Formation of New Halogeno Mixed-metal Clusters by Oxidative Addition of Triphenylphosphinegold(I) Halides to $[Ru_5C(CO)_{15}]$: Crystal and Molecular Structures of $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ and $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ †

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In CH_2Cl_2 the compound $[Ru_5C(CO)_{15}]$ reacts with $[Au(PPh_3)X]$ (X = Cl or Br) to form $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}X]$ which loses one mole of CO to form $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}X)]$, where X functions as a three-electron donor. The crystal structures of $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ and $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ are reported. The complex $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ crystallizes in the triclinic space group $P\bar{1}$ with a = 15.333(3), b = 15.865(3), c = 18.813(7) Å, α = 84.29(4), β = 84.41(4), γ = 61.88(2)°, and Z = 4 with two distinct molecules per asymmetric unit. For 5 487 reflections the structure refined to R 0.0703 and R' 0.0539. The molecule contains a bridged butterfly configuration of ruthenium atoms (seven Ru–Ru bonds) with the gold atom bridging the butterfly 'hinge' bond and the chloride attached terminally to the ruthenium that spans the wing tips of the butterfly. All ruthenium atoms remain bonded to the carbide atom, but the gold and chlorine show no interaction with the carbide. For $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ the space group is monoclinic, $P2_1/c$, with a = 8.967(1), b = 29.767(7), c = 15.010(3) Å, β = 92.16(1)°, and Z = 4. For 2 950 reflections, the refinement converged with R 0.0432 and R' 0.0434. The molecule is best described as a distorted square pyramid of ruthenium atoms in which one apical to basal Ru–Ru bond is replaced by a bridging three-electron donating bromine. The complex is derived from the 15 carbonyl complex by displacement of one of the hinge carbonyls by the halide.

Mixed-metal cluster complexes have gained interest owing to the induced asymmetry in electronic and steric properties arising from the presence of more than one type of metal atom in these clusters. These properties suggest the possibility of stereochemical control of reactions occurring on the cluster and perhaps higher selectivity control in competing reactions. Synthesis of discrete mixed-metal clusters also affords a potential route into heterogeneous mixed-metal catalysts of definite composition.[1]

It has recently been shown that $[Ru_5C(CO)_{15}]$ is reactive to the addition of ligands such as CH_3CN to form $[Ru_5C(CO)_{15}(NCMe)]$ in which the parent square-pyramidal configuration is converted into a bridged butterfly geometry.[2] This geometry also results when HX (X = halogen) is oxidatively added to the cluster.[3] Following recent work on mixed-metal gold clusters,[4] we have employed the reaction of triphenylphosphinegold(I) halides with $[Ru_5C(CO)_{15}]$ in order to obtain mixed ruthenium–gold clusters. Previously, mixed-metal gold clusters have been obtained by the addition of phosphinegold(I) halides to metal carbonylate anions,[4] and in one case gold(I) has been observed to add to neutral $[Os_3(CO)_{10}H_2]$.[5] Complexes are formed between these gold halides and the ruthenium carbide in which all 15 carbonyls are retained [type (I)]. They are observed to lose carbon monoxide reversibly undergoing a rearrangement of the metal framework in the process in which the halide becomes a bridging three-electron donor [type (II)]. As a result of the bridging mode of the halide, the number of metal–metal bonds remains the same as the electron count in the system does not change on losing the CO. Because of the current interest in such complexes, we have performed the crystallographic analyses of $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ and $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$. Observation of the loss of CO from these complexes led us to reinvestigate the reactions of $[Ru_5C(CO)_{15}]$ with HX, and similar CO loss reactions are observed.

† μ_5-Carbido-chloro-μ-triphenylphosphineaurio-*cyclo*-pentakis (tricarbonylruthenium) (7*Ru*–*Ru*, 2*Au*–*Ru*) and μ-bromo-μ_5-carbido-tetradecacarbonyl-μ-triphenylphosphineaurio-*cyclo*-pentaruthenium (7*Ru*–*Ru*, 2*Au*–*Ru*).

Supplementary data available (No. SUP 23527, 60 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Results and Discussion

Crystal Structure Descriptions.—$[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$. This complex crystallizes from CH_2Cl_2–hexane at 0 °C in the triclinic space group $P\bar{1}$ (no. 2) with two independent molecules per asymmetric unit. The possibility that a higher symmetry space group existed for the crystal was tested but no crystallographically reasonable solution was found. Diagrams of the two molecular forms, which are essentially the same, are found in Figure 1(*a*) and (*b*) and diagrams of the metal framework in Figure 2(*a*) and (*b*). Crystal data are given in Table 1, atomic co-ordinates in Table 2, and bond lengths and angles are compiled in Tables 3 and 4. Because of the size of this crystal structure determination, the data are such that detailed comparisons of molecular parameters are not reliable. The data are sufficient, however, to show the basic structure of the complex.

The metal framework consists of an *arachno*-pentagonal bipyramid with all five rutheniums bonded to the carbide. As in the acetonitrile complex of the ruthenium carbide and in $[Os_5C(CO)_{15}I]^-$,[6] the carbide carbon distances to the wing-tip rutheniums seem to be significantly shorter than those to the hinge and bridge ruthenium atoms. There are seven Ru–Ru bonds and the cluster valence electron count is 76 which is consistent with the structure of $[Ru_5C(CO)_{15}(NCMe)]$.[2] This 'bridged butterfly' configuration is also the same as that observed for $[N(PPh_3)_2][Os_5C(CO)_{15}I]$. The chloride occupies a terminal position on the bridging ruthenium similar to

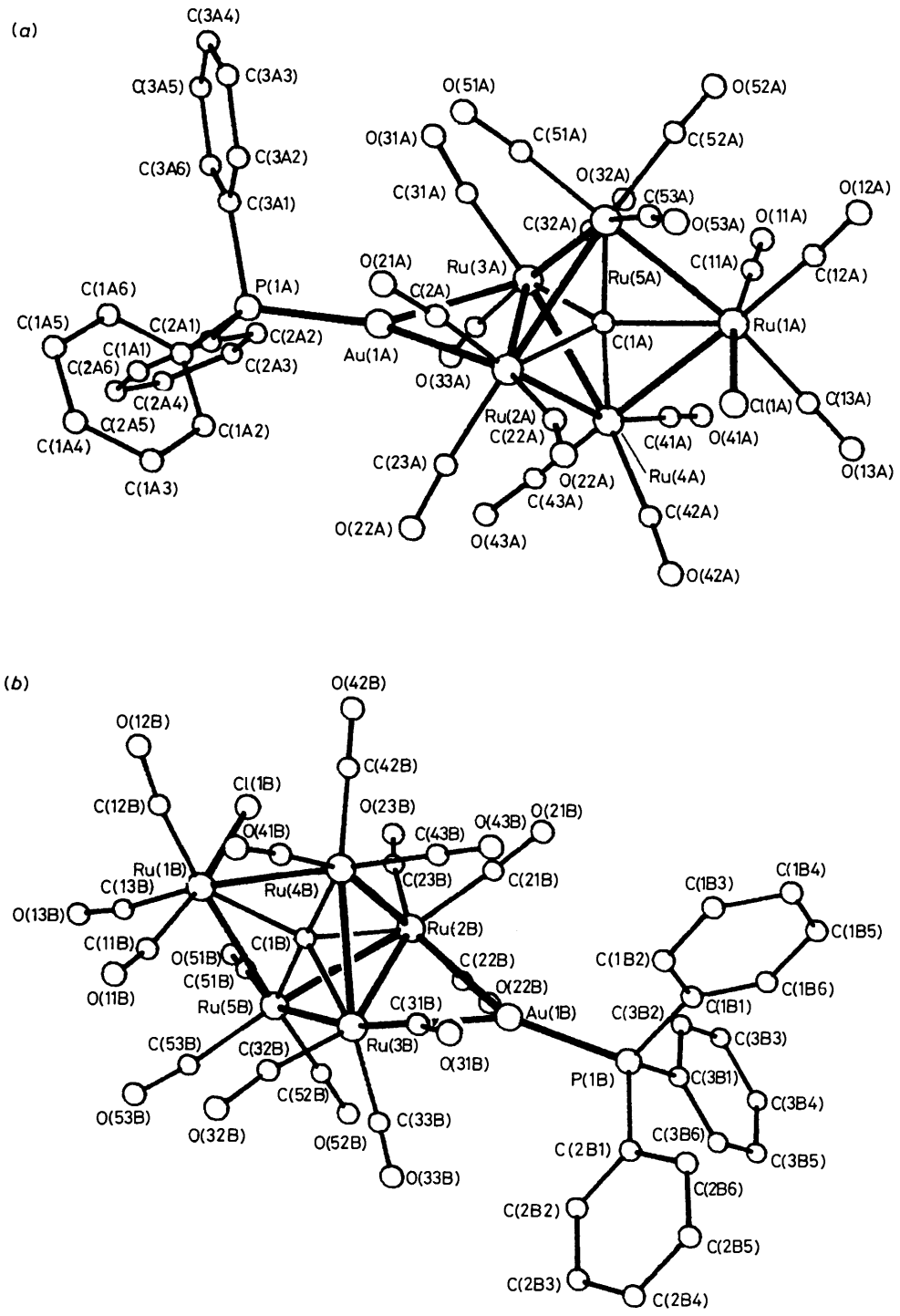


Figure 1. PLUTO diagrams of $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ for (*a*) molecule A and (*b*) molecule B

the configuration of the acetonitrile in the ruthenium–carbide complex and to the iodide in the osmium–carbide complex. The triphenylphosphinegold unit symmetrically bridges the hinge Ru–Ru bond as expected if the gold is considered to be *sp* hybridized, with its orbital directed towards the centre of the hinge bond. There are three carbonyls terminally bonded to each ruthenium. The structure is in kind that proposed for the HX derivatives of $[Ru_5C(CO)_{15}]$.[3]

$[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$. This complex crystallizes in the monoclinic space group $P2_1/c$ and possesses a distorted square-pyramidal arrangement of ruthenium atoms. A diagram of the molecule is shown in Figure 3 and the metal framework is shown in Figure 4. Crystal data are given in Table 1. Atomic co-ordinates appear in Table 5, and bond length and angle data are given in Tables 6 and 7. As with $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$, there are seven Ru–Ru bonds and a 76 electron count for the cluster framework. In the 14 carbonyl product the two electrons lost when CO is

