DALTON

Gold(III) complexes with 1,2-disulfanyl-1,2-dicarba-*closo*-dodecaborane. Synthesis and partial degradation reactions of $[Au(S_2C_2B_{10}H_{10})_2]^-$ salts

Olga Crespo,[a] M. Concepción Gimeno,[a] Peter G. Jones[b] and Antonio Laguna *[,a]

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*
[b] *Institut für Anorganische und Analytische Chemie, Technische Universität, Postfach 3329, 38023 Braunschweig, Germany*

The reaction of 1,2-disulfanyl-1,2-dicarba-*closo*-dodecaborane, under basic conditions, with $[N(PPh_3)_2][AuCl_4]$ or $[AuCl_3(tht)]$–NBu_4Br (molar ratio 2 : 1) (tht = tetrahydrothiophene) resulted in the formation of the homoleptic gold(III) derivative $Q[Au(S_2C_2B_{10}H_{10})_2]$ [Q = $N(PPh_3)_2$ or NBu_4]. Treatment of this complex with hydrazine or phenylhydrazine partially degraded one or both carborane cages, respectively. The complexes $[NBu_4]$-$[Au(S_2C_2B_{10}H_{10})_2]$ and $[NBu_4]_2[Au(S_2C_2B_9H_{10})(S_2C_2B_{10}H_{10})]$ have been characterized by X-ray diffraction studies.

1,2-Dicarba-*closo*-dodecaborane (*o*-carborane) forms a great variety of derivatives as a consequence of the high resistance of the *o*-carborane cage to chemical attack.[1] Despite their cost, such properties make them attractive for various specialized applications. These include the incorporation of high concentrations of boron atoms in tumour-seeking drugs for boron neutron-capture therapy,[2–4] the synthesis of high-temperature polymers,[5] the production of ceramics related to boron carbide,[6] or the synthesis of derivatives with non-linear optical properties.[7] Furthermore, the ability to form *nido* anionic species by treatment with nucleophiles has led to their use in coordination chemistry with potential applications as novel catalysts,[8] radiochemical drugs,[9] *etc*.

We are currently studying various *o*-carborane derivatives as ligands. Here we focus on 1,2-sulfanyl-1,2-dicarba-*closo*-dodecaborane, which has been little studied. Only a few complexes of Co^{II} and Ni^{II} have been previously described,[10,11] and we recently reported some gold(I) derivatives.[12,13] We report on the synthesis of the homoleptic gold(III)-dithiolate species and further studies of the partial degradation of one or both carborane cages. The structural characterization of a complex involving *closo* and *nido* carborane cages allows the comparison of bond distances and angles in the two different cages.

Results and Discussion

The reaction of $(HS)_2C_2B_{10}H_{10}$ with $[N(PPh_3)_2][AuCl_4]$ in 2 : 1 molar ratio in dichloromethane, and in the presence of Na_2CO_3, leads to the homoleptic gold(III) species $[N(PPh_3)_2]$-$[Au(S_2C_2B_{10}H_{10})_2]$ **1a** (Scheme 1). Complex **1a** is a red solid stable to air and moisture and behaves as a 1 : 1 electrolyte in acetone solution. The IR spectrum shows the B–H stretching modes of the *o*-carborane nucleus as a broad band at 2591 cm^{-1}, and also the vibration ν(Au–S) at 341 cm^{-1}. The ^{11}B NMR spectrum displays resonances between δ −2.1 and −10.9, the pattern and the shift being consistent with two disubstituted *o*-carborane cages.

In the negative-ion fast atom bombardment (FAB) spectrum of complex **1a** the anion $[Au(S_2C_2B_{10}H_{10})_2]^-$ appears at m/z = 609 (100%), and also the fragment due to the loss of one dithiolate ligand, $[Au(S_2C_2B_{10}H_{10})]^-$, at m/z = 403 (12%).

