Carbaborane Derivatives of the Late- and Post-transition Elements. Part 1. Preparation and *X*-Ray Crystal Structure of 3-Diethyldithiocarbamato-1,2-dicarba-3-auradodecaborane(11)

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The reaction of $[AuBr_2(S_2CNEt_2)]$ with $Tl[B_9C_2{}^{1,2}Tl^3H_{11}]$ yields the known ion $[3,3'\text{-}Au(B_9C_2{}^{1,2}H_{11})_2]^-$ as its $[Au(S_2CNEt_2)_2]^+$ salt, and also the novel carba-auraborane $B_9C_2{}^{1,2}[Au(S_2CNEt_2)]^3H_{11}$. The latter is shown from single-crystal *X*-ray data to have a distorted structure, in which the metal atom is bonded principally to the three boron atoms of the C_2B_3 open face [Au–B(av.) 2.22(1); Au–C(av.) 2.78(1) Å], which is distinctly non-planar, illustrating the severe distortions which occur within the B_9C_2 framework. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a = 7.3710(6)$, $b = 11.0368(9)$, $c = 21.1564(17)$ Å, and $\beta = 93.22(4)°$. The structure has been refined to R 0.039 for 1 962 independent observed reflections.

COMPLEXES in which carbaboranes, or their ions, are bonded to metals *via* an open face, *e.g.* the C_2B_3 face of the $[B_9C_2H_{11}]^{2-}$ ion, have been extensively studied and a wide range of preparative reactions, chemical properties, and structural types have been reported.[1] Such compounds may be regarded either as heteroboranes in which metal atoms replace boron in a polyhedral skeleton, or as co-ordination compounds in which *nido*-carbaborane anions act as ligands. With the later transition elements, metallacarbaboranes incorporating metals of the cobalt [1] and nickel [2] triads have been well documented, but corresponding derivatives of the Group 1B (Cu, Ag, and Au) and 2B (Zn, Cd, and Hg) elements are less well known. These include the complexes $[3,3'\text{-}M(B_9C_2{}^{1,2}H_{11})_2]^{n-}$ ($M = Cu^{II}$ or Au^{II}, $n = 2$; $M = Cu^{III}$ or Au^{III}, $n = 1$) [3] which have frequently been described as electron-rich 'slipped-sandwich' compounds, since the $[B_9C_2H_{11}]^{2-}$ ligand appears to 'slip' relative to the structure of say $[B_9C_2{}^{1,2}\{Re(CO)_3\}^3H_{11}]^-$, in which the metal atom is situated symmetrically with respect to the C_2B_9 cage.[4] The related complexes $[Cu(B_{10}CH_{11})_2]^{3-}$,[5] $[B_9C_2(HgPh)H_{11}]^-$,[6] $B_4C_2[Au(PPh_3)]H_7$,[7] and $B_4C_2(HgPh)H_7$ have also been reported, although in the derivatives of $[B_4C_2H_7]^-$ the metal is believed to occupy a bridging position between two basal boron atoms.

In order to obtain more information on such compounds, and to study the relative structural consequences of introducing metals with formal d^8, d^{10}, and $d^{10}s^2$ electron configurations, we have investigated a series of reactions between carbaborane anions (in particular the $[B_9C_2{}^{7,8}H_{11}]^{2-}$ ion) and complexes of the late transition elements (Groups 8 and 1B) and post-transition elements (Groups 2B and 3B). We report here results involving the d^8 metal ion Au^{III}. A preliminary account of some of this work has appeared.[8]

RESULTS AND DISCUSSION

The action of the thallium(I) salt $Tl[B_9C_2{}^{1,2}Tl^3H_{11}]$ on the gold(III) dithiocarbamate $[AuBr_2(S_2CNEt_2)]$ in diethyl ether yields two orange-red crystalline metallacarbaboranes which possess the same empirical formula $(Et_2NCS_2AuC_2B_9H_{11})$ from analytical data. Crystallographic characterisation revealed one of these to be the ionic species $[Au(S_2CNEt_2)_2][3,3'\text{-}Au(B_9C_2{}^{1,2}H_{11})_2]$,[9] (1), and we have confirmed the identity of the anion from comparison of its ^{11}B n.m.r. spectrum with published data.[3] The other, diethyl ether-soluble, compound is the novel molecular carba-auraborane $B_9C_2{}^{1,2}[Au(S_2CNEt_2)]^3H_{11}$, (2), whose structure and properties are reported here. The ^{11}B n.m.r. spectrum of (2) in C_6D_6 solution shows doublets, arising from typical carbaborane, J(B–H) couplings, at δ +24.6 [J(B–H) 135 Hz, relative intensity 1], +5.8 (150 Hz, 2), +1.9 (— Hz,† 1), −6.5 (145 Hz, 2), −11.7 (150 Hz, 2), and −21.7 p.p.m. (175 Hz, 1). The pattern of relative intensities (1 : 2 : 1 : 2 : 2 : 1) indicates the existence of a molecular mirror plane in (2), and this conclusion is supported by the ^1H n.m.r. spectrum in C_6D_6 solution which shows only a single resonance due to the carbaborane C–H protons [τ 5.86 (relative intensity 2)] and quartet and triplet signals [τ 7.26 (4) and 9.36 (6) respectively] corresponding to equivalent ethyl groups in the dithiocarbamate ligand.

