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Unprecedented co-ordination mode of the tetrathio-molybdate or -tungstate anions in heterometallic gold complexes. Crystal structures of $[MoS_4(AuAsPh_3)_2]$ and $[WS_4(AuCH_2PPh_3)_2]\cdot CH_2Cl_2$

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Treatment of the tetrathiometalates $[NH_4]_2[MS_4]$ (M = Mo or W) with $[AuCl(AsPh_3)]$ (molar ratio 1:2) gave the trinuclear species $[MS_4(AuAsPh_3)_2]$ (M = Mo **1** or W **2**). Stepwise substitution of the arsine ligand afforded the complexes $[MS_4(AuAsPh_3)(AuPPh_3)]$ (M = Mo **3** or W **4**) or $[MS_4(AuPPh_3)(AuPPh_2Me)]$ (M = Mo **5** or W **6**). The reaction with gold(I) complexes [AuCl(ylide)] follows a different pathway depending on the ylide ligand; with the less sterically demanding CH_2PPh_2Me the species $[MS_4(AuCH_2PPh_2Me)_2]$ (M = Mo **7** or W **8**) with three-co-ordinate gold were formed, but the ylide CH_2PPh_3 led to $[MS_4(AuCH_2PPh_3)_2]$ (M = Mo **9** or W **10**) with one three- and one two-co-ordinate gold centre. The crystal structures of complexes **1** and **10** were determined by X-ray diffraction.

The chemistry of molecular metal sulfides has attracted much attention in the last few years. In particular, tetrathiometalate species have been widely studied as ligands for many transition metals because of their biochemical interest.[1,2] Sulfur-bridged molybdenum compounds are significant in bioinorganic problems and have been studied with respect to the role of this metal in nitrogen fixation,[2–5] in the redox-active molybdoenzymes such as xanthine, aldehyde and sulfite oxidases, and nitrate reductase,[6,7] and in the biological antagonism between copper and molybdenum.[8,9] Furthermore certain thiometalate complexes form structurally related catalytic sites in industrial hydrodesulfurization and hydrodenitrogenation catalysts.[10]

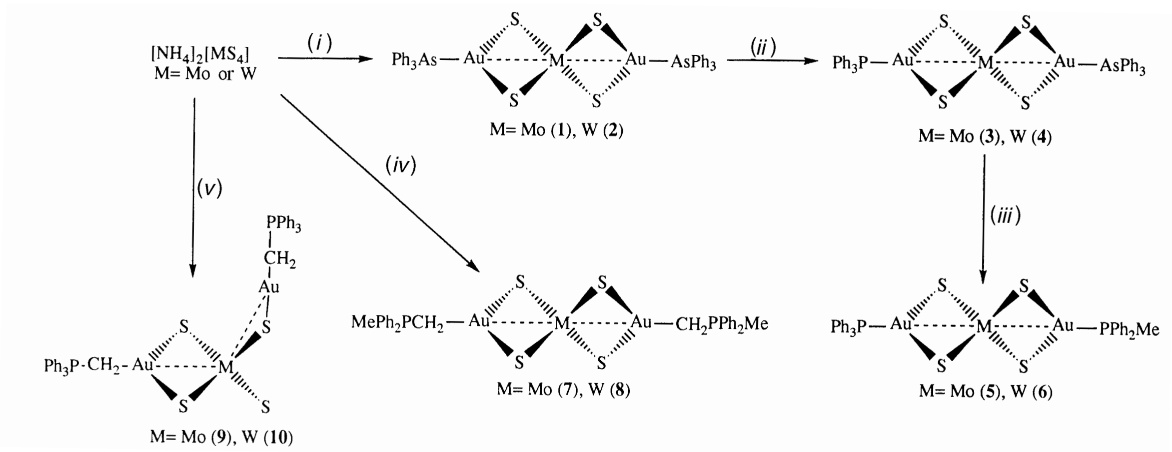
The reactivity of the tetrathiometalates in complex chemistry is especially interesting since they display unique ligand properties. However, only a few examples have been reported with gold: the inorganic ring system[11] $[Au_2(WS_4)]^{2-}$ or the trinuclear species $[MS_4(AuPR_3)_2]$.[12–14] These compounds contain two different metals in close proximity which can lead to unusual structure and bonding relationships and unique reactivity patterns.

