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Cluster chemistry. 61.* Addition of HX (X=Cl, Br,I) or AuCl(PPh$_3$) to an open Ru$_5$ cluster. X-ray structures of Ru$_5$(μ-H)(μ$_5$-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-Br)(CO)$_{13}$ and Ru$_5$(μ-H)(μ$_5$-C$_2$PPh$_2$)(μ$_3$-I)(μ-PPh$_2$)(CO)$_{12}$†

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Reactions of aqueous HX (X=Cl, Br) or of AuCl(PPh$_3$) with Ru$_5$(μ$_5$-C$_2$PPh$_2$)(μ-PPh$_2$)(CO)$_{13}$ result in addition of the 4e-donor set (H+X) or (Au(PPh$_3$)+Cl) with concomitant opening of two Ru–Ru bonds to give complexes containing dimetallated triangular or 'scorpion' cores. Aqueous HI reacts similarly, but in this case the iodide ligand spans three Ru atoms, the (H+I) set acting as 6e-donor. The structures of the two title compounds were confirmed by X-ray crystallographic studies. Ru$_5$(μ-H)(μ$_5$-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-Br)(CO)$_{13}$ is triclinic, space group $P\bar{1}$, $a=9.689(2)$, $b=11.874(2)$, $c=20.005(4)$ Å, $\alpha=84.66(2)$, $\beta=82.90(6)$, $\lambda=67.51(6)°$, $Z=2$; 6478 data with $I>2\sigma(I)$ were refined to $R=0.0368$, $R_w=0.0362$. Ru$_5$(μ-H)(μ$_5$-C$_2$PPh$_2$)(μ$_3$-I)(μ-PPh$_2$)(CO)$_{12}$.CH$_2$Cl$_2$ is monoclinic, space group $P2_1/n$, $a=14.809(4)$, $b=20.721(4)$, $c=17.698(5)$ Å, $\beta=111.42(2)°$, $Z=4$; 7815 data with $I>2\sigma(I)$ were refined to $R=0.0440$, $R_w=0.0416$.

Keywords: ruthenium, gold, oxidative addition, cluster, X-ray structure

INTRODUCTION

The open Ru$_5$ cluster Ru$_5$(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(CO)$_{13}$ (**1**, Scheme 1) reacts with carbon monoxide by addition of two molecules and opening of two Ru–Ru bonds. The initial product, the so-called 'kinetic' isomer of Ru$_5$(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(CO)$_{15}$ (**2k**) is converted to the second 'thermodynamic' isomer (**2t**) by heating in CO. While **2k** loses CO to reform **1** on heating, **2t** is stable under these conditions.[1] Both isomers of **2** contain a metal core consisting of an Ru$_3$ triangle to which two Ru atoms are linked, which we have called a 'scorpion' cluster.

The present paper describes the products formed by addition of the hydrogen halides HX (X=Cl, Br, I) or an isolobal analogue of the first, AuCl(PPh$_3$), to **1**. These reagents commonly add oxidatively across metal–metal bonds in clusters, the 4e ligand combination (H+X) (or Au(PPh$_3$)+Cl) bridging one or two metal–metal bonds in the product. For example, Ru$_3$(CO)$_{12}$ reacts with HX to give Ru$_3$(μ-H)(μ-X)(CO)$_{10}$[2]; for X=I, subsequent displacement of CO by the remaining lone pair on the iodine atom gave Ru$_3$(μ-H)(μ_3-I)(CO)$_9$, in which the halogen atom caps the Ru$_3$ core, acting as a 5e donor.[3]

RESULTS AND DISCUSSION

Four oxidative adducts have been synthesized from the reactions of HX (X=Cl, Br, I) with **1**. The reactions of the aqueous acids with **1** proceeded quickly (5–20 min) at room temperature to give the orange complexes Ru$_5$(μ-H)(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-X)(CO)$_{13}$ [X=Cl (**3**); Br (**4**)] and the purple complex Ru$_5$(μ-H)(μ_5-C$_2$PPh$_2$)(μ_3-I)(μ-PPh$_2$)(CO)$_{12}$ (**5**). The reaction with AuCl(PPh$_3$) (an aurated equivalent of HCl) proceeded more slowly (24 h) to give orange AuRu$_5$(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-Cl)(CO)$_{13}$(PPh$_3$) (**6**) in 41% yield.

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* Part 60: see Ref. 1.

† Supplementary material is lodged with the Cambridge Crystallographic Data Centre, UK.

