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Synthesis and characterisation of gold-(I) and -(III) complexes with 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborate

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The reaction of 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborane with the gold(I) complexes [AuCl(L)] afforded the neutral thiolate derivatives $[Au(SCB_{10}H_{10}CMe)L]$ (L = PPh_3 **1**, PPh_2Me **2** or $AsPh_3$ **3**). Further reaction of **1** with $[Au(O_3SCF_3)(PPh_3)]$ gave the dinuclear species $[Au_2(SCB_{10}H_{10}CMe)(PPh_3)_2][O_3SCF_3]$ **4**. Another dinuclear complex, $[Au_2(SCB_{10}H_{10}CMe)_2(\mu\text{-dppe})]$ **5**, can be synthesized by reaction of $[Au_2Cl_2(\mu\text{-dppe})]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with 2 equivalents of $HSCB_{10}H_{10}CMe$. The anionic derivatives $[N(PPh_3)_2][Au(SCB_{10}H_{10}CMe)Cl]$ **6** and $[N(PPh_3)_2][Au(SCB_{10}H_{10}CMe)_2]$ **7** were obtained by reaction of $HSCB_{10}H_{10}CMe$ with $[N(PPh_3)_2][AuCl_2]$ in a 1 : 1 or 2 : 1 molar ratio, respectively. Finally, by reaction of the thiol with suitable gold(III) precursors the anionic $[NBu_4][Au(C_6F_5)_3(SCB_{10}H_{10}CMe)]$ **8** or the neutral $[Au\{(PPh_2)_2C_2B_9H_{10}\}(SCB_{10}H_{10}CMe)_2]$ **9** derivatives were synthesized. Complexes **1**, **3** and **6** have been characterised by X-ray diffraction studies.

There is a continuing interest in transition-metal complexes, and gold in particular, with thiolate ligands for several reasons. Among these are the relevance to biological systems,[1] the potential of chemistry relating to S–C bond-cleavage reactions and desulfurization,[2] the novel structure of such complexes[3] and the possible applications in organosulfur chemistry. Interest in the co-ordination chemistry of thiolate gold(I) complexes arises in part from the potential use of these derivatives in medicine, including uses as antiarthritic and cancerostatic drugs.[4]

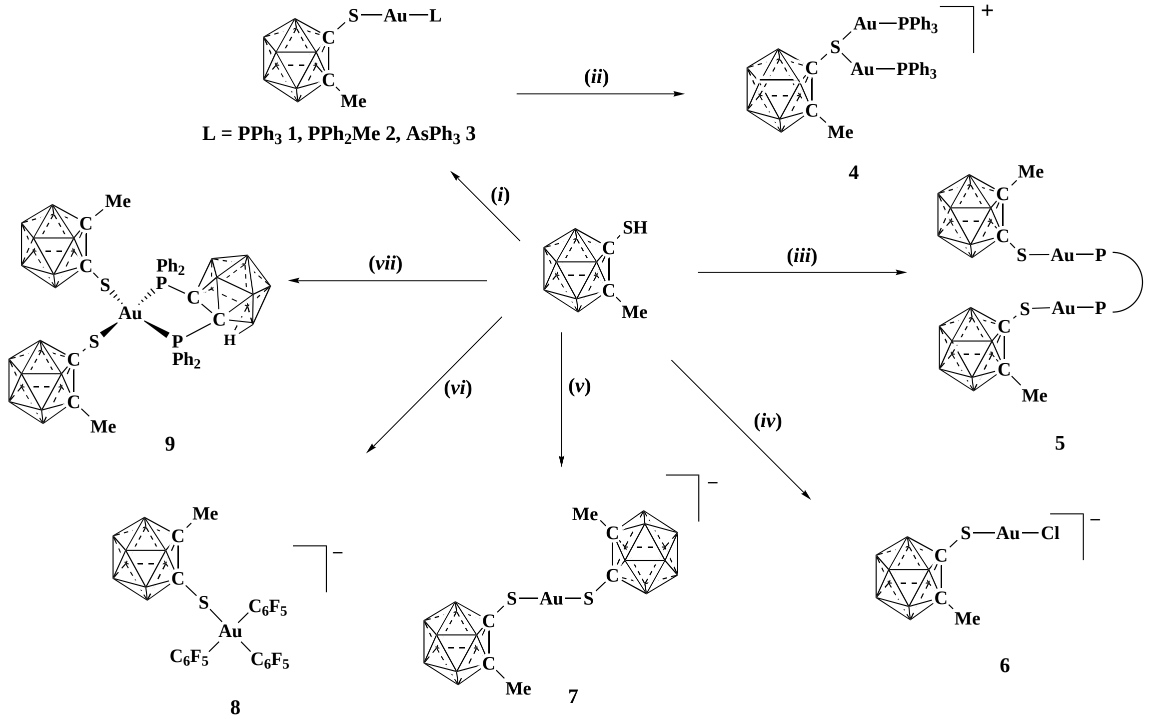
As part of our current program in the chemistry of gold with carborane derivatives,[5] it appears worthwhile to investigate the synthesis and structure of gold 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborate complexes to compare their behaviour with those of other gold thiolate derivatives. Furthermore this dodecaborate has been scarcely studied and only the synthesis of *exo*-thiocarboranes and the study of the partially degraded species have been reported thus far.[6] Here we report on the synthesis of gold-(I) and -(III) complexes with this thiolate which incorporates an *o*-carborane moiety. Furthermore, complexes incorporating an *o*-carborane backbone are receiving much attention for the potential use in tumour-seeking drugs for boron neutron capture therapy.[7]