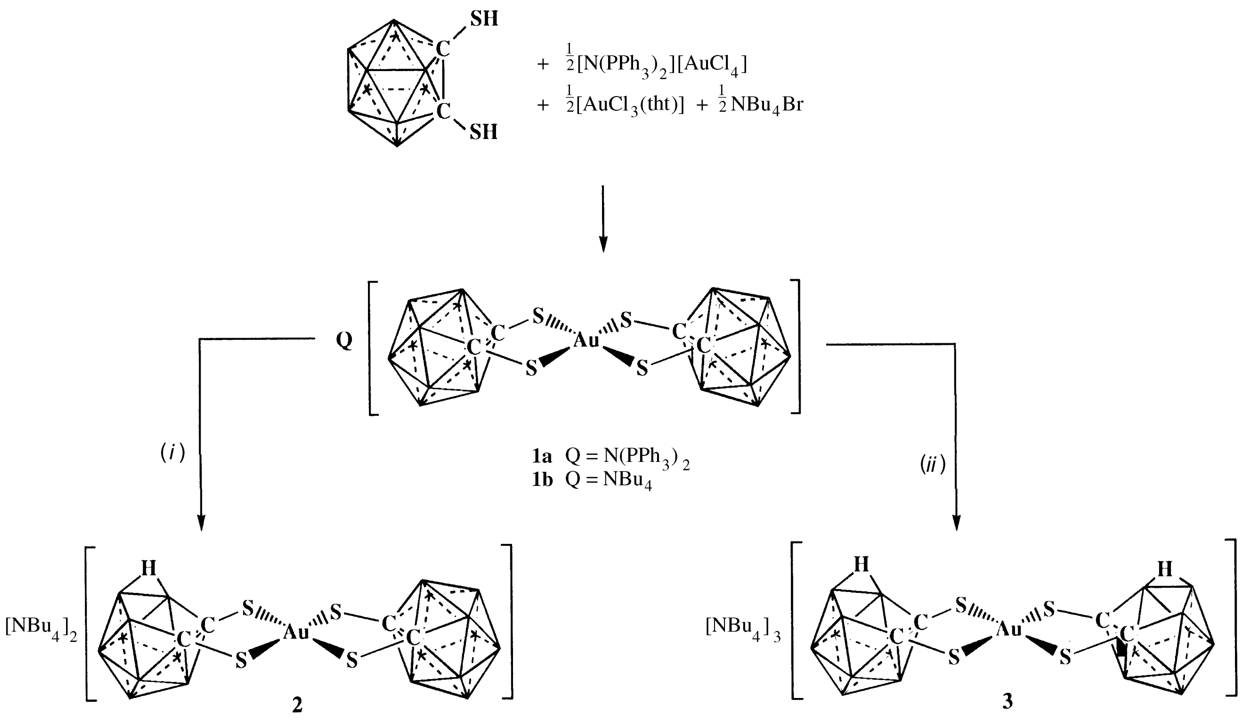
In spite of all our efforts we could not grow crystals of complex **1a** of suitable quality for an X-ray diffraction analysis. We therefore prepared a different salt of the same anion by another procedure, consisting of the reaction of 2 equivalents of $(HS)_2C_2B_{10}H_{10}$ with 1 equivalent of $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) and NBu_4Br, affording $[NBu_4][Au$-$(S_2C_2B_{10}H_{10})]$ **1b**. Complex **1b** possesses similar spectroscopic data to **1a**, but in this case we could grow crystals suitable for an X-ray diffraction study. The anion of **1b** is shown in Fig. 1, with selected bond lengths and angles in Table 1.