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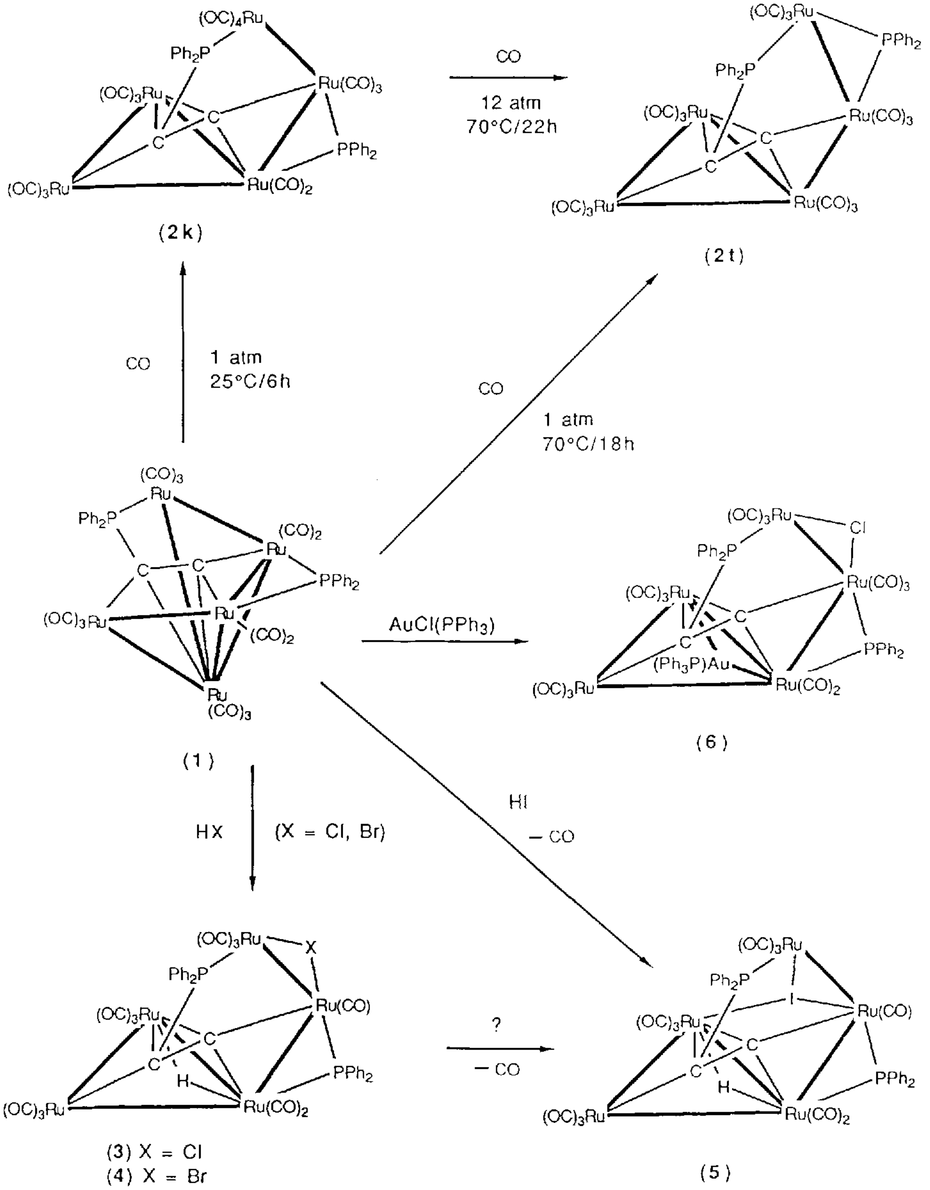

Scheme 1

The infrared spectra of **3**, **4** and **6** all show similar ν(CO) band patterns, the gold derivative having intensities different from the other two. A similar pattern was found for the HI complex. In the ^{1}H NMR spectra, high field signals were found for the hydride ligands at $\delta -21.25$, -20.71 and -25.33 for **3**, **4** and **5**, respectively. These values are within the normal range for μ-hydride ligands. The FAB mass spectra of the four compounds showed molecular ions at m/z 1300 (**3**), 1345 (**4**), 1365 (**5**) and 1759 (**6**), which fragmented by loss of the appropriate number of carbonyl ligands.

To determine the molecular structures of the complexes, X-ray studies were carried out on **4** and **5**. Plots of the two structures are shown in Fig. 1 and 2, and non-hydrogen atomic coordinates are in Tables 1 and 2, respectively, while significant bond distances and angles are collected in Table 3. Both structures are closely related to that of the kinetic isomer **2k**. The metal core consists of an Ru$_3$ triangle spiked by an Ru$_2$ chain in a so-called 'scorpion' geometry. Such a geometry is formed from **1** by the breaking of two Ru–Ru bonds, and is consistent with the addition of the four-electron donor set (H + Br) (**4**), and the six-electron donor set (H + I) (**5**). The addition of HI is accompanied by loss of a carbonyl ligand from Ru(4). In both **4** and **5**, the phosphino-acetylide ligand is attached to Ru(1) by a normal two-electron donor interaction with P(1), and to the Ru(3)Ru(4)Ru(5) triangle by a μ_3,η^2-($\perp$) attachment of the acetylide unit. The interactions between C(2) and Ru(5) are not particularly strong, as may be seen from the bond lengths [2.291(5) Å (**4**) and 2.355(8) Å (**5**)]. There is also a weak interaction between Ru(2) and C(2) [2.276(5) Å (**4**); 2.277(8) Å (**5**)]. A diphenylphosphido group bridges the Ru(2)–Ru(3) vector in each complex, and the carbonyl groups are arranged thus: three to each of Ru(1), Ru(4), Ru(5) in **4**, or Ru(1), Ru(5) in **5**, and two each to the other ruthenium centres. In **4**, the bromide ligand bridges the Ru(2)–Ru(3) bond, and the proton is located on the Ru(4)–Ru(5) edge of the Ru$_3$ triangle. The iodide ligand in **5** is μ_3-bonded to Ru(1), Ru(2) and Ru(4). The proton was not located in **5**, but from the disposition of carbonyl ligands, and by comparison with **4**, it may be assumed that it lies across the Ru(4)–Ru(5) bond.

