Chemistry of the Metal Carbonyls. Part 82.[1] Synthesis of Complexes with Bonds between Rhodium and the Sub-group 6 Metals; *X*-Ray Crystal Structure of $[CrRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)]$ *

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Irradiation with u.v. light of mixtures of $[Cr(CO)_3(\eta\text{-arene})]$ (arene = C_6H_6, $C_6H_3Me_3$-1,3,5, or C_6Me_6) and $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ in tetrahydrofuran (thf) affords the dimetal compounds $[CrRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)(\eta\text{-arene})]$; the complex $[CrRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_9H_7)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ (C_9H_7 = indenyl) has been similarly prepared from $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ and $[Cr(CO)_2(thf)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$. The i.r. and n.m.r. data for these species are reported and discussed in relation to the molecular structure of $[CrRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)]$ which has been established by an *X*-ray diffraction study: crystals are orthorhombic, space group *Pnma* (no. 62), in a unit cell with a = 10.635(4), b = 11.690(3), c = 15.275(5) Å, and Z = 4. The structure has been refined to R 0.051 from 1 584 independent intensities [$I \geqslant 2.5\sigma(I)$]. The molecule is constrained crystallographically to C_s symmetry, the mirror plane being defined by the terminal carbonyl ligand on each metal atom, the Rh–Cr bond [2.757(2) Å], and the centroids of the two cyclic ligands. The pentamethylcyclopentadienyl ligand on the Rh atom is in a *trans* relationship to the η^6-benzene ligand on the Cr atom, and both lie astride (perpendicular to) the mirror plane. The two other carbonyl ligands are terminal to the Cr atom, but are strongly semi-bridging to the Rh atom [Cr–C 1.902(7), Rh–C 2.200(7) Å], and define planes which are nearly perpendicular to the mirror plane. Some distortion of the Rh–C_5 geometry towards a ' diolefin ' type attachment is noted and discussed. Reaction of the compounds $[M(CO)_5(thf)]$ (M = Cr or W) and $[Mo(NCMe)(CO)_5]$ with $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ affords the heteronuclear trimetal cluster complexes $[MRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ in high yield. These species may be regarded as molecules in which an $M(CO)_5$ fragment, isolobal with CH_2, is ' complexed ' by an ethylene-like $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ fragment.

In an important paper, Hoffmann and co-workers[2] showed that the frontier orbitals of the species $Rh(CO)(\eta\text{-}C_5H_5)$ and the molecule $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ are akin to those of CH_2 and C_2H_4, respectively. These isolobal relationships led us to prepare several complexes with bonds between rhodium and other transition metals. Thus the analogy between C_2H_4 and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ prompted the synthesis of $[Pt\{Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2\}_2]$,[3] a compound related to $[Pt(C_2H_4)_3]$.[4] Moreover, the isolation of $[Fe_2Rh(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5Me_5)]$,[1] structurally similar to $[Fe_3(\mu\text{-}CO)_2(CO)_{10}]$[5] and $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$,[6] underlines the isolobal mapping:

$$Rh(CO)(\eta\text{-}C_5Me_5) \leftarrow\!\!\circ\!\!\rightarrow Fe(CO)_4 \leftarrow\!\!\circ\!\!\rightarrow CH_2$$

We have been interested in further extending the employment of the fragment $Rh(CO)(\eta\text{-}C_5Me_5)$ as a building block in heteronuclear metal–metal bond syntheses, and herein we describe experiments leading to compounds in which rhodium is bonded to chromium, molybdenum, or tungsten.

Results and Discussion

In our initial studies we examined reactions between the species $[Cr(CO)_2(thf)(\eta\text{-arene})]$ (thf = tetrahydrofuran; arene = C_6H_6, $C_6H_3Me_3$-1,3,5, or C_6Me_6) and the compound $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$, and between $[Cr(CO)_2(thf)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ and $[Rh(CO)_2(\eta\text{-}C_9H_7)$ (C_9H_7 = indenyl). The complexes $[Cr(CO)_2(thf)(\eta\text{-arene})]$ are readily generated photochemically *in situ* by u.v. irradiation of thf solutions of $[Cr(CO)_3(\eta\text{-arene})]$.[7] They function as sources of $Cr(CO)_2(\eta\text{-arene})$ fragments, since the thf molecule is only weakly co-ordinated to the chromium. With CO they readily revert to the tricarbonylchromium precursors, and hence in reactions with $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ or $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ might abstract CO from rhodium. It was hoped, however, that complexes with Cr–Rh bonds would be formed. This seemed likely because in earlier work[1] the compounds $[(\eta\text{-}C_5H_5)(OC)Mn(\mu\text{-}CO)_2Rh(CO)(\eta\text{-}C_5Me_5)]$ and $[(OC)_3Fe(\mu\text{-}CO)_2Rh(CO)(\eta\text{-}C_5Me_5)]$ were obtained from reactions between $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Mn(CO)_2(thf)(\eta\text{-}C_5H_5)]$ or $[Fe(CO)_4(thf)]$, respectively. Since the species $Fe(CO)_4$, $Mn(CO)_2(\eta\text{-}C_5H_5)$, and $Cr(CO)_2(\eta\text{-arene})$ are isolobal, the $[Cr(CO)_2(thf)(\eta\text{-arene})]$ complexes might show a similar reactivity pattern to the iron- and manganese–thf complexes and with $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ afford dimetal compounds $[(\eta\text{-arene})(OC)Cr(\mu\text{-}CO)_2Rh(CO)(\eta\text{-}C_5Me_5)]$.

