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XXXIX *. GOLD–RUTHENIUM CLUSTERS WITH SULPHUR LIGANDS: SYNTHESIS AND STRUCTURE OF HRu$_3$Au(μ_3-S)(CO)$_9$(PPh$_3$), Ru$_3$Au(μ_3-SBu^t)(CO)$_9$(PPh$_3$) and Ru$_3$Au$_2$(μ_3-S)(CO)$_9$(PPh$_3$)$_2$

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Summary

H$_2$Ru$_3$(μ_3-S)(CO)$_9$ is deprotonated by K[HBBu$^s_3$] to give cluster anions which react with [O{Au(PPh$_3$)}$_3$]$^+$ or with AuCl(PPh$_3$)/Tl$^+$ to give HRu$_3$Au(μ_3-S)(CO)$_9$(PPh$_3$) (1) and Ru$_3$Au$_2$(μ_3-S)(CO)$_9$(PPh$_3$)$_2$ (3). A similar sequence with HRu$_3$(μ_3-SBu^t)(CO)$_9$ leads to Ru$_3$Au(μ_3-SBu^t)(CO)$_9$(PPh$_3$) (2) as the main product although some 1 also forms, indicating S–C cleavage competes with deprotonation of HRu$_3$(μ_3-SBu^t)(CO)$_9$ by [HBBu$^s_3$]$^-$. The X-ray crystal structures of 1, 2 and 3 are described; (1) and (2) have "butterfly" AuRu$_3$ cores with markedly different hinge angles of 119 and 148° respectively, while 3 has a trigonal-bipyramidal Au$_2$Ru$_3$ skeleton. All three clusters have the sulphur atom symmetrically bridging the Ru$_3$ triangular face.

There is now a well-established area of chemistry involving mixed-metal clusters with one, two or three gold atoms incorporated in the metal framework [1,2]. Most interest has centred on gold–ruthenium [3–14] and gold–osmium [15–21] complexes, although species with vanadium [22], manganese [23], rhenium [24], iron [25–30], iridium [31] and platinum [32] are also known, together with several examples which contain more than one type of transition metal [33–37]. An increasing number of clusters which contain ligands such as μ_3-COMe [4], μ_3-C$_2$R or μ_3-C=CHR [6,14], μ_3-cyclododecatrienyl [13], μ_3-PR [3] and μ_3-S [10], in addition to CO, tertiary phosphine or η-C$_5$H$_5$, have been described.

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We now wish to report on our preparation and structural-determination of three related sulphur-containing clusters, namely $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$ (**1**), $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$ (**2**), and $Ru_3Au_2(\mu_3\text{-}S)\text{-}(CO)_9(PPh_3)_2$, (**3**). During the course of this work **1** and **3** were prepared independently by an alternative route involving methane elimination between Ph_3PAuMe and $H_2Ru_3(\mu_3\text{-}S)(CO)_9$, and the structure of a Ph_3P-substituted derivative of **3** was published [10].

(1)   (2)   (3)
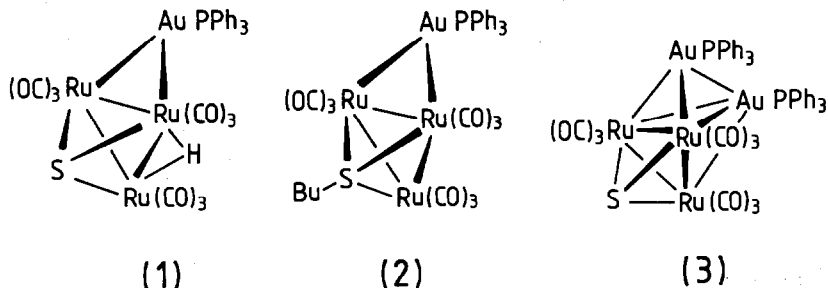
Experimental

General procedures have been described previously [13]. Starting materials $H_2Ru_3(\mu_3\text{-}S)(CO)_9$ [38], $HRu_3(\mu_3\text{-}SBu^t)(CO)_9$ [38] and $[O\{Au(PPh_3)\}_3][BF_4]$ [39], were prepared by literature methods. K-Selectride, $K[HBBu^s_3]$, 0.5 mol l^{-1} in THF, was purchased from Aldrich Chemicals. Infrared spectra were recorded as cyclohexane solutions. Preparative chromatography was performed on silica gel (Merck, PF_{254}) plates. Light petroleum refers to a 60–70°C boiling fraction.