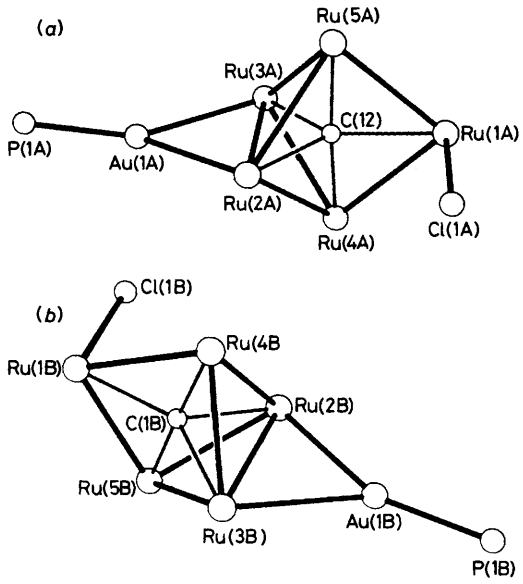


Figure 2. PLUTO diagrams of the metal framework for $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ for (*a*) molecule A and (*b*) molecule B

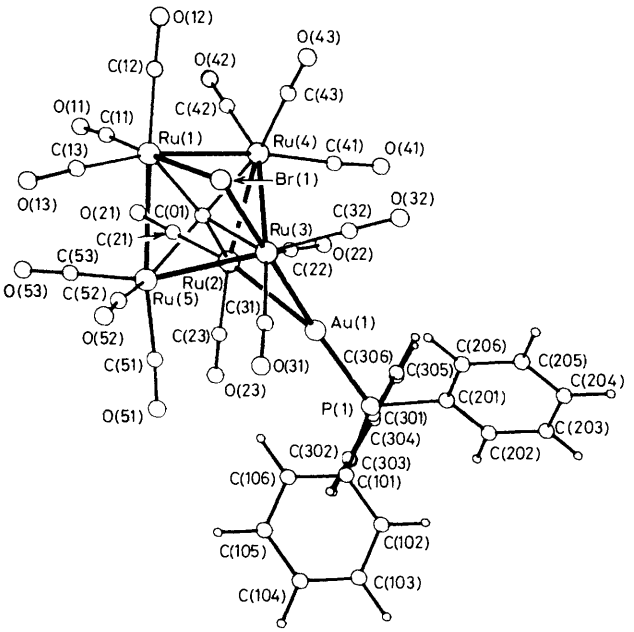


Figure 3. PLUTO diagram of $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$

evolved are regained as the halogen becomes a three-electron donor. The CO that is displaced is bonded to one of the hinge ruthenium atoms in the parent complex and it is this ruthenium to which the bromide becomes bonded. The formation of the second ruthenium–bromine bond alters the otherwise bridged-butterfly configuration so that the geometry becomes more accurately described as a distorted square pyramid. This distortion is seen diagramatically in Figure 5 where the bond angles in the plane containing the hinge and bridging rutheniums are shown for $[Ru_5C(CO)_{15}(NCMe)]$, $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$, $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$, and $[Ru_5C(CO)_{15}]$ (the wing-tip atoms have been omitted in this representation in order to clarify the structural comparisons). As is obvious from Figure 5, the effect of the

Table 1. Crystal data for $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ (I) and $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ (II) *

	(I)	(II)
Chemical formula	$C_{34}H_{15}AuClO_{15}Ru_5$	$C_{33}H_{15}AuBrO_{14}Ru_5$
Crystal colour	Dark red	Orange-yellow
Crystal dimensions/mm	0.39 × 0.27 × 0.23	0.35 × 0.30 × 0.20
a/Å	15.333(3)	8.967(1)
b/Å	15.865(3)	29.767(7)
c/Å	18.813(7)	15.010(3)
α/°	84.29(4)	90.0
β/°	84.41(4)	92.16(1)
γ/°	61.88(2)	90.0
U/Å^3	4 086.5	4 003.6
D_c/g cm^{-3}	2.33	2.40
Z	4 (2 molecules per asymmetric unit)	4
Space group	$P\bar{1}$	$P2_1/c$
Diffractometer	Stoe	Syntex $P2_1$
Number reflections measured	14 358	3 165
Number independent reflections	5 487 ($I > 5\sigma$)	2 950 ($I > 3\sigma$)
R	0.0703	0.0432
R'	0.0539	0.0434
2θ range/°	3—45	3—45
μ(Mo-K_α)/cm^{-1}	54.68	64.96
F(000)	2 680	2 696
Method of correcting for absorption	Azimuthal scans 300 data from 13 independent reflections	Azimuthal scans 402 data from 12 independent reflections
Transmission factors	0.322—0.544	0.663—0.995

* For both complexes: Mo-K_α radiation, λ = 0.710 69 Å, graphite monochromator, D_m not measured.

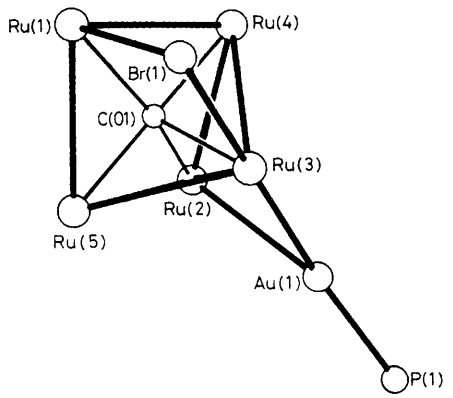


Figure 4. PLUTO diagram of the metal framework of $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$

bromide bridge is to move the bridging ruthenium *ca.* 0.5 Å closer to a hinge ruthenium than it is in the 15 carbonyl-containing complex. Judging from the long Ru(1)–Ru(3) distance [3.403(2) Å] compared to normal Ru–Ru bond lengths [2.70—2.90 Å], no metal–metal bond is formed between Ru(1) and Ru(3) even though that vector is bridged by the bromine. The electron count is sufficient without the formation of such a bond. The triphenylphosphinegold unit

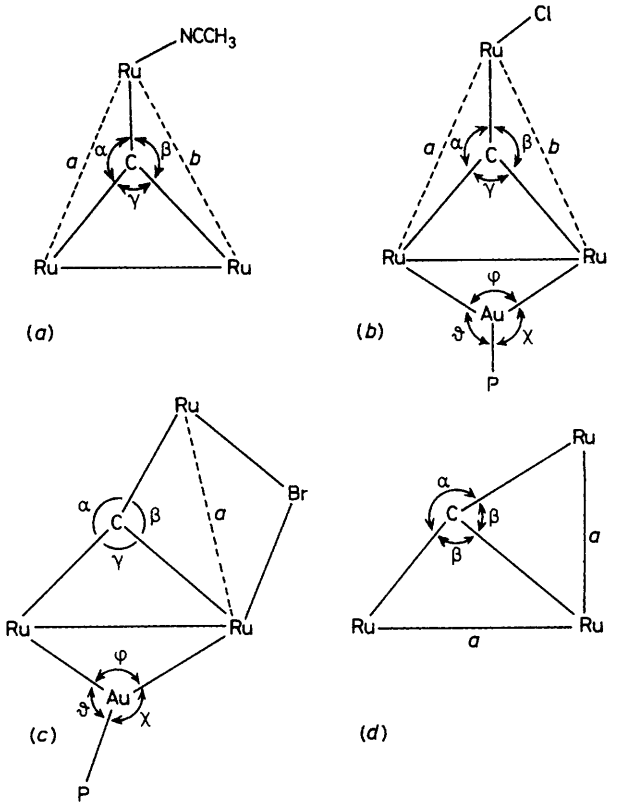
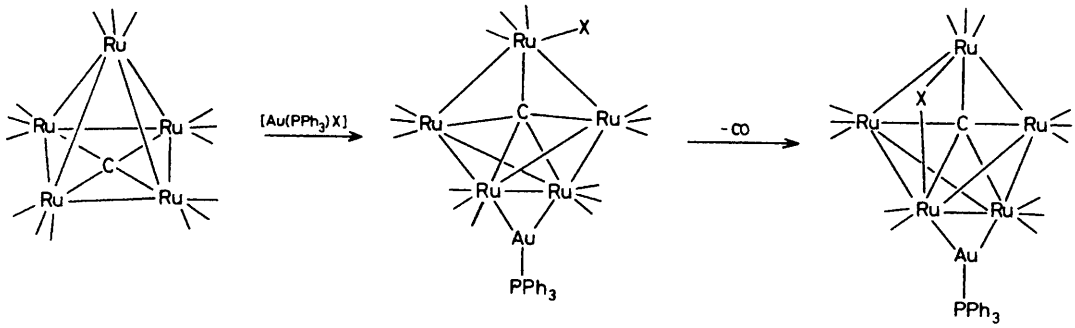


Figure 5. Diagramatic representation of the molecular planes passing through the two hinge ruthenium atoms and the carbide atom for (*a*) $[Ru_5C(CO)_{15}(NCMe)]$ (a = 3.957, b = 3.967 Å, α = 138.3, β = 136.6, γ = 82°), (*b*) $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ (a_A = 3.391, a_B = 3.951, b_A = 3.864, b_B = 3.937 Å, α_A = 133, α_B = 137, β_A = 136, β_B = 135, γ_A = 91.3, γ_B = 88.2°), (*c*) $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ (a = 3.403 Å, α = 155.7, β = 111.7, γ = 92.5°), and for the corresponding orientation in (*d*) for $[Ru_5C(CO)_{15}]$ ($a_{av.}$ = 2.82 Å, $\alpha_{av.}$ = 187, $\beta_{av.}$ = 86.8°)

1.98 Å for Ru(4) and Ru(5), average 2.06 for Ru(1), Ru(2), and Ru(3)], as might be expected since these bonds are derived from the wing-tip ruthenium atoms which are seen to be shorter in the parent complex and in $[Ru_5C(CO)_{15}(NCMe)]$. There are three carbonyls attached to each ruthenium except Ru(3) to which only two carbonyls are bonded. The bond parameters of the carbonyls all fall in the normal range for terminal carbonyl ligands [Ru–C, 1.84(2)—1.93(2); C–O, 1.11(2)—1.18(2); Ru–C–O, 173.7(15)—179.5(14)°].

CO *Elimination Reactions*.—The gold halide adducts are observed to eliminate carbon monoxide as evidenced by the crystallographic determination of $[Ru_5(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$. These reactions are outlined in the Scheme. The ease of CO loss is dependent on the halide. For bromine, the reaction is essentially complete after 28 h in CH_2Cl_2 at room temperature. The chloro-complex does not eliminate CO under the same conditions but will do so in 15 min in heptane at 70 °C. This process is reversible and $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ is regenerated if CO is passed through the hot solution.