Attempts to characterise (2) by its mass spectrum were unsuccessful due to its involatility below the temperature at which it decomposed (115 °C), but, remarkably, pyrolysis of the ionic derivative (1) at 180 °C on the solid probe insert produced a mass spectrum with a cutoff at m/e 480, corresponding to the molecular ion $[B_9C_2\{Au(S_2CNEt_2)\}H_{11}]^+$. The isotope-distribution pattern calculated ‡ for this ion matched the experimental spectrum to within a 4% overall deviation. Analogous rearrangements of salts of the type $[PtL_4][PtX_4]$ (L = ligand, X = halogen) to the molecular isomers $[PtX_2L_2]$ are known to occur simply on heating.[10]

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† No coupling constant can be assigned for this resonance due to overlapping signals in the undecoupled spectrum.

‡ Using the program MASPEC (T. Blair and T. J. Greenhough, 1976).

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Both compounds (1) and (2) underwent reductive-elimination reactions on treatment with pyridine to yield the dimeric gold(I) derivative $[\{Au(S_2CNEt_2)\}_2]$ and $C_5H_5N{\cdot}B_9C_2H_{11}$ [11] which was identified from its ^{11}B n.m.r., i.r., and mass spectra. These reactions, involving a reduction of Au^{III} d^8 to Au^I d^{10}, are the inverse of the oxidative-addition reactions (recently used to synthesise a variety of metallacarbaboranes) in which d^{10} ML_2 species (M = Ni, Pd, or Pt; L = PR_3 or RNC) insert directly into *closo*-carbaboranes.[2] Attempts to produce other gold carbaboranes by treating $[AuBr_2(S_2CNEt)_2]$ with $Na_2[B_8C_2H_{10}]$, and $Na_2[B_{10}C_2H_{12}]$, yielded only dark brown-black solids (suggesting that reduction had occurred) and small amounts of $[\{Au(S_2CNEt_2)\}_2]$ and $[Au(S_2CNEt_2)_2][B_{10}C_2H_{13}]$ respectively. Spectroscopic and preliminary *X*-ray evidence indicated the latter to be a simple salt with no significant interaction between the ions. Trace quantities of $[\{Au(S_2CNEt_2)\}_2]$ and $B_{10}C_2{}^{1,2}H_{12}$ were also identified in the latter reaction.

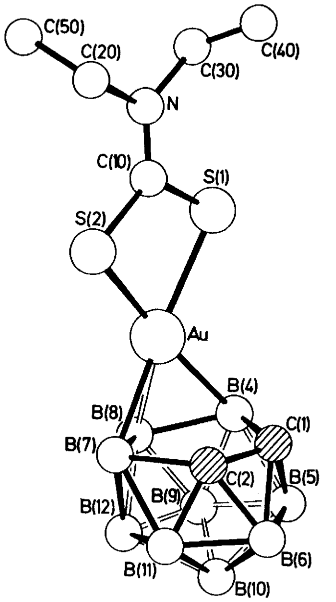

FIGURE 1 Molecular structure of complex (2). Hydrogen atoms are omitted for clarity

TABLE 1

Atomic co-ordinates (× 10^4) for the non-hydrogen atoms with standard deviations in parentheses

	x	*y*	*z*
Au	2 265(1)	3 423(1)	3 790(1)
S(1)	2 372(5)	5 101(3)	4 494(2)
S(2)	4 570(4)	4 730(3)	3 434(2)
N	4 913(14)	6 695(10)	4 180(4)
C(10)	4 116(16)	5 682(11)	4 056(6)
C(20)	6 360(19)	7 178(14)	3 769(7)
C(30)	4 474(18)	7 445(11)	4 731(6)
C(40)	3 385(30)	8 542(15)	4 533(8)
C(50)	8 218(25)	7 063(22)	4 097(9)
C(1)	−1 255(17)	2 983(12)	3 300(7)
C(2)	−85(18)	2 710(13)	2 782(6)
B(4)	−203(21)	2 454(14)	4 050(7)
B(5)	−2 204(19)	1 817(13)	3 603(9)
B(6)	−2 058(20)	1 974(15)	2 777(8)
B(7)	1 956(22)	1 938(14)	3 079(7)
B(8)	1 669(22)	1 484(12)	3 902(7)
B(9)	−442(26)	839(15)	3 910(8)
B(10)	−1 426(22)	583(14)	3 139(8)
B(11)	26(24)	1 277(15)	2 603(7)
B(12)	974(20)	470(14)	3 283(7)

TABLE 2

Final positional (fractional co-ordinates × 10^3) parameters of the hydrogen atoms *

	x	*y*	*z*
H(1)	−188(18)	357(12)	327(6)
H(2)	12(18)	324(12)	249(7)
H(4)	−92(18)	263(13)	451(6)
H(5)	−330(18)	179(12)	382(6)
H(6)	−298(18)	223(13)	242(6)
H(7)	343	200	293
H(8)	258(16)	121(11)	428(6)
H(9)	−61(18)	19(13)	430(6)
H(10)	−217(18)	−22(12)	303(6)
H(11)	15(19)	104(13)	210(6)
H(21)	657(19)	631(13)	343(7)
H(22)	602(19)	801(13)	371(7)
H(31)	573(18)	725(13)	502(6)
H(32)	360(18)	693(13)	500(6)
H(41)	344(25)	896(18)	492(9)
H(42)	425(26)	901(17)	433(9)
H(51)	824(24)	798(18)	437(8)
H(52)	872(24)	732(17)	378(9)

* The hydrogen atoms H(12) [bonded to C(12)], H(43) [bonded to C(40)], and H(53) [bonded to C(50)] were not located, and H(7) was not refined.

