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Binuclear complexes of rhodium or copper with pentamethylcyclopentadienyltricarbonyltungsten. Crystal structure of $(\eta^5\text{-}C_5Me_5)(CO)W(\mu\text{-}CO)_2Rh(PPh_3)_2$

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Abstract

The reaction of $Li[W(CO)_3Cp^\star]$ ($Cp^\star = \eta^5\text{-}C_5Me_5$) with $[RhCl(PPh_3)_3]$ affords $[Cp^\star(CO)W(\mu\text{-}CO)_2Rh(PPh_3)_2]$,**3**, which has been structurally characterised by an X-ray diffraction study, and shown to contain a short W–Rh bond of 2.5820(6) Å and two semi-bridging CO ligands. Variable temperature $^{31}P\{^1H\}$ NMR spectra show that complex **3** is fluxional in solution and undergoes intramolecular interchange of inequivalent PPh_3 with $\Delta G^\ddagger$ca. 30 kJ mol^{-1} at −105°C. Reaction of $Li[W(CO)_3Cp^\star]$ with $[RhCl(PPh_3)_3]$ gives the mono-triphenylphosphine complex $[Cp^\star W(CO)_3Cu(PPh_3)]$, **4a**, which has the same valence electron count as **3** and has been characterised analytically and by IR and NMR spectroscopy. Evidence for a related molybdenum-copper species, **4b**, is also presented. The structural and spectroscopic properties of new products are discussed in relation to those of related heterobinuclear compounds.

Keywords: Rhodium; Copper; Tungsten; Carbonyl; Pentamethylcyclopentadienyl; Fluxionality

1. Introduction

We have previously reported the heteronuclear bimetallic compounds of general formula $[MM'(CO)_3(PPh_3)_2Cp]$ (M = Mo or W; M′ = Rh, Ni or Cu; $Cp = \eta^5\text{-}C_5H_5$) [1,2]. These derivatives have interesting electronic structures, possessing metal–metal bonds of varying multiplicity and semi-bridging carbonyl groups [2,3], and exhibit geometrical non-rigidity in solution involving intramolecular rotational motion around the linkage between the two metallic centres [4]. The rhodium compound $[Cp(CO)W(\mu\text{-}CO)_2Rh(PPh_3)_2]$, **1a**, has also been made by an alternative route from a tungsten carbyne complex, and shown by an X-ray diffraction study [5] to be isomorphous in the solid state with the molybdenum analogue $[Cp(CO)Mo(\mu\text{-}CO)_2Rh(PPh_3)_2]$, **1b** [1]: both complexes possess short, multiple metal–metal bonds. Some Mo–Rh complexes of related structure have also been reported containing pyrazolylgallate or pyrazolylborate ligands, including the structurally characterised $[\{MeGa(pz)_3\}(CO)Mo(\mu\text{-}CO)_2Rh(PPh_3)_2]$ [6].

The copper complex $[CpW(CO)_3Cu(PPh_3)_2]$, **2a**, can exist in two isomeric forms, **A** and **B**, in the solid state, both structurally characterised by X-ray diffraction [1], but the bonds of the Cu atom to two semi-bridging carbonyl ligands and to the Group 6 metal are relatively weak. The molybdenum analogue $[CpMo(CO)_3Cu(PPh_3)_2]$, **2b**, has only been obtained in one crystalline form, and its structure is probably similar to that of conformer **B**. Related complexes containing a cyclopentadienyltricarbonyl Group 6 metal entity bonded to a diaminecopper unit have been reported, and the solid-state structure of $[CpMo(CO)_3Cu(tmed)]$ (tmed = N,N,N′,N′-tetramethylethylenediamine) is analogous to form **B** of complex **2a** [7]; a similar interaction between the Mo and Cu atoms and the CO ligands is found in complex $[\{HB(pz)_3\}Mo(CO)_3Cu(tmed)]$ [8], and the acetate-bridged derivative $[CpMo(CO)_2(\mu\text{-}O_2CMe)_2Cu(NC_5H_4Me\text{-}4)]$ also bears a structural resemblance to the tricarbonyl species [9].

We thought it of interest to investigate the properties of other binuclear carbonyl compounds related to

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the above species, and we describe below some new derivatives in which the cyclopentadienyl group has been replaced by the more bulky and more electron-donating pentamethylcyclopentadienyl ligand.

2. Results and discussion

2.1. Rhodium species

The reaction of Li[W(CO)$_3$Cp*] (Cp* = η^5-C_5Me_5) with [RhCl(PPh$_3$)$_3$] in tetrahydrofuran affords relatively low yields of black prismatic crystals, identified by spectroscopic and analytical means as the pentamethylcyclopentadienyl derivative [Cp*(CO)W(μ-CO)$_2$Rh(PPh$_3$)$_2$] **3**, an analogue of complexes **1**. By-products of this reaction include the yellow rhodium(I) complex [RhCl(CO)(PPh$_3$)$_2$] formed by carbonyl ligand transfer from tungsten to rhodium, possibly via a binuclear intermediate; decomposition of **3** in chlorinated solvents is also a source of this by-product. The carbonyl vibrations in the IR spectrum of solid **3** {ν(CO): 1866, 1790, 1738 cm^{-1} (in Nujol)} agree well with those for complex **1a** {ν(CO): 1871, 1770, 1738 cm^{-1}} and the two low frequencies suggest the presence of bridging CO ligands. The ^{1}H NMR spectrum comprises resonances assignable to protons of two PPh$_3$ ligands and one symmetrical C_5Me_5 group.