As has been described earlier, HX (X = Cl or Br) reacts with the pentanuclear ruthenium carbide to produce adducts of the form $[Ru_5C(CO)_{15}(H)X]$ which are postulated as having the *arachno*-pentagonal bipyramidal geometry based on $\nu(Ru\text{-}C_{carbide})$.[2] At the time of the report it was not known that these complexes eliminate CO, but in the light of the ease with which the gold halide complexes eliminate CO, the possibility was examined. For $[Ru_5C(CO)_{15}(H)X]$ where X = Cl simple heating in nonane at 90 °C for 5 min reconverted the adduct into $[Ru_5C(CO)_{15}]$; however, $[Ru_5C(CO)_{14}(H)Cl]$ was obtained when HCl gas was bubbled through the heated solution. For X = Br, the reaction to form $[Ru_5C(CO)_{14}(H)Br]$ was essentially complete after 18 h in refluxing CH_2Cl_2 or after 45 min in refluxing hexane. In the case of X = I, the 15 carbonyl-containing product could not be obtained, but addition of HI to the pentaruthenium carbide resulted in the immediate formation of $[Ru_5C(CO)_{14}(H)I]$. The ease of conversion to the 14 carbonyl-containing derivative seems to be dependent on the size and electronegativity of the X group



Scheme.

is not symmetrically positioned. The gold atom is closer to the ruthenium to which the bromide is also bonded [Ru(2)–Au(1), 2.850; Ru(3)–Au(1), 2.633 Å]. If the gold is assumed to be *sp* hybridized, then it also appears that that orbital is directed more towards Ru(3) than to Ru(2) as determined by the positioning of the phosphine ligand [P(1)–Au(1)–Ru(2), 137.2(1); P(1)–Au(1)–Ru(3), 157.5(1)°]. The bromide is also asymmetrically situated, being closer to Ru(1) than Ru(3) [2.615(1) *versus* 2.655(1) Å]. The carbide is bonded to all five ruthenium, and the Ru–C distances for Ru(4) and Ru(5) are slightly shorter than those to the remaining metals [average

and follows the order I > Br > Cl, in a fashion similar to that observed for the gold halide adducts. In fact when $[Ru_5C(CO)_{14}(H)I]$ is heated in nonane at 110 °C for 1 h a new complex results which is proposed to be $[Ru_5C(CO)_{13}(H)I]$ based on its mass spectrum, and the i.r. pattern is similar to that of $[Ru_5C(CO)_{13}(H)(SC_2H_5)]$ whose structure was recently determined and will be reported elsewhere. The exact nature of this compound is still, therefore, under investigation. Iodine also forms an adduct with the pentaruthenium carbide, which mass spectroscopy indicates to be $[Ru_5C(CO)_{14}I_2]$. Because the carbonyls are so readily lost from these complexes, it is

Table 2. Atom co-ordinates ($\times 10^4$) for $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$

	Molecule A				Molecule B		
Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Au(1A)	8 126(1)	3 800(1)	4 068(1)	Au(1B)	1 756(1)	6 039(1)	716(1)
Ru(1A)	6 215(2)	8 081(1)	3 766(1)	Ru(1B)	4 308(1)	1 912(1)	1 399(1)
Ru(2A)	8 280(1)	5 415(1)	3 647(1)	Ru(2B)	2 057(1)	4 490(1)	1 583(1)
Ru(3A)	6 438(1)	5 558(1)	4 260(1)	Ru(3B)	3 212(1)	4 227(2)	246(1)
Ru(4A)	6 541(1)	6 436(1)	2 929(1)	Ru(4B)	4 128(1)	3 795(1)	1 557(1)
Ru(5A)	7 200(1)	6 694(1)	4 833(1)	Ru(5B)	2 540(1)	2 886(1)	670(1)
P(1A)	8 911(4)	2 207(4)	4 339(3)	P(1B)	1 036(5)	7 636(5)	445(4)
C(1A1)	10 251(7)	1 592(9)	4 083(8)	C(1B1)	1 437(12)	8 310(12)	963(8)
C(1A2)	10 598(7)	1 886(9)	3 484(8)	C(1B2)	2 443(12)	7 940(12)	1 028(8)
C(1A3)	11 594(7)	1 436(9)	3 320(8)	C(1B3)	2 815(12)	8 437(12)	1 406(8)
C(1A4)	12 245(7)	693(9)	3 755(8)	C(1B4)	2 181(12)	9 303(12)	1 719(8)
C(1A5)	11 898(7)	399(9)	4 354(8)	C(1B5)	1 174(12)	9 673(12)	1 654(8)
C(1A6)	10 902(7)	849(9)	4 518(8)	C(1B6)	802(12)	9 176(12)	1 276(8)
C(2A1)	8 446(10)	1 487(10)	3 980(7)	C(2B1)	1 287(11)	7 883(12)	−484(7)
C(2A2)	7 432(10)	1 904(10)	3 937(7)	C(2B2)	1 196(11)	7 349(12)	−1 025(7)
C(2A3)	6 998(10)	1 375(10)	3 693(7)	C(2B3)	1 342(11)	7 544(12)	−1 733(7)
C(2A4)	7 576(10)	429(10)	3 491(7)	C(2B4)	1 579(11)	8 273(12)	−1 900(7)
C(2A5)	8 590(10)	13(10)	3 534(7)	C(2B5)	1 670(11)	8 807(12)	−1 359(7)
C(2A6)	9 025(10)	541(10)	3 779(7)	C(2B6)	1 523(11)	8 613(12)	−651(7)
C(3A1)	8 787(11)	2 079(11)	5 312(6)	C(3B1)	−300(8)	8 243(10)	632(10)
C(3A2)	9 292(11)	2 402(11)	5 734(6)	C(3B2)	−695(8)	8 130(10)	1 280(10)
C(3A3)	9 220(11)	2 357(11)	6 474(6)	C(3B3)	−1 698(8)	8 646(10)	1 410(10)
C(3A4)	8 643(11)	1 988(11)	6 791(6)	C(3B4)	−2 306(8)	9 275(10)	890(10)
C(3A5)	8 138(11)	1 665(1)	6 369(6)	C(3B5)	−1 911(8)	9 388(10)	242(10)
C(3A6)	8 210(11)	1 711(11)	5 629(6)	C(3B6)	−907(8)	8 872(10)	113(10)
C(1A)	6 881(15)	6 519(15)	3 884(12)	C(1B)	3 346(15)	3 322(15)	1 122(12)
C(11A)	4 992(17)	8 333(17)	4 132(13)	C(11B)	5 173(17)	1 652(18)	509(14)
C(12A)	6 111(17)	9 096(17)	4 345(13)	C(12B)	5 379(18)	1 365(19)	1 907(15)
C(13A)	5 684(17)	8 885(17)	2 970(14)	C(13B)	4 220(18)	788(19)	1 239(15)
C(21A)	9 213(18)	4 741(18)	4 237(14)	C(21B)	2 005(17)	5 454(18)	2 169(14)
C(22A)	9 041(16)	6 023(16)	3 300(13)	C(22B)	669(15)	5 121(15)	1 425(12)
C(23A)	8 788(16)	4 589(16)	2 860(12)	C(23B)	1 698(15)	3 965(15)	2 412(11)
C(31A)	6 622(15)	4 885(16)	5 115(12)	C(31B)	3 651(17)	5 177(17)	132(13)
C(32A)	5 128(17)	6 314(17)	4 587(13)	C(32B)	4 188(19)	3 453(19)	−432(15)
C(33A)	6 117(15)	4 745(15)	3 791(12)	C(33B)	2 274(17)	4 680(17)	−459(13)
C(41A)	5 212(18)	7 129(19)	2 777(14)	C(41B)	4 586(19)	6 732(19)	−1 290(15)
C(42A)	7 067(16)	6 889(17)	2 120(13)	C(42B)	4 253(17)	3 608(17)	2 549(13)
C(43A)	6 713(17)	5 419(17)	2 405(14)	C(43B)	4 098(16)	5 040(16)	1 643(13)
C(51A)	7 843(17)	5 791(17)	5 534(13)	C(51B)	2 040(16)	2 184(17)	1 221(13)
C(52A)	6 113(16)	7 560(16)	5 521(13)	C(52B)	1 341(17)	3 506(17)	278(13)
C(53A)	8 014(16)	7 279(16)	4 914(13)	C(53B)	6 773(19)	7 981(20)	117(15)
O(11A)	4 224(11)	8 483(12)	4 350(10)	O(11B)	5 713(13)	1 460(14)	101(10)
O(12A)	6 115(13)	9 650(12)	4 706(10)	O(12B)	6 041(13)	1 096(14)	2 279(10)
O(13A)	5 391(16)	9 363(14)	2 506(12)	O(13B)	4 169(14)	78(14)	1 253(11)
O(21A)	9 890(11)	4 239(11)	4 596(9)	O(21B)	2 000(16)	6 013(15)	2 550(11)
O(22A)	9 680(11)	6 166(12)	3 096(10)	O(22B)	−132(11)	5 459(14)	1 406(10)
O(23A)	9 145(12)	4 132(11)	2 337(9)	O(23B)	1 320(11)	3 773(12)	2 883(9)
O(31A)	6 677(13)	4 529(12)	5 675(8)	O(31B)	3 985(12)	5 657(12)	−51(12)
O(32A)	4 331(10)	6 727(11)	4 816(12)	O(32B)	4 692(14)	3 003(16)	−918(10)
O(33A)	5 837(13)	4 315(14)	3 479(11)	O(33B)	1 705(12)	4 907(13)	−869(9)
O(41A)	4 417(12)	7 501(15)	2 677(11)	O(41B)	6 250(12)	2 897(14)	1 091(13)
O(42A)	7 447(13)	7 106(13)	1 665(9)	O(42B)	4 329(15)	3 490(14)	3 145(9)
O(43A)	6 796(13)	4 725(13)	2 060(10)	O(43B)	4 085(14)	5 706(12)	1 689(12)
O(51A)	8 247(14)	5 184(13)	5 933(10)	O(51B)	1 670(14)	1 801(14)	1 506(10)
O(52A)	5 506(11)	8 072(13)	5 885(9)	O(52B)	573(12)	3 867(13)	43(11)
O(53A)	8 530(12)	7 600(12)	4 893(10)	O(53B)	6 308(13)	8 534(14)	529(11)
Cl(1A)	7 711(5)	8 050(5)	3 244(4)	Cl(1B)	3 422(5)	2 032(5)	2 547(4)

possible that the complex actually contains 15 carbonyls but loses one in the mass spectroscopy probe. Comparison with the results for the reaction with HI tends to favour the immediate formation of the 14 carbonyl derivative in this instance, however. This reaction is also under further investigation. In contrast, when chlorine or bromine is used in these systems cluster degradation results to give $[Ru_2(CO)_6X_2]$ (X = Cl or Br).