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

Au–B(4)	2.21(2)	C(1)–C(2)	1.46(2)
Au–B(7)	2.23(2)	C(1)–B(4)	1.82(2)
Au–B(8)	2.20(1)	C(2)–B(7)	1.81(2)
Au–C(1)	2.78(1)	B(7)–B(8)	1.84(2)
Au–C(2)	2.79(1)	B(4)–B(8)	1.79(2)
C(1)–B(6)	1.66(2)	B(9)–B(12)	1.78(2)
C(1)–B(5)	1.62(2)	B(12)–B(11)	1.80(2)
C(2)–B(6)	1.67(2)	B(11)–B(6)	1.77(2)
C(2)–B(11)	1.63(2)	B(6)–B(5)	1.76(2)
B(7)–B(11)	1.85(2)	B(5)–B(9)	1.78(2)
B(7)–B(12)	1.84(2)	B(10)–B(12)	1.78(2)
B(8)–B(12)	1.78(2)	B(10)–B(11)	1.77(2)
B(8)–B(9)	1.71(2)	B(10)–B(6)	1.77(2)
B(4)–B(9)	1.81(2)	B(10)–B(5)	1.79(2)
B(4)–B(5)	1.85(2)	B(10)–B(9)	1.77(2)
Au–S(1)	2.375(3)	N–C(20)	1.51(2)
Au–S(2)	2.384(4)	N–C(30)	1.48(2)
S(1)–C(10)	1.75(1)	C(20)–C(50)	1.51(2)
S(2)–C(10)	1.73(1)	C(30)–C(40)	1.50(2)
N–C(10)	1.28(2)		
C(1)–H(1)	0.8(1)	C(20)–H(21)	1.2(1)
C(2)–H(2)	0.9(1)	C(20)–H(22)	1.0(1)
B(4)–H(4)	1.1(1)	C(30)–H(31)	1.1(1)
B(5)–H(5)	1.0(1)	C(30)–H(32)	1.0(1)
B(6)–H(6)	1.0(1)	C(40)–H(41)	0.9(2)
B(7)–H(7) *	1.2	C(40)–H(42)	0.9(2)
B(8)–H(8)	1.1(1)	C(50)–H(51)	1.2(2)
B(9)–H(9)	1.1(1)	C(50)–H(52)	0.8(2)
B(10)–H(10)	1.1(1)		
B(11)–H(11)	1.1(1)		

* H(7) was not included in the least-squares refinement.

Description of the Structure.—Final atomic positional parameters are given in Tables 1 and 2 together with least-squares estimated standard deviations. Bond distances and angles are given in Tables 3 and 4, the

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atomic-numbering scheme in Figure 1, and the equations of some best least-squares planes in Table 5.

TABLE 4

Interbond angles (°) with estimated standard deviations in parentheses

(*a*) Within the polyhedron			
C(2)–Au–C(1)	30.5(4)	C(1)–B(5)–B(4)	63.2(8)
C(2)–Au–B(7)	40.5(5)	B(4)–B(5)–B(9)	59.9(9)
C(1)–Au–B(4)	40.9(5)	B(9)–B(5)–B(10)	59.4(8)
B(4)–Au–B(8)	47.9(6)	B(10)–B(5)–B(6)	59.5(9)
B(7)–Au–B(8)	49.0(5)	B(6)–B(5)–C(1)	58.4(9)
Au–C(1)–B(4)	52.3(6)	C(2)–B(6)–C(1)	52.3(8)
Au–C(2)–B(7)	53.0(6)	C(1)–B(6)–B(5)	56.3(8)
Au–C(1)–C(2)	74.9(7)	B(5)–B(6)–B(10)	61.0(9)
Au–C(2)–C(1)	74.7(7)	B(10)–B(6)–B(11)	60.2(9)
Au–B(4)–C(1)	86.8(7)	B(11)–B(6)–C(2)	56.4(9)
Au–B(7)–C(2)	86.5(8)		
Au–B(7)–B(8)	64.7(6)	B(8)–B(9)–B(4)	60.8(9)
Au–B(4)–B(8)	65.9(7)	B(4)–B(9)–B(5)	61.8(9)
Au–B(8)–B(4)	66.2(6)	B(5)–B(9)–B(10)	60.5(9)
Au–B(8)–B(7)	66.3(6)	B(10)–B(9)–B(12)	60.2(9)
		B(12)–B(9)–B(8)	61.1(9)
C(1)–C(2)–B(6)	63.5(9)		
B(6)–C(1)–C(2)	64.2(9)	B(6)–B(10)–B(11)	60.2(9)
B(4)–C(1)–B(5)	64.6(9)	B(11)–B(10)–B(12)	60.8(9)
B(7)–C(2)–B(11)	64.7(9)	B(12)–B(10)–B(9)	60.2(9)
B(5)–C(1)–B(6)	65.3(10)	B(9)–B(10)–B(5)	60.1(9)
B(11)–C(2)–B(6)	65.2(10)	B(5)–B(10)–B(6)	59.5(9)
B(5)–B(4)–C(1)	52.2(8)		
B(11)–B(7)–C(2)	52.9(8)	C(2)–B(11)–B(7)	62.4(9)
B(9)–B(4)–B(5)	58.3(9)	B(7)–B(11)–B(12)	60.5(8)
B(12)–B(7)–B(11)	58.5(8)	B(12)–B(11)–B(10)	59.8(9)
B(8)–B(4)–B(9)	56.8(9)	B(10)–B(11)–B(6)	59.7(9)
B(8)–B(7)–B(12)	57.9(8)	B(6)–B(11)–C(2)	58.4(9)
B(7)–B(8)–B(12)	61.1(8)		
B(4)–B(8)–B(9)	62.4(9)	B(7)–B(12)–B(8)	61.1(8)
B(12)–B(8)–B(9)	61.4(9)	B(8)–B(12)–B(9)	57.5(9)
		B(9)–B(12)–B(10)	59.6(9)
		B(10)–B(12)–B(11)	59.4(9)
		B(11)–B(12)–B(7)	61.0(9)
C(2)–C(1)–B(4)	110(1)	B(12)–B(9)–B(5)	108(1)
C(1)–C(2)–B(7)	111(1)	B(9)–B(12)–B(11)	105(1)
C(2)–B(7)–B(8)	109(1)	B(12)–B(11)–B(6)	111(1)
C(1)–B(4)–B(8)	110(1)	B(9)–B(5)–B(6)	110(1)
B(4)–B(8)–B(7)	98(1)	B(5)–B(6)–B(11)	105(1)
(*b*) Exo-polyhedral bond angles			
S(1)–Au–S(2)	74.2(1)	C(10)–N–C(20)	121.3(11)
Au–S(1)–C(10)	87.3(4)	C(10)–N–C(30)	122.0(10)
Au–S(2)–C(10)	87.4(4)	S(1)–C(10)–N	123.5(9)
S(1)–C(10)–S(2)	111.1(7)	S(2)–C(10)–N	125.3(9)
C(20)–N–C(30)	116.6(10)	N–C(20)–C(50)	110.1(12)
		N–C(30)–C(40)	111.6(11)