Irradiation of a thf solution of $[Cr(CO)_3(\eta\text{-}C_6H_6)]$ and $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ with u.v. light afforded a red crystalline compound (1) in 70% yield. Similar dimetal compounds (2) and (3) were obtained employing the arenechromium complexes $[Cr(CO)_3(\eta\text{-arene})]$ (arene = $C_6H_3Me_3$-1,3,5 or C_6Me_6), while irradiation of a mixture of $[Cr(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ in thf gave compound (4). The i.r. spectra of compounds (1)—(3) showed a band in the region expected for a bridging CO ligand (Table 1). Compound (4) was evidently less symmetrical showing two such bands (1 830 and 1 797 cm^{-1}). The $^{13}C\text{-}\{^1H\}$ n.m.r. data for the compounds (Table 2), indicating the presence of both terminal and bridged CO groups in these molecules, are informative but discussion is deferred until the results of a single-crystal *X*-ray diffraction study on (1) are described. This study

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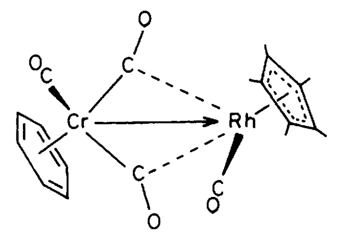
* 2-(1′—6′-η-Benzene)-di-μ-carbonyl-1,2-dicarbonyl-1-(1″—5″-η-pentamethylcyclopentadienyl)rhodiumchromium(*Rh*^{1}–*Cr*^{2}).

Supplementary data available (No. SUP 23473, 20 pp.): thermal parameters, H-atom co-ordinates, complete bond parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



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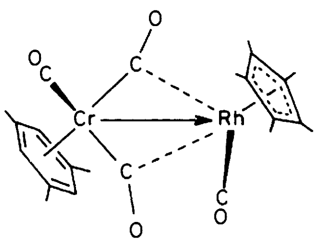

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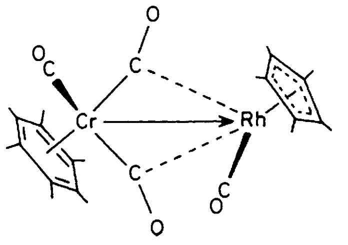

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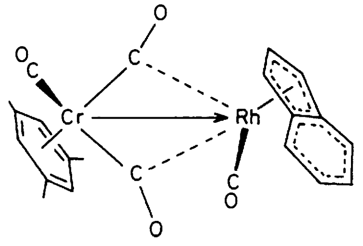

(4)

Table 1. Analytical [a] and physical data for the di- and tri-metal compounds

Compound	M.p. (θ_c/°C)	Colour	$\nu_{max.}$ (CO) [b]/cm^{-1}	Yield (%)	Analysis (%)	
					C	H
(1) $[CrRh(CO)_4(\eta-C_5Me_5)(\eta-C_6H_6)]$	155	Dark red	1 968s, 1 905vs, 1 788s	70	50.3 (50.0)	4.5 (4.4)
(2) $[CrRh(CO)_4(\eta-C_5Me_5)(\eta-C_6H_3Me_3-1,3,5)]$	169	Dark red	1 961s, 1 891s, 1 777m	68	52.9 (52.9)	5.3 (5.2)
(3) $[CrRh(CO)_4(\eta-C_5Me_5)(\eta-C_6Me_6)]$	180 [c]	Dark red	1 964s, 1 875s, 1 764m	69	55.1 (55.3)	5.5 (5.9)
(4) $[CrRh(CO)_4(\eta-C_9H_7)(\eta-C_6H_3Me_3-1,3,5)]$	162 [c]	Dark red	1 978s, 1 903vs, 1 830w (br), 1 797w (br)	55	52.5 (52.6)	3.9 (3.8)
(5) $[CrRh_2(\mu-CO)_2(CO)_5(\eta-C_5Me_5)_2]$	>200 [d]	Purple	2 026s, 1 931vs, 1 755w (br)	94	45.0 (44.8)	4.7 (4.2)
(6) $[MoRh_2(\mu-CO)_2(CO)_5(\eta-C_5Me_5)_2]$	>200 [d]	Purple	2 047m, 1 948vs, 1 943s, 1 938m, 1 750w (br)	96	41.3 (42.2)	4.6 (4.0)
(7) $[WRh_2(\mu-CO)_2(CO)_5(\eta-C_5Me_5)_2]$	>200 [d]	Purple	2 045m, 1 941vs, 1 934vs, 1 747w (br)	90	38.2 (37.9)	4.0 (3.5)