Results and Discussion

The reaction of 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborane with [AuCl(L)] in dichloromethane and in the presence of Na_2CO_3 affords the gold(I) thiolate complexes $[Au(SCB_{10}H_{10}CMe)L]$ (L = PPh_3 **1**, PPh_2Me **2** or $AsPh_3$ **3**) (see Scheme 1). Complexes **1–3** are white solids, air and moisture stable, and they behave as non-conductors in acetone solutions. Their IR spectra show bands arising from the B–H stretching modes of the *o*-carborane cluster between 2572 and 2602 cm^{-1} (s, br). In the ^1H NMR spectra the signal of the SH proton has disappeared. There is a singlet for the carborane methyl protons and for the ligand L a multiplet for the phenyl protons; complex **2** also presents a doublet for the PMe group. The $^{31}P\text{-}\{^1H\}$ NMR spectra show a singlet for the phosphorus atom shifted downfield in comparison with the position of the starting materials. The positive-ion mass spectra of these derivatives show the molecular peak at *m/z* = 649 (**1**, 18), 586 (**2**, 2) and 693 (**3**, 8%), although the most intense peaks are assigned to the fragments $[AuL]^+$, $[AuL_2]^+$ and $[M + AuL]^+$.

The structures of complexes **1** and **3** have been confirmed by an X-ray diffraction study. The molecule of **1** is shown in Fig. 1 with selected bond lengths and angles in Table 1, **3** appears in Fig. 2 with selected bond lengths and angles in Table 2. The complexes are isostructural. In both molecules the gold atoms display a linear geometry with P–Au–S or As–Au–S angles of 179.70(8) or 178.34(4)°. Usually, mononuclear gold(I) thiolate derivatives are associated in pairs through short gold–gold contacts of *ca.* 3 Å. Contrarily, for **1** and **3** no association of the monomers by intermolecular metal–metal interactions is observed. The shortest gold–gold distances are 4.027 Å in **1** and 3.747 Å in **3**. It appears therefore that steric effects preclude the intermolecular approach necessary for the weak $Au^I\cdots Au^I$ interactions, which quite obviously are easily overruled. Similar results have been reported in (phosphine)gold benzenethiolates in which association of the monomers is only observed with unsubstituted benzenethiolates.[8]