The five Ru–Ru bonds are in the ranges 2.808(1)–2.917(1) Å (av. 2.863 Å) (**4**) and 2.775(1)–2.936(1) Å (av. 2.860 Å) (**5**), and have similar variations, the shortest bond in the structures being Ru(4)–Ru(5) and the longest Ru(2)–Ru(3) (**4**) and Ru(1)–Ru(2) (**5**). These variations are also in accordance with the structure of **2k**. The environment around Ru(1) is approximately octahedral with coordination by three CO ligands, P(1), Ru(2) and either Br or I. Since the P(1)→Ru(1) bond [2.397(1) Å (**4**); 2.400(2) Å (**5**)] is a normal two-electron donor link, the metal atom achieves an 18-electron count from this tertiary phosphine and the halide and CO ligands. The Ru(1)–Ru(2) bonds [2.862(1) Å (**4**); 2.936(1) Å (**5**)] are therefore further examples of a supported donor bond. Both structures have 80-electron electron-precise structures, again being similar to the structure of **2k**.

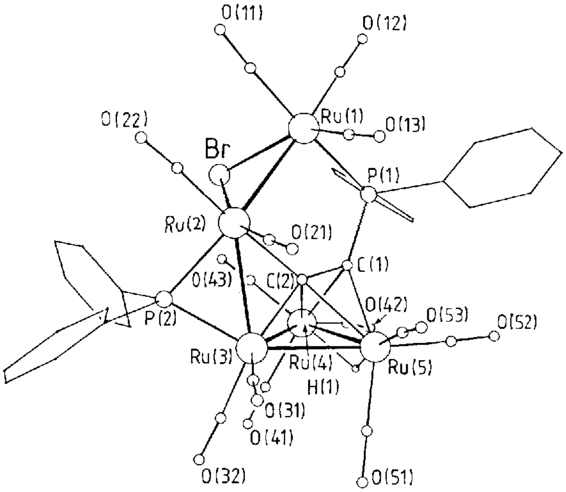

Figure 1 Computer-generated plot of a molecule of Ru$_5$(μ-H)(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-Br)(CO)$_{13}$ (**4**), showing atom-numbering scheme. Non-labelled atoms are carbons.

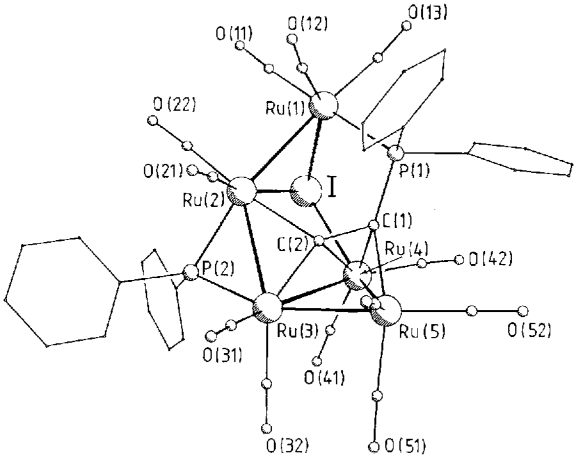

Figure 2 Computer-generated plot of molecule of Ru$_5$(μ-H)(μ_5-C$_2$PPh$_2$)(μ_3-I)(μ-PPh$_2$)(CO)$_{13}$ (**5**), showing atom-numbering scheme. Non-labelled atoms are carbons.

The major structural difference between the two complexes is in the orientation of the metal cores. A least-squares plane passes through C(1), C(2), Ru(1), Ru(2), Ru(3), P(1) (maximum deviation <0.02 Å) in complex **4**. In **5**, there are substantial deviations from the equivalent plane: C(1) 0.06 Å, C(2) −0.10 Å, Ru(1)−0.09 Å, Ru(2) − 0.48 Å, Ru(3) 0.10 Å, P(1) − 0.17 Å, implying that the Ru(2)–Ru(3) bond is twisted towards the iodide atom. The different geometries probably reflect the effect of the μ_3-I spanning the open side Ru(1)Ru(2)Ru(4) in **5**.

Complex **6** has a ν(CO) spectrum similar to that of **3** and analytical and FAB MS data support an analogous formulation. The isolobal relationship $\mathrm{H}^+ \underset{o}{\longleftrightarrow} [\mathrm{Au(PR_3)}]^+$, which has often been used previously to suggest locations of cluster-bound hydrogen atoms,[2] is now used conversely to support our conclusion that **6** is the isolobal analogue of **3**, with the structure illustrated.