Here we report the synthesis of tetrathiometalate gold(I) complexes with ligands other than phosphines. Usually the thioanions $[MS_4]^{2-}$ (M = Mo or W) have been shown to co-ordinate either in a bi- or tetra-dentate manner. We describe an unprecedented co-ordination mode of these metalloligands, as a bridging ligand to two gold atoms, where the gold centres display two- and three-co-ordination in the same molecule.

Results and Discussion

The reaction of $[NH_4]_2[MS_4]$ with $[AuCl(AsPh_3)]$ in dichloromethane progresses with slow dissolution of the thioanions to give dark red (Mo) or yellow (W) solutions of the complexes $[MS_4(AuAsPh_3)_2]$ (M = Mo **1** or W **2**) (Scheme 1). The IR spectra of complexes **1** and **2** show the typical absorptions arising from the arsine ligands,[15] δ(C–As–C), at *ca.* 340vs and 327s cm^{-1} and ν(As–C) at *ca.* 477s and 470s cm^{-1}. Other bands can be assigned to the vibration ν(M–S) at *ca.* 455s cm^{-1}, which, according to literature data, corresponds to bridging sulfur atoms.[1,16] In the positive-ion fast-atom bombardment (FAB) spectra of **1** and **2** the molecular peaks appear at m/z = 1234 (**1**, 18) or 1319 (**2** $[M + H]^+$, 86%).

The structure of complex **1** was confirmed by an X-ray diffraction study. The molecule is shown in Fig. 1, with selected bond lengths and angles in Table 1. The molybdenum atom has an essentially tetrahedral co-ordination geometry with Mo–S



Scheme 1 (*i*) $2[AuCl(AsPh_3)]$; (*ii*) PPh_3; (*iii*) PPh_2Me; (*iv*) $2\,[AuCl(CH_2PPh_2Me)]$; (*v*) $2\,[AuCl(CH_2PPh_3)]$

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Au(1)–As(1)	2.3748(14)	Au(1)–S(2)	2.388(3)
Au(1)–S(1)	2.402(3)	Au(1)···Mo	2.7806(14)
Au(2)–As(2)	2.3714(14)	Au(2)–S(3)	2.379(3)
Au(2)–S(4)	2.401(3)	Au(2)···Mo	2.7685(14)
Mo–S(3)	2.212(3)	Mo–S(2)	2.214(3)
Mo–S(1)	2.217(2)	Mo–S(4)	2.220(3)
As(1)–C(31)	1.917(9)	As(1)–C(11)	1.929(9)
As(1)–C(21)	1.933(9)	As(2)–C(61)	1.915(9)
As(2)–C(51)	1.922(9)	As(2)–C(41)	1.936(9)
As(1)–Au(1)–S(2)	132.95(7)	As(1)–Au(1)–S(1)	126.48(6)
S(2)–Au(1)–S(1)	100.00(9)	As(2)–Au(2)–S(3)	134.63(7)
As(2)–Au(2)–S(4)	124.78(7)	S(3)–Au(2)–S(4)	100.44(9)
S(3)–Mo–S(2)	108.16(11)	S(3)–Mo–S(1)	108.71(10)
S(2)–Mo–S(1)	111.85(10)	S(3)–Mo–S(4)	111.97(10)
S(2)–Mo–S(4)	108.00(11)	S(1)–Mo–S(4)	108.19(10)
Au(2)···Mo···Au(1)	178.38(3)	C(31)–As(1)–C(11)	106.6(4)
C(31)–As(1)–C(21)	104.3(4)	C(11)–As(1)–C(21)	102.0(4)
C(31)–As(1)–Au(1)	109.6(3)	C(11)–As(1)–Au(1)	117.7(3)
C(21)–As(1)–Au(1)	115.5(2)	C(61)–As(2)–C(51)	105.0(3)
C(61)–As(2)–C(41)	103.9(4)	C(51)–As(2)–C(41)	106.6(4)
C(61)–As(2)–Au(2)	108.7(2)	C(51)–As(2)–Au(2)	116.4(3)
C(41)–As(2)–Au(2)	115.1(3)	Mo–S(1)–Au(1)	73.90(8)
Mo–S(2)–Au(1)	74.24(8)	Mo–S(3)–Au(2)	74.08(8)
Mo–S(4)–Au(2)	73.49(8)		