The Au–S bond distances are 2.311(2) Å in complex **1** and 2.272(2) Å in **3**, on the extremes of those found in other gold thiolate complexes such as $[Au(SR)(PPh_3)]$ (R = Ph, $C_6H_2Me_3$-2,4,6, $C_6H_2Et_3$-2,4,6, $C_6H_2Pr^i_3$-2,4,6 or C_6H_4Cl-2)[8,9] which lie in the range 2.284(2)–2.296(2) Å. These values are more similar to that in **1** which has a phosphine as ligand. The fact that the Au–S distance is shorter in **3** may be explained by the higher *trans* influence of the phosphine compared with the arsine ligand. The Au–P bond length in **1** is 2.267(2) Å which compares well with other Au–P bond distances found in linear gold(I) complexes such as the related compounds $[Au(SR)(PPh_3)]$[8,9] [2.255(2)–2.260(3) Å] or $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(PPh_3)_2]$ [2.260(2) Å].[5a] In **3** the Au–As bond distance of 2.3399(8) is similar to that found in $[AuCl(AsPh_3)]$ [2.331(1) Å],[10] although smaller than those in the complexes $[AuMe(AsPh_3)]$ [2.3800(11) Å][11] or $[Au(C_2B_{10}H_{10}CCH_2CH_3)(AsPh_3)]$ [2.3740(8) Å][11] maybe because of the higher *trans* influence of the carboranyl carbon compared with the sulfur atom.



Scheme 1 (*i*) [AuCl(L)]; (*ii*) $[Au(O_3SCF_3)(PPh_3)]$; (*iii*) $\frac{1}{2}[Au_2Cl_2(\mu\text{-dppe})]$; (*iv*) $[N(PPh_3)_2][AuCl_2]$; (*v*) $\frac{1}{2}[N(PPh_3)_2][AuCl_2]$; (*vi*) $[NBu_4][AuBr(C_6F_5)_3]$; (*vii*) $\frac{1}{2}[AuCl_2\{(PPh_2)_2C_2B_9H_{10}\}]$

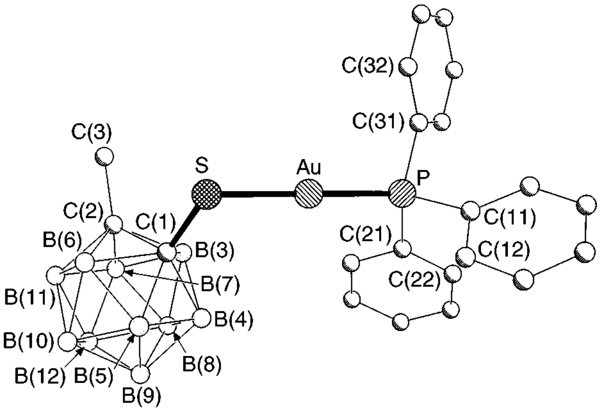


Fig. 1 Molecule of complex **1** in the crystal with the atom numbering scheme; H atoms are omitted for clarity and radii are arbitrary

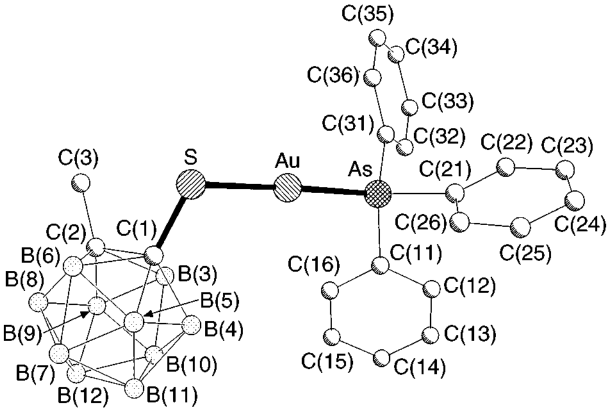


Fig. 2 Molecule of complex **3** in the crystal showing the atom labelling scheme. Details as in Fig. 1

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

Au–P	2.267(2)	Au–S	2.311(2)
S–C(1)	1.774(7)	P–C(11)	1.810(8)
P–C(31)	1.810(8)	P–C(21)	1.815(7)
C(1)–C(2)	1.736(10)	C(2)–C(3)	1.495(11)
P–Au–S	179.70(8)	C(1)–S–Au	103.9(3)
C(11)–P–C(31)	105.7(3)	C(11)–P–C(21)	105.9(3)
C(31)–P–C(21)	105.9(3)	C(11)–P–Au	113.7(3)
C(31)–P–Au	113.7(2)	C(21)–P–Au	111.3(2)
B(5)–C(1)–S	121.4(5)	B(4)–C(1)–S	123.9(5)
B(6)–C(1)–S	115.0(5)	B(3)–C(1)–S	120.3(5)
C(2)–C(1)–S	118.2(5)	C(3)–C(2)–C(1)	117.8(6)