The ability of the halide to exist as a one- or three-electron donor ligand affords a potentially vacant site on the cluster

Table 3. Bond lengths (Å) for $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$

Molecule A		Molecule B	
Au(1A)-Ru(2A)	2.774(4)	Au(1B)-Ru(2B)	2.764(3)
Au(1A)-Ru(3A)	2.811(3)	Au(1B)-Ru(3B)	2.841(3)
Au(1A)-P(1A)	2.277(6)	Au(1B)-P(1B)	2.283(7)
P(1A)-C(1A1)	1.89(1)	P(1B)-C(1B1)	1.79(2)
P(1A)-C(2A1)	1.77(2)	P(1B)-C(2B1)	1.85(2)
P(1A)-C(3A1)	1.85(1)	P(1B)-C(3B1)	1.86(1)
Ru(1A)-Ru(4A)	2.915(4)	Ru(1B)-Ru(4B)	2.890(4)
Ru(1A)-Ru(5A)	2.819(4)	Ru(1B)-Ru(5B)	2.810(4)
Ru(2A)-Ru(3A)	2.965(4)	Ru(2B)-Ru(3B)	2.970(4)
Ru(2A)-Ru(4A)	2.772(4)	Ru(2B)-Ru(4B)	2.867(4)
Ru(2A)-Ru(5A)	2.961(4)	Ru(2B)-Ru(5B)	2.895(4)
Ru(3A)-Ru(4A)	2.866(4)	Ru(3B)-Ru(4B)	2.785(4)
Ru(3A)-Ru(5A)	2.830(5)	Ru(3B)-Ru(5B)	2.863(5)
Ru(1A)-C(1A)	2.20(2)	Ru(1B)-C(1B)	2.08(2)
Ru(2A)-C(1A)	2.10(2)	Ru(2B)-C(1B)	2.17(2)
Ru(3A)-C(1A)	2.05(3)	Ru(3B)-C(1B)	2.10(2)
Ru(4A)-C(1A)	1.91(2)	Ru(4B)-C(1B)	1.91(3)
Ru(5A)-C(1A)	1.93(2)	Ru(5B)-C(1B)	1.92(3)
Ru(1A)-C(11A)	1.86(3)	Ru(1B)-C(11B)	2.04(3)
Ru(1A)-C(12A)	1.91(3)	Ru(1B)-C(12B)	1.76(3)
Ru(1A)-C(13A)	1.87(2)	Ru(1B)-C(13B)	1.88(3)
Ru(2A)-C(21A)	1.74(2)	Ru(2B)-C(21B)	1.88(3)
Ru(2A)-C(22A)	1.94(3)	Ru(2B)-C(22B)	1.93(3)
Ru(2A)-C(23A)	1.90(2)	Ru(2B)-C(23B)	1.94(2)
Ru(3A)-C(31A)	1.86(2)	Ru(3B)-C(31B)	1.93(3)
Ru(3A)-C(32A)	1.91(2)	Ru(3B)-C(32B)	1.91(3)
Ru(3A)-C(33A)	1.84(3)	Ru(3B)-C(33B)	1.86(2)
Ru(4A)-C(41A)	1.85(3)	Ru(4B)-C(41B)	1.83(3)
Ru(4A)-C(42A)	1.98(3)	Ru(4B)-C(42B)	1.88(3)
Ru(4A)-C(43A)	1.82(3)	Ru(4B)-C(43B)	1.97(3)
Ru(5A)-C(51A)	1.84(2)	Ru(5B)-C(51B)	1.90(3)
Ru(5A)-C(52A)	2.05(2)	Ru(5B)-C(52B)	1.81(2)
Ru(5A)-C(53A)	1.90(3)	Ru(5B)-C(53B)	1.97(3)
C(11A)-O(11A)	1.17(3)	C(11B)-O(11B)	1.06(3)
C(12A)-O(12A)	1.13(4)	C(12B)-O(12B)	1.16(3)
C(13A)-O(13A)	1.10(3)	C(13B)-O(13B)	1.17(4)
C(21A)-O(21A)	1.19(3)	C(21B)-O(21B)	1.15(4)
C(22A)-O(22A)	1.17(4)	C(22B)-O(22B)	1.10(3)
C(23A)-O(23A)	1.120(3)	C(23B)-O(23B)	1.16(3)
C(31A)-O(31A)	1.17(3)	C(31B)-O(31B)	1.15(4)
C(32A)-O(32A)	1.17(3)	C(32B)-O(32B)	1.20(3)
C(33A)-O(33A)	1.15(4)	C(33B)-O(33B)	1.11(3)
C(41A)-O(41A)	1.11(3)	C(41B)-O(41B)	1.20(3)
C(42A)-O(42A)	1.16(3)	C(42B)-O(42B)	1.13(3)
C(43A)-O(43A)	1.215(4)	C(43B)-O(43B)	1.05(4)
C(51A)-O(51A)	1.14(3)	C(51B)-O(51B)	1.13(4)
C(52A)-O(52A)	1.14(3)	C(52B)-O(52B)	1.15(3)
C(53A)-O(53A)	1.13(4)	C(53B)-O(53B)	1.14(3)
Ru(1A)-Cl(1A)	2.48(1)	Ru(1B)-Cl(1B)	2.49(1)

as evidenced by the ease with which the original complex can be regenerated on addition of CO. Bound halide may therefore function as a promoter of ligand replacement reactions. The metal framework is obviously flexible, and this may, in part, arise from the stabilization of the carbido-carbon atom.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using carbon monoxide as calibrant, and n.m.r. spectra were obtained on a Varian XL100 or Bruker WM250 spectrometer with $SiMe_4$ as standard for ^1H and $P(OMe)_3$ for ^{31}P spectra. Mass spectra were recorded on an A.E.I. MS 12 spectrometer using tris(perfluoroheptyl)-*s*-triazine as calibrant.

Ruthenium trichloride and tetrachloroauric acid were supplied by Johnson Matthey and Co. Ltd. The complex $[Ru_6C(CO)_{17}]$ was prepared by the literature method.[7] Triphenylphosphinegold(I) chloride was prepared by the reaction of triphenylphosphine with $HAuCl_4$ in acetone. Triphenylphosphinegold(I) bromide was prepared by passing a stream of HBr gas through a stirred solution of triphenylphosphinegold(I) chloride in dichloromethane for 30 min. Purification of the $[Au(PPh_3)Br]$ was achieved by evaporation of the solvent followed by washing with dichloromethane until the solid produced was colourless. The compound $[Ru_5C(CO)_{15}]$ was synthesized as described elsewhere.[3] Reactions were performed under nitrogen in reagent grade solvents. Infrared data for all complexes are given in Table 8.

Preparations.—$[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}X]$ (X = Cl *or* Br). To a stirred solution of $[Ru_5C(CO)_{15}]$ (50 mg, 0.053 mmol) in CH_2Cl_2 (30 cm^3) was added $[Au(PPh_3)Cl]$ (27 mg, 0.054 mmol), yielding a yellow solution of the adduct $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$. Evaporation to dryness followed by recrystallization from dichloromethane–hexane by slow evaporation at 0 °C yielded yellow crystals of the adduct (Found: C, 28.7; H, 1.3; Cl, 4.0; P, 2.4. Calc. for $C_{34}H_{15}AuClO_{15}PRu_5$: C, 28.5; H, 1.0; Cl, 4.0; P, 2.2%). The bromide derivative was prepared similarly.

$[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$. To a stirred solution of $[Ru_5C(CO)_{15}]$ (10 mg, 0.11 mmol) in dichloromethane (10 cm^3) was added $[Au(PPh_3)Br]$ (6 mg, 0.011 mmol) giving a yellow solution of the adduct $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Br]$. Nitrogen was bubbled through the dichloromethane solution with stirring and a slow colour change of yellow to orange was observed. The reaction was monitored by i.r. spectroscopy, and complete conversion to the fourteen carbonyl-containing product was observed after 28 h. Evaporation of the solution to dryness followed by recrystallization from dichloromethane–hexane by slow evaporation at 0 °C yielded dark orange crystals of $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ (Found: C, 28.15; H, 1.50; Br, 6.05; P, 2.10. Calc. for $C_{33}H_{15}AuBrO_{14}PRu_5$: C, 27.35; H, 1.05; Br, 5.50; P, 2.15%). For X = Cl, no reaction was observed when nitrogen was bubbled through a solution of the 15 carbonyl-containing parent for 21 h. Conversion to $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Cl)]$ was effected in refluxing hexane for 15 min.

$[Ru_5C(CO)_{15}I_2]$. To a solution of $[Ru_5C(CO)_{15}]$ (10 mg, 0.011 mmol) in dichloromethane was added a solution of I_2 (2.7 mg, 0.011 mmol) in cyclohexane (2.7 cm^3), yielding a brown solution. Evaporation of the solution by nitrogen gave a brown solid. Mass spectrum: highest mass *m/e* 1 163, mass of $[Ru_5C(CO)_{15}I_2]$ (for Ru = 101 mass units) 1 163 mass units; lowest mass *m/e* 517, mass of Ru_5C 517 mass units (Found: C, 20.8; I, 22.7 Calc. for $C_{15}I_2O_{15}Ru_5$: C, 16.1; I, 21.3%).

$[Ru_5C(CO)_{15}(H)X]$ (X = Cl *or* Br). For X = Cl, a steady stream of HCl gas was bubbled through a stirred solution of $[Ru_5C(CO)_{15}]$ (20 mg) in dichloromethane (20 cm^3) for 30 s. Evaporation of the yellow solution to dryness yielded a yellow solid $[Ru_5C(CO)_{15}(H)Cl]$ (20.5 mg, 98.5%). Mass spectrum: highest mass *m/e* 946, mass of $[Ru_5C(CO)_{15}(H)Cl]$ (for Ru = 101 mass units) 946 mass units; lowest mass *m/e* 517, for Ru_5C (Found: C, 20.9; H, 0.95; Cl, 3.85. Calc. for $C_{16}HClO_{15}Ru_5$: C, 19.7; H, 0.001; Cl, 3.65%). ^1H N.m.r. (−89 and 25 °C): δ −22.1 p.p.m. For X = Br, the reaction was carried out similarly giving $[Ru_5C(CO)_{15}(H)Br]$. Mass spectrum: highest mass *m/e* 1 099 corresponding to $[Ru_5C(CO)_{15}(H)Br_2]$, and the lowest mass seen at *m/e* 517 corresponds to Ru_5C (Found: C, 18.2; H, 0.45. Calc. for $C_{16}HBrO_{15}Ru_5$: C, 18.8; H, 0.001%).

