentadienyl-ring atoms were anisotropic. The phenyl and cyclopentadienyl groups were treated as hexagonal and pentagonal rigid bodies respectively and their associated hydrogen atoms placed on calculated positions ($d_{\mathrm{C-H}}$ 1.08 Å) with fixed thermal parameters ($U = 0.10$ Å^2). In all cases, the cyclopentadienyl groups were disordered. This was modelled satisfactorily by having two coplanar five-membered rings staggered with respect to each other, and refining the atomic occupancies.

The final residuals for (1) were $R = 0.036$ and $R' = 0.074$ where the weights $w = 1.115/[\sigma^2|F| + 0.030\ 69|F|^2]$. A final Fourier difference map showed no features >0.64 e Å^{-3}. The atomic positional parameters, and important bond distances and angles, are listed in Tables 2 and 3 respectively. For (5a), at convergence $R = 0.058$ and $R' = 0.076$, where $w = 0.9707/[\sigma^2|F| + 0.005\ 628|F|^2]$. Although the final Fourier difference map was largely featureless, there were four peaks in the range 1.0—1.4 e Å^{-3} located close to the tungsten atom. Tables 4 and 5 give the atomic fractional co-ordinates, and selected geometrical parameters. Structural refinement of (5b) converged at $R = 0.034$ and $R' = 0.0492$, where $w = 2.0623/[\sigma^2|F| + 0.001\ 388|F|^2]$. A final electron-density difference map showed no peaks >0.5 e Å^{-3} except in the immediate vicinity of the tungsten atom where peaks *ca.* 0.9 e Å^{-3} were observed. Tables 6 and 7 list the fractional atomic co-ordinates and selected geometrical parameters.

All crystallographic calculations were carried out using SHELX 76.[42] Scattering factors and corrections for anomalous scattering were taken from ref. 43.

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