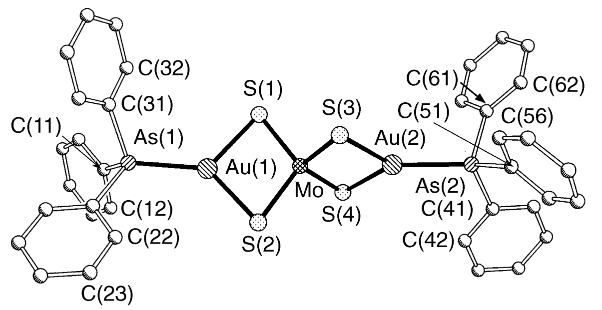
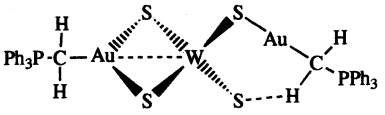


Fig. 1 Structure of complex **1** showing the atom numbering scheme. Radii are arbitrary; hydrogen atoms are omitted for clarity

distances from 2.212(3) to 2.220(3) Å, as expected longer than in the free thioanion.[17] The geometry at the gold centres is trigonal planar but somewhat distorted because of the restricted bite of the metalloligand, with narrow S–Au–S angles of 100.00(9) and 100.44(9)°, similar to those found in complexes with phosphine ligands.[12–14] The Au–S distances are 2.379(3) and 2.402(3) Å and are, as expected, longer than in linearly co-ordinated gold complexes, but normal for these type of complexes.[12–14] The Au–As bond lengths, 2.3748(14) and 2.3714(14) Å, are also normal. The Mo···Au distances are 2.7685(14) and 2.7806(14) Å, shorter than those in the complexes $[MoS_4(AuPR_3)_2]$ at about 2.81 Å. The Mo–S–Au angles, 73.49(8), 73.90(8), 74.08(8) and 74.24(8)°, are slightly narrower than in the phosphine derivatives. It thus seems that in complex **1** any Mo···Au interaction is stronger than in the previously reported complexes with phosphines. Molecular orbital calculations have been described for derivatives of Fe and Co. These show that a delocalized molecular orbital occurs over the M–Mo moiety. The overlap integral function between the metals shows that at a separation of approximately 2.8 Å a direct metal–metal interaction should be considered.[1]

Taking advantage of the substitution lability of the $AsPh_3$ ligand in gold complexes, we have carried out stepwise substitution reactions for phosphine ligands. This synthetic route allows the preparation of asymmetric complexes where the anion $[MS_4]^{2-}$ bridges two different AuL^+ fragments. The reaction of **1** or **2** with PPh_3 in dichloromethane proceeds with substitution of one arsine ligand, giving the complexes $[MS_4(AuAsPh_3)(AuPPh_3)]$ (M = Mo **3** or W **4**). Further reaction of **3** or **4** with 1 equivalent of PPh_2Me gave the mixed-phosphine species $[MS_4(AuPPh_3)(AuPPh_2Me)]$ (M = Mo **5** or W **6**).



Scheme 2 Interaction of one hydrogen atom with the sulfur centre in complex **10**

Complexes **3**–**6** have a similar IR pattern to those of the starting materials, although a shift is observed for the bands arising from $AsPh_3$ (in **3** and **4**; they disappear from **5** and **6**), and also a small change in the ν(M–S) vibrations. The $^{31}P-\{^1H\}$ NMR spectra show a singlet for PPh_3 in complexes **3** and **4**, while two singlets for the two different phosphorus environments appear for **5** and **6**. The chemical shift for these derivatives is similar to that observed for other three-co-ordinated complexes with sulfur-based ligands.[12–14] The positive-ion fast atom bombardment (FAB) spectra show the molecular peaks at $m/z = 1189$ (**3**, 7), 1083 (**5**, 13) and 1168 (**6**, 21%), but not for complex **4**. However all display a marked fragmentation of the molecule caused by addition of $[Au(PR_3)]^+$ cations to the S^{2-} or $[MS_4]^{2-}$ ligands.

We have also examined the reaction of other [AuCl(L)] complexes with the thioanions, and have synthesized the first organometallic gold derivatives of the tetrathiometalates, $[MS_4(AuL)_2]$ ($L = CH_2PPh_2Me$, M = Mo **7** or W **8**; $L = CH_2PPh_3$, M = Mo **9** or W **10**) (with L = ylide). The complexes are red (**7** and **9**) or yellow (**8** and **10**) solids stable to air and moisture. In the IR spectra the ν(Au–Cl) vibrations of the starting materials are no longer observed; new vibrations ν(M–S) appear between 438 and 457 cm^{-1}, but other bands around 500 cm^{-1} may be overlapped with those from the ylide ligand.