The ^{31}P{^{1}H} NMR spectrum of **3** in CD_2Cl_2 at ambient temperature shows a doublet resonance (J(^{103}Rh–P) = 170.7 Hz) assignable to apparently equivalent phosphorus atoms of the two PPh$_3$ ligands bonded directly to rhodium. Additionally, each component of this well-resolved doublet resonance shows small satellite bands (see Fig. 1). The total intensity of the two large outer satellites is ca. 14% of the whole component, and this small doublet signal may be assigned to coupling with ^{183}W (I = 0.5; 14.4% natural abundance); observation of ^{183}W–^{31}P coupling {J(W–

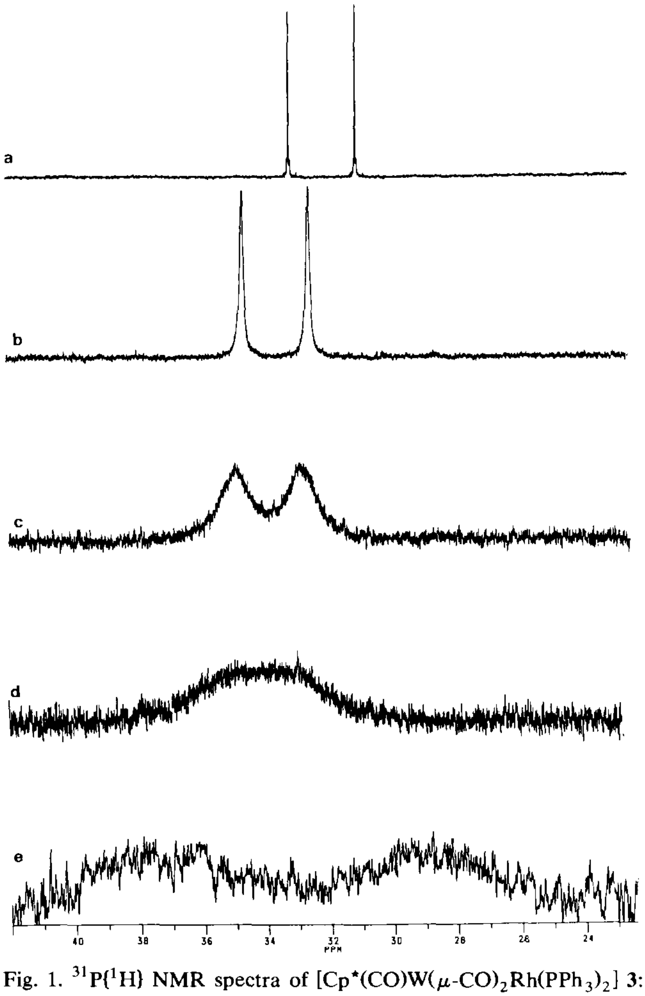


Fig. 1. ^{31}P{^{1}H} NMR spectra of [Cp*(CO)W(μ-CO)$_2$Rh(PPh$_3$)$_2$] **3**: (a) 22°C in CD_2Cl_2; (b) −80°C in CD_2Cl_2; (c) −100°C in CD_2Cl_2; (d) −105°C in CD_2Cl_2; (e) −120°C in CD_2Cl_2/$CFCl_3$.

