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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 $TI[B_9C_2^{1,2}TI^3H_{11}]$ yields the known ion $[3,3'-Au(B_9C_2^{1,2}H_{11})_2]^-$ 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 $\beta = 93.22(4)^\circ$. 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 cobalt¹ and nickel² 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 $[3,3'-M(B_9C_2^{1,2}H_{11})_2]^{n-}$ (M = Cu^{II} or Au^{II}, n = 2; $M = Cu^{III}$ or Au^{III} , n = 1³ which have frequently been described as electron-rich 'slipped-sandwich compounds, since the $[{\rm B_9C_2H_{11}}]^{2-}$ ligand appears to ' slip ' relative to the structure of say $[B_9C_2^{1,2}{Re(CO)_3}^3$ - H_{11}]⁻, in which the metal atom is situated symmetrically with respect to the C_2B_9 cage.⁴ The related complexes $[\check{B_{9}C_{2}(HgPh)H_{11}}]^{-,6}$ $[Cu(B_{10}CH_{11})_2]^{3-,5}$ B₄C₂[Au- (PPh_3)]H₇,⁷ and B₄C₂(HgPh)H₇ 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 posttransition 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

† 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).

¹ G. B. Dunks and M. F. Hawthorne in 'Boron Hydride Chemistry,' ed. E. L. Muetterties, Academic Press, New York, 1975, ch. 11.

² F. G. A. Stone, J. Organometallic Chem., 1975, **100**, 257. ³ L. F. Warren, jun., and M. F. Hawthorne, J. Amer. Chem.

- Soc., 1968, 90, 4823. A. Zalkin, T. E. Hopkins, and D. H. Templeton, Inorg. Chem.,
- 1966, **5**, 1189. ⁵ D. E. Hyatt, J. L. Little, J. T. Moran, F. A. Scholer, and L. J. Todd, J. Amer. Chem. Soc., 1967, 89, 3342.

RESULTS AND DISCUSSION

The action of the thallium(I) salt $Tl[B_9C_2^{1,2}Tl^3H_{11}]$ on the gold(III) dithiocarbamate [AuBr₂(S₂CNEt₂)] in diethyl ether yields two orange-red crystalline metallacarbaboranes which possess the same empirical formula (Et₂NCS₂AuC₂B₉H₁₁) from analytical data. Crystallographic characterisation revealed one of these to be the ionic species [Au(S₂CNEt₂)₂][3,3'-Au(B₉C₂^{1,2}H₁₁)₂],⁹ (1), and we have confirmed the identity of the anion from comparison of its ¹¹B n.m.r. spectrum with published data.³ The other, diethyl ether-soluble, compound is the novel molecular carba-auraborane B₉C₂^{1,2}[Au- (S_2CNEt_2)]³H₁₁, (2), whose structure and properties are reported here. The ¹¹B n.m.r. spectrum of (2) in C₆D₆ solution shows doublets, arising from typical carbaborane, J(B-H) couplings, at $\delta + 24.6 [J(B-H) 135$ 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 C₆D₆ solution which shows only a single resonance due to the carbaborane C-H protons $[\tau 5.86 \text{ (relative intensity 2)}]$ and quartet and triplet signals $[\tau 7.26 (4) \text{ and } 9.36 (6) \text{ respectively}]$ 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 [PtL₄]- $[PtX_{4}]$ (L = ligand, X = halogen) to the molecular isomers [PtX₂L₂] are known to occur simply on heating.¹⁰

⁶ B. M. Mikhailov and T. V. Potapova, Bull. Acad. Sci., U.S.S.R., Chem. Div., 1970, 11, 2484.

U.S.S.K., Chem. Div., 1970, 11, 2484.
⁷ C. P. Magee, L. G. Sneddon, D. C. Beer, and R. N. Grimes, J. Organometallic Chem., 1975, 86, 159.
⁸ H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, J.C.S. Chem. Comm., 1976, 1019.
⁹ H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, Acta Cryst., 1977, B33, 3604.
¹⁰ A. D. Westland J. Chem. Soc. 1965, 3060.

- ¹⁰ A. D. Westland, J. Chem. Soc., 1965, 3060.