The NMR spectra indicate a significant difference between the complexes with both ylides. Compounds **7** and **8** present a singlet in their $^{31}P-\{^1H\}$ NMR spectra, which shows the equivalence of the phosphorus atoms. In the ^1H NMR spectra a doublet for the methylene and another for the methyl group appear as expected. Therefore we can propose a similar structure to those of the complexes mentioned above with the gold(I) centres being three-co-ordinated. However, in the $^{31}P-\{^1H\}$ NMR spectra of **9** and **10** two singlets appear, which means that the two phosphorus atoms are chemically inequivalent. In the ^1H NMR spectra of these derivatives the four protons of the methylene groups are inequivalent; each appears as a doublet of doublets because of the coupling with the other proton and the phosphorus atom. Two of these resonances are overlapped, probably those of the two protons of a methylene group, and the other two have different chemical shifts, one being broad. The reason for this change in the chemical shift and the broadness of one of the signals could arise from an interaction between a hydrogen and one of the sulfur atoms (Scheme 2).

In the positive-ion fast atom bombardment spectra of these derivatives the molecular peaks appear at $m/z = 1048$ (**7**, 17), 1135 (**8**, 15) and 1258 (**10**, 6%). A peak also appears corresponding to the addition of an AuL^+ fragment, $[M + AuL]^+$ at $m/z = 1457$ (**7**, 13), 1545 (**8**, 5) and 1733 (**10**, 4%). The spectrum of complex **9** does not present any peak containing the $[MoS_4]^{2-}$ unit and only shows small fragmentation peaks such as $[AuL]^+$, $[AuL_2]^+$, *etc.*

We have confirmed the structure of complex **10** by an X-ray diffraction study. The molecule is shown in Fig. 2, with selected bond lengths and angles in Table 2. An important structural feature is that the two gold atoms have different co-ordination modes. Atom Au(1) has a trigonal-planar geometry, again distorted because of the restricted bite of the tetrathiometalate ligand, S(1)–Au(1)–S(2) 98.5(3), similar to that of complex **1**. Consequently the angles S–Au–C are greater than 120°. The other gold atom, Au(2), has a linear geometry with an angle S–Au–C of 177.6(8)° similar to the ideal value. The tungsten centre has a tetrahedral co-ordination geometry but now with a more irregular distribution of W–S bond distances. As expected

Table 2 Selected bond lengths (Å) and angles (°) for complex **10**

Au(1)–C(1)	2.10(3)	Au(1)–S(2)	2.427(9)
Au(1)–S(1)	2.453(9)	Au(2)–C(2)	2.10(3)
Au(2)–S(3)	2.322(9)	W–S(4)	2.145(8)
W–S(2)	2.217(8)	W–S(1)	2.226(9)
W–S(3)	2.240(10)	P(1)–C(1)	1.72(3)
P(1)–C(31)	1.80(2)	P(1)–C(11)	1.82(2)
P(1)–C(21)	1.83(2)	P(2)–C(41)	1.73(3)
P(2)–C(2)	1.78(3)	P(2)–C(61)	1.79(2)
P(2)–C(51)	1.82(2)		
C(1)–Au(1)–S(2)	133.1(9)	C(1)–Au(1)–S(1)	128.2(9)
S(2)–Au(1)–S(1)	98.5(3)	C(2)–Au(2)–S(3)	177.6(8)
S(4)–W–S(2)	107.8(3)	S(4)–W–S(1)	109.3(4)
S(2)–W–S(1)	112.6(3)	S(4)–W–S(3)	105.4(4)
S(2)–W–S(3)	111.2(4)	S(1)–W–S(3)	110.1(4)
C(1)–P(1)–C(31)	111.2(14)	C(1)–P(1)–C(11)	110.5(12)
C(31)–P(1)–C(11)	107.2(11)	C(1)–P(1)–C(21)	112.4(14)
C(31)–P(1)–C(21)	108.3(11)	C(11)–P(1)–C(21)	106.9(10)
C(41)–P(2)–C(2)	115.8(13)	C(41)–P(2)–C(61)	108.4(13)
C(2)–P(2)–C(61)	110.3(13)	C(41)–P(2)–C(51)	106.7(13)
C(2)–P(2)–C(51)	110.0(14)	C(61)–P(2)–C(51)	105.1(10)
W–S(1)–Au(1)	74.0(3)	W–S(2)–Au(1)	74.6(3)
W–S(3)–Au(2)	81.9(3)	P(1)–C(1)–Au(1)	115(2)
P(2)–C(2)–Au(2)	111(2)	C(12)–C(11)–P(1)	116.9(11)
C(16)–C(11)–P(1)	122.0(11)	C(22)–C(21)–P(1)	120.3(12)
C(26)–C(21)–P(1)	119.6(13)	C(32)–C(31)–P(1)	119.0(12)
C(36)–C(31)–P(1)	121.0(12)	C(42)–C(41)–P(2)	119(2)
C(46)–C(41)–P(2)	121(2)	C(52)–C(51)–P(2)	122(2)
C(56)–C(51)–P(2)	118(2)	C(62)–C(61)–P(2)	118.7(11)
C(66)–C(61)–P(2)	121.2(11)		