Table 1
Derived geometrical parameters for complex **3**

Bond Lengths (Å) with estimated standard deviations			
Rh(1)–P(1)	2.2878(18)	W(1)–C(40)	2.379(6)
Rh(1)–P(2)	2.2493(17)	W(1)–C(41)	2.350(6)
Rh(1)–W(1)	2.5820(6)	W(1)–C(42)	2.361(6)
Rh(1)–C(2)	2.239(8)	W(1)–C(43)	2.396(6)
Rh(1)–C(3)	2.100(7)	W(1)–C(44)	2.407(6)
P(1)–C(9)	1.838(5)	W(1)–C(40′)	2.383(8)
P(1)–C(15)	1.811(5)	W(1)–C(41′)	2.346(8)
P(1)–C(21)	1.845(5)	W(1)–C(42′)	2.309(8)
P(2)–C(27)	1.814(5)	W(1)–C(43′)	2.325(8)
P(2)–C(33)	1.826(5)	W(1)–C(44′)	2.371(8)
P(2)–C(39)	1.860(6)	C(1)–O(1)	1.172(10)
W(1)–C(1)	1.938(8)	C(2)–O(2)	1.170(9)
W(1)–C(2)	2.002(8)	C(3)–O(3)	1.186(9)
W(1)–C(3)	1.999(7)		
Angles (°) with estimated standard deviations			
P(1)–Rh(1)–P(2)	98.95(6)	Rh(1)–P(2)–C(39)	112.49(19)
P(1)–Rh(1)–W(1)	129.23(5)	C(27)–P(2)–C(33)	104.11(22)
P(1)–Rh(1)–C(2)	125.49(20)	C(27)–P(2)–C(39)	101.04(24)
P(1)–Rh(1)–C(3)	122.24(20)	C(33)–P(2)–C(39)	100.55(23)
P(2)–Rh(1)–W(1)	131.83(5)	P(2)–C(27)–C(22)	119.2(4)
P(2)–Rh(1)–C(2)	107.02(20)	P(2)–C(27)–C(26)	120.8(4)
P(2)–Rh(1)–C(3)	108.31(20)	P(2)–C(33)–C(28)	115.6(3)
W(1)–Rh(1)–C(2)	48.44(19)	P(2)–C(33)–C(32)	124.3(3)
W(1)–Rh(1)–C(3)	49.24(20)	P(2)–C(39)–C(34)	121.6(4)
C(2)–Rh(1)–C(3)	93.9(3)	P(2)–C(39)–C(38)	118.3(4)
Rh(1)–P(1)–C(9)	125.78(18)	Rh(1)–W(1)–C(1)	75.85(24)
Rh(1)–P(1)–C(15)	106.95(17)	Rh(1)–W(1)–C(2)	56.80(21)
Rh(1)–P(1)–C(21)	114.57(17)	Rh(1)–W(1)–C(3)	52.71(21)
C(9)–P(1)–C(15)	103.25(23)	C(1)–W(1)–C(2)	90.6(3)
C(9)–P(1)–C(21)	98.73(23)	C(1)–W(1)–C(3)	95.0(3)
C(15)–P(1)–C(21)	105.59(22)	C(2)–W(1)–C(3)	104.8(3)
P(1)–C(9)–C(4)	116.4(4)	W(1)–C(1)–O(1)	171.3(7)
P(1)–C(9)–C(8)	123.6(4)	Rh(1)–C(2)–W(1)	74.77(25)
P(1)–C(15)–C(10)	123.3(4)	Rh(1)–C(2)–O(2)	119.2(6)
P(1)–C(15)–C(14)	116.7(3)	W(1)–C(2)–O(2)	166.1(6)
P(1)–C(21)–C(16)	119.5(4)	Rh(1)–C(3)–W(1)	78.1(3)
P(1)–C(21)–C(20)	120.4(4)	Rh(1)–C(3)–O(3)	124.5(6)
Rh(1)–P(2)–C(27)	118.43(17)	W(1)–C(3)–O(3)	157.4(6)
Rh(1)–P(2)–C(33)	117.57(16)		

Table 2
Fractional coordinates of atoms with standard deviations

Atom	x	y	z	U_{eq}
Rh(1)	0.23184(5)	0.75067(4)	0.23107(3)	0.0300(3)
P(1)	0.22654(17)	0.92376(13)	0.26258(10)	0.0359(10)
C(4)	0.1710(4)	0.9353(4)	0.4267(3)	0.059(5)
C(5)	0.1903(4)	0.9609(4)	0.4987(3)	0.080(7)
C(6)	0.3030(4)	1.0078(4)	0.4985(3)	0.095(8)
C(7)	0.3964(4)	1.0292(4)	0.4263(3)	0.101(9)
C(8)	0.3771(4)	1.0036(4)	0.3542(3)	0.065(6)
C(9)	0.2644(4)	0.9567(4)	0.3544(3)	0.045(4)
C(10)	0.3058(4)	1.0949(4)	0.1355(3)	0.059(5)
C(11)	0.4000(4)	1.1460(4)	0.0739(3)	0.073(6)
C(12)	0.5298(4)	1.0984(4)	0.0580(3)	0.070(6)
C(13)	0.5653(4)	0.9995(4)	0.1036(3)	0.077(6)
C(14)	0.4711(4)	0.9483(4)	0.1652(3)	0.063(5)
C(15)	0.3413(4)	0.9960(4)	0.1811(3)	0.043(4)
C(16)	−0.0381(5)	0.9631(3)	0.2528(3)	0.055(5)
C(17)	−0.1604(5)	1.0248(3)	0.2587(3)	0.073(6)
C(18)	−0.1779(5)	1.1310(3)	0.2792(3)	0.082(7)
C(19)	−0.0732(5)	1.1757(3)	0.2938(3)	0.077(7)
C(20)	0.0491(5)	1.1140(3)	0.2880(3)	0.057(5)
C(21)	0.0667(5)	1.0078(3)	0.2675(3)	0.042(4)
P(2)	0.31186(16)	0.65287(13)	0.33461(10)	0.0344(9)
C(22)	0.0737(4)	0.6816(4)	0.4454(3)	0.056(5)
C(23)	−0.0135(4)	0.6625(4)	0.5205(3)	0.071(6)
C(24)	0.0251(4)	0.5873(4)	0.5828(3)	0.083(7)
C(25)	0.1509(4)	0.5313(4)	0.5699(3)	0.071(6)
C(26)	0.2382(4)	0.5505(4)	0.4948(3)	0.058(5)
C(27)	0.1996(4)	0.6256(4)	0.4325(3)	0.042(4)
C(28)	0.5618(4)	0.7132(4)	0.29405(21)	0.056(5)
C(29)	0.6762(4)	0.7444(4)	0.30689(21)	0.065(6)
C(30)	0.6811(4)	0.7630(4)	0.38398(21)	0.076(7)
C(31)	0.5717(4)	0.7503(4)	0.44824(21)	0.069(6)
C(32)	0.4573(4)	0.7190(4)	0.43540(21)	0.055(5)
C(33)	0.4523(4)	0.7005(4)	0.35831(21)	0.040(4)
C(34)	0.4910(5)	0.4584(4)	0.3415(3)	0.074(6)
C(35)	0.5358(5)	0.3499(4)	0.3289(3)	0.088(8)
C(36)	0.4695(5)	0.2935(4)	0.2901(3)	0.080(7)
C(37)	0.3583(5)	0.3456(4)	0.2638(3)	0.081(7)
C(38)	0.3135(5)	0.4541(4)	0.2763(3)	0.060(5)
C(39)	0.3798(5)	0.5105(4)	0.3152(3)	0.044(4)
W(1)	0.16300(3)	0.69128(2)	0.11152(2)	0.0380(2)
C(1)	0.1471(8)	0.8507(7)	0.0895(4)	0.055(5)
O(1)	0.1349(7)	0.9454(4)	0.0666(4)	0.084(5)
C(2)	0.3506(8)	0.6886(6)	0.1173(4)	0.047(5)
O(2)	0.4653(5)	0.6793(5)	0.1055(3)	0.064(4)
C(3)	0.0614(7)	0.6848(5)	0.2266(4)	0.045(4)
O(3)	−0.0253(5)	0.6639(5)	0.2837(3)	0.059(4)
C(40)	0.1918(6)	0.6441(5)	−0.0209(3)	0.0433(0)
C(41)	0.2013(6)	0.5456(5)	0.0342(3)	0.0433(0)
C(42)	0.0769(6)	0.5365(5)	0.0886(3)	0.0433(0)
C(43)	−0.0094(6)	0.6294(5)	0.0672(3)	0.0433(0)
C(44)	0.0617(6)	0.6959(5)	−0.0005(3)	0.0433(0)
C(45)	0.3018(6)	0.6867(5)	−0.0897(3)	0.0905(25)
C(46)	0.3231(6)	0.4641(5)	0.0347(3)	0.0905(25)
C(47)	0.0422(6)	0.4435(5)	0.1577(3)	0.0905(25)
C(48)	−0.1526(6)	0.6534(5)	0.1093(3)	0.0905(25)
C(49)	0.0078(6)	0.8037(5)	−0.0436(3)	0.0905(25)
C(40′)	0.2167(7)	0.6111(6)	−0.0108(5)	0.0462(0)
C(41′)	0.1631(7)	0.5319(6)	0.0546(5)	0.0462(0)
C(42′)	0.0315(7)	0.5722(6)	0.0874(5)	0.0462(0)
C(43′)	0.0037(7)	0.6764(6)	0.0424(5)	0.0462(0)
C(44′)	0.1182(7)	0.7004(6)	−0.0183(5)	0.0462(0)
C(45′)	0.3552(7)	0.6019(6)	−0.0635(5)	0.115(4)
C(46′)	0.2342(7)	0.4230(6)	0.0841(5)	0.115(4)
C(47′)	−0.0631(7)	0.5141(6)	0.1584(5)	0.115(4)
C(48′)	−0.1258(7)	0.7493(6)	0.0567(5)	0.115(4)
C(49′)	0.1327(7)	0.8036(6)	−0.0805(5)	0.115(4)