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

Au(1)–S(1)	2.319(2)	Au(1)–S(2)	2.321(2)
S(1)–C(1)	1.778(6)	S(2)–C(2)	1.784(6)
C(1)–C(2)	1.641(8)	Au(1′)–S(2′)	2.318(2)
Au(1′)–S(1′)	2.321(2)	S(1′)–C(1′)	1.791(5)
S(2′)–C(2′)	1.791(5)	C(1′)–C(2′)	1.640(7)
S(1)–Au(1)–$S(2^I)$	87.37(6)	S(1)–Au(1)–S(2)	92.63(6)
C(1)–S(1)–Au(1)	102.1(2)	C(2)–S(2)–Au(1)	102.2(2)
C(2)–C(1)–S(1)	119.0(4)	B(5)–C(1)–S(1)	121.4(4)
B(4)–C(1)–S(1)	119.8(4)	B(6)–C(1)–S(1)	119.0(4)
B(3)–C(1)–S(1)	117.0(4)	C(1)–C(2)–S(2)	118.6(4)
B(8)–C(2)–S(2)	120.3(4)	B(9)–C(2)–S(2)	120.6(4)
B(6)–C(2)–S(2)	118.1(4)	B(3)–C(2)–S(2)	117.5(4)
S(2′)–Au(1′)–S(1′)	92.59(6)	S(2′)–Au(1′)–$S(1'^{II})$	87.41(6)
C(1′)–S(1′)–Au(1′)	101.8(2)	C(2′)–S(2′)–Au(1′)	102.7(2)
C(2′)–C(1′)–S(1′)	119.3(3)	B(3′)–C(1′)–S(1′)	118.5(4)
B(5′)–C(1′)–S(1′)	119.2(4)	B(4′)–C(1′)–S(1′)	120.9(3)
B(6′)–C(1′)–S(1′)	116.1(3)	C(1′)–C(2′)–S(2′)	117.9(3)
B(11′)–C(2′)–S(2′)	120.8(4)	B(7′)–C(2′)–S(2′)	121.0(4)
B(3′)–C(2′)–S(2′)	117.3(3)	B(6′)–C(2′)–S(2′)	116.9(3)

Symmetry transformations used to generate equivalent atoms: I $-x, -y, -z$; II $-x + 1, -y + 1, -z + 1$.

The asymmetric unit consists of an NBu_4^+ cation and two $[Au(S_2C_2B_{10}H_{10})]^-$ anions, each with the gold atoms on an inversion centre. In both anions the gold centre has a square-planar geometry with similar bond lengths and angles. The ligand bite angles, 87.37(6) and 87.41(6)° (corresponding S···S distances 3.355 and 3.353 Å), are narrower than the exterior S–Au–S angles, in contrast to observations in other gold(III) derivatives containing dithiolate ligands, *e.g.* $[N(PPh_3)_2]$-$[Au(C_3S_5)_2]$ [91.88(5) and 91.76(5)°] (C_3S_5 = 4,5-disulfanyl-1,3-dithiole-2-thionate)[14] or $[Au(PPh_2Me)_2][Au(3,4\text{-}S_2C_6H_3Me)_2]$ [90.02(12)°].[15] The Au–S bond distances are 2.319(2) and 2.321(2) Å in one molecule and 2.318(2) and 2.321(2) Å in the other; these values, although similar to those in $[N(PPh_3)_2]$-$[Au(C_3S_5)_2]$ [2.321(2)–2.326(2) Å],[14] are slightly longer than



Scheme 1 (*i*) N_2H_4, NBu_4Br; (*ii*) $PhHNNH_2$, $2NBu_4Br$

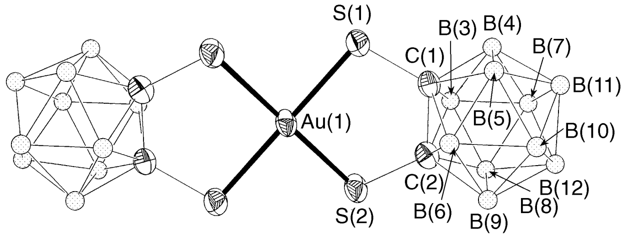


Fig. 1 One of the two independent anions of complex **1b** in the crystal, showing the numbering scheme of the independent atoms. Hydrogen atoms are omitted for clarity; radii are arbitrary