The gold–diethyldithiocarbamate moiety. The gold-diethyldithiocarbamate moiety is planar (apart from the terminal methyl groups) to within ±0.03 Å, the deviations from planarity being consistent with a small torsion of *ca.* 2° about the C(10)–N bond. A similar torsion has been observed in the *NN*-diethyldithiocarbamate ion of $Na[S_2CNEt_2]\cdot3H_2O$.[12] The usual *anti* configuration is adopted by the methyl groups, the ligand as a whole exhibiting two-fold symmetry to within the experimental error.

Significant differences[13] $[3\sigma : \sigma = (\sigma_1{}^2 + \sigma_2{}^2)^{\frac{1}{2}}]$ from the 'free' ligand molecule, in an essentially ionic environment, occur in the angles around C(10), and in the N–C(10) distance, which is 1.283(16) Å here and 1.344(8) Å in the ion;[12] these variations are consistent with chelation, and an increase in double-bond character of the C–N bond on co-ordination respectively. The Au–S distances [2.375(3) and 2.384(4) Å] are significantly longer than in the $[Au(S_2CNEt_2)_2]^+$ cation [2.330(2) Å],[9] implying a relatively high '*trans*' effect for the $B_9C_2H_{11}$ group. The Au–S_2 plane is twisted by 3.5° with respect to the Au–B(4),B(7) plane, probably as a result of crystal-packing forces.

The metal–cage interaction. The metal–cage distances in this distorted gold(III) carbaborane, (2), are typical of the non-symmetrically bonded $B_9C_2{}^{1,2}$ complexes so far structurally characterised,[9,14,15] the M–C distances being much greater than the M–B. There are no significant differences between the metal–cage distances here and those in the gold(III) sandwich compound $[Au(B_9C_2{}^{1,2}H_{11})_2]^-$,[9] (1). Although the M–B(unique) [B(8) here] distance differs by 4σ from the other two M–B distances in (1), and by 10σ in the copper(II) (d^9) sandwich structure $[Cu(B_9C_2{}^{1,2}H_{11})_2]^{2-}$,[14] all the M–B distances are essentially the same here.

The B_9C_2 *framework.* The B_9C_2 framework exhibits mirror symmetry to within the error of the experiment. There are, however, significant deviations from the cage geometry found in a symmetrically bonded complex such as $[Re(CO)_3(B_9C_2H_{11})]^-$,[5] (3), the majority of which involve the carbon atoms.

The C–B bond lengths in the C_2B_3 face are lengthened from 1.71(1) and 1.71(1) Å in (3) to 1.81(2) and 1.82(2) Å in (2). The bond distances between the carbon atoms and the non-facial boron atoms B(5) and B(11) are shorter here [1.62(2) and 1.63(2) Å] than in (3) [1.72(1) and 1.74(1) Å] and the C–B(6) distances [1.72(1) and 1.71(1) Å] in (3) differ by *ca.* 2σ from those here [1.67(2) and 1.66(2) Å]. The C–C bond length in (2) is 1.46(2) Å, again significantly shorter than in (3) [1.61(1) Å], and the C_2B_3 face, which is planar in (3), exhibits a dihedral angle [planes (3) and (4), Table 5] of 162.8°.

Significant differences between (3) and (2) which do not involve the carbon atoms occur in the facial B–B–B angle, 106° in (3) and 98(1)° in (2), in the average B(7),B(4)–non-facial B distance [1.77 Å in (3) and 1.84 Å in (2)], and in the lower B_5 plane [plane (2), Table 5] which is planar in (3) but in (2) shows a B_4–B_2 dihedral angle [planes (5) and (6), Table 5] of 170.8°.