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Au–S	2.272(2)	Au–As	2.3399(8)
S–C(1)	1.753(6)	As–C(11)	1.910(6)
As–C(21)	1.911(6)	As–C(31)	1.915(6)
C(1)–C(2)	1.713(8)	C(2)–C(3)	1.508(8)
S–Au–As	178.34(4)	C(1)–S–Au	103.7(2)
C(11)–As–C(21)	103.9(2)	C(11)–As–C(31)	104.3(2)
C(21)–As–C(31)	105.2(2)	C(11)–As–Au	111.6(2)
C(21)–As–Au	115.3(2)	C(31)–As–Au	115.4(2)
B(5)–C(1)–S	121.7(4)	B(4)–C(1)–S	124.5(4)
B(6)–C(1)–S	114.8(4)	B(3)–C(1)–S	120.5(4)
C(2)–C(1)–S	118.7(4)	C(3)–C(2)–C(1)	117.3(5)
C(12)–C(11)–As	121.2(5)	C(16)–C(11)–As	118.8(5)

As mentioned above, the mass spectra of complexes **1–3** indicate that the fragment $[M + AuPPh_3]^+$ is stable, and thus we have carried out a further reaction of complex **1** with $[Au(O_3SCF_3)(PPh_3)]BF_4$ which gives the dinuclear species $[Au_2(SCB_{10}H_{10}CMe)(PPh_3)_2][O_3SCF_3]$ **4**. Although we have not got structural confirmation of **4** we propose a structure where the thiolate ligand bridges both gold atoms; this type of derivative is well known in the chemistry of gold thiolate complexes.[12] Compound **4** behaves as a 1:1 electrolyte in acetone solutions. Its IR spectrum shows, apart from the ν(B–H) bands, others arising from the O_3SCF_3 anion, $\nu_{asym}(SO_3)$ at 1265vs (br), $\nu_{sym}(CF_3)$ at 1223s and $\nu_{asym}(CF_3)$ at 1150s cm^{-1}. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows one singlet for the two equivalent phosphorus atoms. In the positive-ion FAB mass spectrum of **4** the cation molecular peak appears at $m/z = 1108$ (25%) with coincident experimental and calculated isotopic distribution.

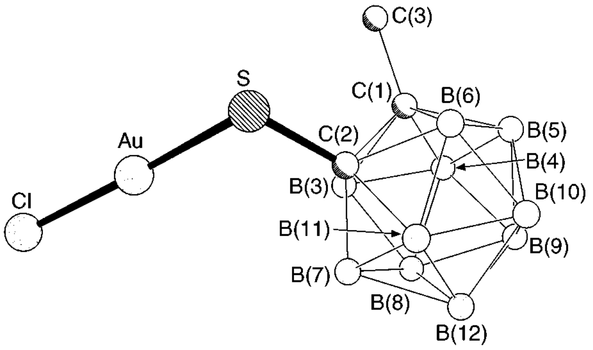


Fig. 3 The anion of complex **6** in the crystal with the atom labelling scheme. Details as in Fig. 1

Table 3 Selected bond lengths (Å) and angles (°) for complex **6**

Au–S	2.260(2)	Au–Cl	2.2794(14)
S–C(2)	1.780(5)	C(1)–C(3)	1.503(6)
C(1)–C(2)	1.710(7)		
S–Au–Cl	176.39(5)	C(2)–S–Au	106.1(2)
C(3)–C(1)–C(2)	117.6(4)	B(11)–C(2)–S	120.8(3)
B(7)–C(2)–S	124.1(4)	B(3)–C(2)–S	120.2(3)
C(1)–C(2)–S	118.0(3)	B(6)–C(2)–S	114.9(3)

The fragments $[Au(PPh_3)_2]^+$ and $[Au(PPh_3)]^+$ are present at *m/z* 721 (100) and 459 (72%), respectively; also a peak at *m/z* 1409 (12%) appears which corresponds to the cation $[S(AuPPh_3)_3]^+$.