Table 1 Final positional and equivalent thermal parameters for Ru$_5$(μ-H)(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-Br)(CO)$_{13}$ (**4**)

Atom	*x*	*y*	*z*	U_{eq}
Ru(1)	0.5109(1)	−0.2533(1)	0.1970(1)	0.017
Ru(2)	0.3834(1)	0.0074(1)	0.1823(1)	0.013
Ru(3)	0.1561(1)	0.1807(1)	0.2714(1)	0.013
Ru(4)	0.0105(1)	0.0096(1)	0.3159(1)	0.013
Ru(5)	0.2142(1)	0.0405(1)	0.3939(1)	0.014
Br	0.2733(1)	−0.1325(1)	0.1380(1)	0.018
P(1)	0.3665(2)	−0.2546(1)	0.3031(1)	0.015
P(2)	0.1897(2)	0.1950(1)	0.1572(1)	0.014
C(1)	0.2507(6)	−0.1001(5)	0.3225(3)	0.013
C(2)	0.2499(6)	−0.0050(5)	0.2827(3)	0.015
C(11)	0.6298(8)	−0.2633(6)	0.1111(4)	0.034
O(11)	0.7043(7)	−0.2752(6)	0.0614(3)	0.060
C(12)	0.5639(7)	−0.4267(6)	0.2003(3)	0.027
O(12)	0.6038(6)	−0.5309(4)	0.2032(2)	0.038
C(13)	0.6512(7)	−0.2234(6)	0.2424(3)	0.027
O(13)	0.7404(5)	−0.2093(5)	0.2697(2)	0.037
C(21)	0.5141(7)	0.0540(6)	0.2238(3)	0.022
O(21)	0.5974(5)	0.0800(5)	0.2477(2)	0.035
C(22)	0.5038(7)	0.0090(6)	0.0999(3)	0.022
O(22)	0.5776(5)	0.0200(5)	0.0531(2)	0.036
C(31)	0.2680(7)	0.2769(6)	0.2848(3)	0.021
O(31)	0.3390(5)	0.3302(4)	0.2953(3)	0.033
C(32)	−0.0246(7)	0.3145(6)	0.2818(3)	0.022
O(32)	−0.1357(5)	0.3987(4)	0.2849(3)	0.035
C(41)	−0.1765(7)	0.1503(6)	0.3187(3)	0.020
O(41)	−0.2899(5)	0.2270(4)	0.3242(2)	0.028
C(42)	−0.0835(7)	−0.0875(6)	0.3716(3)	0.022
O(42)	−0.1482(5)	−0.1348(4)	0.4065(2)	0.030
C(43)	−0.0363(6)	−0.0401(6)	0.2355(3)	0.018
O(43)	−0.0772(5)	−0.0665(4)	0.1907(2)	0.028
C(51)	0.1179(7)	0.2000(6)	0.4297(3)	0.024
O(51)	0.0558(6)	0.2928(4)	0.4520(2)	0.037
C(52)	0.2236(7)	−0.0695(6)	0.4724(3)	0.022
O(52)	0.2317(6)	−0.1377(5)	0.5170(2)	0.037
C(53)	0.4073(7)	0.0475(6)	0.3998(3)	0.021
O(53)	0.5164(5)	0.0571(5)	0.4063(3)	0.037
C(61)	0.1758(4)	−0.3546(4)	0.3766(2)	0.020
C(62)	0.0632(4)	−0.4022(4)	0.3852(2)	0.025
C(63)	0.0118(4)	−0.4298(4)	0.3291(2)	0.026
C(64)	0.0729(4)	−0.4097(4)	0.2644(2)	0.029
C(65)	0.1855(4)	−0.3621(4)	0.2557(2)	0.021
C(66)	0.2369(4)	−0.3345(4)	0.3118(2)	0.018
C(71)	0.5314(4)	−0.4567(3)	0.3819(2)	0.025
C(72)	0.6344(4)	−0.5181(3)	0.4286(2)	0.032
C(73)	0.6960(4)	−0.4539(3)	0.4626(2)	0.030
C(74)	0.6548(4)	−0.3283(3)	0.4499(2)	0.030
C(75)	0.5518(4)	−0.2670(3)	0.4032(2)	0.022
C(76)	0.4901(4)	−0.3312(3)	0.3692(2)	0.018
C(81)	0.3673(4)	0.3315(3)	0.1153(2)	0.030
C(82)	0.3931(4)	0.4343(3)	0.0867(2)	0.039
C(83)	0.2771(4)	0.5320(3)	0.0593(2)	0.037
C(84)	0.1354(4)	0.5270(3)	0.0605(2)	0.036
C(85)	0.1095(4)	0.4242(3)	0.0890(2)	0.025
C(86)	0.2255(4)	0.3264(3)	0.1164(2)	0.020
C(91)	0.0869(3)	0.1523(4)	0.0415(2)	0.020
C(92)	−0.0203(3)	0.1448(4)	0.0035(2)	0.028
C(93)	−0.1678(3)	0.1729(4)	0.0318(2)	0.025
C(94)	−0.2081(3)	0.2085(4)	0.0982(2)	0.028
C(95)	−0.1009(3)	0.2160(4)	0.1363(2)	0.023
C(96)	0.0466(3)	0.1879(4)	0.1079(2)	0.014
H(1)	0.032(8)	0.051(7)	0.397(4)	0.050