While there are no significant (3σ) differences between the B_9C_2 frameworks in (1) and (2), it is interesting to note that the deviations from the framework in (3) are all smaller for the gold(III) sandwich structure, (1), than for (2).

Molecular packing. The molecular packing is illustrated in Figure 2. All the intramolecular contacts < 3.5 Å involve hydrogen atoms; H–H and X–H contact distances < 2.6 and 3.0 Å respectively are given in Table 6.

Bonding and the molecular distortions. On the basis of the electron-counting rules for metallacarbaboranes,

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TABLE 5

Some best least-squares planes expressed in the form $PI + QJ + RK = S$

	Plane (1)		Plane (2)		Plane (3)		Plane (4)		Plane (5)		Plane (6)		Plane (7)	
P	0.508 3		0.536 8		0.451 9		0.620 2		0.561 7		0.465 3		0.657 6	
Q	0.839 4		0.816 4		0.882 2		0.717 6		0.791 5		0.873 8		−0.479 8	
R	0.192 7		0.213 0		0.132 7		0.316 8		0.241 1		0.141 7		0.580 8	
S	3.486 4		2.105 3		3.237 9		4.262 5		2.273 5		1.875 3		3.636 0	
Atoms defining the plane (unit weight) and distances (Å) from the plane	C(1)	−0.049	B(12)	−0.029	C(1)	−0.003	B(7)	0	B(11)	0.004	B(11)	0	Au	0.003
													S(1)	−0.025
	C(2)	−0.043	B(9)	−0.014	C(2)	0.003	B(8)	0	B(12)	−0.007	B(6)	0	S(2)	0.019
													C(10)	0.009
	B(7)	0.109	B(5)	0.051	B(7)	−0.002	B(4)	0	B(9)	0.007	B(5)	0.	C(20)	−0.024
													C(30)	0.025
	B(8)	−0.133	B(6)	−0.069	B(4)	0.002			B(5)	−0.005			N	0.002
	B(4)	0.115	B(11)	0.061										
σ		0.108		0.055		0.003		0		0.007		0		0.021
Other atoms and distances (Å) from the plane	Au	1.848	Au	3.339	Au	1.709	Au	1.741	Au	3.332	Au	3.127	B(7)	−0.178
	H(1)	0.253	H(9)	−0.518	H(1)	0.356	H(7)	0.631	H(11)	−0.366	H(11)	−0.302	B(4)	−0.382
	H(2)	0.425	H(5)	−0.320	H(2)	0.522	H(8)	0.421	H(9)	−0.460	H(6)	−0.156	B(10)	−1.03
	H(7)	0.665	H(6)	−0.341	H(7)	0.514	H(4)	0.083	H(5)	−0.383	H(5)	−0.346	B(12)	0.359
	H(8)	0.083	H(11)	−0.291	H(4)	0.038							B(9)	0.197
	H(4)	0.168												
Acute angles (°) between the planes	(1)–(2)	2.4	(1)–(7)	87.5	(2)–(7)	85.1	(4)–(5)	6.9	(6)–(7)	88.2				
	(1)–(3)	5.3	(2)–(3)	7.7	(3)–(4)	17.2	(4)–(6)	16.2						
	(1)–(4)	11.9	(2)–(4)	9.5	(3)–(5)	10.3	(4)–(7)	75.7						
	(1)–(5)	5.0	(2)–(5)	2.6	(3)–(6)	1.0	(5)–(6)	9.2						
	(1)–(6)	4.3	(2)–(6)	6.7	(3)–(7)	87.2	(5)–(7)	82.5						

suggested by Jones *et al.*,[16] it might be anticipated that complex (2) would have a *closo* structure, but since such proposals depend on the validity of the 18-electron rule, the failure of this approach in certain circumstances is not unexpected. In particular, a large *d*–*p* promotion energy would reduce the availability of *p* orbitals for bonding, and in d^8 ions this factor often favours the formation of planar four-co-ordinate 16-electron species.[17]

TABLE 6

Intramolecular contact distances: X–H < 3.0 Å, H–H < 2.6 Å

Atom (1)	Atom (2)	Distance (Å)
S(2)	$H(1^{I})$	2.953
Au	$H(31^{II})$	2.935
H(8)	$H(31^{II})$	2.531
H(51)	$H(9^{III})$	2.584
H(52)	$H(11^{IV})$	2.522
H(4)	$H(32^{IV})$	2.342
H(2)	$H(10^{VI})$	2.564

Symmetry code:

I $1 + x, y, z$

II $1 - x, 1 - y, 1 - z$

III $1 + x, 1 + y, z$

IV $-x, 1 - y, 1 - z$

V $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

VI $-x, \frac{1}{2} + y, \frac{1}{2} - z$

In the formally 18-electron gold(III) derivative (2) the same factor results in the placing of two electrons in the metal–cage d_{xz},e_1 π-antibonding orbital (e_1*), and we have suggested that an interaction [8] between this highest filled molecular orbital and the vacant $d_{x^2-y^2},e_2$ δ-antibonding orbital (e_2*) (roughly equivalent to 'back donation' from d_{xz} to e_2) could lead to the observed distortions, namely (*a*) a shortening of the C–C bond, (*b*) a lengthening of the facial B–C bonds, (*c*) a distortion of the structure so as to increase the M–C distances without appreciably affecting the M–B bonds, and (*d*) a tilting of the dithiocarbamate ligand away from the z axis, towards the carbon atoms (Figure 3).