P) = 8.1 Hz} indicates that complex **3** retains its integrity as a binuclear system in solution at room temperature. The smaller inner satellites arise from ^{13}C–^{31}P couplings. It is of interest that $^{31}P\{^1H\}$ NMR spectra of complexes **1** at ambient temperatures gave broader signals from which satellite bands were not resolved [1,4].

Low temperature $^{31}P\{^1H\}$ NMR spectra show that complex **3** is fluxional (see Fig. 1) and exhibits typical coalescence behaviour associated with a two-site exchange of inequivalent ^{31}P nuclei. Coalescence occurs at −105°C, and at −120°C (in $CD_2Cl_2/CFCl_3$) the spectrum becomes two broad resonances (δ = ca. 37.0 and 29.5 ppm). This is consistent with the presence of two inequivalent PPh_3 ligands undergoing slow exchange on the NMR timescale at the latter temperature but, unfortunately, within the limits of the experimentally available temperature range further resolution of these bands into expected multiplets from Rh–P and P–P coupling was not observed. These results are consistent with the occurrence of an intramolecular pseudo-rotational process similar to that previously proposed for complex **1a** [4]. The NMR parameters for complex **3** yield an approximate value for the activation free energy of $\Delta G^{\ddagger} = 30$ kJ mol^{-1} at −105°C for this

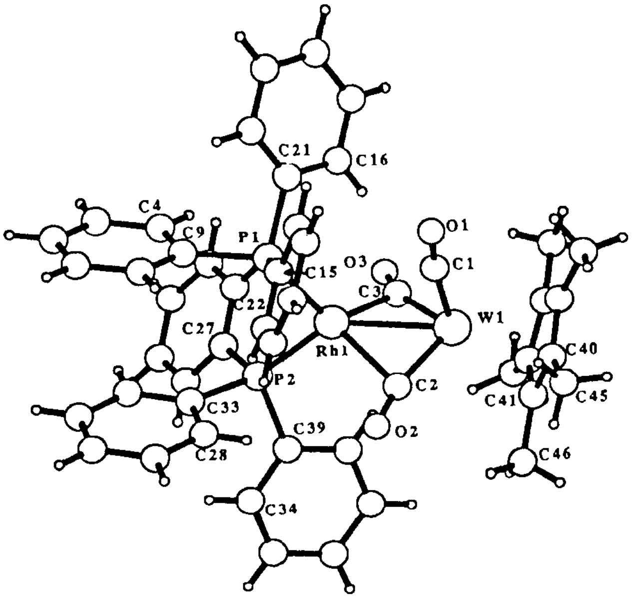
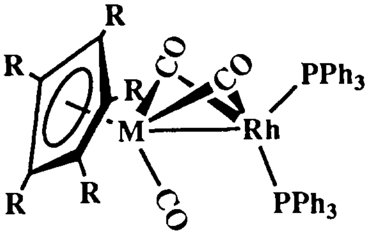
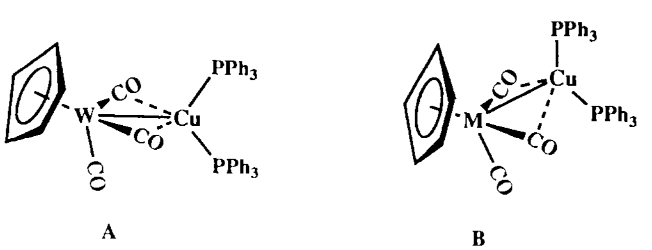