The treatment of $HSCB_{10}H_{10}CMe$ with $[Au_2Cl_2(\mu\text{-dppe})]$ (molar ratio 2:1) [dppe = 1,2-bis(diphenylphosphino)ethane] in dichloromethane and in the presence of Na_2CO_3 leads to the dinuclear species $[Au_2(SCB_{10}H_{10}CMe)_2(\mu\text{-dppe})]$ **5**. The ^1H NMR spectrum shows a singlet for the methyl protons and a multiplet for the methylene protons of the dppe ligand. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum only a singlet appears because of the equivalence of the phosphorus atoms of the diphosphine. The positive-ion FAB mass spectrum shows the highest peak at *m/z* = 983 which corresponds to the fragment $[Au_2(SCB_{10}H_{10}CMe)(\mu\text{-dppe})]^+$ arising by loss of one thiolate ligand.

Anionic derivatives have been synthesized from the reaction of $HSCB_{10}H_{10}CMe$ with $[N(PPh_3)_2][AuCl_2]$ in molar ratios 1:1 and 1:2 to give $[N(PPh_3)_2][AuCl(SCB_{10}H_{10}CMe)]$ **6** and $[N(PPh_3)_2][Au(SCB_{10}H_{10}CMe)_2]$ **7**. Their IR spectra show bands arising from the ν(B–H) frequencies at 2599s (br) and 2566s (br) cm^{-1}, respectively; for complex **6** also appears the vibration ν(Au–Cl) at 329 cm^{-1}. Both behave as 1:1 electrolytes in acetone solutions. The ^1H NMR spectra show resonances due to the BH protons as a very broad band over 2 ppm, the multiplets of the phenyl protons and a singlet arising from the methyl protons. The $^{31}P\text{-}\{^1H\}$ NMR spectra present only a singlet for the two equivalent phosphorus of the cation $[N(PPh_3)_2]^+$. The negative-ion mass spectra of complexes **6** and **7** show the anion peaks $[Au(SCB_{10}H_{10}CMe)Cl]^-$ at *m/z* = 420 (**6**, 11%) and $[Au(SCB_{10}H_{10}CMe)_2]^-$ at *m/z* = 576 (**7**, 100%). In both spectra there are peaks of higher nuclearity such as $[Au_2(SCB_{10}H_{10}CMe)_2]^-$, $[Au_2(SCB_{10}H_{10}CMe)_3]^-$ or $[Au_3(SCB_{10}H_{10}CMe)_4]^-$.

The structure of complex **6** has been established by an X-ray diffraction study. The anion is shown in Fig. 3 and selected bonds and angles are collected in Table 3. The co-ordination around the gold atom is almost linear, S–Au–Cl 176.39(5)°. The Au–Cl length, 2.2794(14) Å, is similar to those observed in other linear gold(I) complexes such as $[AuCl(C_5H_{10}N_2S)]$ [Au–Cl 2.26(1) Å][13] or $[AuCl(PPh_3)]$ [2.279(3) Å].[14] The Au–S bond length of 2.260(2) Å is consistent with other S donors co-ordinated *trans* to Cl such as $[AuCl(SPPh_3)]$ [Au–S 2.256(1) Å][15] or $[AuCl(C_5H_{10}N_2S)]$ [Au–S 2.25(1) Å][13] and slightly shorter than those found in the related compound $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(PPh_3)_2]$ [Au–S 2.329(2) Å].[5a] As far as we are aware this is the first crystal structure report of an anionic gold compound bonded to a chlorine and a sulfur donor ligand.

We have also synthesized gold(III) derivatives with the 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborate ligand. The treatment of equimolar amounts of $[NBu_4][AuBr(C_6F_5)_3]$ with 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborane in the presence of Na_2CO_3 gives $[NBu_4][Au(C_6F_5)_3(SCB_{10}H_{10}CMe)]$ **8**. Complex **8** behaves as 1:1 electrolyte in acetone solutions. Its IR spectrum shows, apart from ν(B–H) at 2597vs (br), bands arising from the pentafluorophenyl groups bonded to gold(III) at 1510vs, 971vs, 811s and 795s and the ν(Au–S) vibration at 313s cm^{-1}. The ^{19}F NMR spectrum shows the typical pattern of a tris(pentafluorophenyl) group; there are two multiplets for the *m*-, two triplets for the *p*- and two multiplets for the *o*-fluorine nuclei in the ratio 2:1. Each group of signals belongs to the mutually *trans* pentafluorophenyl rings and to the C_6F_5 group *cis* to them, respectively.