The addition of HX (X = Cl, Br or I) or AuCl(PPh$_3$) to **1** thus appears to proceed by oxidative addition at Ru(2), followed by migration of the H or Au(PPh$_3$) groups to bridge one edge of the closed Ru$_3$ triangle that results. Halide ligands in ruthenium clusters may be found in terminal or in μ_2- or μ_3-bridging modes, but the non-face-capping μ_3 coordination mode found in **5** has not been observed previously. The only other structurally characterized clusters containing μ_3-I groups, Ru$_3$(μ-H)(μ_3-I)(CO)$_9$[3] and [Na(18-crown-6)][Ru$_3$(μ_3-I)(CO)$_9$],[4] have the ligand in a triangular face-capping position. As both these clusters were derived from a Ru$_3$(μ-I)(CO)$_{10}$ precursor by CO loss, it seems likely that **5** is also formed through CO loss from a intermediate related to **4**, probably Ru$_5$(μ-H)(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-I)(CO)$_{13}$. The FAB mass spectrum of **5** supports this idea, as an ion [M + CO]$^+$ is formed after short periods in the FAB beam. However, no intermediates were detected in the formation of **5**.

EXPERIMENTAL

Syntheses

Ru$_5$(μ-H)(μ$_5$-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-Cl)(CO)$_{13}$ (3)

Two drops of HCl (aq. 33%; 58 mg, *ca* 1.61 mmol) were added to a solution of **1** (100 mg, 0.079 mmol) dissolved in acetone/CH$_2$Cl$_2$ (1:1, 20 ml). After stirring for 20 min no starting material remained (spot TLC). At this stage CH$_2$Cl$_2$ (20 ml) and water (10 ml) were added to the orange solution. The organic layer was then extracted with a further two aliquots of water, dried over MgSO$_4$ and evaporated to dryness. Crystallization (CH$_2$Cl$_2$/petroleum spirit) gave Ru$_5$(μ-H)(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(μ-Cl)(CO)$_{13}$ (**3**;

Table 2 Final positional and equivalent thermal parameters for $Ru_5(\mu\text{-H})(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-I})(\mu\text{-}PPh_2)(CO)_{12}$ (**5**)

Atom	x	y	z	U_{eq}
I(1)	0.49108(4)	0.25037(2)	0.08106(3)	0.019
Ru(1)	0.64691(5)	0.19384(3)	0.05768(4)	0.015
Ru(2)	0.65184(5)	0.23242(3)	0.21878(4)	0.015
Ru(3)	0.65970(5)	0.36348(3)	0.27527(4)	0.016
Ru(4)	0.54445(5)	0.37684(3)	0.10676(4)	0.015
Ru(5)	0.72043(5)	0.44136(3)	0.16993(4)	0.017
P(1)	0.7137(1)	0.2964(1)	0.0423(1)	0.014
P(2)	0.6001(1)	0.2758(1)	0.3177(1)	0.017
C(1)	0.6879(5)	0.3507(4)	0.1092(5)	0.020
C(2)	0.6824(5)	0.3320(4)	0.1791(5)	0.016
C(11)	0.5954(7)	0.1104(4)	0.0700(5)	0.026
O(11)	0.5670(5)	0.0601(3)	0.0739(4)	0.044
C(12)	0.7758(7)	0.1644(4)	0.1088(5)	0.024
O(12)	0.8534(5)	0.1448(3)	0.1327(4)	0.034
C(13)	0.6237(6)	0.1733(4)	−0.0538(5)	0.025
O(13)	0.6195(6)	0.1563(3)	−0.1156(4)	0.044
C(21)	0.7793(7)	0.2210(4)	0.2871(5)	0.023
O(21)	0.8580(5)	0.2160(3)	0.3321(4)	0.039
C(22)	0.6228(6)	0.1469(4)	0.2366(5)	0.023
O(22)	0.6081(5)	0.0956(3)	0.2525(4)	0.032
C(31)	0.7773(7)	0.3697(4)	0.3666(5)	0.025
O(31)	0.8512(5)	0.3759(3)	0.4183(4)	0.042
C(32)	0.5960(6)	0.4307(4)	0.3088(5)	0.027
O(32)	0.5585(5)	0.4718(3)	0.3285(4)	0.038
C(41)	0.4449(6)	0.4066(4)	0.1423(5)	0.024
O(41)	0.3858(4)	0.4264(3)	0.1611(4)	0.030
C(42)	0.4826(6)	0.4012(4)	−0.0045(6)	0.025
O(42)	0.4446(5)	0.4190(3)	−0.0692(4)	0.040
C(51)	0.7073(7)	0.5135(5)	0.2341(6)	0.032
O(51)	0.6976(6)	0.5578(3)	0.2691(5)	0.052
C(52)	0.7339(7)	0.4920(4)	0.0838(6)	0.030
O(52)	0.7430(6)	0.5223(3)	0.0330(5)	0.047
C(53)	0.8547(7)	0.4380(4)	0.2307(5)	0.025
O(53)	0.9356(5)	0.4369(3)	0.2700(4)	0.043
C(111)	0.9009(3)	0.2996(3)	0.1578(3)	0.019
C(112)	1.0007(3)	0.2889(3)	0.1852(3)	0.029
C(113)	1.0444(3)	0.2717(3)	0.1303(3)	0.043
C(114)	0.9882(3)	0.2651(3)	0.0481(3)	0.047
C(115)	0.8883(3)	0.2757(3)	0.0206(3)	0.026
C(116)	0.8447(3)	0.2930(3)	0.0755(3)	0.017
C(211)	0.5858(3)	0.3198(2)	−0.1159(3)	0.021
C(212)	0.5518(3)	0.3545(2)	−0.1884(3)	0.030
C(213)	0.6068(3)	0.4051(2)	−0.2010(3)	0.031
C(214)	0.6957(3)	0.4210(2)	−0.1411(3)	0.031
C(215)	0.7296(3)	0.3863(2)	−0.0686(3)	0.022
C(216)	0.6746(3)	0.3357(2)	−0.0560(3)	0.017
C(311)	0.6882(4)	0.2969(2)	0.4845(3)	0.026
C(312)	0.7340(4)	0.2785(2)	0.5654(3)	0.027
C(313)	0.7518(4)	0.2134(2)	0.5853(3)	0.028
C(314)	0.7239(4)	0.1667(2)	0.5243(3)	0.034
C(315)	0.6780(4)	0.1851(2)	0.4434(3)	0.028
C(316)	0.6602(4)	0.2502(2)	0.4235(3)	0.020
C(411)	0.4290(4)	0.2054(2)	0.2896(3)	0.029
C(412)	0.3344(4)	0.1969(2)	0.2868(3)	0.037
C(413)	0.2830(4)	0.2493(2)	0.3003(3)	0.035
C(414)	0.3262(4)	0.3101(2)	0.3166(3)	0.038
C(415)	0.4209(4)	0.3185(2)	0.3193(3)	0.031
C(416)	0.4722(4)	0.2662(2)	0.3058(3)	0.021
Cl(1)[a]	0.2511(5)	−0.0090(3)	0.0086(4)	0.069
Cl(2)[a]	0.3641(6)	0.0749(4)	0.1342(6)	0.113
C(3)[a]	0.354(2)	0.009(1)	0.083(2)	0.063
Cl(4)[b]	0.638(2)	0.0571(9)	0.686(1)	0.109
Cl(5)[b]	0.471(2)	−0.046(1)	0.397(1)	0.115
Cl(6)[b]	0.495(2)	0.031(1)	0.399(1)	0.126
Cl(7)[b]	0.459(1)	−0.001(1)	0.460(1)	0.115