More recently, however, extensive E.H.T.M.O. calculations have been reported[18] which suggest that the 'slipped' structure arises in part from overlap of a filled cage e_1 orbital, localised principally on the unique facial

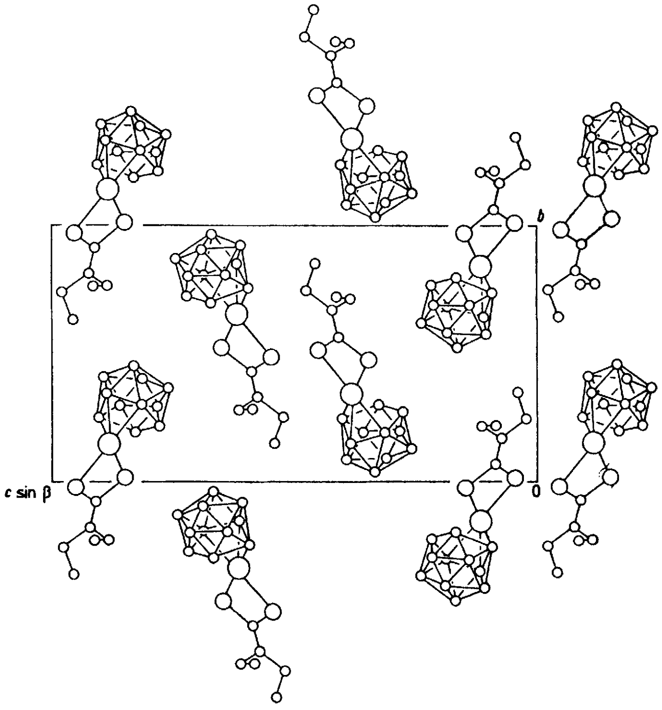

FIGURE 2 Molecular packing, viewed along the a axis towards the origin

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boron atom, with a vacant metal sp_z hybrid orbital[19] similar to an earlier suggestion in which sd_{z^2},e_1 overlap was postulated.[3] In terms of molecular orbitals this is equivalent to mixing $e_1,e_1{}^*$ with $(sp_z,a_1),(sp_z,a_1)^*$ orbitals, an interaction which also seems likely for d^{10} metallacarbaboranes in which the d–s promotion energy is relatively low.[20] Such calculations further suggest that in fact the $e_2{}^*$ set lie too high in energy to contribute significantly to the bonding.[19]

In the sandwich structure $[3,3'\text{-M}(B_9C_2{}^{1,2}H_{11})_2]^{n-}$ (M = Cu^{II}, $n = 2$; M = Au^{III}, $n = 1$), where the metal atom is *not* symmetrically bonded to the five atoms of the $C_2{}^{1,2}B_3$ face, as it is in $[Re(CO)_3(B_9C_2H_{11})]^-$ or $[NMe_4][Ni(B_9C_2{}^{1,2}H_{11})_2]$,[21] a description based on an antiparallel slip of the cages has long been used to express the deviations from the symmetrically bonded case. In these so-called ' slipped-sandwich ' structures the ' slip ' is defined in terms of the position of the metal atom in relation to the centroid of a mean facial C_2B_3 plane. For a symmetrically bonded complex the metal atom is situated directly above this centroid while the distance of the projection of the metal atom on to this plane in a distorted complex is the ' slip ' parameter in Å. Examples of ' slip ' parameters so derived are 0.7 Å for the gold(III) sandwich,[9] 0.6 Å for the copper(II) analogue,[14] and 0.7 Å for the present structure. While the ' slip ' parameter provides an approximate idea of the gross deviations from the symmetrically bonded structure, it cannot be considered as an adequate description since no indication of the framework distortions is included. Further, since the non-symmetrically bonded $B_9C_2{}^{1,2}$ metallacarbaboranes so far structurally characterised all exhibit distinct non-planarity of the C_2B_3 face, the approximation to planarity is misleading in terms of the positional relation of the metal atom to the facial atoms.

The lower B_5 plane is itself appreciably non-planar in (2), but consideration of the relatively undistorted B_4 fragment it contains gives a ' slip ' parameter of 0.5 Å. Thus, if slip is to be defined, it is adequately done in terms of the best least-squares plane through these four boron atoms. A marked decrease in the M–B(unique) bond distance in relation to a hypothetical symmetrically bonded structure is implied by this ' slip,' but since no M–B distances for the same metal in both distorted and symmetrically bonded $B_9C_2{}^{1,2}$ metallacarbaboranes are available this implication remains uncertain, and an alternative description may therefore be more appropriate.

The M–B bond distances in (2) appear similar to those expected for a hypothetical symmetrically bonded $B_9C_2{}^{1,2}Au$ metallacarbaborane, and the deviations from such a structure may thus be envisaged as arising from a tilting of the cage, about an axis parallel to the C–C bond and through B_u (so maintaining M–B_u 2.2 Å) accompanied by distortions centred mainly on the carbon atoms (Figure 3). Using this model, the projection of the metal on to the lower B_5 plane is geometrically equivalent to ' slip,' and we suggest that the ' slip ' figure so derived is perhaps better interpreted for the present structure as arising from the tilt, the 0.49 Å ' slip ' being equivalent to a tilt of *ca.* 10° here. The value for (1) is 0.52 Å, and the angle of tilt for each cage is *ca.* 12°. Both the values given are derived from the four planar boron atoms [plane (5), Table 5]. A description based on tilt and distortion provides a useful geometrical description, but neither this nor ' slip ' can be preferred at present in the absence of more structural data on similar compounds.