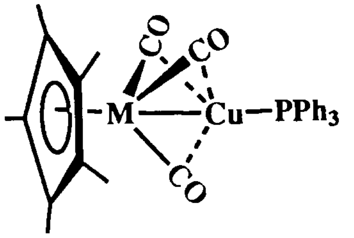
Fig. 2. Molecular structure of [Cp*(CO)W(μ-CO)$_2$Rh(PPh$_3$)$_2$] **3**, with atom numbering as in Table 1. Only the major site occupancies of the disordered Cp* unit are shown for clarity.



1a R = H; M = W
1b R = H; M = Mo
3 R = Me; M = W



2a M = W
2b M = Mo



4a M = W
4b M = Mo

interchange, and this compares with $\Delta G^{\ddagger} = 27.9 \pm 0.8$ kJ mol^{-1} at -108°C for the cyclopentadienyl analogue **1a**.

A single crystal of non-solvated **3**, obtained from CH_2Cl_2/petroleum ether at -15°C, was subjected to an X-ray diffraction study and the structure of a single molecule is depicted in Fig. 2. Table 1 lists important bond lengths and angles and Table 2 the atomic fractional co-ordinates. The molecular structure of **3** is very similar to those $[Cp(CO)M(\mu\text{-}CO)_2Rh(PPh_3)_2]$ (M = W, **1a** [5], and M = Mo **1b** [1]). Table 3 presents a comparative listing of some geometrical parameters of complexes **3**, **1a**, **1b** and the closely related methyltris(1-pyrazolyl)gallate complex, $[\{MeGa(pz)_3\}(CO)Mo(\mu\text{-}CO)_2Rh(PPh_3)_2]$. Two CO groups in **3** are semi-bridging to Rh, being closer to linear with respect to tungsten {angles W–C–O: 166.1(6)° and 157.4(6)°} than to rhodium {angles Rh–C–O: 119.2(6)° and 124.5(6)°}, and the difference in Rh–C distances {2.239(8)° and 2.100(7) Å} suggests more asymmetry in this bridging than in species **1a** and **1b**. The Rh–W bond length, 2.5820(6) Å, is marginally shorter than in the non-methylated cyclopentadienyl compound **1a**. The dihedral angle between W-Rh-C(2) and W-Rh-C(3) planes is 152.0°, and the two triphenylphosphine ligands are in inequivalent positions, with the P–Rh–P plane rotated by 5.7° from the Rh–W–C(1) plane. The pentamethylcyclopentadienyl ligand shows typical η^5-coordination, although rotational disorder has been modelled on two sites of 55% and 45% occupancy. The solid-state structure of **3** is consistent with the IR spectrum and with the low temperature NMR data for the species in solution.

These results indicate that substitution of the cyclopentadienyl by the pentamethylcyclopentadienyl ligand has only a small influence on the structural parameters of complexes $[Cp'(CO)W(\mu\text{-}CO)_2Rh(PPh_3)_2]$, although the stability seemed to be lower for the pentamethylcyclopentadienyl complex.

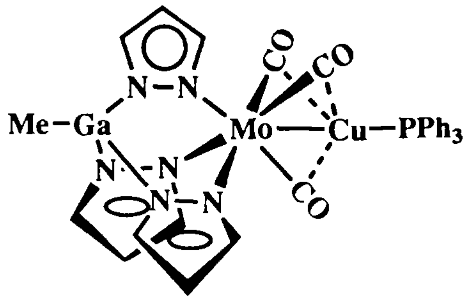
2.2. Copper species

After several crystallisations of the product from the reaction of $Li[W(CO)_3Cp^*]$ with $[CuCl(PPh_3)_3]$ in te-

Table 3
Comparison of some geometrical parameters in the solid state of structurally related M–Rh complexes (M = W or Mo)