[a] Calculated values are given in parentheses. [b] In hexane. [c] With decomposition. [d] Sublimed with decomposition.

was made to establish the molecular structure of the new chromium–rhodium dimetal species.*

The structure is shown in the Figure with the crystallographic numbering. Bond lengths and angles are in Table 3. The molecule is constrained crystallographically to C_s symmetry, the mirror plane being defined by the atoms Cr, Rh, C(1), C(4), C(11), O(11), C(12), and O(12). The centroids of the two cyclic ligands also lie in the mirror plane. As the carbonyl C(10)–O(10) is ' terminal ' to the chromium atom and ' semi-bridging ' to the rhodium atom, its mirror image C(10′)–O(10′) is necessarily similarly related to the two metal atoms. The Cr–Rh bond may, therefore, be regarded as a donor bond of order 1 with Cr as the donor; the effects of any associated polarity were discussed in our earlier paper on the structure of $[MnRh(\mu-CO)_2(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)]$.[1] The length of the Cr–Rh bond is 2.757(2) Å. In the semi-bridging carbonyls, the difference between the two metal–carbon distances is not large [Cr–C(10) 1.902(7), Rh–C(10) 2.200(7) Å] while the distortion from linearity relative to the Cr atom is considerable [Cr–C(10)–O(10) 154.4(6), Rh–C(10)–O(10) 121.4(5)°]. The planes defined by Cr, Rh, and the two bridging carbonyl ligands are both nearly, but not quite, perpendicular to the molecular mirror plane {interplanar angle 171° with the concave side facing the terminal carbonyl ligand on the Cr atom [C(12), O(12)]}. The metal–carbon bond length for the terminal carbonyl ligand on the chromium atom is appreciably shorter [1.844(11) Å] than that for the semi-bridging carbonyl [1.902(7) Å]. The pentamethylcyclopentadienyl ring and the benzene ring are in a *trans* relationship to one another, and the planes of the two ring systems are parallel within 2°. The methyl groups of the pentamethylcyclopentadienyl ligand bend back slightly from the plane of the C_5 ring, away from

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* First attempts at a crystal-structure study were made on the complex $[CrRh(\mu-CO)_2(CO)_2(\eta-C_5Me_5)(\eta-C_6Me_6)]$ (3). The crystals were monoclinic, with a = 8.354(3), b = 15.291(5), c = 9.833(2) Å, β = 103.95(2)°, and Z = 4, but the molecules appeared to be positionally disordered in such a manner that the two metal atom sites are interchangeably occupied by Cr or Rh, with associated reversal of all attached ligands.

Table 2. Hydrogen-1 and ^{13}C n.m.r. data[a]