$[Ru_5C(CO)_{14}(H)Br]$. When nitrogen was bubbled through a

Table 4. Bond angles (°) for $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$

Molecule A		Molecule B		Molecule A		Molecule B	
Ru(2A)–Au(1A)–Ru(3A)	64.1(5)	Ru(3B)–Au(1B)–Ru(2B)	64.0(1)	Ru(5A)–Ru(3A)–C(32A)	96.5(9)	Ru(5B)–Ru(3B)–C(32B)	98.2(10)
Ru(2A)–Au(1A)–P(1A)	147.5(2)	Ru(2B)–Au(1B)–P(1B)	153.0(2)	Ru(2A)–Ru(3A)–C(33A)	109.3(7)	Ru(2B)–Ru(3B)–C(33B)	103.8(8)
Ru(3A)–Au(1A)–P(1A)	146.6(2)	Ru(3B)–Au(1B)–P(1B)	142.9(2)	Ru(4A)–Ru(3A)–C(33A)	90.0(7)	Ru(4B)–Ru(3B)–C(33B)	163.1(7)
Au(1A)–Ru(2A)–Ru(3A)	58.5(1)	Au(1B)–Ru(2B)–Ru(3B)	59.3(1)	Ru(5A)–Ru(3A)–C(33A)	170.7(7)	Ru(5B)–Ru(3B)–C(33B)	88.4(10)
Au(1A)–Ru(2A)–Ru(4A)	100.5(1)	Au(1B)–Ru(2B)–Ru(4B)	91.9(1)	Ru(1A)–Ru(4A)–C(41A)	83.6(10)	Ru(1B)–Ru(4B)–C(41B)	86.6(11)
Au(1A)–Ru(2A)–Ru(5A)	99.9(1)	Au(1B)–Ru(2B)–Ru(5B)	107.4(1)	Ru(2A)–Ru(4A)–C(41A)	159.5(8)	Ru(2B)–Ru(4B)–C(41B)	164.1(10)
Au(1A)–Ru(3A)–Ru(2A)	57.3(1)	Au(1B)–Ru(3B)–Ru(2B)	56.7(1)	Ru(3A)–Ru4(A)–C(41A)	97.5(9)	Ru(3B)–Ru(4B)–C(41B)	101.8(9)
Au(1A)–Ru(3A)–Ru(4A)	97.4(1)	Au(1B)–Ru(3B)–Ru(4B)	92.0(1)	Ru(1A)–Ru(4A)–C(42A)	91.3(8)	Ru(1B)–Ru(4B)–C(42B)	90.8(9)
Au(1A)–Ru(3A)–Ru(5A)	102.2(1)	Au(1B)–Ru(3B)–Ru(5B)	106.1(1)	Ru(2A)–Ru(4A)–C(42A)	97.3(6)	Ru(2B)–Ru(4B)–C(42B)	94.4(8)
Ru(4A)–Ru(1A)–Ru(5A)	84.0(1)	Ru(5B)–Ru(1B)–Ru(4B)	84.4(1)	Ru(3A)–Ru(4A)–C(42A)	160.6(7)	Ru(3B)–Ru(4B)–C(42B)	157.7(8)
Ru(3A)–Ru(2A)–Ru(4A)	59.8(1)	Ru(3B)–Ru(2B)–Ru(4B)	57.0(1)	Ru(1A)–Ru(4A)–C(43A)	178.6(8)	Ru(1B)–Ru(4B)–C(43B)	176.1(7)
Ru(3A)–Ru(2A)–Ru(5A)	57.1(1)	Ru(3B)–Ru(2B)–Ru(5B)	58.4(1)	Ru(2A)–Ru(4A)–C(43A)	93.8(7)	Ru(2B)–Ru(4B)–C(43B)	97.0(6)
Ru(2A)–Ru(3A)–Ru(4A)	56.7(1)	Ru(2B)–Ru(3B)–Ru(4B)	59.6(1)	Ru(1A)–Ru(5A)–C(51A)	179.7(5)	Ru(1B)–Ru(5B)–C(51B)	89.0(7)
Ru(2A)–Ru(3A)–Ru(5A)	61.4(1)	Ru(2B)–Ru(3B)–Ru(5B)	59.5(1)	Ru(2A)–Ru(5A)–C(51A)	94.6(7)	Ru(2B)–Ru(5B)–C(51B)	101.0(7)
Ru(4A)–Ru(3A)–Ru(5A)	84.7(1)	Ru(5B)–Ru(3B)–Ru(4B)	85.4(1)	Ru(3A)–Ru(5A)–C(51A)	91.9(10)	Ru(3B)–Ru(5B)–C(51B)	162.5(8)
Ru(1A)–Ru(4A)–Ru(2A)	87.4(1)	Ru(1B)–Ru(4B)–Ru(2B)	86.7(1)	Ru(1A)–Ru(5A)–C(52A)	87.0(6)	Ru(1B)–Ru(5B)–C(52B)	174.5(8)
Ru(1A)–Ru(4A)–Ru(3A)	85.8(1)	Ru(1B)–Ru(4B)–Ru(3B)	85.8(1)	Ru(2A)–Ru(5A)–C(52A)	163.1(8)	Ru(2B)–Ru(5B)–C(52B)	90.3(8)
Ru(2A)–Ru(4A)–Ru(3A)	63.4(1)	Ru(3B)–Ru(4B)–Ru(2B)	63.4(1)	Ru(3A)–Ru(5A)–C(52A)	103.1(8)	Ru(3B)–Ru(5B)–C(52B)	97.7(10)
Ru(1A)–Ru(5A)–Ru(2A)	85.7(1)	Ru(1B)–Ru(5B)–Ru(2B)	87.7(1)	Ru(1A)–Ru(5A)–C(53A)	86.6(7)	Ru(1B)–Ru(5B)–C(53B)	85.8(8)
Ru(1A)–Ru(5A)–Ru(3A)	88.4(1)	Ru(1B)–Ru(5B)–Ru(3B)	85.9(1)	Ru(2A)–Ru(5A)–C(53A)	97.3(7)	Ru(2B)–Ru(5B)–C(53B)	155.4(11)
Ru(2A)–Ru(5A)–Ru(3A)	61.5(1)	Ru(3B)–Ru(5B)–Ru(2B)	62.1(1)	Ru(3A)–Ru(5A)–C(53A)	158.6(7)	Ru(3B)–Ru(5B)–C(53B)	93.7(11)
Ru(4A)–Ru(1A)–C(1A)	41.0(6)	Ru(4B)–Ru(1B)–C(1B)	41.4(8)	C(1A)–Ru(1A)–C(11A)	96.1(10)	C(1B)–Ru(1B)–C(11B)	95.5(9)
Ru(5A)–Ru(1A)–C(1A)	43.0(6)	Ru(5B)–Ru(1B)–C(1B)	43.1(8)	C(1A)–Ru(1A)–C(12A)	135.3(9)	C(1B)–Ru(1B)–C(12B)	133.9(13)
Ru(3A)–Ru(2A)–C(1A)	43.7(8)	Ru(3B)–Ru(2B)–C(1B)	45.0(6)	C(1A)–Ru(1A)–C(13A)	130.8(10)	C(1B)–Ru(1B)–C(13B)	129.5(11)
Ru(4A)–Ru(2A)–C(1A)	43.5(6)	Ru(4B)–Ru(2B)–C(1B)	41.8(7)	C(1A)–Ru(2A)–C(21A)	127.8(10)	C(1B)–Ru(2B)–C(21B)	123(10)
Ru(5A)–Ru(2A)–C(1A)	40.5(6)	Ru(5B)–Ru(2B)–C(1B)	41.5(7)	C(1A)–Ru(2A)–C(22A)	106.4(10)	C(1B)–Ru(2B)–C(22B)	137.1(10)
Ru(2A)–Ru(3A)–C(1A)	45.0(5)	Ru(2B)–Ru(3B)–C(1B)	46.8(5)	C(1A)–Ru(2A)–C(23A)	132.2(9)	C(1B)–Ru(2B)–C(23B)	106.4(8)
Ru(4A)–Ru(3A)–C(1A)	41.8(7)	Ru(4B)–Ru(3B)–C(1B)	43.3(7)	C(1A)–Ru(3A)–C(31A)	132.9(11)	C(1B)–Ru(3B)–C(31B)	129.4(10)
Ru(5A)–Ru(3A)–C(1A)	42.9(7)	Ru(5B)–Ru(3B)–C(1B)	42.1(7)	C(1A)–Ru(3A)–C(32A)	105.2(10)	C(1B)–Ru(3B)–C(32B)	106.1(10)
Ru(1A)–Ru(4A)–C(1A)	48.9(7)	Ru(1B)–Ru(4B)–C(1B)	46.0(6)	C(1A)–Ru(3A)–C(33A)	131.2(10)	C(1B)–Ru(3B)–C(33B)	128.8(12)
Ru(2A)–Ru(4A)–C(1A)	49.0(5)	Ru(2B)–Ru(4B)–C(1B)	49.1(5)	C(1A)–Ru(4A)–C(41A)	112.7(10)	C(1B)–Ru(4B)–C(41B)	117.5(12)
Ru(3A)–Ru(4A)–C(1A)	45.6(8)	Ru(3B)–Ru(4B)–C(1B)	49.0(7)	C(1A)–Ru(4A)–C(42A)	120.6(12)	C(1B)–Ru(4B)–C(42B)	115.3(12)
Ru(1A)–Ru(5A)–C(1A)	51.0(7)	Ru(1B)–Ru(5B)–C(1B)	47.8(6)	C(1A)–Ru(4A)–C(43A)	131.7(10)	C(1B)–Ru(4B)–C(43B)	136.6(9)
Ru(2A)–Ru(5A)–C(1A)	44.9(5)	Ru(2B)–Ru(5B)–C(1B)	48.5(5)	C(1A)–Ru(5A)–C(51A)	129.3(11)	C(1B)–Ru(5B)–C(51B)	118.9(11)
Ru(3A)–Ru(5A)–C(1A)	46.4(8)	Ru(3B)–Ru(5B)–C(1B)	47.2(7)	C(1A)–Ru(5A)–C(52A)	120.0(9)	C(1B)–Ru(5B)–C(52B)	132.9(11)
Ru(1A)–C(1A)–Ru(2A)	132.7(13)	Ru(1B)–C(1B)–Ru(2B)	136.9(12)	C(1A)–Ru(5A)–C(53A)	116.8(11)	C(1B)–Ru(5B)–C(53B)	112.3(12)
Ru(1A)–C(1A)–Ru(3A)	136.0(10)	Ru(1B)–C(1B)–Ru(2B)	134.9(10)	C(11A)–Ru(1A)–C(12A)	86.6(12)	C(11B)–Ru(1B)–C(12B)	88.2(11)
Ru(2A)–C(1A)–Ru(3A)	91.3(9)	Ru(3B)–C(1B)–Ru(2B)	88.2(7)	C(11A)–Ru(1A)–C(13A)	92.9(11)	C(11B)–Ru(1B)–C(13B)	89.4(12)
Ru(1A)–C(1A)–Ru(4A)	90.1(8)	Ru(1B)–C(1B)–Ru(4B)	92.6(9)	C(12A)–Ru(1A)–C(13A)	93.4(11)	C(12B)–Ru(1B)–C(13B)	96.4(13)
Ru(2A)–C(1A)–Ru(4A)	87.4(8)	Ru(2B)–C(1B)–Ru(4B)	89.1(9)	C(21A)–Ru(2A)–C(22A)	88.5(13)	C(21B)–Ru(2B)–C(22B)	94.1(10)
Ru(3A)–C(1A)–Ru(4A)	92.6(12)	Ru(3B)–C(1B)–Ru(4B)	87.7(11)	C(21A)–Ru(2A)–C(23A)	97.4(10)	C(21B)–Ru(2B)–C(23B)	87.7(11)
Ru(1A)–C(1A)–Ru(5A)	86.0(9)	Ru(1B)–C(1B)–Ru(5B)	89.1(10)	C(22A)–Ru(2A)–C(23A)	87.11(1)	C(22B)–Ru(2B)–C(23B)	83.0(9)
Ru(2A)–C(1A)–Ru(5A)	94.7(9)	Ru(2B)–C(1B)–Ru(5B)	90.0(9)	C(31A)–Ru(3A)–C(32A)	85.7(10)	C(31B)–Ru(3B)–C(32B)	89.1(13)
Ru(3A)–C(1A)–Ru(5A)	90.7(9)	Ru(3B)–C(1B)–Ru(5B)	90.7(9)	C(31A)–Ru(3A)–C(33A)	92.9(11)	C(31B)–Ru(3B)–C(33B)	98.2(12)
Ru(4A)–C(1A)–Ru(5A)	176.0(15)	Ru(5B)–C(1B)–Ru(4B)	178.2(11)	C(32A)–Ru(3A)–C(33A)	92.2(11)	C(32B)–Ru(3B)–C(33B)	90.4(10)
Ru(4A)–Ru(1A)–Cl(1A)	90.4(2)	Ru(4B)–Ru(1B)–Cl(1B)	91.6(2)	C(41A)–Ru(4A)–C(42A)	101.2(11)	C(42B)–Ru(4B)–C(41B)	100.0(11)