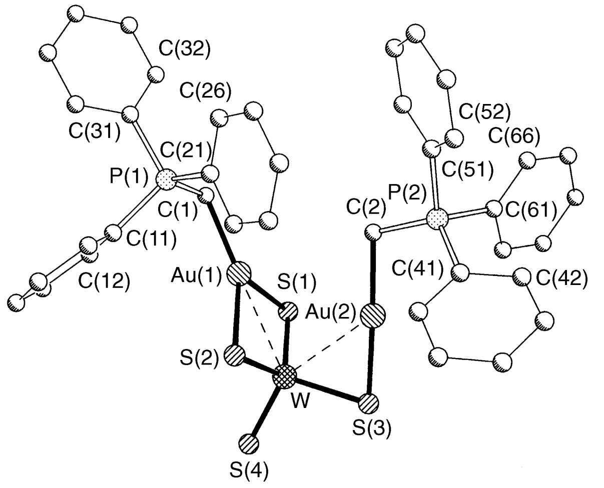


Fig. 2 Structure of complex **10** showing the atom numbering scheme. Details as in Fig. 1

the shortest, 2.145(8) Å, corresponds to the terminal sulfur and the longest, 2.240(10) Å, to the sulfur co-ordinated at the linear gold centre. The other distances W–S, 2.226(9) and 2.217(8) Å, are similar to those in complex **1**. The angles at the sulfur atoms bridging two metallic centres are very narrow, Au(1)–S(1)–W 74.0(3), Au(1)–S(2)–W 74.6(3) and W–S(3)–Au(2) 81.9(3)°, thus favouring a tungsten–gold interaction: the contact distances are Au(1)–W 2.820(2) Å and Au(2)–W 2.991(2) Å, whereby the first is of the same order as those found in the phosphino derivatives with a trigonal gold atom. The second, although longer, is still 'short' and indicates that three-co-ordination is not a precondition for a metal–metal interaction. The gold–gold distance is 3.582(3) Å and is longer than those in dinuclear gold(I) compounds with bridging ligands.[18] The Au–S bond lengths also depend on the co-ordination mode of the metal; Au(1)–S(1) 2.453(9) and Au(1)–S(2) 2.427(9) Å are slightly longer than those in complex **1**, but lie in a similar range to those in three-co-ordinate gold complexes with a bidentate sulfur-based ligand such as $[\{\mathrm{Au(CS)(PPh_3)}\}_6]$.[19]

Experimental

Infrared spectra were recorded in the range 2000–200 $\mathrm{cm^{-1}}$ on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. The C, H and S analyses were carried out with a Perkin-Elmer 240C microanalyser. The NMR spectra were recorded on Varian 300 Unity and Bruker 300 spectrometers in $\mathrm{CDCl_3}$. Chemical shifts are relative to $\mathrm{SiMe_4}$ (^{1}H, external) and 85% $\mathrm{H_3PO_4}$ (^{31}P, external). Mass spectra were recorded on a VG Autospec using FAB techniques and 3-nitrobenzyl alcohol as matrix. The starting materials $[\mathrm{AuCl(AsPh_3)}]$,[20] $[\mathrm{AuCl(CH_2PPh_3)}]$,[21] and $[\mathrm{AuCl(CH_2PPh_2Me)}]$[21] were prepared by published procedures; $[\mathrm{Au(O_3SCF_3)(PR_3)}]$ ($\mathrm{PR_3 = PPh_3}$ or $\mathrm{PPh_2Me}$) were prepared from $[\mathrm{AuCl(PR_3)}]$[22] and $\mathrm{AgO_3SCF_3}$.