[a] Site occupancy 0.5. [b] Site occupancy 0.25.

87 mg, 0.067 mmol, 85%). The analytical sample was purified by preparative TLC (2:1 petroleum spirit/CH_2Cl_2) of this product. A major orange band (R_f 0.52) was separated from three trace bands and crystallized (CH_2Cl_2/petroleum spirit) to give pure orange crystalline **3** (30 mg, 0.023 mmol, 29%), m.p. 193–194°C. Analysis: Calcd for $C_{39}H_{21}ClO_{13}P_2Ru_5$: C, 36.03; H, 1.63%; M_r 1300. Found: C, 36.55; H, 1.84%; M_r 1300 (mass spectrometry). IR (cyclohexane): ν(CO) 2087w, 2070s, 2061s, 2050(sh), 2023vs, 2014(sh), 2009(sh), 1998(sh), 1976m, 1958(sh), 1948(sh), 1944m cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.5–6.7 (m, 20H, Ph); −21.25 (s, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (CH_2Cl_2): δ 292.9 (s, C_α); 205.4(s), 203.3 (s), 199.2 (m), 197.6 (m), 196.1 (s), 194.6 (m), 191.8 (s), 189.2 (m), 185.1 (s), 183.9 (s), 176.0 (s) (Ru–CO); 154.3 (d, $J_{P\text{-}C} = 15$ Hz, C_β); 141.2–128.6 (m, Ph). FAB MS: 1300, $[M]^+$; ions formed by stepwise loss of 13 CO groups.

An attempted protonation of **1** with $HBF_4.Et_2O$ was unsuccessful. After 5 h at room temperature with an excess of acid no reaction was observed and unreacted starting material was recovered.

$Ru_5(\mu\text{-H})(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-Br})(CO)_{13}$ (4)

Three drops of HBr (aq. 48%, *ca* 4.5 mmol) were added to **1** (100 mg, 0.079 mmol) dissolved in acetone/CH_2Cl_2 (1:1, 20 ml). After stirring for 20 min the orange solution was poured into water (30 ml), and the organic layer then separated, dried over $MgSO_4$ and evaporated to dryness. Preparative TLC (2:1 petroleum spirit/CH_2Cl_2) of this product gave a major orange band (R_f 0.67) which was collected and crystallized

(CH_2Cl_2/EtOH), giving light orange crystals of $Ru_5(\mu\text{-H})(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-Br})(CO)_{13}$ (**4**) (60 mg, 0.045 mmol, 56%), m.p. 195–197 °C (crystals darkened at 175 °C). Analysis: Calcd for $C_{39}H_{21}BrO_{13}P_2Ru_5$: C, 34.83; H, 1.57%; M_r 1345. Found: C, 34.58; H, 1.57%; M_r 1345 (mass spectrometry). IR (cyclohexane): ν(CO) 2088w, 2071s, 2063s, 2051(sh), 2037(sh), 2031(sh), 2025vs, 2020(sh), 2014(sh), 2000(sh), 1989(sh), 1981m, 1962(sh), 1954w cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.9–6.9 (m, 20H, Ph); −20.71 (s, 1H, Ru*H*). FAB MS: 1345, $[M]^{+\cdot}$; ions formed by stepwise loss of 13 CO groups.