Compound	^1H (δ)	^{13}C (δ)
(1) $[CrRh(CO)_4(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)]$[b]	1.82 (s, 15 H, C_5Me_5), 5.32 (m, 6 H, C_6H_6)	262.0 [d, μ-CO, *J*(RhC) 20], 238.5 (CrCO), 189.7 [d, RhCO, *J*(RhC) 87], 105.0 [d, C_5Me_5, *J*(RhC) 3], 98.0 (C_6H_6), 9.6 (Me)
(2) $[CrRh(CO)_4(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$[b]	1.84 (s, 15 H, C_5Me_5), 2.14 (s, 9 H, Me-1,3,5), 4.72 (m, 3 H, C_6H_3)	262.7 [d, μ-CO, *J*(RhC) 21], 238.6 (CrCO), 190.1 [d, RhCO, *J*(RhC) 88], 113.4 (C_6Me_3), 104.8 [d, C_5Me_5, *J*(RhC) 4], 94.3 (C_6H_3), 19.8 (Me-1,3,5), 9.5 (C_5Me_5)
(3) $[CrRh(CO)_4(\eta\text{-}C_5Me_5)(\eta\text{-}C_6Me_6)]$	1.86 (s, 15 H, C_5Me_5), 2.13 (s, 18 H, C_6Me_6)	263.6 [d, μ-CO, *J*(RhC) 20], 239.9 (CrCO), 191.1 [d, RhCO, *J*(RhC) 89], 107.9 (C_6Me_6), 105.1 [d, C_5Me_5, *J*(RhC) 3], 16.1 (C_6Me_6), 9.6 (C_5Me_5)
(4) $[CrRh(CO)_4(\eta\text{-}C_9H_7)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$[c]	2.12 (s, 9 H, Me-1,3,5), 4.74 (s, 3 H, C_6H_3), 5.70 (m, 2 H, C_9H_7), 6.08 (m, 1 H, C_9H_7), 7.16 (m, 4 H, C_9H_7)	255.7 [d, μ-CO, *J*(RhC) 20], 249.0 [d, μ-CO, *J*(RhC) 20], 237.8 (CrCO), 190.6 [d, RhCO, *J*(RhC) 90], 126.3—117.9 (CH of C_6 ring of C_9H_7), 115.0 (*C*Me), 105.0, 104.9 (C of C_9H_7), 95.4 (CH of $C_6H_3Me_3$), 84.8, 84.0, 81.3 (CH of C_5 ring of C_9H_7), 20.1 (Me)
(5) $[CrRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$	1.77 (s, 15 H, C_5Me_5)	245.7 [t, μ-CO, *J*(RhC) 45], 230.6 (1 CO, CrCO), 221.8 (4 CO, CrCO), 104.4 (C_5Me_5), 8.1 (Me)
(6) $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$[b]	1.75 (s, 15 H, C_5Me_5)	246.2 [t, μ-CO, *J*(RhC) 44], 215.0 (1 CO, MoCO), 206.8 (4 CO, MoCO), 103.1 (C_5Me_5), 8.2 (Me)
(7) $[WRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$	1.71 (s, 15 H, C_5Me_5)	241.7 [t, μ-CO, *J*(RhC) 49], 203.5 [1 CO, *J*(WC) 166], 199.7 [4 CO, *J*(WC) 121], 103.7 (C_5Me_5), 8.3 (Me)

[a] Measured in $CDCl_3$ at room temperature, unless otherwise stated. Chemical shifts (δ) in p.p.m., and for ^{13}C-{^1H} these are relative to $SiMe_4$, positive values representing shifts to high frequency. Coupling constants are in Hz. [b] ^{13}C-{^1H} spectrum measured in CD_2Cl_2–CH_2Cl_2 solution at −50 °C. [c] ^{13}C-{^1H} spectrum measured in CD_2Cl_2–CH_2Cl_2 solution at −60 °C.

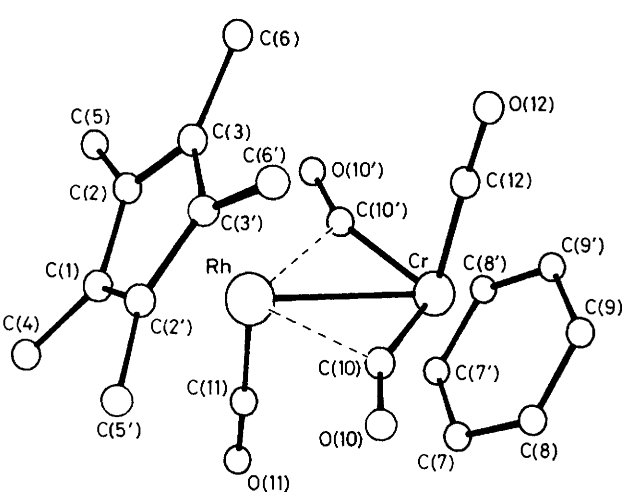


Figure. Molecular structure of $[CrRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)]$ (1) showing the crystallographic numbering

the rhodium atom [root mean square (r.m.s.) deviation 0.107 Å]. For other examples of this phenomenon and for a discussion of the structure of $[CrNi(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ in relation to that of $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$, which would be equally relevant in the present context, see ref. 1.

Finally, in the structure of $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ it was noted that a distinct distortion of the C_5Me_5 ring towards a ' diolefin ' structure was apparent.[1]

Table 3. Bond lengths (Å) and angles (°) for the compound $[CrRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)]$ (1)

Rh–Cr	2.757(2)	Cr–C(7)	2.232(7)
Rh–C(1)	2.198(9)	Cr–C(8)	2.234(8)
Rh–C(2)	2.294(6)	Cr–C(9)	2.220(8)
Rh–C(3)	2.332(6)	Cr–C(12)	1.844(11)
Rh–C(11)	1.851(9)	Cr–C(10)	1.902(7)
Rh–C(10)	2.200(7)	C(7)–C(8)	1.433(11)
C(1)–C(2)	1.444(8)	C(8)–C(9)	1.385(11)
C(2)–C(3)	1.415(9)	C(7)–C(7')	1.383(16)
C(3)–C(3')	1.458(12)	C(9)–C(9')	1.439(16)
C(1)–C(4)	1.517(13)	C(10)–O(10)	1.185(9)
C(2)–C(5)	1.523(9)	C(11)–O(11)	1.141(12)
C(3)–C(6)	1.503(10)	C(12)–O(12)	1.146(14)