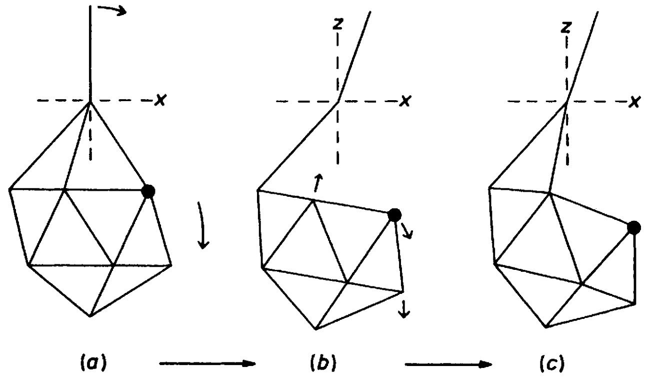

FIGURE 3 Proposed relation between the observed structure and a hypothetical symmetrically bonded analogue; (*a*) symmetrical structure showing direction of ' tilt '; (*b*) ' tilted ' structure showing cage deformations; (*c*) observed structure

EXPERIMENTAL

Boron-11 n.m.r. spectra were obtained at 28.9 MHz, using a Bruker WH90 Fourier-transform spectrometer [$\delta(OEt_2{\cdot}BF_3) = 0$, downfield shifts quoted as positive], and ^1H n.m.r. spectra were recorded on a Perkin-Elmer R12 instrument. Infrared spectra were obtained on Perkin-Elmer 621 and 457 spectrophotometers, and mass spectra were recorded at 70 eV on a V.G. Micromass 12 spectrometer.* Elemental analyses were by the Butterworth Microanalytical Consultancy Ltd. The starting materials $Na_2[B_8C_2H_{10}]$,[22] $Tl_2[B_9C_2H_{11}]$,[23] $Na_2[B_{10}C_2H_{12}]$,[24] and $[AuBr_2(S_2CNEt_2)]$,[25] were prepared by literature methods. Solvents were dried and distilled *in vacuo* before use; reactions were carried out *in vacuo* or in an atmosphere of dry nitrogen, and melting points were measured with the sample in a sealed tube *in vacuo*.

Preparation of $B_9C_2{}^{1,2}[Au(S_2CNEt_2)]^3H_{11}$, (2), *and* $[Au(S_2CNEt_2)_2][3,3'\text{-}Au(B_9C_2{}^{1,2}H_{11})_2]$, (1).—Dry diethyl ether (200 cm^3) was distilled on to a mixture of $[AuBr_2(S_2CNEt_2)]$ (6.60 g, 13.1 mmol) and $Tl[B_9C_2{}^{1,2}Tl^3H_{11}]$ (7.08 g, 13.1 mmol), and the reaction mixture was stirred at room

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

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temperature for 30 min, giving a red solution and maroon precipitate. Filtration in air, followed by removal of solvent under reduced pressure and recrystallisation of the solid residue from dichloromethane–pentane, afforded orange crystals of (2), 0.73 g (12%), m.p. 115 °C (decomp.) (Found: C, 17.7; H, 4.2; Au, 41.1; B, 20.2; N, 2.9. $C_7H_{21}AuB_9NS_2$ requires C, 17.6; H, 4.4; Au, 41.3; B, 20.4; N, 2.9%). The i.r. spectrum (Nujol) contained bands at 3 063w and 3 048w [carbaborane ν(CH)], 2 622w, 2 612m, 2 580s, and 2 542vs [ν(BH)], and 1 537vs cm^{-1} [dithiocarbamate ν(CN)].

The maroon precipitate from the original reaction mixture was extracted with tetrahydrofuran (thf) (3 × 100 cm^3) and pentane (100 cm^3) was added slowly to the filtered extract, giving dark red crystals of (1), 1.32 g (21%), m.p. 167 °C (decomp.) (Found: C, 17.7; H, 4.4; Au, 41.5; B, 20.7; N, 3.0%). The i.r. spectrum (Nujol) contained bands at 3 051vw [carbaborane ν(CH)], 2 603m, 2 581s, 2 562s, 2 549s, 2 519vs, and 2 490m [ν(BH)], and 1 561vs cm^{-1} [dithiocarbamate ν(CN)]. Evaporation of the thf–pentane supernatant gave a yellow crystalline material, identified by its i.r. spectrum [ν(CN) at 1 497 cm^{-1}] as $[\{Au(S_2CNEt_2)\}_2]$ [25] (0.26 g, 6%).

Reactions of $[AuBr_2(S_2CNEt_2)]$.—*With* $Na_2[B_8C_2H_{10}]$. Solid $[AuBr_2(S_2CNEt_2)]$ (0.505 g, 1.0 mmol) was added to a cold (−20 °C) solution of $Na_2[B_8C_2H_{10}]$ [derived from $B_8C_2{}^{1,2}H_{10}$ (0.121 g, 1.0 mmol)] in thf (25 cm^3), and the reaction mixture warmed to 25 °C with stirring. The solution turned black, and the only gold-containing product isolated was $[\{Au(S_2CNEt_2)\}_2]$ (0.15 g, 44%).