Reaction of [HRu$_3$(μ_3-S)(CO)$_9$]$^-$ with [O{ Au(PPh$_3$)}$_3$]$^+$

A solution of $H_2Ru_3(\mu_3\text{-}S)(CO)_9$ (200 mg. 0.34 mmol) in THF (15 ml) was treated with $K[HBBu^s_3]$ (0.34 mmol). After 2 min the orange solution was treated with solid $[O\{Au(PPh_3)\}_3][BF_4]$ (167 mg, 0.113 mmol). After ca. 20 h, solvent was evaporated. A benzene extract of the residue was filtered and chromatographed, eluting with benzene/cyclohexane (1/1). Band 1 (R_f 0.83), orange-yellow, (20 mg). $\nu(CO)$ 2088m, 2066vs, 2040vs, 2024w, 2004sh, 1998s, 1985w, 1983m cm^{-1}, not identified. Band 2 (R_f 0.72), orange $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$ (10 mg, 3%), m.p. 159°C (dec), recrystallised from heptane. (Found: C, 31.21; H, 1.22. $C_{27}H_{16}Au$-O_9PRu_3S calcd.: C, 30.95; H, 1.54%). $\nu(CO)$ 2084s, 2063vs, 2050m, 2038vs, 2010m, 1996vs, 1191m, 1958m cm^{-1}; ^1H NMR: δ (CDCl$_3$) 7.5 m, 15H, Ph; -19.85 s, 1 H, Ru-H. Band 3 (R_f 0.62) red, $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$, (70 mg, 14%) m.p. 186°C (dec), recrystallised from diethyl ether. (Found: C, 35.70; H, 1.80; $C_{45}H_{30}Au_2O_9P_2Ru_3S$ calcd.: C, 35.87; H, 2.07%.) $\nu(CO)$ 2060s, 2035vs, 2025vs, 1986w, 1973s, 1964s cm^{-1}; ^1H NMR: δ (CDCl$_3$) 7.1 m, Ph. Band 4, (R_f 0.48), purple, (trace only), $\nu(CO)$ 2061s, 2032 vs, 2020vs, 2002m, 1993m, 1984m, 1970m, 1962s, cm^{-1}, not identified.

Reaction of [HRu$_3$(μ_3-S)(CO)$_9$]$^-$ with AuCl(PPh$_3$)/TlPF$_6$

A solution of $[HRu_3(\mu_3\text{-}S)(CO)_9]^-$ (0.51 mmol) in THF (20 ml), prepared as above, was treated sequentially with AuCl(PPh$_3$) (252 mg, 0.51 mmol) and TlPF$_6$

(178 mg, 0.51 mmol). After stirring overnight TlCl was filtered and the filtrate evaporated in vacuo. The residue was extracted with acetone and chromatographed, eluting with acetone/light petroleum (3/7). Band 1, yellow, $H_2Ru_3(\mu_3\text{-S})(CO)_9$; Band 2 ($R_f$ 0.82), orange, $HRu_3Au(\mu_3\text{-S})(CO)_9(PPh_3)$ (150 mg, 28%). Band 3, red, $Ru_3Au_2(\mu_3\text{-S})(CO)_9(PPh_3)_2$ (99 mg, 13%).

Reaction of [Ru$_3$(μ_3-SBu^t)(CO)$_9$]$^-$ with AuCl(PPh$_3$)/TlPF$_6$

$HRu_3(\mu_3\text{-SBu}^t)(CO)_9$ (150 mg, 0.23 mmol) was dissolved in THF (15 ml) and $K[HBBu^s_3]$ (0.23 mmol) was added. After 5 min conversion to $[Ru_3(\mu_3\text{-SBu}^t)(CO)_9]^-$ was complete (TLC); $AuCl(PPh_3)$ (115 mg, 0.23 mmol) and $TlPF_6$ (81 mg, 023 mmol) were added and the mixture stirred for 2 h. After filtration and evaporation, the residue was extracted with CH_2Cl_2. Chromatography, eluting with acetone/light petroleum (3/7) gave 7 bands. Band 1 (R_f 0.96), 3, (R_f 0.69) and 7 (R_f 0.31) were present in trace amounts only, and were not identified. Band 2 (R_f 0.89), traces, $HRu_3(\mu_3\text{-SBu}^t)(CO)_9$. Band 4 ($R_f$ 0.64) yellow/orange, $HRu_3Au(\mu_3\text{-S})(CO)_9(PPh_3)$, (10 mg, 4%). band 5 ($R_f$ 0.58), orange, $Ru_3Au(\mu_3\text{-SBu}^t)(CO)_9(PPh_3)$, (72 mg, 28%), m.p. 154°C (dec), recrystallised from heptane. (Found: C, 33.82; H, 1.86; $C_{31}H_{24}AuO_9PRu_3S$ calcd.: C, 33.73; H, 2.19%) $\nu(CO)$ 2066s, 2030vs, 2024sh, 1998vs, 1983sh, 1975s, 1964s, cm^{-1}; ^1H NMR: δ (CDCl$_3$) 7.51–7.24 m, 15H, Ph; 1.48S, 9H, Bu^t. Band 6 (R_f 0.39), red, $Ru_3Au_2(\mu_3\text{-S})(CO)_9(PPh_3)_2$, (11 mg, 3%).

Reaction of HRu$_3$(μ_3-SBu^t)(CO)$_9$ with K[HBBu$^s_3$] and subsequent protonation with H$_3$PO$_4$

A solution of $[Ru_3(\mu_3\text{-SBu}^t)(CO)_9]^-$ was generated from $HRu_3(\mu_3\text{-SBu}^t)(CO)_9$ (100 mg, 0.155 mmol) and $K[HBBu^s_3]$ (0.155 mmol) in THF (10 ml) for 5 min.