Table 4 (*continued*)

Molecule A		Molecule B		Molecule A		Molecule B	
Ru(5A)–Ru(1A)–Cl(1A)	95.0(2)	Ru(5B)–Ru(1B)–Cl(1B)	91.3(2)	C(41A)–Ru(4A)–C(43A)	95.1(12)	C(43B)–Ru(4B)–C(41B)	89.5(12)
C(1A)–Ru(1A)–Cl(1A)	93.9(7)	C(1B)–Ru(1B)–Cl(1B)	91.7(6)	C(42A)–Ru(4A)–C(43A)	89.3(12)	C(42B)–Ru(4B)–C(43B)	90.0(11)
C(11A)–Ru(1A)–Cl(1A)	170.0(8)	C(11B)–Ru(1B)–Cl(1B)	172.6(6)	C(51A)–Ru(5A)–C(52A)	92.8(9)	C(51B)–Ru(5B)–C(52B)	86.3(11)
C(12A)–Ru(1A)–Cl(1A)	86.7(9)	C(12B)–Ru(1B)–Cl(1B)	85.7(9)	C(51A)–Ru(5A)–C(53A)	93.3(12)	C(51B)–Ru(5B)–C(53B)	102.6(13)
C(13A)–Ru(1A)–Cl(1A)	80.1(9)	C(13B)–Ru(1B)–Cl(1B)	87.2(9)	C(52A)–Ru(5A)–C(53A)	97.4(11)	C(52B)–Ru(5B)–C(53B)	98.1(11)
Au(1A)–Ru(2A)–C(1A)	102.3(8)	Au(1B)–Ru(2B)–C(1B)	103.6(6)	Ru(1A)–C(11A)–O(11A)	178.8(15)	Ru(1B)–C(11B)–O(11B)	171.2(22)
Au(1A)–Ru(3A)–C(1A)	102.3(5)	Au(1B)–Ru(3B)–C(1B)	102.8(5)	Ru(1A)–C(12A)–O(12A)	174.9(20)	Ru(1B)–C(12B)–O(12B)	172.8(26)
Au(1A)–Ru(2A)–C(21A)	71.2(11)	Au(1B)–Ru(2B)–C(21B)	72.5(8)	Ru(1A)–C(13A)–O(13A)	178.0(31)	Ru(1B)–C(13B)–O(13B)	171.3(24)
Au(1A)–Ru(2A)–C(22A)	151.1(6)	Au(1B)–Ru(2B)–C(22B)	76.3(8)	Ru(2A)–C(21A)–O(21A)	174.9(20)	Ru(2B)–C(21B)–O(21B)	176.9(22)
Au(1A)–Ru(2A)–C(23A)	75.7(8)	Au(1B)–Ru(2B)–C(23B)	150.0(5)	Ru(2A)–C(22A)–O(22A)	163.6(17)	Ru(2B)–C(22B)–O(22B)	172.8(21)
Au(1A)–Ru(3A)–C(31A)	73.9(6)	Au(1B)–Ru(3B)–C(31B)	69.0(6)	Ru(2A)–C(23A)–O(23A)	173.1(25)	Ru(2B)–C(23B)–O(23B)	168.1(15)
Au(1A)–Ru(3A)–C(32A)	152.4(9)	Au(1B)–Ru(3B)–C(32B)	150.8(9)	Ru(3A)–C(31A)–O(31A)	174.5(17)	Ru(3B)–C(31B)–O(31B)	167.4(21)
Au(1A)–Ru(3A)–C(33A)	70.8(5)	Au(1B)–Ru(3B)–C(33B)	74.6(8)	Ru(3A)–C(32A)–O(32A)	175.4(22)	Ru(3B)–C(32B)–O(32B)	170.9(23)
Ru(4A)–Ru(1A)–C(11A)	96.7(9)	Ru(4B)–Ru(1B)–C(11B)	92.8(9)	Ru(3A)–C(33A)–O(33A)	173.4(15)	Ru(3B)–C(33B)–O(33B)	175.9(27)
Ru(5A)–Ru(1A)–C(11A)	92.7(7)	Ru(5B)–Ru(1B)–C(11B)	95.0(7)	Ru(4A)–C(41A)–O(41A)	176.4(28)	Ru(4B)–C(41B)–O(41B)	176.8(32)
Ru(4A)–Ru(1A)–C(12A)	175.1(6)	Ru(4B)–Ru(1B)–C(12B)	92.6(11)	Ru(4A)–C(42A)–O(42A)	174.7(18)	Ru(4B)–C(42B)–O(42B)	179.6(27)
Ru(5A)–Ru(1A)–C(12A)	92.3(7)	Ru(5B)–Ru(1B)–C(12B)	175.7(8)	Ru(4A)–C(43A)–O(43A)	177.3(23)	Ru(4B)–C(43B)–O(43B)	179.8(28)
Ru(4A)–Ru(1A)–C(13A)	90.0(9)	Ru(4B)–Ru(1B)–C(13B)	170.8(8)	Ru(5A)–C(51)A–O(51A)	175.0(23)	Ru(5B)–C(51B)–O(51B)	173.5(20)
Ru(5A)–Ru(1A)–C(13A)	172.2(7)	Ru(5B)–Ru(1B)–C(13B)	86.4(7)	Ru(5A)–C(52A)–O(52A)	177.1(23)	Ru(5B)–C(52B)–O(52B)	176.9(26)
Ru(3A)–Ru(2A)–C(21A)	107.8(10)	Ru(3B)–Ru(2B)–C(21B)	114.5(9)	Ru(5A)–C(53A)–O(53A)	173.0(21)	Ru(5B)–C(53B)–O(53B)	173.6(22)
Ru(4A)–Ru(2A)–C(21A)	167.7(10)	Ru(4B)–Ru(2B)–C(21B)	85.5(8)	Au(1A)–P(1A)–C(1A1)	114.0(6)	Au(1B)–P(1B)–C(1B1)	114.8(6)
Ru(5A)–Ru(2A)–C(21A)	88.4(8)	Ru(5B)–Ru(2B)–C(21B)	168.8(8)	Au(1A)–P(1A)–C(2A1)	117.5(5)	Au(1B)–P(1B)–C(2B1)	112.5(6)
Ru(3A)–Ru(2A)–C(22A)	150.0(6)	Ru(3B)–Ru(2B)–C(22B)	112.6(7)	Au(1A)–P(1A)–C(3A1)	107.2(5)	Au(1B)–P(1B)–C(3B1)	112.6(7)
Ru(4A)–Ru(2A)–C(22A)	102.3(6)	Ru(4B)–Ru(2B)–C(22B)	167.7(7)	C(1A1)–P(1A)–C(3A1)	109.0(7)	C(1B1)–P(1B)–C(3B1)	102.0(8)
Ru(5A)–Ru(2A)–C(22A)	99.9(7)	Ru(5B)–Ru(2B)–C(22B)	96.7(7)	C(1A1)–P(1A)–C(2A1)	104.6(7)	C(1B1)–P(1B)–C(2B1)	103.9(10)
Ru(3A)–Ru(2A)–C(23A)	114.4(9)	Ru(3B)–Ru(2B)–C(23B)	150.6(6)	C(2A1)–P(1A)–C(3A1)	103.9(9)	C(2B1)–P(1B)–C(3B1)	110.3(8)
Ru(4A)–Ru(2A)–C(23A)	89.2(6)	Ru(4B)–Ru(2B)–C(23B)	109.3(6)	P(1A)–C(1A1)–C(1A2)	121.3(5)	P(1B)–C(1B1)–C(1B2)	116.5(5)
Ru(5A)–Ru(2A)–C(23A)	171.1(8)	Ru(5B)–Ru(2B)–C(23B)	96.3(7)	P(1A)–C(1A1)–C(1A6)	118.6(5)	P(1B)–C(1B1)–C(1B6)	123.5(5)
Ru(2A)–Ru(3A)–C(31A)	112.7(7)	Ru(2B)–Ru(3B)–C(31B)	111.6(7)	P(1A)–C(2A1)–C(2A2)	115.9(4)	P(1B)–C(2B1)–C(2B2)	118.6(7)
Ru(4A)–Ru(3A)–C(31A)	169.3(7)	Ru(4B)–Ru(3B)–C(31B)	86.2(7)	P(1A)–C(2A1)–C(2A6)	124.0(4)	P(1B)–C(2B1)–C(2B6)	121.3(7)
Ru(5A)–Ru(3A)–C(31A)	91.0(9)	Ru(5B)–Ru(3B)–C(31B)	170.1(7)	P(1A)–C(3A1)–C(3A2)	116.1(7)	P(1B)–C(3B1)–C(3B2)	122.3(6)
Ru(2A)–Ru(3A)–C(32A)	150.1(9)	Ru(2B)–Ru(3B)–C(32B)	152.5(7)	P(1A)–C(3A1)–C(3A6)	123.9(7)	P(1B)–C(3B1)–C(3B6)	117.6(6)
Ru(4A)–Ru(3A)–C(32A)	104.4(7)	Ru(4B)–Ru(3B)–C(32B)	106.0(8)				