Table 3 Selected bond distances (Å) and angles (°) for **4** and **5**

	Structure	
Parameter	**4**^{a}	**5**^{b}
Ru(1)–Ru(2)	2.862(1)	2.936(1)
Ru(2)–Ru(3)	2.917(1)	2.881(1)
Ru(3)–Ru(4)	2.909(1)	2.858(1)
Ru(3)–Ru(5)	2.821(1)	2.848(1)
Ru(4)–Ru(5)	2.808(1)	2.775(1)
Ru(1)–P(1)	2.397(1)	2.400(2)
Ru(2)–P(2)	2.359(1)	2.332(3)
Ru(3)–P(2)	2.268(1)	2.264(2)
Ru(4)–C(1)	2.203(5)	2.176(9)
Ru(5)–C(1)	2.195(6)	2.129(8)
Ru(2)–C(2)	2.276(5)	2.277(8)
Ru(3)–C(2)	2.042(6)	1.962(9)
Ru(5)–C(2)	2.291(5)	2.355(8)
Ru(1)–X	2.565(1)	2.751(1)
Ru(2)–X	2.560(1)	2.740(1)
P(1)–C(1)	1.796(5)	1.774(9)
C(1)–C(2)	1.316(8)	1.33(1)
Ru(1)–Ru(2)–Ru(3)	129.0(1)	125.2(1)
Ru(2)–Ru(3)–Ru(5)	98.3(1)	106.8(1)
Ru(2)–Ru(3)–Ru(4)	92.7(1)	78.2(1)
Ru(3)–Ru(4)–Ru(5)	59.1(1)	60.7(1)
Ru(3)–Ru(5)–Ru(4)	62.2(1)	61.1(1)
Ru(4)–Ru(3)–Ru(5)	58.7(1)	58.2(1)
Ru(1)–P(1)–C(1)	108.8(2)	106.8(3)
Ru(2)–P(2)–Ru(3)	78.1(1)	77.6(1)
Ru(1)–X–Ru(2)	67.9(1)	64.7(1)
Ru(4)–C(1)–Ru(5)	79.4(2)	80.2(3)
Ru(2)–C(2)–Ru(3)	84.8(2)	85.3(3)
Ru(3)–C(2)–Ru(4)	84.5(2)	87.0(3)
Ru(3)–C(2)–Ru(5)	81.0(2)	82.0(3)
C(1)–C(2)–Ru(2)	131.0(4)	129.7(6)
C(2)–C(1)–Ru(5)	77.0(4)	83.0(1)

[a] Ru(4)–H(1) 1.79(8); Ru(5)–H(1) 1.72; X = Br. [b] Ru(4)–I 2.727(1); Ru(1)–I–Ru(4) 103.1(1); Ru(2)–I–Ru(4) 83.0(1); X = I.

$Ru_5(\mu\text{-H})(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-I})(\mu\text{-}PPh_2)(CO)_{12}$ (5)

Two drops of HI (aq. 57%, *ca* 2.8 mmol) were added to a solution of **1** (100 mg, 0.079 mmol) dissolved in CH_2Cl_2/acetone (1:1, 20 ml). An instant colour change to a dark orange–brown was observed and 5 min later the solution was added to water (30 ml). The organic layer was extracted with water and then dried over $MgSO_4$. After removing the solvent under reduced pressure the residue was purified by TLC (2:1 petroleum spirit/CH_2Cl_2). A major burgundy-coloured band [R_f 0.71) was separated from two other trace bands and an orange baseline. This product was then crystallized (CH_2Cl_2/heptane) to give $Ru_5(\mu\text{-H})(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-I})(\mu\text{-}PPh_2)(CO)_{12}.0.33C_7H_{16}$ (**5**) (75 mg, 0.055 mmol, 70%), m.p. 187–189°C (darkened at 112°C). Analysis: Calcd for $C_{38}H_{21}IO_{12}P_2Ru_5.0.33C_7H_{16}$: C, 34.67; H, 1.90%; M_r 1364 (unsolvated). Found: C, 34.86; H, 1.81%; M_r 1364 (mass spectrometry, $1365 = [M+H]^+$). IR (cyclohexane): ν(CO) 2081w, 2061s, 2021vs, 2006vw, 1996w, 1982w, 1953vw cm^{-1}. ^{1}H NMR (acetone-d^6): δ 8.2–7.4 (m, 20H, Ph); 1.28(m, 3H, CH_2, C_7H_{16}); 0.88 (m, 2H, CH_3, C_7H_{16}); −25.33 (s, 1H, Ru*H*). FAB MS: 1365, $[M]^+$; ions formed by stepwise loss of 12 CO groups. This complex also forms an ion at *m*/*z* 1391, $[M+CO]^+$ after short periods in the FAB beam.