Syntheses

$[\mathrm{MS_4(AuAsPh_3)_2}]$ (M = Mo 1 or W 2). To a dichloromethane solution (20 $\mathrm{cm^3}$) of $[\mathrm{AuCl(AsPh_3)}]$ (0.108 g, 0.2 mmol) was added $[\mathrm{NH_4}]_2[\mathrm{MS_4}]$ (0.15 mmol, M = Mo or W). The suspension was stirred for 2 h and then filtered to remove unchanged $[\mathrm{NH_4}]_2[\mathrm{MS_4}]$. The solution was concentrated *in vacuo* to *ca.* 5 $\mathrm{cm^3}$ and addition of diethyl ether (10 $\mathrm{cm^3}$) gave a red (**1**) or yellow (**2**) solid which was filtered off. Complex **1**: 80% yield (Found: C, 34.85; H, 2.50; S, 9.45. Calc. for $\mathrm{C_{36}H_{30}As_2Au_2MoS_4}$: C, 35.15; H, 2.45; S, 10.4%). Complex **2**: 90% yield (Found: C, 32.7; H, 2.25; S, 9.45. Calc. for $\mathrm{C_{36}H_{30}As_2Au_2S_4W}$: C, 32.8; H, 2.3; S, 9.7%).

$[\mathrm{MS_4(AuAsPh_3)(AuPPh_3)}]$ (M = Mo 3 or W 4). To a solution of complex **1** or **2** (0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$) was added slowly a solution of $\mathrm{PPh_3}$ (0.026 g, 0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$). The mixture was stirred for 10 min and then the solvent was concentrated to *ca.* 5 $\mathrm{cm^3}$. Addition of diethyl ether (10 $\mathrm{cm^3}$) gave the complexes as red (**3**) or yellow (**4**) solids. Complex **3**: 85% yield; ^{31}P-{^{1}H} NMR δ 42.9 (s) (Found: C, 36.05; H, 2.5; S, 10.35. Calc. for $\mathrm{C_{36}H_{30}AsAu_2MoPS_4}$: C, 36.45; H, 2.55; S, 10.8%). Complex **4**: 90% yield; ^{31}P-{^{1}H} NMR δ 43.7 (s) (Found: C, 33.55; H, 2.4; S. 10.5. Calc. for $\mathrm{C_{36}H_{30}AsAu_2PS_4W}$: C, 33.9; H, 2.35; S, 10.05%).

$[\mathrm{MS_4(AuPPh_3)(AuPPh_2Me)}]$ (M = Mo 5 or W 6). To a solution of complex **3** or **4** (0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$) was added slowly a solution of $\mathrm{PPh_2Me}$ (0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$). The mixture was stirred for 10 min and then the solvent was concentrated to *ca.* 5 $\mathrm{cm^3}$. Addition of diethyl ether (10 $\mathrm{cm^3}$) gave the complexes as red (**5**) or yellow (**6**) solids. Complex **5**: 84% yield; ^{31}P-{^{1}H} NMR δ 42.8 (s, $\mathrm{PPh_3}$) and 24.2 (s, $\mathrm{PPh_2Me}$); ^{1}H NMR δ 2.50 [d, 3 H, Me, *J*(PH) 10.01 Hz] (Found: C, 34.6; H, 2.8; S, 11.45. Calc. for $\mathrm{C_{31}H_{28}Au_2MoP_2S_4}$: C, 34.45; H, 2.6; S, 11.85%). Complex **6**: 56% yield; ^{31}P-{^{1}H} NMR δ 43.6 (s, $\mathrm{PPh_3}$) and 24.9 (s, $\mathrm{PPh_2Me}$); ^{1}H NMR δ 2.48 [d, 3 H, Me, *J*(PH) 8.54 Hz] (Found: C, 32.1; H, 2.55; S, 10.5. Calc. for $\mathrm{C_{31}H_{28}Au_2P_2S_4W}$: C, 31.85; H, 2.4; S, 11.0%).