TABLE 1

CRYSTAL DATA FOR COMPLEXES 1–3

	1	2	3
Formula:	$C_{27}H_{16}AuO_9PRu_3S$	$C_{31}H_{24}AuO_9PRu_3S$	$C_{45}H_{30}Au_2O_9P_2Ru_3S$
M_r:	1047.64	1103.75	1505.90
Crystal class:	Monoclinic	Triclinic	Monoclinic
Space group:	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	12.983(2)	10.307(4)	12.763(3)
b (Å)	17.646(4)	16.082(2)	27.568(5)
c (Å)	14.962(2)	12.781(3)	15.617(4)
α (degrees)	90	109.86(2)	90
β (degrees)	106.05(1)	111.66(2)	121.81(2)
γ (degrees)	90	95.55(2)	90
U (Å^3)	3294.2	1791.1	4669.5
Z	4	2	4
D_c (g cm^{-3})	2.11	2.05	2.14
μ(Mo-K_α) (cm^{-1})	58	54	73
$F(000)$	1968	1048	2835
Scan range	$3° < 2\theta < 45°$	$0° < 2\theta < 45°$	$1° < 2\theta < 43°$
Unique data	4253	5032	5271
Data, $I > 3\sigma(I)$	3337	4295	3345
Final R, R_w	0.042,0.044	0.031,0.035	0.045,0.045
Weight, $w = 1.0[\sigma^2 F + pF^2]^{-1}$	$p = 0.0005$	$p = 0.0002$	$p = 0.0012$

TABLE 2

FINAL POSITIONAL PARAMETERS FOR AuRu$_3$(μ_3-S)(H)(CO)$_9$(Ph$_3$P) (1)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Au(1)	0.2522(1)	0.2378(1)	0.6055(1)	O(7)	−0.127(1)	−0.015(1)	0.619(1)
Ru(1)	0.0448(1)	0.2193(1)	0.6158(1)	O(8)	0.167(1)	−0.0328(8)	0.8579(8)
Ru(2)	0.2322(1)	0.1781(1)	0.7686(1)	O(9)	0.223(1)	−0.0145(7)	0.5817(9)
Ru(3)	0.0878(1)	0.0678(1)	0.6891(1)	H(1)	0.037(0)	0.118(0)	0.581(0)
P(1)	0.3620(2)	0.2732(2)	0.5156(2)	C(11)	0.4774(6)	0.3292(5)	0.5743(6)
S(1)	0.0517(3)	0.1757(2)	0.7667(2)	C(12)	0.5185(6)	0.3850(5)	0.5276(6)
C(1)	0.054(1)	0.2333(9)	0.491(1)	C(13)	0.6098(6)	0.4254(5)	0.5743(6)
C(2)	−0.110(1)	0.216(1)	0.577(1)	C(14)	0.6600(6)	0.4101(5)	0.6677(6)
C(3)	0.054(1)	0.325(1)	0.643(1)	C(15)	0.6189(6)	0.3544(5)	0.7143(6)
C(4)	0.347(1)	0.1333(9)	0.731(1)	C(16)	0.5276(6)	0.3139(5)	0.6676(6)
C(5)	0.285(1)	0.134(1)	0.889(1)	C(21)	0.2892(7)	0.3271(5)	0.4163(6)
C(6)	0.285(1)	0.2763(9)	0.808(1)	C(22)	0.2927(7)	0.3095(5)	0.3263(6)
C(7)	−0.050(2)	0.021(1)	0.645(1)	C(23)	0.2303(7)	0.3504(5)	0.2508(6)
C(8)	0.138(1)	0.004(1)	0.795(1)	C(24)	0.1644(7)	0.4088(5)	0.2653(6)
C(9)	0.170(1)	0.0150(9)	0.621(1)	C(25)	0.1609(7)	0.4265(5)	0.3553(6)
O(1)	0.0487(8)	0.2399(8)	0.4138(8)	C(26)	0.2233(7)	0.3856(5)	0.4308(6)
O(2)	−0.1992(9)	0.214(1)	0.5524(9)	C(31)	0.4176(7)	0.1928(4)	0.4709(6)
O(3)	0.057(1)	0.3862(9)	0.666(1)	C(32)	0.3544(7)	0.1277(4)	0.4509(6)
O(4)	0.4143(9)	0.0998(7)	0.7119(9)	C(33)	0.3921(7)	0.0639(4)	0.4147(6)
O(5)	0.319(1)	0.1112(7)	0.9625(8)	C(34)	0.4929(7)	0.0652(4)	0.3986(6)
O(6)	0.318(1)	0.3357(7)	0.8311(9)	C(35)	0.5561(7)	0.1303(4)	0.4186(6)
				C(36)	0.5184(7)	0.1941(4)	0.4548(6)