Table 5. Atom co-ordinates ($\times 10^4$) for $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$

Atom	X/a	Y/b	Z/c
Au(1)	3 420(1)	970(1)	3 285(1)
Ru(1)	1 827(1)	2 212(1)	5 952(1)
Ru(2)	4 481(1)	1 656(1)	4 333(1)
Ru(3)	1 748(1)	1 336(1)	4 495(1)
Ru(4)	3 690(2)	1 418(1)	6 013(1)
Ru(5)	2 329(1)	2 243(1)	4 072(1)
Br(1)	−333(2)	1 650(1)	5 541(1)
C(01)	3 012(15)	1 834(5)	5 045(9)
C(11)	3 410(18)	2 577(6)	6 269(10)
C(12)	1 270(18)	2 156(6)	7 170(11)
C(13)	557(18)	2 701(6)	5 706(11)
C(21)	6 064(18)	2 123(6)	4 784(10)
C(22)	6 269(17)	1 176(6)	4 507(10)
C(23)	5 541(18)	1 739(6)	3 148(11)
C(31)	444(19)	1 336(6)	3 484(11)
C(32)	1 483(20)	728(6)	4 828(11)
C(41)	4 487(18)	835(6)	5 879(11)
C(42)	5 181(17)	1 681(6)	6 792(10)
C(43)	2 436(20)	1 188(7)	6 882(12)
C(51)	2 654(18)	2 186(6)	2 858(10)
C(52)	267(17)	2 390(6)	3 805(10)
C(53)	3 098(18)	2 841(6)	4 155(10)
O(11)	4 415(12)	2 808(4)	6 424(8)
O(12)	1 029(15)	2 110(4)	7 912(7)
O(13)	−121(16)	3 026(5)	5 519(8)
O(21)	6 716(12)	2 421(4)	5 097(8)
O(22)	7 167(13)	908(4)	4 592(9)
O(23)	6 034(13)	1 777(4)	2 465(7)
O(31)	−415(15)	1 357(5)	2 894(8)
O(32)	1 326(17)	357(4)	5 023(9)
O(41)	4 900(15)	466(4)	5 843(8)
O(42)	6 042(16)	1 834(4)	7 251(8)
O(43)	1 652(14)	1 044(5)	7 374(8)
O(51)	2 811(13)	2 172(4)	2 095(7)
O(52)	−932(13)	2 456(6)	3 613(8)
O(53)	3 484(14)	3 221(4)	4 200(8)
P(1)	3 980(5)	534(2)	2 085(3)
C(101)	3 026(13)	727(3)	1 072(8)
C(102)	2 761(13)	457(3)	324(8)
C(103)	1 992(13)	630(3)	−425(8)
C(104)	1 488(13)	1 073(3)	−426(8)
C(105)	1 752(13)	1 344(3)	323(8)
C(106)	2 521(13)	1 171(3)	1 072(8)
C(201)	3 384(11)	−44(4)	2 213(7)
C(202)	3 916(11)	−387(4)	1 679(7)
C(203)	3 344(11)	−821(4)	1 750(7)
C(204)	2 239(11)	−911(4)	2 355(7)
C(205)	1 706(11)	−568(4)	2 889(7)
C(206)	2 279(11)	−134(4)	2 818(7)
C(301)	5 920(14)	502(4)	1 852(7)
C(302)	6 500(14)	686(4)	1 083(7)
C(303)	8 030(14)	668(4)	952(7)
C(304)	8 982(14)	465(4)	1 590(7)
C(305)	8 402(14)	281(4)	2 358(7)
C(306)	6 872(14)	299(4)	2 489(7)

refluxing solution of $[Ru_5C(CO)_{15}(H)Br]$ for 18 h the colour of the solution changed from yellow to orange. The reaction was followed by i.r. spectroscopy. The reaction to give $[Ru_5C(CO)_{14}(H)Br]$ was complete in that time and no further changes were observed upon heating for an additional 4 h. Alternatively $[Ru_5C(CO)_{14}(H)Br]$ was prepared by bubbling nitrogen through a refluxing solution of the 15 carbonyl-containing parent in hexane for 45 min. ^1H N.m.r. δ −28.44 p.p.m.

$[Ru_5C(CO)_{14}(H)I]$. A steady stream of HI gas was bubbled through a solution of $[Ru_5C(CO)_{15}]$ (30 mg) in hexane (60 cm^3) for 40 min, during which time a gradual colour change of red to orange was observed. The reaction was followed by i.r. spectroscopy. At the end of that time, reaction to give $[Ru_5C(CO)_{14}(H)I]$ was complete. No further change was observed in the i.r. spectrum after continued stirring for 2 h. The mass spectrum displayed a parent ion peak at mass 1 037 (for Ru = 101 mass units). Loss of CO was also observed down to the Ru_5C core.

Table 6. Bond lengths (Å) for $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$

Au(1)–Ru(2)	2.850(2)	Au(1)–Ru(3)	2.633(2)
Au(1)–P(1)	2.290(4)	Ru(1)–Ru(3)	3.403(3)
Ru(1)–Ru(4)	2.892(3)	Ru(1)–Ru(5)	2.877(3)
Ru(2)–Ru(3)	2.951(3)	Ru(2)–Ru(4)	2.849(3)
Ru(2)–Ru(5)	2.866(3)	Ru(3)–Ru(4)	2.826(3)
Ru(3)–Ru(5)	2.829(3)	Ru(1)–C(01)	2.09(1)
Ru(2)–C(01)	2.06(1)	Ru(3)–C(01)	2.02(1)
Ru(4)–C(01)	1.99(1)	Ru(5)–C(01)	1.98(1)
Ru(1)–Br(1)	2.615(1)	Ru(3)–Br(1)	2.655(1)
Ru(1)–C(11)	1.84(2)	Ru(1)–C(12)	1.92(2)
Ru(1)–C(13)	1.88(2)	Ru(2)–C(21)	1.88(2)
Ru(2)–C(22)	1.93(2)	Ru(2)–C(23)	1.92(2)
Ru(3)–C(31)	1.88(2)	Ru(3)–C(32)	1.90(2)
Ru(4)–C(41)	1.89(2)	Ru(4)–C(42)	1.91(2)
Ru(4)–C(43)	1.88(2)	Ru(5)–C(51)	1.86(2)
Ru(5)–C(52)	1.93(2)	Ru(5)–C(53)	1.91(2)
C(11)–O(11)	1.15(2)	C(12)–O(12)	1.15(2)
C(13)–O(13)	1.17(2)	C(21)–O(21)	1.15(2)
C(22)–O(22)	1.14(2)	C(23)–O(23)	1.14(2)
C(31)–O(31)	1.15(2)	C(32)–O(32)	1.15(2)
C(41)–O(41)	1.16(2)	C(42)–O(42)	1.11(2)
C(43)–O(43)	1.12(2)	C(51)–O(51)	1.16(2)
C(52)–O(52)	1.12(2)	C(53)–O(53)	1.18(2)
P(1)–C(101)	1.81(1)	P(1)–C(201)	1.81(1)
P(1)–C(301)	1.79(1)		

$[Ru_5C(CO)_{14}(H)Cl]$. A steady stream of HCl gas was bubbled through a heptane solution of $[Ru_5C(CO)_{15}(H)Cl]$ at 90 °C. Conversion to $[Ru_5C(CO)_{14}(H)Cl]$ was complete after 1 h.

$[Ru_5C(CO)_{13}(H)I]$. Nitrogen was bubbled through a solution of $[Ru_5C(CO)_{14}(H)I]$ in nonane at 110 °C. A colour change from orange to brown was observed and the i.r. spectrum of the reaction solution was monitored until no further changes were observed. On bubbling CO through the solution of $[Ru_5C(CO)_{13}(H)I]$ for 10 min, $[Ru_5C(CO)_{15}]$ was regenerated.

Crystal Structure Determinations.—Crystal structure data are located in Table 1. Cell parameters were determined during preliminary data collection and alignment procedures and were refined using standard programs. Initial data reduction on the Stoe diffractometer was performed using programs provided by Dr. W. Clegg. Data were corrected for absorption and Lorentz polarization effects. The structures were solved using direct methods and refined by blocked-cascade least-squares routines provided by Professor G. M. Sheldrick. Phenyl rings were refined as rigid bodies with C–C distances of 1.395 Å and C–C–C of 120°. Phenyl ring hydrogen atom positions were also fixed in the case of $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ at 1.08 Å from the corresponding carbon atoms with C–C–H of 120°. The hydrogen atoms were not included in the refinement of the $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$ structure owing to the size of the structure and the small effect inclusion would have had in the overall data quality. Scattering factor parameters were obtained from standard references.[8]

Table 7. Bond angles (°) for $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$