$[\mathrm{MoS_4(AuL)_2}]$ ($\mathrm{L = CH_2PPh_2Me}$, M = Mo 7 or W 8; $\mathrm{L = CH_2PPh_3}$, M = Mo 9 or W 10). To a solution of $[\mathrm{AuCl(CH_2PPh_2Me)}]$ (0.089 g, 0.2 mmol) or $[\mathrm{AuCl(CH_2PPh_3)}]$ (0.102 g, 0.2 mmol) in dichloromethane (20 $\mathrm{cm^3}$) was added $[\mathrm{NH_4}]_2[\mathrm{MS_4}]$ (0.1 mmol). The suspension was stirred for 2 h and then filtered over Celite. The solution was concentrated under vacuum to *ca.* 5 $\mathrm{cm^3}$ and addition of diethyl ether (15 $\mathrm{cm^3}$) gave the complexes **7**–**10**. For **9** it was necessary to add water (10 $\mathrm{cm^3}$) to the dichloromethane and the complex was obtained in the organic layer. Complex **7**: 70% yield; ^{31}P-{^{1}H} NMR δ 30.2; ^{1}H NMR δ 2.82 [d, 2 H, $\mathrm{CH_2}$, *J*(PH) 11.66] and 2.52 [d, 3 H, Me, *J*(PH) 12.99 Hz] (Found: C, 32.3; H, 2.7; S, 12.15. Calc. for $\mathrm{C_{28}H_{30}Au_2MoP_2S_4}$: C, 32.15; H, 2.9; S, 12.25%). Complex **8**: 72% yield; ^{31}P-{^{1}H} NMR δ 30.2; ^{1}H NMR δ 2.60 [d, 2 H, $\mathrm{CH_2}$, *J*(PH) 11.72] and 2.49 [d, 3 H, Me, *J*(PH) 12.94 Hz] (Found: C, 29.8; H, 2.85; S, 11.45. Calc. for $\mathrm{C_{28}H_{30}Au_2P_2S_4W}$: C, 29.65; H, 2.65; S, 11.3%). Complex **9**: 85%

yield; ^{31}P-{^{1}H} NMR δ 33.1 and 32.9; ^{1}H NMR δ 3.08 (dd), 3.05 (dd), 2.87 (br) and 2.76 (dd) (Found: C, 38.6; H, 2.8; S, 10.5. Calc. for $C_{38}H_{34}Au_2MoP_2S_4$: C, 39.0; H, 2.95; S, 10.95%). Complex **10**: 87% yield; ^{31}P-{^{1}H} NMR δ 33.1 and 32.5; ^{1}H NMR δ 2.81 (br), 2.76 (m) and 2.40 (m) (Found: C, 36.3; H, 2.9; S, 10.2. Calc. for $C_{38}H_{34}Au_2P_2S_4W$: C, 36.25; H, 2.7; S, 10.2%).

Crystallography

Compound 1. *Crystal data.* $C_{36}H_{30}As_2Au_2MoS_4$, $M = 1230.55$, triclinic, space group $P\bar{1}$, $a = 9.452(4)$, $b = 10.690(4)$, $c = 19.735(7)$ Å, $\alpha = 87.98(3)$, $\beta = 80.18(3)$, $\gamma = 67.73(2)°$, $U = 1817.3(12)$ Å^3, $Z = 2$, $D_c = 2.249$ Mg m^{-3}, $F(000) = 1152$, λ(Mo-Kα) = 0.710 73 Å, μ = 10.45 mm^{-1}, $T = -130$ °C.

Data collection and reduction. Single crystals of compound **1** in the form of orange plates were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **1**. A crystal of dimensions 0.65 × 0.30 × 0.10 mm was mounted on a Stoe-STAD14 diffractometer, and used to collect 6508 intensities to $2\theta_{max}$ 50° (monochromated Mo-Kα radiation). An absorption correction based on ψ scans was applied, with transmission factors 0.53–1.0. Merging equivalents gave 6419 independent reflections (R_{int} 0.02). Cell constants were refined from ± ω angles of 54 reflections in the range 2θ 20–22°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F^2 (program system SHELXL 93).[23] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included using a riding model. Refinement proceeded to $wR(F^2) = 0.104$ for 406 parameters and 336 restraints (to ring planarity and light atom U values), conventional $R(F) = 0.041$, $S(F^2) = 1.071$, maximum Δρ 1.0 e Å^{-3}.