TABLE 3

FINAL POSITIONAL PARAMETERS FOR AuRu$_3$(μ_3-SBu^t)(CO)$_9$(Ph$_3$P) (2)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Au(1)	0.3171(0)	0.2492(0)	0.4974(0)	O(22)	−0.1283(6)	−0.0098(4)	0.0411(5)
Ru(1)	0.1732(1)	0.3547(0)	0.3855(0)	O(23)	0.3493(6)	0.0975(4)	0.2452(5)
Ru(2)	0.0850(1)	0.1531(0)	0.2701(0)	O(31)	0.3337(6)	0.2427(4)	0.1116(6)
Ru(3)	0.0525(1)	0.2569(0)	0.1313(0)	O(32)	0.0099(7)	0.4165(4)	0.0553(6)
S(1)	−0.0530(2)	0.2570(1)	0.2616(1)	O(33)	−0.1349(6)	0.1101(4)	−0.1251(5)
P(1)	0.5007(2)	0.2557(1)	0.6721(2)	C(51)	0.5703(5)	0.3685(2)	0.7963(4)
C(1)	−0.2329(8)	0.2596(5)	0.2619(7)	C(52)	0.6299(5)	0.3807(2)	0.9194(4)
C(2)	−0.259(1)	0.3484(8)	0.262(1)	C(53)	0.6806(5)	0.4686(2)	1.0128(4)
C(3)	−0.222(1)	0.256(1)	0.380(1)	C(54)	0.6717(5)	0.5443(2)	0.9831(4)
C(4)	−0.340(1)	0.1776(8)	0.150(1)	C(55)	0.6121(5)	0.5321(2)	0.8599(4)
C(11)	0.3648(9)	0.3825(5)	0.4025(7)	C(56)	0.5614(5)	0.4442(2)	0.7665(4)
C(12)	0.1889(8)	0.3949(5)	0.5522(7)	C(61)	0.6549(4)	0.2228(3)	0.6513(4)
C(13)	0.1407(9)	0.4624(5)	0.3661(8)	C(62)	0.6312(4)	0.1378(3)	0.5590(4)
C(21)	0.0665(8)	0.1019(4)	0.3804(7)	C(63)	0.7477(4)	0.1075(3)	0.5433(4)
C(22)	−0.0480(7)	0.0510(5)	0.1249(6)	C(64)	0.8880(4)	0.1622(3)	0.6199(4)
C(23)	0.2526(7)	0.1199(4)	0.2565(6)	C(65)	0.9117(4)	0.2472(3)	0.7122(4)
C(31)	0.2286(8)	0.2488(4)	0.1203(7)	C(66)	0.7951(4)	0.2775(3)	0.7278(4)
C(32)	0.0249(8)	0.3582(5)	0.0852(7)	C(71)	0.4417(5)	0.1828(3)	0.7362(4)
C(33)	−0.0681(8)	0.1649(5)	−0.0292(7)	C(72)	0.3164(5)	0.1909(3)	0.7528(4)
O(11)	0.4788(6)	0.3992(4)	0.4073(6)	C(73)	0.2650(5)	0.1368(3)	0.8015(4)
O(12)	0.1921(8)	0.4209(4)	0.6483(5)	C(74)	0.3390(5)	0.0746(3)	0.8335(4)
O(13)	0.1240(8)	0.5303(4)	0.3566(7)	C(75)	0.4642(5)	0.0664(3)	0.8169(4)
O(21)	0.0493(7)	0.0628(4)	0.4366(6)	C(76)	0.5156(5)	0.1206(3)	0.7682(4)

Complete conversion was confirmed by TLC. H_3PO_4 (5 drops) was added and the mixture stirred for one hour. After evaporation, a CH_2Cl_2 (10 ml) extract of the residue was washed with water (5×10 ml) and dried by azeotropic distillation with benzene and ethanol. Subsequent chromatography (acetone/light petroleum, (1/9)) gave 3 bands. Band 1 (R_f 0.92), yellow, trace. ν(CO) 2068 vs, 2044m, 2028s, 2010m, 1979m cm^{-1} not identified. Band 2 (R_f 0.83 $H_2Ru_3(\mu_3$-S)(CO)$_9$ (9 mg, 10%). Band 3, (R_f 0.69) HRu$_3(\mu_3$-SBu^t)(CO)$_9$ (50 mg, 50%).

X-Ray Crystal structure determination. Suitable crystals of **1**, **2** or **3** were mounted on a Nicolet P3 diffractometer, and accurate lattice parameters were determined using 25 high-angle reflections with Mo-K_α X-radiation; data are summarised in Table 1. The structures were solved by direct methods, difference map techniques, and routinely refined by full-matrix least-squares methods. Phenyl rings were treated as rigid groups with isotropic temperature factors for the carbon atoms and with hydrogen atoms in calculated positions; all other atoms were assigned anisotropic thermal parameters. For **1**, the hydrido ligand was located directly as the highest peak in the penultimate difference map and was included in