Both compounds (1) and (2) underwent reductiveelimination 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 ¹¹B 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



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

TABLE 1

Atomic co-ordinates (\times 10⁴) for the non-hydrogen atoms with standard deviations in parentheses

	х	У	z
Au	$2\ 265(1)$	$3\ 423(1)$	3790(1)
S(1)	$2\ 372(5)$	$5\ 101(3)$	4494(2)
S(2)	4570(4)	4730(3)	3 434(2)
N	4913(14)	6 695(10)	4 180(4)
C(10)	4116(16)	$5\ 682(11)$	4056(6)
C(20)	6 360(19)	7 178(14)	3 769(7)
C(30)	4474(18)	7445(11)	4 731(6)
C(40)	3 385(30)	8542(15)	4533(8)
C(50)	8 218(25)	7063(22)	$4\ 097(9)$
C(1)	-1255(17)	2 983(12)	3 300(7)
C(2)	-85(18)	2710(13)	2782(6)
$\mathbf{B}(4)$	-203(21)	2 454(14)	$4\ 050(7)$
$\mathbf{B}(5)$	-2204(19)	1817(13)	3 603(9)
$\mathbf{B}(6)$	-2.058(20)	1 974(15)	2777(8)
$\mathbf{B}(7)$	1 956(22)	1 938(14)	3 079(7)
B(8)	1669(22)	1 484(12)	3 902(7)
$\mathbf{B}(9)$	-442(26)	839(15)	3 910(8)
$\mathbf{B}(10)$	-1426(22)	583(14)	3 139(8)
$\mathbf{B}(11)$	26(24)	$1\ 277(15)$	2603(7)
$\mathbf{B}(12)$	974(20)	470(14)	$3\ 283(7)$

a variety of metallacarbaboranes) in which d^{10} ML₂ species (M = Ni, Pd, or Pt; L = PR₃ or RNC) insert directly into *closo*-carbaboranes.² Attempts to produce other gold carbaboranes by treating [AuBr₂(S₂CNEt)₂] with Na₂[B₈C₂H₁₀], and Na₂[B₁₀C₂H₁₂], yielded only dark brown-black solids (suggesting that reduction had occurred) and small amounts of [{Au(S₂CNEt₂)}₂] and ¹¹ D. C. Young, D. V. Howe, and M. F. Hawthorne, J. Amer. Chem. Soc., 1969, **91**, 859.

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 $[Au(S_2CNEt_2)_2][B_{10}C_2H_{13}]$ respectively. Spectroscopic and preliminary X-ray evidence indicated the latter to

TABLE 2

Final positional (fractional co-ordinates \times 10³) parameters of the hydrogen atoms *

	x	у	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)	4 37(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

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

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

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.