Cr–Rh–C(11)	88.3(3)	Rh–Cr–C(12)	94.9(3)
Cr–Rh–C(10)	43.3(2)	Rh–Cr–C(10)	52.5(2)
C(11)–Rh–C(10)	92.0(3)	C(12)–Cr–C(10)	89.3(3)
Rh–C(11)–O(11)	177.7(9)	Cr–C(12)–O(12)	177.9(10)
Rh–C(10)–O(10)	121.4(5)	Cr–C(10)–O(10)	154.4(6)

The same type of distortion is present in (1): the Rh–C distances differ by more than 0.1 Å, with Rh–C(1) < Rh–C(2) < Rh–C(3) (Table 3). The ring C–C distances, although not very accurately determined, fit in with this ' diolefin ' distortion, C(2)–C(3) and C(2')–C(3') being the two short bonds.

The CO bridge system present in compound (1) is thus similar to that in $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and $[FeRh(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)]$,[1] and is of the type established some years ago for $[V_2(\mu\text{-}CO)_2(CO)_3(\eta\text{-}C_5H_5)_2]$.[8] The semi-bridging configuration adopted by the two CO ligands is accounted for by assuming it provides a mechanism whereby the charge transfer in the V $\longrightarrow$ V and M $\longrightarrow$ Rh (M = Cr, Mn, or Fe) bonds can be redistributed *via* back bonding to the π^* orbitals of the CO groups.[9] The metal–metal interaction in compounds (1)—(4) can be regarded as arising from donation of an electron pair from an 18-electron $[Cr(CO)_3(\eta\text{-arene})]$ species to the 16-electron group Rh(CO)(η-C_5Me_5). We have previously referred to the isolobal relationship between the latter fragment and CH_2, and in this context complexes (1)—(4), and the above mentioned rhodium–manganese and –iron compounds, are related to ylides represented by the canonical forms (a) and (b). In the

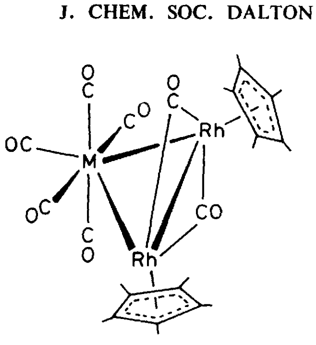
$$\underset{(a)}{R_3P\rightarrow CH_2} \longleftrightarrow \underset{(b)}{R_3P{=}CH_2}$$

molecules $[Mn(CO)_3(\eta\text{-}C_5H_5)]$, $[Cr(CO)_3(\eta\text{-arene})]$, and $[Fe(CO)_5]$ the highest occupied molecular orbital (h.o.m.o.) is predominantly centred on the metal so that it can function as an electron-pair donor, as does phosphorus in PR_3. In the ylides the polarity of the P–C bond is reduced by resonance (a) $\longleftrightarrow$ (b), and in the dimetal compounds charge transfer is compensated by back bonding *via* the semi-bridging CO ligands.

The $^{13}C\text{-}\{^1H\}$ n.m.r. data (Table 2) for compounds (1)—(4) became readily interpretable once the molecular structure of (1) had been established by *X*-ray diffraction. In the spectra of (1)—(3) there are resonances for CO ligands in three different environments, as expected. Moreover, $^{103}Rh\text{-}^{13}C$ coupling allows assignments to be made. Thus for compound (1) the doublet signal at 189.7 p.p.m. [*J*(RhC) 87 Hz] must be due to the terminally bonded RhCO group.[1] The peak at 238.5 p.p.m. since it has no $^{103}Rh\text{-}^{13}C$ coupling is assigned to the CrCO group,[10] while the third resonance at δ 262 p.p.m. appearing as a doublet [*J*(RhC) 20 Hz] is as anticipated for the presence of the Cr(μ-CO)Rh bridging system. In $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ the resonance for the μ-CO ligands in the ^{13}C n.m.r. spectrum occurs as a doublet at δ 252.2 p.p.m. [*J*(RhC) 22 Hz].[1] The spectra of compounds (2) and (3) show similar features, and include resonances for the η-C_5Me_5 and arene ligands.