TABLE 4

FINAL POSITIONAL PARAMETERS FOR Au$_2$Ru$_3(\mu_3$-S)(CO)$_9$(Ph$_3$P)$_2$ (3)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Au(1)	0.1787(1)	0.8487(1)	0.2160(1)	C(111)	−0.0476(11)	0.7905(3)	−0.0124(9)
Au(2)	0.0565(1)	0.9227(1)	0.2721(1)	C(122)	0.2425(10)	0.7901(5)	−0.0066(8)
Ru(1)	0.2505(1)	0.9469(1)	0.2386(1)	C(123)	0.3443(10)	0.7886(5)	−0.0173(8)
Ru(2)	0.2958(1)	0.8845(1)	0.4119(1)	C(124)	0.4597(10)	0.7755(1)	0.0642(8)
Ru(3)	0.2445(2)	0.9865(1)	0.4058(1)	C(125)	0.4734(10)	0.7638(5)	0.1565(8)
P(1)	−0.1534(4)	0.9133(2)	0.2026(4)	C(126)	0.3717(10)	0.7653(5)	0.1673(8)
P(2)	0.1319(5)	0.7835(3)	0.1096(4)	C(121)	0.2562(10)	0.7784(5)	0.0857(8)
S(1)	0.4124(5)	0.9498(2)	0.4083(4)	C(132)	0.1797(11)	0.6829(5)	0.1468(9)
C(11)	0.9382(20)	0.9438(2)	0.1161(15)	C(133)	0.1682(11)	0.6384(5)	0.1838(9)
O(12)	0.0079(15)	0.9510(5)	0.0371(11)	C(134)	0.0999(11)	0.6352(5)	0.2298(9)
C(12)	0.2894(21)	1.0084(8)	0.2103(17)	C(135)	0.0429(11)	0.6764(5)	0.2388(9)
O(12)	0.3184(17)	1.0438(6)	0.1948(13)	C(136)	0.0544(11)	0.7209(5)	0.2018(9)
C(13)	0.3406(20)	0.9128(8)	0.1900(15)	C(131)	0.1228(11)	0.7241(5)	0.1558(9)
O(13)	0.3960(15)	0.8969(8)	0.1587(13)	C(212)	−0.3277(12)	0.8838(4)	0.0045(9)
C(21)	0.1711(19)	0.8415(7)	0.3952(14)	C(213)	−0.3861(12)	0.8492(4)	−0.0716(9)
O(21)	0.1004(14)	0.8141(6)	0.3932(11)	C(214)	−0.3473(12)	0.8009(4)	−0.0524(9)
C(22)	0.4068(19)	0.8371(8)	0.4169(14)	C(215)	−0.2501(12)	0.7874(4)	0.0429(9)
C(22)	0.4802(14)	0.8110(6)	0.4233(13)	C(216)	−0.1917(12)	0.8220(4)	0.1189(9)
C(23)	0.3698(19)	0.8865(7)	0.5542(17)	C(211)	−0.2306(12)	0.8703(4)	0.0998(9)
O(23)	0.4130(18)	0.8854(7)	0.6367(12)	C(222)	−0.3093(10)	0.8708(4)	0.2595(9)
C(31)	0.0868(18)	1.0017(8)	0.3815(19)	C(223)	−0.3401(10)	0.8572(4)	0.3296(7)
O(31)	−0.0044(16)	1.0165(6)	0.3719(15)	C(224)	−0.2564(10)	0.8647(4)	0.4322(7)
C(32)	0.2781(22)	1.0510(9)	0.3838(16)	C(225)	−0.1421(10)	0.8858(4)	0.4647(7)
O(32)	0.2902(18)	1.0907(6)	0.3727(13)	C(226)	−0.1113(10)	0.8994(4)	0.3946(7)
C(33)	0.3161(22)	0.9938(8)	0.5471(22)	C(221)	−0.1949(10)	0.8919(4)	0.2920(7)
O(33)	0.3603(18)	1.0006(7)	0.6319(14)	C(232)	−0.2012(11)	1.0005(5)	0.1004(9)
C(112)	−0.0702(11)	0.7506(3)	−0.0728(9)	C(233)	−0.2609(11)	1.0448(5)	0.0625(9)
C(113)	−0.1729(11)	0.7576(3)	−0.1694(9)	C(234)	−0.3549(11)	1.0590(5)	0.0776(9)
C(114)	−0.2130(11)	0.8045(3)	−0.2055(9)	C(235)	−0.3891(11)	1.0290(5)	0.1307(9)
C(115)	−0.1504(11)	0.8444(3)	−0.1450(9)	C(236)	−0.3294(11)	0.9847(5)	0.1685(9)
C(116)	−0.0476(11)	0.8374(3)	−0.0484(9)	C(231)	−0.2355(11)	0.9705(5)	0.1534(9)
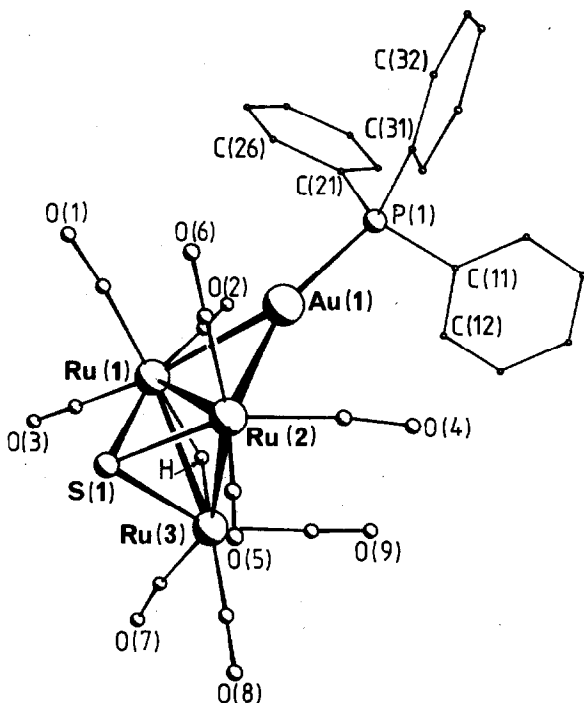
Fig. 1. A view of $HRu_3Au(\mu_3\text{-S})(CO)_9(PPh_3)$.

TABLE 5

SELECTED BOND PARAMETERS FOR $Ru_3Au(\mu_3\text{-S})(H)(CO)_9PPh_3$ (1), $Ru_3Au(\mu_3\text{-SBu}^t)(CO)_9PPh_3$, (2), AND $Ru_3Au_2(\mu_3\text{-S})(CO)_9(PPh_3)_2$ (3)