$AuRu_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-Cl})(CO)_{13}(PPh_3)$ (6)

A mixture of **1** (60 mg, 0.047 mmol) and AuCl(PPh_3) (50 mg, 0.10 mmol) was stirred in acetone/CH_2Cl_2 (1 : 1, 20 ml) at room temperature for 24 h. The solvent was then removed under vacuum and the residue purified by TLC (4:1 petroleum spirit/CH_2Cl_2) giving a minor brown band (R_f0.62) identified (IR, FAB MS) as **1** (5 mg, 0.004 mmol, 8%). A major orange band (R_f0.37) was also collected and crystallized (CH_2Cl_2/petroleum spirit) as $AuRu_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-Cl})(CO)_{13}(PPh_3)$ (**6**) (34 mg, 0.019 mmol, 41%), m.p. 162°C (dec.) Analysis: Calcd for $C_{57}H_{35}AuClO_{13}P_3Ru_5$: C, 38.93; H, 2.01%; M_r 1759. Found: C, 38.71; H, 2.06%; M_r 1759 (mass spectrometry). IR (cyclohexane): ν(CO) 2066m, 2050m, 2038vs, 2013m, 2001(sh), 1992m, 1980(sh), 1970m, 1953(sh), 1932w cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.9–6.5 (m, Ph). FAB MS: 1759, $[M]^+$; ions formed by stepwise loss of 13 CO groups.

X-ray crystallography

For both structures space groups were defined by preliminary precession photography, while cell dimensions and intensity data were obtained on a Nicolet P3 diffractometer using Mo-Kα X-radiation ($\lambda = 0.7107$ Å). In the final cycles of refinement for each, all non-hydrogen atoms were assigned anisotropic temperature factors, the phenyl rings were treated as rigid hexagons (D_{C-C} 1.395 Å) with their hydrogen atoms in calculated positions with a common isotropic temperature factor. All calculations were performed using SHELXS-86 or SHELX76 programs.[5] Individual details are given below.

Structure of $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}Br)(CO)_{13}$ (4)

Crystal data: $C_{39}H_{21}BrO_{13}P_2Ru_5$, M 1344.8, triclinic, space group $P\bar{1}$, a 9.689(2), b 11.874(2), c 20.005(4) Å, α 84.66(2), β 82.90(6), γ 67.51(6)°, U 2107.7(7) Å^3. D_c 2.12 g cm^{-3} for $Z = 2$, $F(000)$ 1288, μ(Mo-Kα) 27.5 cm^{-1}, T 173 K. Deep-orange crystals from CH_2Cl_2/Pr^iOH, crystal size 0.5 mm × 0.4 mm × 0.2 mm. Total of 8166 unique reflections (ω-scans) in range $4° < 2\theta < 52°$, 6478 with $I > 2\sigma(I)$ used after correction for absorption (ϕ-scan method, transmission factors 0.969 (max), 0.588(min)). Solved by automatic Patterson interpretation for Ru and Br positions. The bridging H atom was revealed as the largest peak in the penultimate difference map and included in the refinement with fixed temperature factor and free coordinates. $R = 0.0368$, R_w 0.0362, $w = [\sigma^2(F) + 0.000519F^2]^{-1}$. Largest final shift 0.02σ, largest residual feature 0.76 e Å^{-3}.

Structure of $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}I)(\mu\text{-}PPh_2)(CO)_{12}$ (5)

Crystal data: $C_{38}H_{21}IO_{12}P_2Ru_5.CH_2Cl_2$, M 1448.7, monoclinic, space group $P2_1/n$, a 14.809(4), b 20.721(4), c 17.698(5) Å, β 111.42(2)°, U 5055.6 Å^3. D_c 1.90 g cm^{-3} for $Z = 4$, $F(000)$ 2760, μ(Mo-Kα) 22 cm^{-1}, T 143 K. Deep-red crystals from CH_2Cl_2/petroleum spirit, crystal size 0.70 mm × 0.15 mm × 0.09 mm. Total of 8921 unique reflections (ω-scans) in range $4° < 2\theta < 50°$, 7815 with $I > 2\sigma(I)$ used after correction for absorption (ϕ-scan method, transmission factors 0.83(max), 0.71(min)). Solved by direct methods. The penultimate difference map showed significant electron density which was modelled as a molecule of CH_2Cl_2 equally distributed over two sites; in the first the orientation was ordered and so the carbon and chlorine atoms were included with half-occupancy each, while at the other site there was disorder with four quarter-occupied chlorine positions with insufficient central electron density reasonably to assign to the carbon atom. The bridging H atom could not be located but from the disposition of the CO ligands, and by comparison with the Br analogue above, can be assumed to lie across the Ru(4)–Ru(5) bond. $R = 0.0440$, R_w 0.0416, $w = [\sigma^2(F) + 0.00021F^2]^{-1}$. Largest final shift 0.5σ, largest residual feature 1.5 e Å^{-3} near the disordered solvent molecule.

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