Not unexpectedly the spectroscopic properties of compound (4) are somewhat different and this is presumably due to the η-C_9H_7 group introducing asymmetry. The *X*-ray results for (1) establish a mirror plane through the metal–metal bond and the centroids of the C_5 and C_6 rings of the η-C_5Me_5 and η-C_6H_6 ligands, respectively. Hence the bridging CO groups are equivalently disposed, leading to the appearance of one band in the i.r. spectrum for these groups, and one resonance in the ^{13}C n.m.r. spectrum. The presence of the η-C_9H_7 ligand in compound (4) could, and seemingly does, render the two μ-CO ligands non-equivalent since there is no longer necessarily a mirror plane through the bridge system. Consequently, in the i.r. spectrum this compound shows two bands in the bridging CO region at 1 830 and 1 797 cm^{-1}. Moreover, in the ^{13}C n.m.r. spectrum measured at −60 °C the $Cr(\mu\text{-}CO)_2Rh$ system gives rise to two resonances, each occurring as a doublet, due to $^{103}Rh\text{-}^{13}C$ coupling (Table 2). On warming, however, these two signals collapse at −40 °C suggesting the onset of dynamic behaviour. At higher temperatures the solutions decompose, and so detailed studies were not possible, but rotation of the Rh(CO)(η-C_9H_7) group about the Cr–Rh axis, or rotation of the η-C_9H_7 ligand itself, could render the two bridging CO ligands equivalent.

The relationship between the building blocks of organic chemistry (CH_3, CH_2, CH) and metal–ligand fragments of inorganic complex compounds is not a one-to-one mapping.[11] Thus a d^6 ML_5 octahedral fragment, *e.g.* $Cr(CO)_5$, is isolobal both with CH_3^+ and with CH_2. The latter analogy is generally the more useful in suggesting new preparative work. We[12] and others[13,14] have shown that CH_2 from diazomethane adds to $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ to give the ' dimetallacyclopropane ' complex $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$. Because of the analogy between $M(CO)_5$ [$M(d^6)$ = Cr, Mo, or W] and CH_2 it seemed likely that $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)]$ would likewise combine with pentacarbonylmetal (d^6) fragments, affording heteronuclear trimetal complexes.



M
(5) Cr
(6) Mo
(7) W

Ultraviolet irradiation of a thf solution of $[Cr(CO)_6]$, to generate $[Cr(CO)_5(thf)]$ *in situ*,[15] followed by addition of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ afforded the purple crystalline complex (5). The molybdenum analogue (6) was isolated from the reaction between $[Mo(NCMe)(CO)_5]$ and the dirhodium compound, while the tungsten complex (7) was prepared in a similar manner to (5). Compounds (5)—(7), isolated in yields of 90% or greater, were readily characterised by microanalysis and their spectroscopic properties (Tables 1 and 2).

In the i.r. spectra of compounds (5)—(7) there is a band near 1 750 cm^{-1} attributable to the CO ligands bridging the rhodium–rhodium bond. In accord with this, the ^{13}C n.m.r. spectra each show a CO resonance at *ca.* δ 245 p.p.m. which appears as a triplet, due to $^{103}Rh\text{-}^{13}C$ coupling to two equivalent rhodium nuclei. The ^{13}C n.m.r. spectra of the compounds in the CO region also show that these ligands are not undergoing site exchange. For example, in the spectrum of (7) there are two resonances due to tungsten-ligated CO groups at δ 203.5 and 199.7 p.p.m. of relative intensity 1 : 4, and showing ^{183}W satellite peaks. This pattern could be interpreted as that expected for a structure in which the tungsten is in an essentially octahedral environment with one CO ligand *trans* to the $Rh(\mu\text{-}CO)_2Rh$ group and four which are *cis* to it. However, for the compounds (5)—(7) there are alternative conformations for the Rh_2 group relative to the $M(CO)_5$ fragment. The most likely configuration is one in which the Rh–Rh vector does not eclipse a *trans* OC–M–CO group but is rotated with respect to these groups by 45°. The pattern observed for the ^{13}CO resonances in the ^{13}C n.m.r. spectra of compounds (5)—(7) is in accord with such a configuration. However, the resonances for the carbonyl ligands of the $M(CO)_4$ group would also appear as two signals of relative intensity 1 : 4 if the dirhodium fragment were rotating on the n.m.r. time-scale about an axis through the metal atom M and perpendicular to the Rh–Rh vector. Such dynamic behaviour would be akin to metal–olefin rotation. The spectrum of compound (6) (Table 2) recorded at −50 °C, however, shows only one peak (δ 206.8 p.p.m.) for the $Mo(CO)_4$ group, suggesting either a very low-energy pathway for rotation of the Rh_2 group[16] or a static structure in which the Rh–Rh axis lies in the staggered 45° orientation described above.