M–Rh Complex	M–Rh (Å)	$M\text{–}C_{term}$ (Å)	$M\text{–}C_{\mu}$ (Å)	$Rh\text{–}C_{\mu}$ (Å)	$M\text{–}C_{term}\text{–}O$ (°)	$M\text{–}C_{\mu}\text{–}O$ (°)	$Rh\text{–}C_{\mu}\text{–}O$ (°)	Rh–P (Å)	P–Rh–P (°)
$[Cp^*(CO)W(\mu\text{-}CO)_2\text{-}Rh(PPh_3)_2]$ **3** [a]	2.5820(6)	1.938(8)	2.002(8) 1.999(7)	2.239(8) 2.100(7)	171.3(7)	166.1(6) 157.4(6)	119.2(6) 124.5(6)	2.2878(18) 2.2493(17)	98.95(6)
$[Cp(CO)W(\mu\text{-}CO)_2\text{-}Rh(PPh_3)_2]$ **1a** [b]	2.587(1)	1.94(1)	1.990(9) 2.009(7)	2.116(8) 2.158(8)	176(1)	164.0(7) 162.0(6)	118.9(6) 120.1(6)	2.315(2) 2.263(2)	103.8(1)
$[Cp(CO)Mo(\mu\text{-}CO)_2\text{-}Rh(PPh_3)_2]$ **1b** [c]	2.588(1)	1.943(6)	1.980(6) 2.026(5)	2.182(6) 2.092(5)	174.7(5)	164.7(5) 159.4(4)	118.6(5) 122.7(4)	2.242(1) 2.321(1)	103.3(0)
$[\{MeGa(pz)_3\}(CO)\text{-}Mo(\mu\text{-}CO)_2\text{-}Rh(PPh_3)_2]$ [d]	2.6066(5)	1.982(5)	1.971(6) 2.034(5)	2.334(5) 2.079(5)	173.9(5)	167.4(4) 153.2(4)	117.9(4) 128.1(4)	2.2491(13) 2.2836(12)	95.27(5)

[a] This work; [b] From ref. [5]; [c] From ref. [1]; [d] From ref. [6].



5

trahydrofuran at ambient temperature, a pure heteronuclear complex of formula $[\mathrm{Cp^{*}W(CO)_3Cu(PPh_3)}]$ **4a** was obtained as yellow crystals. The formula assignment is based on the results of elemental analysis and on the relative intensities of proton resonances from $\mathrm{C_5Me_5}$ and $\mathrm{PPh_3}$ ligands in the ^{1}H NMR spectrum. It is of interest that under similar conditions the main product isolated from reaction between $\mathrm{Na[W(CO)_3Cp]}$ and $\mathrm{[CuCl(PPh_3)_3]}$ is the bis-triphenylphosphine complex $\mathrm{[CpW(CO)_3Cu(PPh_3)_2]}$, **2a**. The IR spectrum of **4a** shows two relatively low frequency ν(CO) bands in solution and in the solid state {e.g.: 1887, 1787 cm^{-1} (Nujol)} and these suggest the presence of bridging CO groups or of a largely ionic $[\mathrm{Cp^{*}W(CO)_3}]^-$ unit. The ambient temperature ^{31}P{^{1}H} NMR spectrum of **4a** comprises a broadened singlet resonance at $\delta = 8.1$ ppm, but at lower temperatures this reversibly passes through coalescence points to be resolved into three singlets of relative intensities 6.3 : 1 : 2.6 at 13.1, 1.8 and -4.2 ppm, respectively, at -90°C in $\mathrm{CD_2Cl_2}$. The $\mathrm{C_5Me_5}$ resonance in the ^{1}H NMR spectrum at ambient temperature is a singlet, but at lower temperatures two smaller singlet resonances are also evident. These NMR observations indicate the existence of an equilibrium between species in solution, which may account for the difficulty in crystallising pure samples of **4a** and for its tendency to decompose readily in solution. Attempts to isolate pure samples of the analogous molybdenum complex $[\mathrm{Cp^{*}Mo(CO)_3Cu(PPh_3)}]$, **4b**, were unsuceessful, but the spectroscopic properties of the product from reactions between $[\mathrm{Li[Mo(CO)_3Cp^{*}]}]$ and $\mathrm{[CuCl(PPh_3)_3]}$ supported the formation of **4b** as the major binuclear carbonyl complex.

The mono-triphenylphosphine complex $\mathrm{[\{MeGa(pz)_3\}Mo(CO)_3Cu(PPh_3)]}$, **5**, [6] and a tris(1-pyrazolyl)borate analogue [8] have been reported. Complex **5** has a 3 : 3 : 1 structure, with an approximate three-fold axis along the near-linear Mo–Cu–P atomic arrangement (see diagram), with a short Mo–Cu bond and the Cu atom interacting with all three CO ligands in semi-bridging modes [6]. A similar bonding arrangement is found in the trimetallic anion $\mathrm{[Cu(Mo\{CO\}_3\{HB(pz)_3\})_2]^-}$, in which the central Cu atom is linearly bonded to the two Mo atoms and is semi-bridged by all six CO groups [10], and this bonding is also likely to arise in the anions $\mathrm{[Cu\{M(CO)_3Cp\}_2]^-}$ (M = Cr, Mo, W) [11] which have not been structurally characterised. The IR spectrum of **5** shows ν(CO) bands {1898, 1798 cm^{-1} ($\mathrm{CH_2Cl_2}$); 1890, 1805, 1780 cm^{-1} (Nujol)} that are similar to those of **4a** and, considering the related stoichiometries, it is likely that both have a similar coordination geometry around Cu. Unfortunately, X-ray data collected from crystals of **4a** were of too poor quality to allow refinement of the structure.

It is noteworthy that the gold complex of similar stoichiometry, $\mathrm{[CpW(CO)_3Au(PPh_3)]}$, is structurally different from complex **5**, and adopts a typical "four-legged piano stool" arrangement of ligands around the tungsten atom, with the cyclopentadienyl group at the apex and the three CO ligands and the $\mathrm{Au(PPh_3)}$ group occupying the basal positions [12]. There are no interactions between Au and CO ligands in this structure, and the ν(CO) vibrations are at higher frequencies than in complexes **4** or **5**.