Finally, we have also synthesized another gold(III) derivative by reaction of $[AuCl_2\{(PPh_2)_2C_2B_9H_{10}\}]$ with 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborane in the presence of Na_2CO_3. The resulting complex $[Au\{(PPh_2)_2C_2B_9H_{10}\}(SCB_{10}H_{10}CMe)_2]$ **9** is neutral and thus behaves as non-conductor in acetone solutions. The IR spectrum shows a very broad band centred around 2570 cm^{-1} for the ν(B–H) frequencies of the two carborane types. The ^1H NMR spectrum shows a singlet for the methyl protons, a multiplet for the phenyl protons and a broad signal around δ −2 assigned to the extra hydrogen atom in the pentagonal open C_2B_3 face. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum only one signal at very low field appears which corresponds to the equivalent phosphorus atoms of the diphosphine.

Experimental

Instrumentation

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. The analyses (C and H) were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG autospec instrument, with the FAB technique, using nitrobenzyl alcohol as matrix. The NMR spectra were recorded on Varian Unity 300 and Bruker ARX 300 spectrometers in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), 85% H_3PO_4 (^{31}P, external) and $CFCl_3$ (^{19}F, external).

Materials

The starting materials $HSCB_{10}H_{10}CMe$,[6] $[AuCl(PR_3)]$,[16] $[N(PPh_3)_2][AuCl_2]$,[17] $[NBu_4][AuBr(C_6F_5)_3]$[18] and $[AuCl_2\{(PPh_2)_2C_2B_9H_{10}\}]$[19] were prepared by published procedures; $[Au(O_3SCF_3)(PPh_3)]$ was obtained from $[AuCl(PPh_3)]$ by reaction with AgO_3SCF_3 and $[Au_2Cl_2(\mu\text{-dppe})]$ from 2 equivalents of $[AuCl(tht)]$[20] (tht = tetrahydrothiophene) and 1 equivalent of the diphosphine.

Syntheses

$[Au(SCB_{10}H_{10}CMe)L]$ (L = PPh_3 1, PPh_2Me 2, or $AsPh_3$ 3). To a solution of $HSCB_{10}H_{10}CMe$ (0.019 g, 0.1 mmol) in dichloromethane (30 cm^3) was added $[AuCl(PPh_3)]$ (0.049 g, 0.1 mmol), $[AuCl(PPh_2Me)]$ (0.043 g, 0.1 mmol) or $[AuCl(AsPh_3)]$ (0.053 g, 0.1 mmol) and an excess of Na_2CO_3 (0.53 g, 5 mmol). The mixture was stirred for 30 min, the excess of Na_2CO_3 filtered off and the solution concentrated to *ca.* 5 cm^3. Addition of diethyl ether (10 cm^3) gave complexes **1**–**3** as white solids. Complex **1**: yield 74% (Found: C, 38.45; H, 4.05; S, 4.95. Calc. for $C_{21}H_{28}AuB_{10}PS$: C, 38.90; H, 4.35; S, 4.95%). Λ_M 0.8 Ω^{-1} cm^2 mol^{-1}; ^1H NMR δ 2.25 (s, 3 H, Me) and 7.3–7.6 (m, br, 15

Table 4 Details of the data collection and structure refinement for complexes **1**, **3** and **6***

	1·$0.5CH_2Cl_2$	**3**·$0.5CH_2Cl_2$	**6**·CH_2Cl_2
Chemical Formula	$C_{21.5}H_{29}AuB_{10}ClPS$	$C_{21.5}H_{29}AsAuB_{10}ClS$	$C_{40}H_{45}AuB_{10}Cl_3NP_2S$
M	690.99	734.94	1045.19
Crystal habit	Colourless prism	Colourless prism	Colourless tablet
Crystal size/mm	0.40 × 0.30 × 0.20	0.45 × 0.45 × 0.20	0.50 × 0.40 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/c$
a/Å	16.445(6)	16.400(3)	11.2536(12)
b/Å	20.060(7)	19.868(5)	27.985(3)
c/Å	16.886(7)	16.771(3)	15.0641(14)
β/°	98.50(3)	98.52(2)	107.789(6)
U/Å^3	5509(4)	5404(2)	4517.4(8)
Z	8	8	4
D_c/Mg m^{-3}	1.666	1.807	1.537
$F(000)$	2680	2824	2072
μ(Mo-Kα)/mm^{-1}	5.583	6.848	3.583
Transmission	0.776–0.886	0.444–0.917	0.591–1.000
No. reflections measured	6508	6860	9172
No. unique reflections	4847	4732	7934
R_{int}	0.0311	0.058	0.0304
$R^a[F, F > 4\sigma(F)]$	0.0398	0.040	0.0361
R'^b (F^2, all reflections)	0.0951	0.0957	0.0606
No. reflections used	4847	4731	7934
No. parameters	271	330	474
No. restraints	64	271	123
S	0.904	1.008	0.824
Maximum $\Delta\rho$/e Å^{-3}	2.099	2.195	0.570