Compound 10. *Crystal data.* $C_{39}H_{36}Au_2Cl_2P_2S_4W$, $M = 1343.54$, triclinic, space group $P\bar{1}$, $a = 12.869(4)$, $b = 12.927(4)$, $c = 15.646(6)$ Å, $\alpha = 105.01(3)$, $\beta = 91.04(3)$, $\gamma = 111.71(3)°$, $U = 2316.8(13)$ Å^3, $Z = 2$, $D_c = 1.926$ Mg m^{-3}, $F(000) = 1260$, λ(Mo-Kα) = 0.710 73 Å, μ = 9.18 mm^{-1}, $T = -100$ °C.

Data collection and reduction. Single crystals in the form of red plates were obtained by slow diffusion of hexane into a dichloromethane solution of complex **10**. A crystal of dimensions 0.45 × 0.20 × 0.03 mm was mounted on a Siemens R3 diffractometer, and used to collect 6300 intensities to $2\theta_{max}$ 45° (monochromated Mo-Kα radiation) of which 5991 were independent (R_{int} 0.15, a high value because all equivalents were weak). An empirical absorption correction was applied with the program SHELXA,[24] with transmission factors 0.058–0.52. Cell constants were refined from setting angles of 46 reflections in the range 2θ 20–22°.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined as above. Only the heaviest atoms were refined anisotropically; carbon atoms were refined isotropically. The complex crystallizes with one molecule of dichloromethane, but the carbon atom could not be located. Refinement proceeded to $wR(F^2) = 0.249$ for 170 parameters, conventional $R(F) = 0.091$, $S(F^2) = 0.94$, maximum Δρ 2.6 e Å^{-3} (near the gold atoms). The R values are poor because of the weakly diffracting nature of the crystal.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/307.

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References

1 A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem.*, *Int. Ed. Engl.*, 1981, **20**, 934.
2 D. Coucouvanis, *Acc. Chem. Res.*, 1981, **14**, 201.
3 R. A. D. Wentworth, *Coord. Chem. Rev.*, 1976, **18**, 1.
4 R. H. Holm, *Chem. Soc. Rev.*, 1981, **10**, 455.
5 A. Müller and W. E. Newton, *Nitrogen Fixation*: *Chemical*, *Biochemical*, *Genetics*, Plenum Press, New York, 1981.
6 J. T. Spence, *Coord. Chem. Rev.*, 1969, **4**, 475.
7 L. E. Bennett, *Prog. Inorg. Chem.*, 1976, **18**, 1.
8 C. F. Mills, *Chem. Ber.*, 1979, **15**, 512.
9 S. Sarkar and S. B. S. Mishra, *Coord. Chem. Rev.*, 1984, **59**, 239.
10 T. R. Halbert, S. A. Cohen and E. I. Stiefel, *Organometallics*, 1985, **4**, 1689.
11 A. Müller, H. Dornfeld, G. Henkel, B. Krebs and M. P. A. Viegers, *Angew. Chem.*, *Int. Ed. Engl.*, 1978, **17**, 52.
12 J. C. Huffman, R. S. Roth and A. R. Siedle, *J. Am. Chem. Soc.*, 1976, **98**, 4340.
13 E. M. Kinsch and D. W. Stephan, *Inorg. Chim. Acta*, 1985, **96**, L87.
14 J. M. Charnock, S. Bristow, J. R. Nicholson, C. D. Garner and W. Clegg, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 303.
15 E. Maslowsky, jun., *Vibrational Spectra of Organometallic Compounds*, Wiley-Interscience, New York, 1977.
16 S. B. Sharma and I. N. Tewari, *Synth. React. Metal-Org. Chem.*, 1992, **22**, 217.
17 A. Müller, H. Bögge, E. Königer-Ahlborn and W. Hellmann, *Inorg. Chem.*, 1979, **18**, 2301.
18 P. G. Jones, *Gold Bull.*, 1981, **14**, 102, 159; 1983, **16**, 114; 1986, **19**, 46.
19 H. K. Yip, A. Schier, J. Riede and H. Schmidbaur, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2333.
20 A. D. Westland, *Can. J. Chem.*, 1969, **47**, 4135.
21 R. Usón, A. Laguna, M. Laguna, A. Usón and M. C. Gimeno, *Inorg. Chim. Acta*, 1986, **114**, 91.
22 R. Usón and A. Laguna, *Inorg. Synth.*, 1982, **21**, 71.
23 G. M. Sheldrick, SHELXL 93, A program for crystal structure refinement, University of Göttingen, 1993.
24 G. M. Sheldrick, SHELXA, A program for absorption corrections, unpublished work.

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