The pentamethylcyclopentadienyl ligand promotes the formation of monophosphine complexes $[\mathrm{Cp^{*}M(CO)_3Cu(PPh_3)}]$, **4**, and not bis-phosphine complexes corresponding to the species $\mathrm{[CpM(CO)_3Cu(PPh_3)_2]}$, **2**, obtained as the major products from reactants containing the simple cyclopentadienyl ligand. This difference could be the result of unfavorable steric interactions between cyclopentadienyl methyl groups and phenyl groups of a $\mathrm{PPh_3}$ ligand in a conformation of type **B** found for complex **2a** and related species. Also, the smaller $\mathrm{Cu(PPh_3)}$ entity has the same 13-valence electron count as $\mathrm{Rh(PPh_3)_2}$ which coordinates to $[\mathrm{Cp^{*}M(CO)_3}]$ within the cone of the three CO groups to form a stronger multiple bond. The bonding between metal centres in complexes **4** probably involves a dative interaction from the Group 6 metal to Cu and weak back-donation of electrons from the Cu centre to the three CO ligands, as suggested by MO calculations on related systems [3].

3. Experimental details

All reactions were carried out using Schlenk techniques under dry nitrogen using freshly distilled, predried solvents, as previously described [1]. The reagents $\mathrm{RhCl(PPh_3)_3}$ [13], $\mathrm{CuCl(PPh_3)_3}$ [14] and pentamethylcyclopentadiene [15] were prepared by published methods, and $\mathrm{W(CO)_6}$, CuCl, $\mathrm{RhCl_3.3H_2O}$ and $\mathrm{PPh_3}$ were obtained commercially (Aldrich, BDH or Strem Chemicals) and used as supplied. *n*-Butyllithium in hexane (Aldrich) was standardised by titration against diphenylacetic acid [16]. Solutions of the salts $\mathrm{Li[M(CO)_3Cp^{*}]}$ (M = W or Mo) were prepared by refluxing a solution of $M(CO)_6$ and LiCp* (from *n*-butyllithium and pentamethylcyclopentadiene) in THF for 50 h (M = W) or 24 h (M = Mo), as previously described [17], and the conversion was monitored by IR spectroscopy {ν(CO): M = W, 1887, 1790, 1701; M = Mo, 1886, 1791, 1709 cm^{-1}}. Silica gel used for column chromatography was 70–230 mesh (Merck), and petroleum ether was of b.p. 60–80°C, unless otherwise specified. NMR spectra were recorded on a Bruker WP 200 SY spectrometer at 200 MHz or 81.0 MHz for ^1H or ^{31}P, respectively, with $SiMe_4$ or 85% aqueous H_3PO_4 as reference, and at ca. 20°C unless otherwise stated. IR spectra were obtained on a Perkin Elmer FT1600 spectrometer, and elemental analyses were carried out at UMIST, Manchester, UK.

3.1. Preparation of $[Cp^*(CO)W(\mu\text{-}CO)_2Rh(PPh_3)_2]$

A solution of $Li[W(CO)_3Cp^*]$ (0.38 mmol) in THF (3 cm^3) was added to $[RhCl(PPh_3)_3]$ (0.30 g, 0.32 mmol) and the mixture was stirred at room temperature for 1 h. Deoxygenated water (20 cm^3) was added during 2 min to give a black solid and a cloudy white solution. After decantation of the liquid phase, the solid was filtered off, washed well with water and dried in vacuo, and then extracted with CH_2Cl_2 (20 cm^3). The extract was filtered to remove yellow insoluble material, then evaporated to dryness to give an impure product, which was redissolved in the minimum amount of CH_2Cl_2. The solution was layered with an equal volume of petroleum ether and kept at room temperature for ca. 3 d to give black microcrystals of the title compound. After decantation of the supernatant liquid the crystals where washed well with petroleum ether and dried in vacuo, yield 0.035 g (10%). Anal. Found: C, 56.0; H, 4.3. $C_{49}H_{45}O_3P_2RhW$ calc.: C, 57.1; H 4.4%; {slight contamination by traces of CH_2Cl_2 was indicated by the ^1H NMR spectrum in $CDCl_3$: calc. for $C_{49}H_{45}O_3P_2RhW\text{-}0.25(CH_2Cl_2)$: C, 56.2; H, 4.4%}. IR ν(CO): (CH_2Cl_2) 1868, 1734; (nujol) 1866, 1790 and 1738 cm^{-1}. NMR (CD_2Cl_2): ^1H δ 7.0–7.45 (complex m, 30H, PPh_3), 1.95 (s, 15H, C_5Me_5). $^{31}P\{^1H\}$ δ 32.1 {d, J(Rh–P) = 170.7 Hz, 2P; doublet satellites J(W–P) = 8.1 Hz}.