	Bond lengths (Å)				Bond angles (degrees)		
	1	**2**	**3**		**1**	**2**	**3**
Au(1)–Ru(1)	2.759(1)	2.773(1)	2.821(2)	Ru(1)–Au(1)–Ru(2)	64.5(1)	64.4(1)	64.6(1)
Au(1)–Ru(2)	2.736(1)	2.766(1)	2.783(2)	Au(1)–Ru(1)–Ru(2)	57.3(1)	57.7(1)	57.1(1)
Ru(1)–Ru(2)	2.933(1)	2.950(1)	2.996(2)	Au(1)–Ru(2)–Ru(1)	58.1(1)	57.9(1)	58.3(1)
Ru(1)–Ru(3)	2.885(1)	2.782(1)	2.869(2)	Ru(1)–Ru(2)–Ru(3)	61.1(1)	58.0(1)	58.4(1)
Ru(2)–Ru(3) ·	2.737(1)	2.780(1)	2.878(2)	Ru(2)–Ru(1)–Ru(3)	56.1(1)	57.9(1)	58.7(1)
Ru(1)–S(1)	2.363(4)	2.298(2)	2.351(5)	Ru(1)–Ru(3)–Ru(2)	62.8(1)	64.1(1)	62.8(1)
Ru(2)–S(1)	2.336(4)	2.302(2)	2.355(5)	Ru(1)–S(1)–Ru(2)	77.2(1)	79.8(1)	79.1(1)
Ru(3)–S(1)	2.344(4)	2.300(2)	2.352(6)	Ru(1)–S(1)–Ru(3)	75.6(1)	74.5(1)	75.2(1)
Ru(1)–H(1)	1.84(2)			Ru(2)–S(1)–Ru(3)	71.6(1)	74.3(1)	75.4(2)
Ru(2)–H(1)	1.79(2)			Ru(1)–S(1)–C(1)		133.1(2)	
Au(2)–Au(1)			2.967(2)	Ru(2)–S(1)–C(1)		133.4(2)	
Au(2)–Ru(1)			2.867(2)	Ru(3)–S(1)–C(1)		137.3(2)	
Au(2)–Ru(2)			2.859(2)				
Au(2)–Ru(3) ·			2.817(2)				
C(1)–S(1)		1.861(7)					

All other bonds were unexceptional:
Ru–C (1.90 Å), C–O (1.14 Å),
Au–P (2.29 Å), P–C (1.81 Å) and C–C (1.50 Å).

Dihedral angles (degrees)			
$\begin{bmatrix} Au(1)\text{–}Ru(1)\text{–}Ru(2) \\ Ru(1)\text{–}Ru(2)\text{–}Ru(3) \end{bmatrix}$	119.4	147.5	146.5
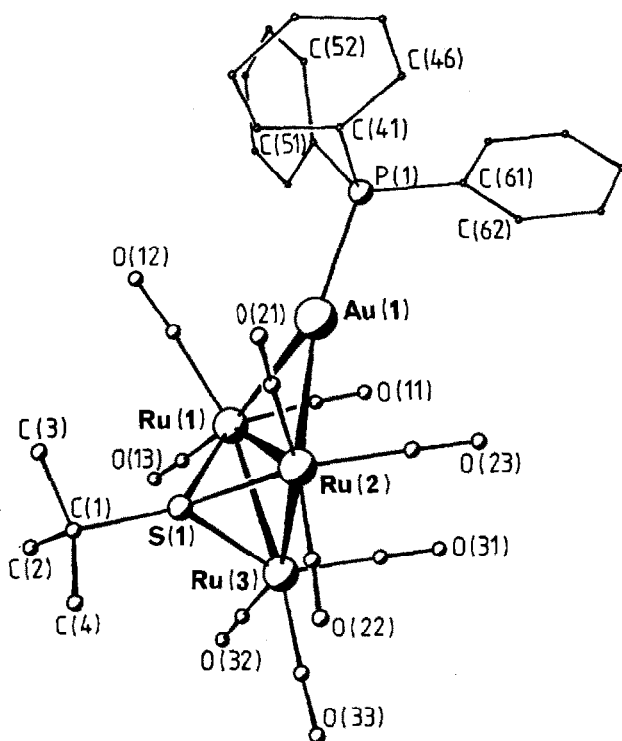
Fig. 2. The structure of Ru$_3$Au(μ_3-SBu^t)(CO)$_9$(PPh$_3$).
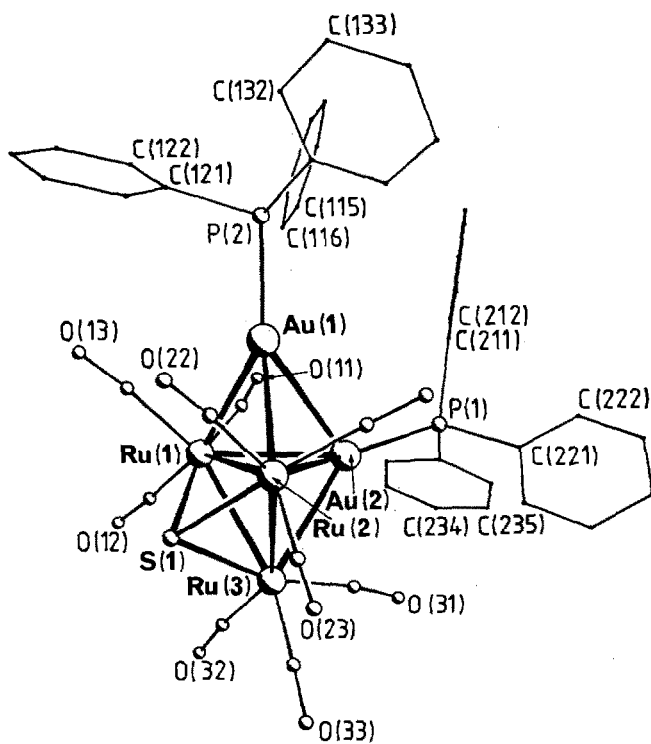
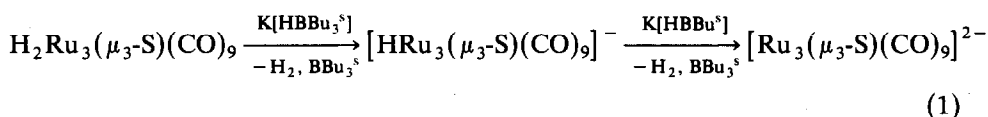Fig. 3. The structure of Ru$_3$Au$_2$(μ_3-S)(CO)$_9$(PPh$_3$)$_2$.