* Details in common: −100 °C; $2\theta_{max}$ 50°: $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R'(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants adjusted by the program; $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, where n is the number of data and p the number of parameters.

H); $^{31}P-\{^1H\}$ NMR δ 35.1 (s). Complex **2**: yield 72% (Found: C, 34.15; H, 4.50; S, 4.95. Calc. for $C_{16}H_{26}AuB_{10}PS$: C, 34.45; H, 4.70; S, 5.45%). Λ_M 1.5 Ω^{-1} cm^2 mol^{-1}; ^1H NMR δ 2.07 [d, 3 H, PMe, J(PH) 9.90 Hz], 2.19 (s, 3 H, Me) and 7.4–7.7 (m, br, 10 H); $^{31}P-\{^1H\}$ NMR δ 21.8 (s). Complex **3**: yield 81% (Found: C, 35.95; H, 3.50; S, 3.70. Calc. for $C_{21}H_{28}AsAuB_{10}S$: C, 36.40; H, 4.05; S, 4.65%); Λ_M 3 Ω^{-1} cm^2 mol^{-1}; ^1H NMR δ 2.26 (s, 3 H, Me) and 7.3–7.6 (m, br, 15 H).

$[Au_2(SCB_{10}H_{10}CMe)(PPh_3)_2][O_3SCF_3]$ 4. To a freshly prepared dichloromethane solution (20 cm^3) of $[Au(O_3SCF_3)(PPh_3)]$ (0.061 g, 0.1 mmol) was added $[Au(SCB_{10}H_{10}CMe)(PPh_3)]$ (0.080g, 0.1 mmol) and the solution was stirred for 30 min. The solvent was removed *in vacuo* and addition of diethyl ether (10 cm^3) gave complex **4** as a white solid. Yield 65% (Found: C, 39.55; H, 3.70; S, 2.25. Calc. for $C_{40}H_{43}Au_2B_{10}F_3O_3PS_2$: C, 39.20; H, 3.60; S, 2.70%). Λ_M 85 Ω^{-1} cm^2 mol^{-1}. ^1H NMR: δ 2.18 (s, 3 H, Me) and 7.2–7.6 (m, br, 30 H). $^{31}P-\{^1H\}$ NMR: δ 34.9 (s).

$[Au_2(SCB_{10}H_{10}CMe)_2(\mu\text{-dppe})]$ 5. To a solution of $HSCB_{10}H_{10}CMe$ (0.038 g, 0.2 mmol) in dichloromethane (30 cm^3) was added $[Au_2Cl_2(\mu\text{-dppe})]$ (0.086 g, 0.1 mmol) and an excess of Na_2CO_3 (0.53 g, 5 mmol). The mixture was stirred for 30 min and then filtered to remove the sodium carbonate. Concentration of solvent to *ca.* 5 cm^3 and addition of diethyl ether afforded complex **5** as a white solid. Yield 77% (Found: C, 32.75; H, 4.40; S, 5.30. Calc. for $C_{32}H_{50}Au_2B_{20}P_2S_2$: C, 32.80; H, 4.30; S, 5.45%). ^1H NMR: δ 2.25 (s, 6 H, Me), 2.67 (s, br, 4 H) and 7.3–7.5 (m, br, 20 H). $^{31}P-\{^1H\}$ NMR: δ 35.0 (s).