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 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 po	lyhedron
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$\begin{array}{c} C(2)-Au-C(1) \\ C(2)-Au-B(7) \\ C(1)-Au-B(4) \\ B(4)-Au-B(8) \\ B(7)-Au-B(8) \\ \end{array}$	$\begin{array}{c} 30.5(4) \\ 40.5(5) \\ 40.9(5) \\ 47.9(6) \\ 49.0(5) \end{array}$	$\begin{array}{c} C(1) - B(5) - B(4) \\ B(4) - B(5) - B(9) \\ B(9) - B(5) - B(10) \\ B(10) - B(5) - B(6) \\ B(6) - B(5) - C(1) \end{array}$	$\begin{array}{c} 63.2(8)\\ 59.9(9)\\ 59.4(8)\\ 59.5(9)\\ 58.4(9)\end{array}$
Au-C(1)-B(4)Au-C(2)-B(7)Au-C(1)-C(2)Au-C(2)-C(1)Au-B(4)-C(1)Au-B(7)-C(2)	52.3(6) 53.0(6) 74.9(7) 74.7(7) 86.8(7) 86.8(7)	$\begin{array}{c} C(2) - B(6) - C(1) \\ C(1) - B(6) - B(5) \\ B(5) - B(6) - B(10) \\ B(10) - B(6) - B(11) \\ B(11) - B(6) - C(2) \end{array}$	52.3(8) 56.3(8) 61.0(9) 60.2(9) 56.4(9)
$ \begin{array}{l} Au - B(7) - B(8) \\ Au - B(4) - B(8) \\ Au - B(8) - B(4) \\ Au - B(8) - B(4) \\ Au - B(8) - B(7) \end{array} $	64.7(6) 65.9(7) 66.2(6) 66.3(6)	$\begin{array}{c} B(8)-B(9)-B(4)\\ B(4)-B(9)-B(5)\\ B(5)-B(9)-B(10)\\ B(10)-B(9)-B(12)\\ B(12)-B(9)-B(8) \end{array}$	$\begin{array}{c} 60.8(9) \\ 61.8(9) \\ 60.5(9) \\ 60.2(9) \\ 61.1(9) \end{array}$
C(1)-C(2)-B(6) = B(6)-C(1)-C(2) = B(4)-C(1)-B(5) = B(7)-C(2)-B(11) = B(5)-C(1)-B(6) = B(11)-C(2)-B(6) = B(5)-B(4)-C(1) = B(5)-B(4)-B(5) = B(4)-C(1) = B(5)-B(4)-B(4)-B(5)-B(4)-B(4)-B(4)-B(4)-B(4)-B(4)-B(4)-B(4	$\begin{array}{c} 63.5(9) \\ 64.2(9) \\ 64.6(9) \\ 64.7(9) \\ 65.3(10) \\ 65.2(10) \\ 52.2(9) \end{array}$	$\begin{array}{c} B(6){-}B(10){-}B(11)\\ B(11){-}B(10){-}B(12)\\ B(12){-}B(10){-}B(9)\\ B(9){-}B(10){-}B(5)\\ B(5){-}B(10){-}B(6) \end{array}$	$\begin{array}{c} 60.2(9) \\ 60.8(9) \\ 60.2(9) \\ 60.1(9) \\ 59.5(9) \end{array}$
$\begin{array}{l} B(3) & B(4) & C(1) \\ B(11) - B(7) - C(2) \\ B(9) - B(4) - B(5) \\ B(12) - B(7) - B(11) \\ B(8) - B(7) - B(11) \\ B(8) - B(7) - B(12) \\ B(7) - B(8) - B(12) \end{array}$	52.2(8) 52.9(8) 58.3(9) 58.5(8) 56.8(9) 57.9(8) 61.1(8)	$\begin{array}{c} C(2) - B(11) - B(7) \\ B(7) - B(11) - B(12) \\ B(12) - B(11) - B(10) \\ B(10) - B(11) - B(6) \\ B(6) - B(11) - C(2) \end{array}$	$\begin{array}{c} 62.4(9) \\ 60.5(8) \\ 59.8(9) \\ 59.7(9) \\ 58.4(9) \end{array}$
B(4)-B(8)-B(9)' B(12)-B(8)-B(9)	62.4(9) 61.4(9)	$\begin{array}{c} {\rm B(7){-}B(12){-}B(8)} \\ {\rm B(8){-}B(12){-}B(9)} \\ {\rm B(9){-}B(12){-}B(10)} \\ {\rm B(10){-}B(12){-}B(11)} \\ {\rm B(11){-}B(12){-}B(7)} \end{array}$	$\begin{array}{c} 61.1(8) \\ 57.5(9) \\ 59.6(9) \\ 59.4(9) \\ 61.0(9) \end{array}$
$\begin{array}{l} C(2) - C(1) - B(4) \\ C(1) - C(2) - B(7) \\ C(2) - B(7) - B(8) \\ C(1) - B(4) - B(8) \\ B(4) - B(8) - B(7) \end{array}$	110(1) 111(1) 109(1) 110(1) 98(1)	$\begin{array}{c} {\rm B}(12){\rm -B}(9){\rm -B}(5)\\ {\rm B}(9){\rm -B}(12){\rm -B}(11)\\ {\rm B}(12){\rm -B}(11){\rm -B}(6)\\ {\rm B}(9){\rm -B}(5){\rm -B}(6)\\ {\rm B}(5){\rm -B}(6){\rm -B}(11) \end{array}$	$108(1) \\ 105(1) \\ 111(1) \\ 110(1) \\ 105(1)$
(b) Exo-polyhedr S(1)-Au-S(2) Au-S(1)-C(10) Au-S(2)-C(10) S(1)-C(10)-S(2) C(20)-N-C(30)	ral bond angle: 74.2(1) 87.3(4) 87.4(4) 111.1(7) 116.6(10)	s C(10)-N-C(20) C(10)-N-C(30) S(1)-C(10)-N S(2)-C(10)-N N-C(20)-C(50) N-C(20)-C(50)	$121.3(11) \\ 122.0(10) \\ 123.5(9) \\ 125.3(9) \\ 110.1(12) \\ 111.6(11) \\ 111.6($