Compounds (5)—(7) join a growing family of trimetal clusters in which the 'ethylene-like'[2] molecule $[Rh_2(\mu\text{-CO})_2(\eta\text{-C}_5Me_5)_2]$ bonds to a 'carbene-like' metal fragment, *e.g* Pt(cod) (cod = cyclo-octa-1,5-diene),[12] $Fe(CO)_4$,[1] and $Rh(CO)(\eta\text{-C}_5Me_5)$.[1]

Experimental

The n.m.r. spectra were measured on JNM PS-100, FX 90Q, or FX 200 spectrometers, as appropriate, and i.r. spectra on a Nicolet MX-1 FT spectrometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen or argon, using freshly distilled solvents. Light petroleum refers to that fraction of b.p. 30—40 °C. Chromatography was on alumina columns. Methods previously described were used to prepare $[Rh(CO)_2(\eta\text{-C}_5Me_5)]$,[17] $[Rh_2(\mu\text{-CO})_2(\eta\text{-C}_5Me_5)_2]$,[1] $[Cr(CO)_3(\eta\text{-arene})]$,[18] and $[Mo(NCMe)(CO)_5]$.[19] The photochemical reactions were carried out in a jacketed quartz Schlenk tube cooled with ice–water, under a stream of argon with magnetic stirring. A 450-W medium-pressure mercury-vapour lamp was used for irradiation. Analytical and other data for the new compounds are given in Table 1.

Preparation of Dimetal Complexes.—(*a*) The compounds $[Cr(CO)_3(\eta\text{-C}_6H_6)]$ (0.36 g, 1.70 mmol) and $[Rh(CO)_2(\eta\text{-C}_5Me_5)]$ (0.54 g, 1.8 mmol) in thf (100 cm^3) were irradiated for 4 h. After removal of solvent *in vacuo* the residue was dissolved in dichloromethane–light petroleum (1 : 5) and chromatographed at −25 °C. The first band eluted contained unreacted $[Rh(CO)_2(\eta\text{-C}_5Me_5)]$, but this was followed by a solution which afforded red *microcrystals* of $[CrRh(\mu\text{-CO})_2(CO)_2(\eta\text{-C}_5Me_5)(\eta\text{-C}_6H_6)]$ (1) (0.57 g).

(*b*) In a similar manner, $[Cr(CO)_3(\eta\text{-C}_6H_3Me_3\text{-}1,3,5)]$ (0.47 g, 1.85 mmol) and $[Rh(CO)_2(\eta\text{-C}_5Me_5)]$ (0.56 g, 1.90 mmol) gave red *microcrystals* of $[CrRh(\mu\text{-CO})_2(CO)_2(\eta\text{-C}_5Me_5)(\eta\text{-C}_6H_3Me_3\text{-}1,3,5)]$ (2) (0.64 g).

(*c*) As previously, $[Cr(CO)_3(\eta\text{-C}_6Me_6)]$ (0.81 g, 2.70 mmol) and $[Rh(CO)_2(\eta\text{-C}_5Me_5)]$ (0.82 g, 2.80 mmol) yielded red *microcrystals* of $[CrRh(\mu\text{-CO})_2(CO)_2(\eta\text{-C}_5Me_5)(\eta\text{-C}_6Me_6)]$ (3) (1.05 g).

(*d*) As in the synthesis of compound (1), a mixture of $[Cr(CO)_3(\eta\text{-C}_6H_3Me_3\text{-}1,3,5)]$ (1.0 g, 3.9 mmol) and $[Rh(CO)_2(\eta\text{-C}_9H_7)]$ (1.1 g, 4.0 mmol) afforded red *microcrystals* of $[CrRh(\mu\text{-CO})_2(CO)_2(\eta\text{-C}_9H_7)(\eta\text{-C}_6H_3Me_3\text{-}1,3,5)]$ (4) (1.11 g).

Preparation of the Trimetal Compounds.—(*a*) The compound $[Cr(CO)_6]$ (0.67 g, 3.05 mmol) in thf (100 cm^3) was irradiated for 0.5 h, and the solution treated with $[Rh_2(\mu\text{-CO})_2(\eta\text{-C}_5Me_5)_2]$ (0.53 g, 1.0 mmol) and stirred for 24 h. Removal of solvent *in vacuo* gave a residue which was dissolved in diethyl ether–light petroleum (1 : 5) and chromatographed, affording purple *microcrystals* of $[CrRh_2(\mu\text{-CO})_2(CO)_5(\eta\text{-C}_5Me_5)_2]$ (5) (0.68 g).