$[N(PPh_3)_2][Au(SCB_{10}H_{10}CMe)Cl]$ 6 and $[N(PPh_3)_2][Au(SCB_{10}H_{10}CMe)_2]$ 7. To a solution of $[N(PPh_3)_2][AuCl_2]$ (0.080 g, 0.1 mmol) in dichloromethane (30 cm^3) was added $HSCB_{10}H_{10}CMe$ (0.019 g, 0.1 mmol or 0.038 g, 0.2 mmol) and an excess of Na_2CO_3 (0.53 g, 5 mmol). The mixture was stirred for 30 min and then filtered to remove the sodium carbonate. Concentration of solvent to *ca.* 5 cm^3 and addition of diethyl ether (10 cm^3) afforded complex **6** or **7**, respectively, as white solids. Complex **6**: yield 78% (Found: C, 48.20; H, 4.90; N, 1.45; S, 2.95. Calc. for $C_{39}H_{43}AuB_{10}ClNP_2S$: C, 48.75; H, 4.50; N, 1.45; S, 3.35%). Λ_M 102 Ω^{-1} cm^2 mol^{-1}; ^1H NMR δ 2.20 (s, 3 H, Me) and 7.4–7.7 (m, br, 30 H); $^{31}P-\{^1H\}$ NMR δ 21.2 (s). Complex **7**: yield 89% (Found: C, 45.05; H, 5.30; N, 1.25; S, 5.60. Calc. for $C_{42}H_{56}AuB_{20}NP_2S_2$: C, 45.25; H, 5.05; N, 1.25; S, 5.75%). Λ_M 83 Ω^{-1} cm^2 mol^{-1}; ^1H NMR δ 2.21 (s, 6 H, Me) and 7.4–7.8 (m, br, 30 H); $^{31}P-\{^1H\}$ NMR δ 21.2 (s).

$[NBu_4][Au(C_6F_5)_3(SCB_{10}H_{10}CMe)]$ 8. To a dichloromethane solution (25 cm^3) of $[NBu_4][AuBr(C_6F_5)_3]$ (0.102 g, 0.1 mmol) was added $HSCB_{10}H_{10}CMe$ (0.019 g, 0.1 mmol) and the mixture stirred for 1 h. Concentration of the solvent *in vacuo* and addition of hexane (10 cm^3) gave complex **8** as a white solid. Yield 73% (Found: C, 38.96; H, 4.15; N, 1.15; S, 3.80. Calc. for $C_{37}H_{49}AuB_{10}F_{15}NS$: C, 39.32; H, 4.37; N, 1.23; S, 3.15%). Λ_M 84 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR: δ −121.8 (m, 4 F, *o*-F), −122.6 (m, 2 F, *o*-F), −160.1 [t, 2 F, *p*-F, J(FF) 20.0], −159.0 [t, F, *p*-F, J(FF) 20.2 Hz], −163.2 (m, 4 F, *m*-F) and −162.8 (m, 2 F, *m*-F).

$[Au\{(PPh_2)_2C_2B_9H_{10}\}(SCB_{10}H_{10}CMe)_2]$ 9. To a solution of $HSCB_{10}H_{10}CMe$ (0.038 g, 0.2 mmol) in dichloromethane (30 cm^3) was added $[AuCl_2\{(PPh_2)_2C_2B_9H_{10}\}]$ (0.077 g, 0.1 mmol) and an excess of Na_2CO_3 (0.53 g, 5 mmol). The mixture was stirred for 30 min and then filtered to remove the sodium carbonate. Concentration of solvent to *ca.* 5 cm^3 and addition of hexane (10 cm^3) afforded complex **9** as a yellow solid. Yield 62% (Found: C, 35.55; H, 4.80; S, 5.87. Calc. for $C_{32}H_{56}AuB_{29}P_2S_2$: C, 35.63; H, 5.23; S, 5.95%). ^1H NMR: δ −2.0 (m, br, 1 H), 1.99 (s, 6 H, Me) and 7.2–8.4 (m, br, 20 H). $^{31}P-\{^1H\}$ NMR: δ 98.2 (s).

Crystallography

The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Siemens P4 diffractometer. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å), scan type ω (**1**,**6**), θ–2θ (**3**). Cell constants were refined from setting angles of *ca*. 60 reflections in the range 2θ 10–25°. Absorption corrections were applied on the basis of ψ scans. Structures were solved by the heavy-atom method and refined on F^2 using the program SHELXL 93.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. A system of restraints to light-atom displacement-factor components and local ring symmetry was used. Further details are given in Table 4.

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