The gold-diethyldithiocarbamate moiety. The golddiethyldithiocarbamate 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[S₂CNEt₂]·3H₂O.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 ¹³ M. Colapletro, A. Domenicano, and A. Vaciago, *Chem. Comm.*, 1968, 572. 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 $[\text{Au}(\text{S}_2\text{CNEt}_2)_2]^+$ cation [2.330(2) Å],⁹ implying a relatively high 'trans ' effect for the B₉C₂H₁₁ group. The Au-S₂ 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-(B₉C₂^{1,2}H₁₁)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) (d⁹) sandwich structure [Cu(B₉C₂^{1,2}H₁₁)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 B₅ plane [plane (2), Table 5] which is planar in (3) but in (2) shows a B₄–B₂ dihedral angle [planes (5) and (6), Table 5] of 170.8°.

While there are no significant (3σ) differences between the B₉C₂ 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,

- ¹⁴ R. M. Wing, J. Amer. Chem. Soc., 1967, 89, 5599.
- ¹⁵ R. M. Wing, J. Amer. Chem. Soc., 1968, 90, 4828.

¹³ D. W. J. Cruickshank, Acta Cryst., 1949, 2, 65.

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TABLE 5

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

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

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	
Int	ramolecular con	tact distan H−H < 2.	ces: X-H < 3.0 Å 6 Å	λ,
	Atom (1) S(2) Au H(8) H(51) H(52) H(4) H(2)	$\begin{array}{l} {\rm Atom}~(2)\\ {\rm H}(1^{\rm I})\\ {\rm H}(31^{\rm II})\\ {\rm H}(31^{\rm II})\\ {\rm H}(9^{\rm III})\\ {\rm H}(11^{\rm IV})\\ {\rm H}(32^{\rm IV})\\ {\rm H}(10^{\rm VI}) \end{array}$	Distance (Å) 2.953 2.935 2.531 2.584 2.522 2.342 2.564	
Symme I II III	etry code: 1 + x, y, z 1 - x, 1 - y, 1 1 + x, 1 + y, z	z	$ \begin{array}{ccc} \text{IV} & -x, \ 1 - y, \ 1 \\ \text{V} & 1 - x, \ \frac{1}{2} + y, \\ \text{VI} & -x, \ \frac{1}{2} + y, \ \frac{1}{2} \end{array} $	$\frac{-z}{\frac{1}{2}-z}$

In the formally 18-electron gold(III) derivative (2) the same factor results in the placing of two electrons in the metal-cage $d_{xz}, e_1 \pi$ -antibonding orbital (e_1^*) , and we have suggested that an interaction ⁸ between this highest filled molecular orbital and the vacant $d_{x^2-y^2}, e_2 \delta$ -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

¹⁶ C. J. Jones, W. T. Evans, and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1973, 543.

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 reported¹⁸ which suggest that the



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

' slipped ' structure arises in part from overlap of a filled cage e_1 orbital, localised principally on the unique facial

¹⁸ D. M. P. Mingos, M. I. Forsyth, and A. J. Welch, J.C.S. Chem. Comm., 1977, 605.

¹⁷ R. S. Nyholm, Proc. Chem. Soc., 1961, 273.

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 $[3,3'-M(B_9C_2^{1,2}H_{11})_2]^{n-1}$ $(M = Cu^{II}, n = 2; M = Au^{III}, n = 1)$, 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 $[Re(CO)_{3}(B_{9}C_{2}H_{11})]^{-}$ 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

* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J.

 D. M. P. Mingos, J.C.S. Dalton, 1977, 602.
 J. D. Dunitz and L. E. Orgel, Adv. Inorg. Chem. Radiochem., 1960, **2**, 1.

²¹ F. V. Hansen, R. G. Hazell, C. Hyatt, and G. D. Stucky, Acta Chem. Scand., 1973, 27, 1210.
 ²² B. Stibr, J. Plesek, and S. Hermanek, Coll. Czech. Chem.

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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 B₅ 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



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

preferred at present in the absence of more structural data on similar compounds.