With $Na_2[B_{10}C_2H_{12}]$. The complex $[AuBr_2(S_2CNEt_2)]$ (1.680 g, 3.33 mmol) was added to a solution of $Na_2[B_{10}C_2H_{12}]$ (derived from $B_{10}C_2{}^{1,2}H_{12}$) (0.481 g, 3.34 mmol) in CH_2Cl_2 (25 cm^3), and the mixture was stirred at room temperature for 40 min. The dark brown solution was filtered in air and evaporated under reduced pressure, leaving a dark oily residue. Recrystallisation from CH_2Cl_2–OEt_2 gave a low yield of orange crystals, identified by i.r. and ^1H and ^{11}B n.m.r. spectroscopy as $[Au(S_2CNEt_2)_2][B_{10}C_2H_{13}]$ [containing the anion (1) of ref. 26], 0.042 g (4.0%) (Found: C, 22.6; H, 5.3; Au, 30.4; B, 16.6; N, 4.0. $C_8H_{33}AuB_{10}N_2S_4$ requires C, 22.6; H, 5.1; Au, 30.8; B, 16.9; N, 4.4%). The compounds $B_{10}C_2{}^{1,2}H_{12}$ and $[\{Au(S_2CNEt_2)\}_2]$ were qualitatively identified in the supernatant, by mass and i.r. spectrometry respectively.

Reactions of (1) *and* (2) *with Pyridine*.—Pyridine (1 cm^3) was added to a solution of complex (2) (36.8 mg, 0.077 mmol) in CH_2Cl_2 (1 cm^3), giving an immediate yellow precipitate. The solution was diluted with OEt_2 (5 cm^3) and filtered, to give $[\{Au(S_2CNEt_2)\}_2]$ (24.1 mg, 91%). Evaporation of the filtrate gave $C_5H_5N{\cdot}B_9C_2H_{11}$ [12] (14.3 mg, 88%), identified by i.r., ^{11}B n.m.r., and mass spectrometry.[11] Complex (1) also reacted with pyridine, although more slowly (*ca.* 1 h at 25 °C), and gave identical products.

Crystal-structure Determination.—A sample of complex (1) was recrystallised from diethyl ether (*in vacuo*) and a prismatic crystal of axial dimensions *ca.* 0.42 × 0.03 × 0.08 mm was selected and mounted with the [100] direction approximately parallel to the ϕ axis of the goniometer. Accurate unit-cell dimensions were obtained by a least-squares analysis of the 2θ values of 60 reflections ($20 < 2\theta < 35°$) centred in the counter of a Syntex $P2_1$ four-circle diffractometer using graphite-monochromated zirconium-filtered Mo-K_α radiation.

Crystal data. $C_7H_{21}AuB_9NS_2$, $M = 477.3$, Monoclinic, $a = 7.3710(6)$, $b = 11.0368(9)$, $c = 21.1564(17)$ Å, $\beta = 93.22(4)°$, $U = 1\,718.4(1)$ Å^3, $D_m = 1.85$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.844$ g cm^{-3}, $F(000) = 904$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 87.5 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ when l is odd, $0k0$ when k is odd.

Diffractometer data provided a total of 3 275 independent reflections of which 1 962 had $|I_0| > 3\sigma(I_0)$ and were classified as observed, the θ—2θ scan method being used out to $2\theta_{max.} = 52°$. The standard deviation $\sigma(I_0)$ was calculated from $\sigma(I_0) = S[(C + BG)/R^2]^{\frac{1}{2}}$ where S is the scan speed, which varied between 1 and 29.3° min^{-1}, C is the total scan count, BG the sum of the background counts, and R the ratio of total background to total scan counting times. The scan width was from 1° below the α_1 peak to 1° above α_2, at each of which points the background was measured for one quarter of the total scan time (R 0.5).

Unobserved reflections were deleted during data processing, where the Lorentz and polarisation corrections were applied in the usual manner. An analytical absorption correction was applied by use of ABSCOR,[27] transmission factors for the correction of $|F_o|$ varying between 0.71 and 0.87. All the computations using the corrected data were made on a CDC 7600 computer at the University of Manchester Computer Centre with the programs described in ref. 28.

Solution and refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. Atomic-scattering factors for gold, sulphur, carbon, nitrogen, and boron were taken from ref. 29, and those for hydrogen from ref. 30. The anomalous scattering components for gold and sulphur were taken from ref. 31.

The gold and sulphur atoms were located from a three-dimensional Patterson synthesis, and a Fourier synthesis phased on these atoms revealed the remaining non-hydrogen atoms. Least-squares refinement using anisotropic thermal parameters $U = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ gave R 0.049, the minimized function being $\Sigma w(|F_o| - |F_c|)^2$ with unit weights. All but three of the hydrogen atoms were located from difference-Fourier syntheses, and of those found all except the poorly determined H(7) were included in the refinement, their isotropic temperature factors being constrained to be invariant at 130% of the converged isotropic parameter of the atom to which they were bonded. A weighting scheme of the form $w = \{1 + [(|F_o| - B)/A]^2\}^{-1}$, with $B = 60$ and $A = 50$, was introduced and the refinement converged to the final R 0.039, the weighted residual R' being 0.047. The standard deviation of an observation of unit weight (σ_1) was 1.21. A difference-Fourier synthesis computed after the final cycle of least-squares revealed large fluctuations (+1.5 to −0.8 eÅ^{-3}) in the region of the gold atom. No significance could be attached to these peaks which are thought to be mainly

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due to errors in the absorption correction arising from inaccuracies in the crystal-size measurements, and the spherical-atom approximation imposed by the atomic-scattering factors employed. The high-intensity low-angle reflections exhibited quite large positive and negative ΔF values which could not be accounted for by considering extinction to be a problem.

Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22189 (39 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.