(*b*) In a similar manner, $[W(CO)_6]$ (0.20 g, 0.57 mmol) was irradiated in thf (100 cm^3) and $[Rh_2(\mu\text{-CO})_2(\eta\text{-C}_5Me_5)_2]$ (0.15 g, 0.28 mmol) added, giving, after chromatography, purple *microcrystals* of $[WRh_2(\mu\text{-CO})_2(CO)_5(\eta\text{-C}_5Me_5)_2]$ (7) (0.22 g).

(*c*) The compound $[Rh_2(\mu\text{-CO})_2(\eta\text{-C}_5Me_5)_2]$ (0.41 g, 0.77 mmol) was added to a thf (20 cm^3) solution of $[Mo(NCMe)(CO)_5]$ (0.26 g, 0.94 mmol) and the mixture stirred at room temperature for 4 h. Removal of the solvent *in vacuo* afforded a residue which was dissolved in diethyl ether–light petroleum (1 : 5) and chromatographed. Evaporation of the eluate gave *microcrystals* of $[MoRh_2(\mu\text{-CO})_2(CO)_5(\eta\text{-C}_5Me_5)_2]$ (6) (0.56 g).

Table 4. Atomic positional parameters (fractional co-ordinates) for $[CrRh(\mu\text{-CO})_2(CO)_2(\eta\text{-C}_5Me_5)(\eta\text{-C}_6H_6)]$ (1)

Atom	*x*	*y*	*z*
Rh	0.161 27(7)	0.250 00 *	0.028 07(4)
Cr	0.399 90(14)	0.250 00	−0.042 55(9)
C(1)	−0.016 5(8)	0.250 00	0.101 5(6)
C(2)	0.050 2(6)	0.350 2(6)	0.131 4(4)
C(3)	0.161 5(7)	0.312 3(6)	0.173 1(4)
C(4)	−0.145 3(9)	0.250 00	0.058 9(7)
C(5)	0.006 6(7)	0.474 0(6)	0.124 3(5)
C(6)	0.256 8(8)	0.387 5(6)	0.217 6(5)
C(7)	0.370 8(8)	0.190 8(8)	−0.179 9(5)
C(8)	0.475 1(9)	0.129 6(7)	−0.143 3(5)
C(9)	0.574 9(8)	0.188 5(7)	−0.106 3(5)
C(10)	0.304 3(7)	0.121 3(7)	−0.005 4(5)
O(10)	0.285 4(6)	0.022 2(4)	0.004 4(4)
C(11)	0.097 9(9)	0.250 00	−0.084 8(6)
O(11)	0.054 9(9)	0.250 00	−0.153 2(5)
C(12)	0.481 1(10)	0.250 00	0.064 1(8)
O(12)	0.535 0(9)	0.250 00	0.129 0(6)

* Those atoms lying in the mirror plane have their *y* co-ordinates fixed at 0.25.

Crystal-structure Determination of $[CrRh(\mu\text{-CO})_2(CO)_2(\eta\text{-C}_5Me_5)(\eta\text{-C}_6H_6)]$ (1).—Crystals of (1) grow as dark red parallelepipeds. Diffracted intensities were recorded at ambient temperature from a crystal of dimensions 0.35 × 0.30 × 0.10 mm. Of the total 2 287 independent reflections measured (ω scan) on a Nicolet *P*3*m* four-circle diffractometer, 1 584 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure. The crystal showed no signs of decay (as monitored by three check reflections) during 37 h of exposure to *X*-rays. The intensity data were corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $C_{20}H_{21}CrO_4Rh$, $M = 479.9$, Orthorhombic, $a = 10.635(4)$, $b = 11.690(3)$, $c = 15.275(5)$ Å, $U = 1\,899(1)$ Å^3, $Z = 4$, $D_c = 1.68$ g cm^{-3}, $F(000) = 968$, space group *Pnma* (no. 62), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 14.4 cm^{-1}.

The metal atoms were located from a Patterson synthesis, and all other atoms by electron-density difference syntheses. The structure was solved in space group $Pn2_1a$, but the atom locations indicated the higher symmetry *Pnma* with crystallographically required mirror symmetry for the molecule. Refinement with a fixed isotropic thermal parameter ($U = 8.0 \times 10^{-2}$ Å^2) for all hydrogen atoms, and anisotropic thermal parameters for all other atoms, led to *R* 0.051 (*R′* 0.051). A weighting scheme of the form $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$ gave a satisfactory weight analysis. Atomic scattering factors were taken from ref. 20 for hydrogen and from ref. 21 for all other atoms. In the case of Rh and Cr these were corrected for the real and imaginary parts of anomalous dispersion.[21] All computations were carried out within the laboratory on an Eclipse (Data General) minicomputer with the SHELXTL system of programs.[22] Atom co-ordinates for all non-hydrogen atoms are in Table 4.

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