Ru(2)-Au(1)-Ru(3)	65.0(1)	Ru(2)-Au(1)-P(1)	137.2(1)	Ru(5)-Ru(2)-C(21)	92.5(5)	C(01)-Ru(2)-C(21)	95.1(6)
Ru(3)-Au(1)-P(1)	157.5(1)	Au(1)-Ru(2)-Ru(3)	54.0(1)	Au(1)-Ru(2)-C(22)	79.9(5)	Ru(3)-Ru(2)-C(22)	111.7(5)
Au(1)-Ru(2)-Ru(4)	98.1(1)	Au(1)-Ru(2)-Ru(5)	91.7(1)	Ru(4)-Ru(2)-C(22)	87.5(5)	Ru(5)-Ru(2)-C(22)	169.7(5)
Au(1)-Ru(3)-Ru(1)	139.6(1)	Au(1)-Ru(3)-Ru(2)	61.1(1)	C(01)-Ru(2)-C(22)	131.1(6)	C(21)-Ru(2)-C(22)	97.1(7)
Au(1)-Ru(3)-Ru(4)	104.0(1)	Au(1)-Ru(3)-Ru(5)	97.3(1)	Au(1)-Ru(2)-C(23)	74.7(5)	Ru(3)-Ru(2)-C(23)	117.2(5)
Ru(3)-Ru(1)-Ru(5)	52.7(1)	Ru(3)-Ru(1)-Ru(4)	52.6(1)	Ru(4)-Ru(2)-C(23)	172.5(5)	Ru(5)-Ru(2)-C(23)	94.4(5)
Ru(4)-Ru(1)-Ru(5)	86.9(1)	Ru(3)-Ru(2)-Ru(4)	58.3(1)	C(01)-Ru(2)-C(23)	137.8(6)	C(21)-Ru(2)-C(23)	91.8(7)
Ru(3)-Ru(2)-Ru(5)	58.2(1)	Ru(4)-Ru(2)-Ru(5)	87.9(1)	C(22)-Ru(2)-C(23)	89.0(7)	Au(1)-Ru(3)-C(31)	78.3(5)
Ru(1)-Ru(3)-Ru(2)	78.9(1)	Ru(1)-Ru(3)-Ru(4)	54.4(1)	Ru(1)-Ru(3)-C(31)	121.0(6)	Ru(2)-Ru(3)-C(31)	119.5(5)
Ru(2)-Ru(3)-Ru(4)	59.1(1)	Ru(1)-Ru(3)-Ru(5)	54.0(1)	Ru(4)-Ru(3)-C(31)	175.0(6)	Ru(5)-Ru(3)-C(31)	86.2(6)
Ru(2)-Ru(3)-Ru(5)	59.4(1)	Ru(4)-Ru(3)-Ru(5)	89.1(1)	Br(1)-Ru(3)-C(31)	92.7(5)	C(01)-Ru(3)-C(31)	130.6(7)
Ru(2)-Ru(4)-Ru(3)	62.7(1)	Ru(1)-Ru(4)-Ru(3)	73.0(1)	Au(1)-Ru(3)-C(32)	82.4(5)	Ru(1)-Ru(3)-C(32)	124.2(5)
Ru(1)-Ru(4)-Ru(2)	89.9(1)	Ru(1)-Ru(5)-Ru(2)	89.8(1)	Ru(2)-Ru(3)-C(32)	117.3(5)	Ru(4)-Ru(3)-C(32)	87.1(5)
Ru(1)-Ru(5)-Ru(3)	73.2(1)	Ru(2)-Ru(5)-Ru(3)	62.4(1)	Ru(5)-Ru(3)-C(32)	176.0(5)	Br(1)-Ru(3)-C(32)	94.7(5)
Ru(3)-Ru(1)-C(01)	33.5(4)	Ru(4)-Ru(1)-C(01)	43.4(4)	C(01)-Ru(3)-C(32)	131.8(6)	C(31)-Ru(3)-C(32)	97.6(8)
Ru(5)-Ru(1)-C(01)	43.5(4)	Ru(3)-Ru(2)-C(02)	43.2(4)	Ru(1)-Ru(4)-C(41)	165.1(5)	Ru(2)-Ru(4)-C(41)	89.1(5)
Ru(4)-Ru(2)-C(01)	44.2(4)	Ru(5)-Ru(2)-C(01)	33.7(4)	Ru(3)-Ru(4)-C(41)	93.3(5)	C(01)-Ru(4)-C(41)	126.9(6)
Ru(1)-Ru(3)-C(01)	34.7(4)	Ru(2)-Ru(3)-C(01)	44.2(4)	Ru(1)-Ru(4)-C(42)	94.3(5)	Ru(2)-Ru(4)-C(42)	99.9(5)
Ru(4)-Ru(3)-C(01)	44.6(4)	Ru(5)-Ru(3)-C(01)	44.5(4)	Ru(3)-Ru(4)-C(42)	157.7(5)	C(01)-Ru(4)-C(42)	112.4(6)
Ru(1)-Ru(4)-C(01)	46.2(4)	Ru(2)-Ru(4)-C(01)	46.3(4)	C(41)-Ru(4)-C(42)	100.5(7)	Ru(1)-Ru(4)-C(43)	87.7(6)
Ru(3)-Ru(4)-C(01)	45.7(4)	Ru(1)-Ru(5)-C(01)	46.5(4)	Ru(2)-Ru(4)-C(43)	161.6(5)	Ru(3)-Ru(4)-C(43)	99.3(5)
Ru(2)-Ru(5)-C(01)	46.0(4)	Ru(3)-Ru(5)-C(01)	45.7(4)	C(01)-Ru(4)-C(43)	124.0(7)	C(41)-Ru(4)-C(43)	88.7(8)
Ru(1)-C(01)-Ru(2)	155.7(7)	Ru(1)-C(01)-Ru(3)	111.7(6)	C(42)-Ru(4)-C(43)	98.4(7)	Ru(1)-Ru(5)-C(51)	172.9(5)
Ru(2)-C(01)-Ru(3)	92.5(6)	Ru(1)-C(01)-Ru(4)	90.4(5)	Ru(2)-Ru(5)-C(51)	85.8(5)	Ru(3)-Ru(5)-C(51)	99.7(5)
Ru(2)-C(01)-Ru(4)	89.5(5)	Ru(3)-C(01)-Ru(4)	89.6(6)	C(01)-Ru(5)-C(51)	127.6(7)	Ru(1)-Ru(5)-C(52)	91.5(4)
Ru(1)-C(01)-Ru(5)	90.0(6)	Ru(2)-C(01)-Ru(5)	90.3(5)	Ru(2)-Ru(5)-C(52)	155.4(5)	Ru(3)-Ru(5)-C(52)	94.5(5)
Ru(3)-C(01)-Ru(5)	89.8(5)	Ru(4)-C(01)-Ru(5)	179.4(7)	C(01)-Ru(5)-C(52)	124.0(6)	C(51)-Ru(5)-C(52)	90.1(7)
Ru(1)-Br(1)-Ru(3)	80.4(1)	Ru(3)-Ru(1)-Br(1)	50.3(1)	Ru(1)-Ru(5)-C(53)	92.0(5)	Ru(2)-Ru(5)-C(53)	106.2(5)
Ru(4)-Ru(1)-Br(1)	84.7(1)	Ru(5)-Ru(1)-Br(1)	86.1(1)	Ru(3)-Ru(5)-C(53)	160.7(5)	C(01)-Ru(5)-C(53)	115.0(6)
Ru(1)-Ru(3)-Br(1)	49.3(1)	Ru(2)-Ru(3)-Br(1)	128.2(1)	C(51)-Ru(5)-C(53)	94.6(7)	C(52)-Ru(5)-C(53)	98.3(7)
Ru(4)-Ru(3)-Br(1)	85.3(1)	Ru(5)-Ru(3)-Br(1)	86.3(1)	Ru(1)-C(11)-O(11)	176.7(14)	Ru(1)-C(12)-O(12)	175.4(14)
Br(1)-Ru(1)-C(01)	83.8(4)	Br(1)-Ru(3)-C(01)	84.0(4)	Ru(1)-C(13)-O(13)	173.7(15)	Ru(2)-C(21)-O(21)	174.5(15)
Au(1)-Ru(2)-C(01)	97.0(4)	Au(1)-Ru(3)-C(01)	105.1(4)	Ru(2)-C(22)-O(22)	176.3(14)	Ru(2)-C(23)-O(23)	175.9(14)
Au(1)-Ru(3)-Br(1)	170.0(1)	Ru(3)-Ru(1)-C(11)	128.1(5)	Ru(3)-C(31)-O(31)	175.3(16)	Ru(3)-C(32)-O(32)	179.4(14)
Ru(4)-Ru(1)-C(11)	92.0(5)	Ru(5)-Ru(1)-C(11)	94.9(5)	Ru(4)-C(41)-O(41)	174.9(14)	Ru(4)-C(42)-O(42)	179.5(14)
Br(1)-Ru(1)-C(11)	176.5(5)	C(01)-Ru(1)-C(11)	94.6(6)	Ru(4)-C(43)-O(43)	177.2(14)	Ru(5)-C(51)-O(51)	176.3(15)
Ru(3)-Ru(1)-C(12)	123.1(5)	Ru(4)-Ru(1)-C(12)	94.0(5)	Ru(5)-C(52)-O(52)	176.0(14)	Ru(5)-C(53)-O(53)	175.8(14)
Ru(5)-Ru(1)-C(12)	173.2(5)	Br(1)-Ru(1)-C(12)	87.3(5)	Au(1)-P(1)-C(101)	111.7(4)	Au(1)-P(1)-C(201)	112.3(4)
C(01)-Ru(1)-C(12)	137.0(6)	C(11)-Ru(1)-C(12)	91.8(7)	C(101)-P(1)-C(201)	105.0(5)	Au(1)-P(1)-C(301)	115.3(4)
Ru(3)-Ru(1)-C(13)	118.0(5)	Ru(4)-Ru(1)-C(13)	170.1(5)	C(101)-P(1)-C(301)	106.5(6)	C(201)-P(1)-C(301)	105.2(6)
Ru(5)-Ru(1)-C(13)	84.1(5)	Br(1)-Ru(1)-C(13)	90.6(5)	P(1)-C(101)-C(102)	123.6(3)	P(1)-C(101)-C(106)	116.4(3)
C(01)-Ru(1)-C(13)	127.5(6)	C(11)-Ru(1)-C(13)	92.8(7)	P(1)-C(201)-C(202)	121.7(3)	P(1)-C(201)-C(206)	118.1(4)
C(12)-Ru(1)-C(13)	94.5(7)	Au(1)-Ru(2)-C(21)	166.2(5)	P(1)-C(301)-C(302)	122.4(4)	P(1)-C(301)-C(306)	117.6(4)
Ru(3)-Ru(2)-C(21)	138.3(5)	Ru(4)-Ru(2)-C(21)	95.2(5)				

Table 8. Infrared data

Complex	Solvent	ν(CO)/cm^{-1}
$[Ru_5C(CO)_{15}(H)Cl]$	Hexane	2 117w, 2 092s, 2 078s, 2 075vs, 2 059w, 2 039m, 2 034 (sh), 2 019w, 2 008w, 2 001w
$[Ru_5C(CO)_{15}(H)Br]$	Hexane	2 112w, 2 089s, 2 075s (sh), 2 073vs, 2 059w, 2 036m, 2 031 (sh), 2 017w, 2 007w, 2 000w
$[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Cl]$	CH_2Cl_2	2 106m, 2 072 (sh) br, 2 065vs, 2 045s, 2 037 (sh), 2 016m, br, 1 994w
$[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Br]$	CH_2Cl_2	2 100w, 2 067vs, 2 056 (sh), 2 040 (sh), 2 033s, 2 016w
$[Ru_5C(CO)_{14}(H)Br]$	Hexane	2 109w, 2 084s, 2 066vs, 2 058m

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