those in other dithiolate complexes such as $[PClPh_3][Au\{S_2C_2(CF_3)_2\}_2]$ (2.288 Å)[16] and $[Au(PEt_3)_2][Au(1,2\text{-}S_2C_6H_4)_2]$ (2.305 Å).[17] The S–C bond lengths range from 1.778(6) to 1.791(5) Å and the C–C distances in the carborane are 1.641(8) and 1.640(7) Å. The chelate rings display an envelope conformation, with the gold atoms 0.62 and 0.63 Å out of the plane of the respective C_2S_2 group.

The electrochemical behaviour of complex **1b** has been studied by cyclic voltammetry at a platinum electrode in CH_2Cl_2. The cyclic voltammogram, at a scan rate of 100 mV s^{-1}, shows a quasi-reversible reduction wave with peak potential −0.726 V; the peak separation is 78.3 mV and the cathodic to anodic current ratio 0.993 : 1. We believe that it is a single-electron process in which the gold(III) complex is reduced to the gold(II) species.

We have studied the partial degradation reaction of this complex. First we refluxed ethanol solutions of the complex, a method that gives excellent results for 1,2-bis(diphenylphosphine)-*o*-carborane complexes,[18] but only a mixture of the starting material and degraded products were obtained. Then we carried out the reaction of **1b** with an excess of hydrazine in dichloromethane and in the presence of NBu_4Br, which led to some decomposition to metallic gold, consistent with the reducing nature of the hydrazine, and a blue solid that analyses for $[NBu_4]_2[Au(S_2C_2B_9H_{10})(S_2C_2B_{10}H_{10})]$ **2**; in this derivative only one of the carborane groups has been degraded. Complex **2** is moderately stable in solution, although it can be stored in the solid state for a long time; it behaves as a 2 : 1 electrolyte in acetone. In its IR spectrum B–H stretching frequencies appear as a broad band shifted to low frequency, as previously observed for partially degraded carborane moieties. The ^{11}B NMR spectrum shows the presence of two different carborane cages, one *closo* and one *nido*. The resonances appear between δ −2.5 to −36.1; some are overlapped. In the ^{1}H NMR spectrum the signal assigned to the bridging proton B–H–B at δ −2.42 is consistent with the partially degraded nature of one of the carborane cages.

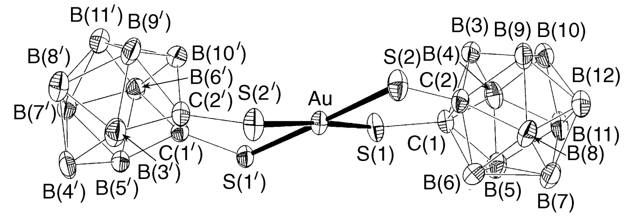


Fig. 2 The anion of complex **2** in the crystal, showing the atom labelling scheme. Hydrogen atoms are omitted for clarity; radii are arbitrary

In the negative-ion (FAB) mass spectrum of complex **2** the molecular peak does not appear, but the fragments due to the loss of one or two NBu_4^+ groups are present at *m/z* = 841 {45, $[Au(S_2C_2B_9H_{10})(S_2C_2B_{10}H_{10})(NBu_4)]^-$} and 599 {47%, $[Au(S_2C_2B_9H_{10})(S_2C_2B_{10}H_{10})]^-$}.