the final refinement with fixed parameters. For all three analyses final difference maps showed no significant features.

All calculations were performed using the SHELX-76 programmes [40]. Final positional parameters and selected bond length and angles are given in Tables 2–5, while perspective views of each of the molecules are shown in Fig. 1–3. Tables of thermal parameters and structure factors are available on request (BKN).
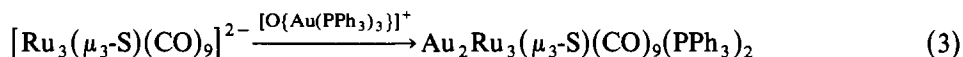
Results and discussion

Preparations

The cluster $H_2Ru_3(\mu_3\text{-}S)(CO)_9$ is rapidly and cleanly deprotonated by $K[HBBu_3^s]$ in THF to give the anions $[HRu_3(\mu_3\text{-}S)(CO)_9]^-$ and $[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-}$ (eq. 1).

$$H_2Ru_3(\mu_3\text{-}S)(CO)_9 \xrightarrow[-H_2,\ BBu_3^s]{K[HBBu_3^s]} [HRu_3(\mu_3\text{-}S)(CO)_9]^- \xrightarrow[-H_2,\ BBu_3^s]{K[HBBu_3^s]} [Ru_3(\mu_3\text{-}S)(CO)_9]^{2-}$$

$$(1)$$

This route to cluster anions is proving to have wide applicability [7,13] and is generally simpler and more specific than the deprotonation reactions with other bases, such as KOH. The degree of deprotonation can be largely controlled by stoichiometric addition of $K[HBBu_3^s]$. Addition of $[O\{Au(PPh_3)\}_3]^+$ to the anion results in formation of the mixed metal clusters **1** and **3** (eq. 2 and 3), which were

$$[HRu_3(\mu_3\text{-}S)(CO)_9]^- \xrightarrow{[O\{Au(PPh_3)\}_3]^+} AuRu_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3) \qquad (2)$$

$$[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-} \xrightarrow{[O\{Au(PPh_3)_3\}]^+} Au_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)_2 \qquad (3)$$

separated by chromatography. The overall yields were only moderate, with the Au_2Ru_3 cluster **3** being the dominant product. A better route to the mono-gold cluster **1** involves the reaction between the anions and $AuCl(PPh_3)$ in the presence of $Tl[PF_6]$ as a halide-abstractor [5,20]. Although we have found previously that the trigold-oxonium reagent commonly adds up to three $Au(PPh_3)$ moieties to mono-anionic clusters [7,13,35], we have found no evidence for the formation of such species in the present work.

In an analogous sequence, $HRu_3(\mu_3\text{-}SBu^t)(CO)_9$ was deprotonated by $K[HBBu_3^s]$, and the reaction with $AuCl(PPh_3)/Tl[PF_6]$ afforded $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$ (**2**) in reasonable yields. In addition, significant quantities of the $\mu_3\text{-}S$ cluster (**1**) were isolated, which indicated that cleavage of the S–C bond of the $\mu_3\text{-}SBu^t$ group was occurring during the deprotonation step. This was confirmed in a separate experiment; a mixture of $HRu_3(\mu_3\text{-}SBu^t)(CO)_9$ and $[HBBu_3^s]^-$ was allowed to react to completion and the resulting cluster anions protonated by H_3PO_4. The products were $HRu_3(\mu_3\text{-}SBu^t)(CO)_9$ and $H_2Ru_3(\mu_3\text{-}S)(CO)_9$ in a 5/1 ratio.

Although complexes **1** and **3** were also characterised by fast atom bombardment (FAB) mass spectrometry [41] it was decided to confirm the identifies of **1–3** by full crystal structure analyses.

The structure of $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$ (1)

The overall geometry is shown in Fig. 1. There is a triangular array of ruthenium atoms capped on one face by the $\mu_3\text{-}S$ ligand. The Au(PPh$_3$) group bridges one

Ru–Ru edge, generating a butterfly metal core, while the hydride ligand, located in the structure analysis, lies across an adjacent edge. The structure is therefore that expected on replacing one of the hydrido ligands of $H_2Ru_3(\mu_3-S)(CO)_9$ [42] by an isolobal $Au(PPh_3)$ moiety [27].

The Au–Ru distances (average 2.748 Å) are towards the shorter end of the range normally found for such bonds. The Ru–Ru bond lengths are all different which is expected since each Ru is chemically distinct. The shortest (Ru(2)–Ru(3), 2.737 Å) is unbridged while the H-bridged (Ru(1)–Ru(3), 2.885 Å) and the Au-bridged (Ru(1)–Ru(2), 2.933 Å) examples are progressively longer, in accord with normal trends. Despite the inequivalence of the three ruthenium atoms the μ_3-S ligand is only slightly displaced away from the most highly-substituted Ru(1); individual Ru–S distances are slightly but significantly shorter than in $H_2Ru_3(\mu_3-S)(CO)_9$ [42].