3.2. Preparation of $[Cp^*W(CO)_3Cu(PPh_3)]$

A solution of $Li[W(CO)_3Cp^*]$ (1.13 mmol) in THF (17 cm^3) was added to $[CuCl(PPh_3)_3]$ (1.00 g, 1.13 mmol) and the mixture was stirred at room temperature for 2 h. The solvent was evaporated under vacuum, and the residue was washed with petroleum ether, then extracted with CH_2Cl_2 (35 cm^3). The extract was filtered to remove insoluble brown material, and the clear yellow filtrate was reduced in volume under vacuum to 10 cm^3, petroleum ether (20 cm^3) was added, and the mixture was cooled to −15°C. Initially a fine white solid was deposited, and this was removed by filtration. The resulting filtrate was reduced to smaller volume and, after a further 2 d at −15°C, deposited yellow crystals of the title compound, contaminated by some orange crystals {probably $[WCl(CO)_3Cp^*]$}. Partial separation of these products was achieved by hand; two further recrystallisations from CH_2Cl_2/petroleum ether gave a pure sample of yellow product, but in low yield (0.037 g; 4.5%). Anal. Found: C, 51.2; H, 4.2; $C_{31}H_{30}CuO_3PW$ calc. C, 51.1; H, 4.1%. IR ν(CO): (CH_2Cl_2) 1898, 1795; (nujol) 1887, 1787 cm^{-1}. NMR: ^1H ($CDCl_3$) δ 7.3–7.9 (complex, 15H, PPh_3), 2.03 (two s, 15H, C_5Me_5); (CD_2Cl_2) −90°C: δ 7.0–7.5 (complex m, 15H, PPh_3), 2.03, 1.95 and 1.70 (three s, rel. int. ca. 5.3 : 1.8 : 1, total 15 H, C_5Me_5). $^{31}P\{^1H\}$: (CD_2Cl_2) 22°C δ 8.1 (s); −90°C δ 13.1, 1.8 and −4.2 (three s, rel. int. ca. 6.3 : 1 : 2.6).

3.3. Reaction of $Li[Mo(CO)_3Cp^*]$ with $[CuCl(PPh_3)_3]$

In a procedure similar to that described above, $Li[Mo(CO)_3Cp^*]$ (1.5 mmol) in THF (20 cm^3) was treated with $[CuCl(PPh_3)_3]$ (1.33 g, 1.5 mmol). The yellow solid obtained after several recrystallisations was mainly $[Cp^*Mo(CO)_3Cu(PPh_3)]$ but it was contaminated with by-products and could not be obtained analytically or spectroscopically pure. IR ν(CO): (nujol) 1894, 1790 cm^{-1}. NMR ($CDCl_3$) ^1H major bands: δ ca. 7.3–7.9 (complex, PPh_3), 1.95 (s, C_5Me_5).

3.4. Crystal structure determination of $[Cp^*(CO)W(\mu\text{-}CO)_2Rh(PPh_3)_2]$

A single crystal of **3** (from dichloromethane-petroleum ether at −15°C ca. 0.25 × 0.3 × 0.175 mm), mounted in a Lindemann tube, was used for X-ray data collection.

3.4.1. Crystal data

$C_{49}H_{45}O_3P_3RhW$., $M = 1030.6$, dark red prisms, triclinic, space group $P1$ (No. 2), $a = 10.5579\ (22)°$, $b = 12.3856\ (23)$ Å, $c = 17.163\ (3)$ Å, $\alpha = 80.292\ (16)°$, $\beta = 75.864\ (20)°$, $\gamma = 81.937\ (17)°$, $U = 2133.7\ (5)$ Å^3, $Z = 2$, $D_c = 1.604$ g cm^{-3}, $F(000) = 1024$, μ(Mo–$K\alpha$) = 88.70 cm^{-1}.

3.4.2. Data collection

The intensity data were collected on an Enraf-Nonius CAD4 diffractometer over the hemisphere (θ range: 1.50–23.0°; h: −11-+11, k: −13-+13, l: 0-18) using graphite monochromated Mo–Kα X-radiation (λ = 0.710693 Å) and ω-2θ scanning. Of the 6,172 unique data measured, 5121 had $I > 2\sigma(I)$ and were used in subsequent structural solution and refinement. Corrections were applied for Lorentz, polarisation and absorption effects (DIFABS [18]).

3.4.3. Structure solution

The approximate locations of the W and Rh atoms were initially determined by direct methods (SHELXS-86 [18]). After two cycles of refinement, the remaining non-hydrogen atoms (P, O, C) were subsequently located from a difference Fourier map phased on the refined heavy atom positions. The structure was refined by full-matrix least-squares methods (SHELX76 [18]) using anisotropic temperature factors for all the non-hydrogen atoms apart from the carbon atoms of the disordered Cp* moiety. All the hydrogen atoms were located on difference Fourier maps and included in the refinement process at idealised positions. The phenyl and cyclopentadienyl rings were treated as idealised hexagons (C–C 1.395 Å) and pentagons (C–C 1.420 Å) respectively. The atoms of Cp* group, which were disordered over two sites with a relative occupancy of 0.56; 0.44, were refined as members of a rigid group with group temperature factors. Fixed isotropic temperature factors were used for the hydrogen atoms ($U_{iso} = 0.10$ Å^2). At convergence, the discrepancy factors R and R_w were 0.034 and 0.045 respectively. The weighting scheme, $w^{-1} = [\sigma^2(F) + 0.000419\ (F)^2]$ was found to give satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level less that ±0.3 e Å^{-3}), apart from a cluster of residuals peaks of ca. 1.06–0.76 e Å^{-3} located close to the W and Rh atoms.

Incidental crystallographic calculations and compilation of tables were carried out using the computer program CALC [18] and the drawing of the molecule was prepared using the crystallographic plotting program PLUTO [18]. Lists of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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