Crystals of complex **2** were obtained by slow diffusion of diisopropyl ether into a dichloromethane solution, and the proposed structure was confirmed by X-ray diffraction analysis; the anion is shown in Fig. 2, with selected bond lengths and angles in Table 2. The gold centre again has a square-planar geometry with four sulfur donor atoms; the mean deviation of these atoms from the best plane is 0.028 Å. The bite angles of both dithiolate ligands are very dissimilar, 88.40(4) and 93.81(4)° (corresponding S · · · S distances 3.227 and 3.400 Å), the narrower corresponding to the degraded ligand, and the wider angle is also very different from those in the starting material (see above). The Au–S distances are also distinct for each type of ligand: 2.3127(13) and 2.3158(11) Å for the *nido* and 2.3264(12) and 2.3291(13) Å for the *closo* ligand. The reason could be the additional negative charge of the *nido* ligand, which slightly reduces the strength of the sulfur–carbon

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

Au–S(2′)	2.3127(13)	Au–S(1′)	2.3158(11)
Au–S(2)	2.3264(12)	Au–S(1)	2.3291(13)
S(1)–C(1)	1.780(4)	S(2)–C(2)	1.776(4)
S(1′)–C(1′)	1.799(4)	S(2′)–C(2′)	1.795(4)
C(1)–C(2)	1.671(5)	C(1′)–C(2′)	1.548(5)
S(2′)–Au–S(1′)	88.40(4)	S(2′)–Au–S(2)	88.59(4)
S(1′)–Au–S(2)	176.97(4)	S(2′)–Au–S(1)	176.21(5)
S(1′)–Au–S(1)	89.21(4)	S(2)–Au–S(1)	93.81(4)
C(1)–S(1)–Au	102.41(13)	C(2)–S(2)–Au	102.64(13)
C(1′)–S(1′)–Au	103.01(14)	C(2′)–S(2′)–Au	102.62(13)
C(2)–C(1)–S(1)	119.1(3)	B(5)–C(1)–S(1)	121.9(3)
B(4)–C(1)–S(1)	120.1(3)	B(3)–C(1)–S(1)	116.6(3)
B(6)–C(1)–S(1)	118.6(3)	C(1)–C(2)–S(2)	119.0(3)
B(8)–C(2)–S(2)	121.4(3)	B(9)–C(2)–S(2)	119.5(3)
B(6)–C(2)–S(2)	118.4(3)	B(3)–C(2)–S(2)	116.9(3)
C(2′)–C(1′)–S(1′)	117.7(3)	B(5′)–C(1′)–S(1′)	117.7(3)
B(6′)–C(1′)–S(1′)	118.8(3)	B(10′)–C(1′)–S(1′)	115.7(3)
C(1′)–C(2′)–S(2′)	117.9(3)	B(3′)–C(2′)–S(2′)	116.6(3)
B(10′)–C(2′)–S(2′)	118.0(3)	B(9′)–C(2′)–S(2′)	121.7(3)

bonds; in agreement with this the C–S bond lengths in the *nido* ligand are 1.799(4) and 1.795(4) Å, and those in the *closo* moiety 1.776(4) and 1.780(4) Å. The chelate rings again display an envelope conformation, which is more pronounced in the *nido* ligand; the gold atoms lie 0.46 and 0.83 Å out of the plane of the respective C_2S_2 group. The C–C bond distances are 1.671(5) Å for the *closo* and 1.548(5) Å for the *nido* ligand. The appreciable C–C shortening from the parent carborane complex to the partially degraded species is expected since a filled orbital derived from $6a_1$ $[B_{11}H_{11}]^{4-}$ (orbital labelling as by Mingos)[19] is formed upon partial degradation.[20] The 'additional' H atom of the open $B_3H_4C_2$ face (see Experimental section) bridges the B(3′)–B(4′) bond, which is the longest B–B bond at 1.858(7) Å. We have observed a similar open-face structure in a related light-atom derivative, where the H atom position is more reliable.[21]