The structure of $Ru_3Au(\mu_3-SBu^t)(CO)_9(PPh_3)$ (2)

The overall geometry of **2** is shown in Fig. 2. Again the $Au(PPh_3)$ group bridges one edge of an isosceles triangle of ruthenium atoms, which is capped by the μ_3-SBu^t ligand. The butterfly angle for this cluster is unusually large (see below).

The μ_3-SBu^t group is symmetrically bonded to all three ruthenium atoms, with the Bu^t-S vector making an angle of 87.2° with the Ru_3 plane. The Ru–S distances are 0.05 Å shorter than those found in **1** as a result of stronger bonding from the formally $5e$ donor ligand, compared with the $4e$ μ_3-S ligand in **1**. However, the Ru–S bonds in **2** are ca. 0.03 Å longer than those in $Ru_3(\mu_3-SBu^t)(\mu_3-C_7H_7)(CO)_6$, in which the electron-withdrawing C_7H_7 ligand encourages even stronger $S \rightarrow Ru_3$ donation [38].

The $AuRu_2$ triangle of **2** is slightly larger than the equivalent part of **1** but it is unclear whether this arises because of the different hinge angle, or whether the electronic properties of the sulphur ligands are responsible. The Ru(1)–Ru(3) and Ru(2)–Ru(3) bond lengths of **2** lie between those of the H-bridged and non-bridged ones of **1**.

The structure of $Ru_3Au_2(\mu_3-S)(CO)_9(PPh_3)_2$ (3)

This complex is illustrated in Fig. 3. It consists of an Au_2Ru_3 trigonal-bipyramidal core with Au atoms in an apical and an equatorial site. This metallic unit is symmetrically capped on the Ru_3 face by a μ_3-S atom. The cluster is formally derived from **1** by removing the H ligand and inserting the second $Au(PPh_3)$ group between the wing tips of the $AuRu_3$ butterfly. This change results in slightly increased Au–Ru, Ru–Ru and S–Ru bond lengths, although the effects are surprisingly small. The Au–Au bond length of 2.967 Å is unexceptional as are all the Au–Ru bonds, which range from 2.783–2.866 Å. Individual differences arise no doubt from the packing requirements of adjacent ligands. Not unexpectedly the overall geometry differs in only minor detail from that of $Ru_3Au_2(\mu_3-S)(CO)_8(PPh_3)_3$ [10].

The butterfly angle in 1 and 2

The most striking difference between **1** and **2** is the $AuRu_2/Ru_3$ dihedral angles of 119.4° in the former and 147.5° in the latter. This means that in **1** the Au(1), Ru(1), Ru(2) and S atoms are nearly coplanar whereas the Au(1)Ru(1)Ru(2)/

TABLE 6

DIHEDRAL ANGLES IN $AuRu_3$ BUTTERFLY CLUSTERS

$AuRu_3(\mu\text{-H})(\mu_3\text{-S})(CO)_9(PPh_3)$	119.4°	this work
$AuRu_3(\mu_3\text{-SBu}^t)(CO)_9(PPh_3)$	147.5°	this work
$AuRu_3(\mu\text{-H})(\mu_3\text{-PPh})(CO)_9(PMe_2Ph)$	106.2°	[3]
$AuRu_3(\mu_3\text{-COMe})(CO)_{10}(PPh_3)$	117°	[4]
$AuRu_3(\mu\text{-H})_2(\mu_3\text{-COMe})(CO)_9(PPh_3)$	111.8°	[4]
$AuRu_3(\mu\text{-Cl})(CO)_{10}(PPh_3)$	117.2°	[12]
$AuRu_3(\mu_3\text{-C}_2Bu^t)(CO)_9(PPh_3)$	129.3°	[6]

Ru(1)Ru(2)S(1) dihedral angle in **2** is 146.5°. This marked change in butterfly angle has remarkably little effect on the dispositions of the CO ligands (see Fig. 1 and 2). The hinge angle of **2** is in fact very similar to the Au(1)Ru(1)Ru(2)/Ru(1)Ru(2)Ru(3) dihedral angle in **3** (146.5°) where the extra Au(PPh$_3$) group holds the wing tips apart.

Although the butterfly angle in such tetranuclear clusters has been shown to be very flexible [29], the difference of 28° in this parameter for **1** and **2** is presumably caused by the electronic differences between μ_3-S and μ_3-SBu^t ligands. Table 6 lists the butterfly angles found for a range of related clusters and it is clear that the normal range is 106–120°, so that the angle observed for **1** conforms to precedent whereas that of **2** is unusually large. Carty et al. [43] have shown a correlation between dihedral angles in tetranuclear butterfly cluster and the formal electron count; 62 electron clusters exhibiting 90–117° while 64 electron clusters give 140–180° angles. However, all the clusters in Table 6 give a formal 62-electron count. An extension of Carty et al.'s conclusions would suggest that the 5-electron μ_3-SBu^t group is more strongly electron-donating to the cluster core than the ligands associated with the other clusters in Table 6. Consistent with this, it was noted above that the Ru–S bonds in **2** are relatively short.

Acknowledgements

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