EXPERIMENTAL

Boron-11 n.m.r. spectra were obtained at 28.9 MHz, using a Bruker WH90 Fourier-transform spectrometer $[\delta(OEt_2 BF_2) = 0$, 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 $\mathrm{Na_2[B_8C_2H_{10}],^{22} \quad Tl_2[B_9C_2H_{11}],^{23} \quad \mathrm{Na_2[B_{10}C_2H_{12}],^{24}}}$ and [AuBr₂(S₂CNEt₂)],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.

 (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

²³ J. L. Spencer, M. Green, and F. G. A. Stone, J.C.S. Chem. Comm., 1972, 1178.

24 D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 1973, 95, 1109.

25 H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. van der Kerk, J. Organometallic Chem., 1964, 2, 236.

Comm., 1973, 38, 338.

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. C7H21AuB9NS2 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 [v(BH)], and 1 537vs cm⁻¹ [dithiocarbamate v(CN)].

The maroon precipitate from the original reaction mixture was extracted with tetrahydrofuran (thf) $(3 \times 100$ cm³) and pentane (100 cm³) 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 v(CH)], 2 603m, 2 581s, 2 562s, 2 549s, 2 519vs, and 2 490m [v(BH)], and 1 561vs cm^{-1} [dithiocarbamate v(CN)]. Evaporation of the thfpentane supernatant gave a yellow crystalline material, identified by its i.r. spectrum $[v(CN) \text{ at } 1497 \text{ cm}^{-1}]$ 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 [AuBr₂(S₂CNEt₂)] (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 cm³), 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 CH₂Cl₂ (25 cm³), 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 CH₂Cl₂-OEt₂ gave a low yield of orange crystals, identified by i.r. and ¹H and ¹¹B n.m.r. spectroscopy as [Au(S₂CNEt₂)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 cm³) was added to a solution of complex (2) (36.8 mg, 0.077 mmol) in CH₂Cl₂ (1 cm³), giving an immediate yellow precipitate. The solution was diluted with OEt_2 (5 cm³) and filtered, to give $[{Au(S_2CNEt_2)}_2]$ (24.1 mg, 91%). Evaporation of the filtrate gave C₅H₅N·B₉C₂H₁₁¹² (14.3 mg, 88%), identified by i.r., ¹¹B 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. $0.42 \times 0.03 \times$ 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 leastsquares analysis of the 20 values of 60 reflections (20 < $2\theta < 35^{\circ}$) centred in the counter of a Syntex P2₁ four-circle diffractometer using graphite-monochromated zirconiumfiltered 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) Å³, $D_{\rm m} = 1.85$ 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, $\mu(Mo-K_{\alpha}) = 87.5$ cm⁻¹. Space group $P2_1/c$ from systematic absences: hol when l is odd, 0k0 when k is odd.

Diffractometer data provided a total of 3 275 independent reflections of which 1962 had $|I_0| > 3\sigma(I_0)$ and were classified as observed, the θ -2 θ scan method being used out to $2\theta_{\text{max}} = 52^{\circ}$. 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 $|F_0|$ 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 threedimensional Patterson synthesis, and a Fourier synthesis phased on these atoms revealed the remaining nonhydrogen atoms. Least-squares refinement using anisotropic thermal parameters $U = \exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}h^2b^{*2} +$ $U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$] gave R 0.049, the minimized function being $\Sigma w(|F_0| - |F_c|)^2$ 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 $w = \{1 + \lceil (|F_0| B/A]^{2}^{-1}$, 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 leastsquares revealed large fluctuations $(+1.5 \text{ to } -0.8 \text{ e}\text{Å}^{-3})$ in the region of the gold atom. No significance could be attached to these peaks which are thought to be mainly

28 'X-Ray '76,' Technical Report TR-446, ed. J. M. Stewart, Computer Science Centre, University of Maryland, 1976. ²⁹ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321. ³⁰ R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem.*

Phys., 1968, **42**, 3175. ³¹ D. T. Cromer and O. Liberman, J. Chem. Phys., 1970, **53**,

1891.

²⁶ G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, J.C.S. Chem. Comm., 1972, 899.

²⁷ N. W. Alcock, in 'Crystallographic Computing,' eds. F. R. Ahmed, S. R. Hall, and C. P. Huber, Munksgaard, Copenhagen, 1970, pp. 271-278.

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.