Treatment of complex **1b** with further hydrazine and/or for longer periods of time did not lead to the doubly degraded species. We then tried the reaction with other bases such as phenylhydrazine, which gives the desired complex $[NBu_4]_3[Au(S_2C_2B_9H_{10})_2]$ **3** as a green solid. Complex **3** is not very stable in solution, but behaves in acetone solution as a 3:1 electrolyte. The ^{11}B and ^1H NMR spectra are consistent with the presence of two partially degraded carborane cages. In the negative-ion mass spectrum the molecular peak does not appear, and neither does the species arising from the loss of one or two NBu_4^+ groups, but the anion containing the two partially degraded species $[Au(S_2C_2B_9H_{10})_2]^-$ is present at $m/z = 587$ (38%). Other fragments correspond to the addition of one or two boron atoms and appear at $m/z = 599$ (45) and 610 (100%), respectively.

We could not grow crystals of sufficient quality to confirm the structure of complex **3**, although in all the cases the same unit cell could be determined; $a = 10.991$, $b = 12.015$, $c = 21.688$ Å, $\alpha = 78.91$, $\beta = 78.51$ and $\gamma = 72.32°$, $U = 2892$ Å^3. For a triclinic cell with $Z = 2$ this indicates approximately 80 non-hydrogen atoms, agreeing well with the calculated 78 for $[NBu_4]_3[Au(S_2C_2B_9H_{10})_2]$.

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. Carbon and hydrogen analyses were carried out with a Perkin-Elmer 2400 microanalyser. Mass spectra were recorded on a VG autospec instrument with the FAB technique, using 3-nitrobenzyl alcohol as matrix, NMR spectra on a Varian Unity 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external) and $BF_3 \cdot OEt_2$ (^{11}B, external). Cyclic voltammetric experiments were performed by employing an EG&G PARC model 273 potentiostat. A three-electrode system was used, consisting of a platinum-disc working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The measurements were carried out in CH_2Cl_2 solutions with 0.1 mol dm^{-3} NBu_4PF_6 as supporting electrolyte. Under the present experimental conditions, the ferrocenium–ferrocene couple was located at 0.47 V. The starting materials $(HS)_2C_2B_{10}H_{10}$,[22] $[N(PPh_3)_2][AuCl_4]$ and $[AuCl_3(tht)]$[23] were prepared by published procedures.

Synthesis

$Q[Au(S_2C_2B_{10}H_{10})_2]$ [$Q = N(PPh_3)_2$ 1a or NBu_4 1b]. To a solution of $(HS)_2C_2B_{10}H_{10}$ (0.041 g, 0.2 mmol) in dichloromethane (30 cm^3) was added $[N(PPh_3)_2][AuCl_4]$ (0.087 g, 0.1 mmol) and an excess of Na_2CO_3 (0.1 g, 1 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 complex **1a** as a red solid in 65% yield (Found: C, 41.75; H, 4.55; N, 1.15. Calc. for $C_{40}H_{50}AuB_{20}NP_2S_4$: C, 41.85; H, 4.4; N, 1.2%). Λ_M 129 Ω^{-1} cm^2 mol^{-1}. ^{11}B NMR: δ −2.7 (2B), −6.1 (2B), −7.5 (4B) and −10.1 (12B).

To a solution of $(HS)_2C_2B_{10}H_{10}$ (0.041 g, 0.2 mmol) in dichloromethane (30 cm^3) was added $[AuCl_3(tht)]$ (0.1 mmol, 0.039 g), NBu_4Br (0.1 mmol, 0.032 g) and an excess of Na_2CO_3. The suspension was stirred for 30 min and then filtered, concentrated to *ca.* 5 cm^3 and addition of hexane (10 cm^3) gave complex **1b** as a red solid in 60% yield (Found: C, 28.55; H, 6.55; N, 1.7. Calc. for $C_{20}H_{56}AuB_{20}NS_4$: C, 28.2; H, 6.6; N, 1.7%). Λ_M 132 Ω^{-1} cm^2 mol^{-1}.

$[NBu_4]_2[Au(S_2C_2B_9H_{10})(S_2C_2B_{10}H_{10})]$ 2. To a dichloromethane solution (20 cm^3) of $[NBu_4][Au(S_2C_2B_{10}H_{10})_2]$ (0.1 mmol, 0.85 g) was added an excess of $N_2H_4.H_2O$ (50 μl, 1.6 mmol). The solution was stirred for 2 h, filtered over Celite to eliminate metallic gold and then the solvent was removed *in vacuo*; after addition of diethyl ether (10 cm^3) complex **2** was isolated as a blue solid in 63% yield (Found: C, 39.5; H, 8.75; N, 3.0. Calc. for $C_{36}H_{92}AuB_{19}N_2S_4$: C, 39.9; H, 8.55; N, 2.6%). Λ_M 190 Ω^{-1} cm^2 mol^{-1}. NMR: ^1H, δ −2.4 (br, Δ = 186 Hz); ^{11}B, δ −2.5 (1B), −8.1 (2B), −9.6 (5B), −12.6 (4B), −19.2 (3B), −22.5 (2B), −33.0 (1B) and −36.1 (1B).

$[NBu_4]_3[Au(S_2C_2B_9H_{10})_2]$ 3. To a dichloromethane solution (20 cm^3) of $[NBu_4][Au(S_2C_2B_{10}H_{10})_2]$ (0.1 mmol, 0.85 g) was added an excess of $PhNHNH_2$ (0.16 cm^3, 1.6 mmol). The solution was stirred for 2 h. The solution was filtered over Celite to eliminate metallic gold and then the solvent was removed *in vacuo*; after addition of diethyl ether (10 cm^3) complex **3** was isolated as a green solid in 57% yield (Found: C, 47.55; H, 10.0; N, 3.2. Calc. for $C_{52}H_{128}AuB_{18}N_3S_4$: C, 47.5; H, 9.8; N, 3.2%). Λ_M 274 Ω^{-1} cm^2 mol^{-1}. NMR: ^1H, δ −2.1 (br, Δ = 150 Hz); ^{11}B, δ −9.5 (4B), −13.7 (6B), −16.5 (4B), −31.2 (2B) and −36.0 (2B).

Crystallography

The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Siemens R3 diffractometer with an LT-2 low-temperature attachment. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å). Scan type ω. Cell constants were refined from setting angles of *ca.* 50 reflections in the range 2θ 20–23°. 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.[24] All non-hydrogen atoms were refined anisotropically for complex **2**; for **1b** the boron atoms were refined

Table 3 Data collection and structure refinement details for complexes **1b** and **2** *

	1b	**2**
Chemical formula	$C_{20}H_{56}AuB_{20}NS_4$	$C_{36}H_{92}AuB_{19}N_2S_4$
M	852.06	1083.71
Crystal habit	Red tablet	Blue tablet
Crystal size/mm	0.50 × 0.40 × 0.25	0.60 × 0.40 × 0.20
a/Å	11.428(3)	13.947(2)
b/Å	11.489(4)	15.087(3)
c/Å	16.272(5)	15.572(3)
α/°	97.06(3)	100.89(2)
β/°	93.84(3)	95.18(2)
γ/°	111.95(3)	116.67(2)
U/Å^3	1951.7(10)	2817.5(9)
D_c/Mg m^{-3}	1.450	1.277
F(000)	852	1120
T/°C	−95	−100
μ(Mo-Kα)/mm^{-1}	4.0	2.79
Transmission	0.53–0.97	0.624–0.953
No. reflections measured	6901	12 491
No. unique reflections	6874	9885
R_{int}	0.028	0.031
$R[F, F > 4\sigma(F)]$	0.035	0.033
wR (F^2, all reflections)	0.101	0.067
No. parameters	318	571
No. restraints	34	404
S	1.099	0.929
Maximum Δρ/e Å^{-3}	1.53	0.906

* Details in common: space group $P\bar{1}$; $Z = 2$; $2\theta_{max} = 50°$; $R\ (F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR\ (F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, 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.

isotropically. Hydrogen atoms were included using a riding model where possible; the open face hydrogens of **2** were refined 'freely' but with terminal and bridging BH separately constrained equal. Further details are given in Table 3.

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 186/392.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (No. PB94-0079) and the Fonds der Chemischen Industrie for financial support.

References

1 V. I. Bregadze, *Chem. Rev.*, 1992, **92**, 2005.
2 R. F. Barth, A. H. Soloway and R. G. Fairchild, *Cancer Res.*, 1990, **50**, 1061.
3 M. F. Hawthorne, *Pure Appl. Chem.*, 1991, **63**, 327.
4 K. Shelly, D. A. Feakes, M. F. Hawthorne, P. G. Schmidt, T. A. Krisch and W. F. Bauer, *Proc. Natl. Acad. Sci. USA.*, 1992, **89**, 9039.
5 D. A. Brown, H. M. Colquhoun, J. A. Daniels, J. A. H. McBride, I. R. Stephenson and K. Wade, *J. Mater. Chem.*, 1992, **2**, 793 and refs. therein.
6 L. G. Sneddon, M. G. Mirabelli, A. T. Lynch, P. J. Fazen, K. Su and J. S. Beck, *Pure Appl. Chem.*, 1991, **63**, 407.
7 D. M. Murphy, D. M. P. Mingos, J. L. Haggitt, H. R. Powell, S. A. Westcott, T. B. Marder, N. J. Taylor and D. R. Kanio, *J. Mater. Chem.*, 1993, **3**, 139.
8 M. F. Hawthorne, J. F. Liebman, A. Greenberg and R. E. Willians (Editors), *Advances in Boron and the Boranes*, VCH, New York, 1988, ch. 10, p. 225.
9 R. J. Paxton, B. G. Beatty, M. F. Hawthorne, A. Varadarajan, L. E. Willians, F. L. Curtis, C. B. Knobler, J. D. Beatty and J. E. Shively, *Proc. Natl. Acad. Sci. USA*, 1991, **88**, 3387.
10 H. D. Smith, jun., *J. Am. Chem. Soc.*, 1965, **87**, 1817.
11 H. D. Smith, jun., M. A. Robinson and S. Papetti, *Inorg. Chem.*, 1967, **6**, 1014.
12 O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *J. Chem. Soc., Chem. Commun.*, 1993, 1697.
13 O. Crespo, M. C. Gimeno, P. G. Jones, B. Ahrens and A. Laguna, *Inorg. Chem.*, in the press.
14 P. G. Jones, E. Cerrada, M. C. Gimeno and M. Laguna, *Z. Kristallogr.*, 1994, **209**, 827.
15 M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna and R. Terroba, *Inorg. Chem.*, 1994, **33**, 3932.
16 J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2636.
17 M. Nakamoto, H. Koijman, M. Paul, W. Hiller and H. Schmidbaur, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1341.
18 O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Inorg. Chem.*, 1996, **35**, 1361.
19 D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1977, 602.
20 F. Teixidor, J. Rius, A. M. Romerosa, C. Miravitlles, L. Escriche, E. Sanchez, C. Viñas and J. Casabó, *Inorg. Chim. Acta*, 1990, **176**, 287.
21 P. G. Jones, O. Crespo, M. C. Gimeno and A. Laguna, *Acta Crystallogr., Sect. C*, in the press.
22 H. D. Smith, jun., C. O. Obenland and S. Papetti, *Inorg. Chem.*, 1967, **5**, 1013.
23 E. A. Allen and W. Wilkinson, *Spectrochim. Acta, Part A*, 1972, **28**, 2257.
24 G. M. Sheldrick, SHELXL 93, A Program for Crystal Structure Refinement, University of Göttingen, 1993.

Received 28*th October* 1996; *Paper* 6/07329H