# Synthesis and *X*-Ray Crystal Structure of 3-Diethyldithiocarbamato-3-aura-1,2-dicarbadodecaborane. A 'Slipped' 18-electron Metallacarborane

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*Summary* Reaction of $Tl_2(7,8\text{-}C_2B_9H_{11})$ with $Et_2NCS_2AuBr_2$ affords the known ion $(1,2\text{-}C_2B_9H_{11})_2Au^-$, and also the novel 18-electron species $(1,2\text{-}C_2B_9H_{11})Au(S_2CNEt_2)$ which is shown from *X*-ray data to have the 'slipped' structure previously found only in 20- or 21-electron systems; a similar structure is also deduced for the 18 electron compound $(Ph_3P)_2Pt(1,2\text{-}C_2B_9H_{11})$.

A VARIETY of metallacarboranes are known where a metal atom is bonded into the open $C_2B_3$ face of the *nido*-carborane anion, $7,8\text{-}C_2B_9H_{11}{}^{2-}$, thus completing an $MC_2B_9$ icosahedral framework. It is expected,[1] and found from *X*-ray studies,[2] that only those derivatives in which the metal atom is associated with up to 18 electrons (e) [*i.e.* $(2n + 14)$e for an $n$-vertex polyhedral metallacarborane] *e.g.* $[(1,2\text{-}C_2B_9H_{11})\text{-}Re(CO)_3]^-$, will possess symmetrical *closo*-structures with the metal situated above the centre of the $C_2B_3$ face. However, for the relatively few electron-rich metallacarboranes, *e.g.* $[(1,2\text{-}C_2B_9H_{11})_2M]^{n-}$ ($M = Ni^{II}$, $Pd^{II}$, $Cu^{II}$, $Au^{II}$, $n = 2$; $Cu^{III}$, $Au^{III}$, $n = 1$)[3] which possess more than 18e (considering $7,8\text{-}C_2B_9H_{11}{}^{2-}$ as a 6e donor) it is generally assumed that severe distortions will occur as has been demonstrated for the $Ni^{II}$, $Cu^{II}$, and $Cu^{III}$ systems,[4] which have 'slipped-sandwich' structures. We have now prepared two 18e metallacarboranes containing the $d^8$ ions $Au^{III}$ and $Pt^{II}$, and a 20e $Au^{III}$ compound to test the validity of these assumptions.

Treatment of dibromo(diethyldithiocarbamato)gold(III) with $Tl_2(7,8\text{-}C_2B_9H_{11})$[5] ($Et_2O$, 25 °C, 0·5 h) gave a red solution from which the neutral complex $(1,2\text{-}C_2B_9H_{11})\text{-}Au(S_2CNEt_2)$, (I) was isolated as an orange crystalline solid (12% yield, m.p. 115 °C decomp.). Also formed was a maroon precipitate containing the $(1,2\text{-}C_2B_9H_{11})_2Au^-$ ion as its $(Et_2NCS_2)_2Au^+$ salt (II) (21% yield, m.p. 167 °C decomp.), together with a small amount of gold(I) diethyldithiocarbamate, $(Et_2NCS_2Au)_2$, indicating that some reduction of gold(III) occurred during the reaction.

Single crystal *X*-ray studies of the 18e and 20e metallacarboranes (I) and (II) show that not only does the anion of (II) adopt a 'slipped' structure as had been suggested previously,[4] but also that (I) unexpectedly exhibits a similar metal-cage interaction (Figure 1).

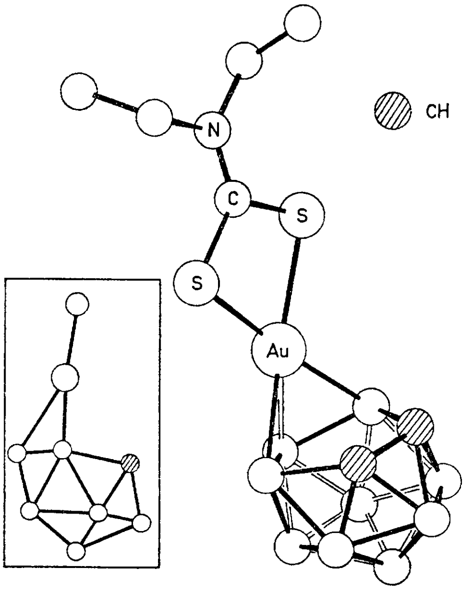

FIGURE 1. Molecular structure of $3\text{-}(Et_2NCS_2)\text{-}3,1,2\text{-}AuC_2B_9H_{11}$. Hydrogen atoms are omitted for clarity. Inset shows a portion of the structure projected parallel to the cage C–C bond.

*Crystal data* (I): $(1,2\text{-}C_2B_9H_{11})Au(S_2CNEt_2)$, $M = 477{\cdot}3$, monoclinic, space group $P2_1/c$, $a = 7{\cdot}3710(6)$, $b = 11{\cdot}0368(9)$, $c = 21{\cdot}1564(17)$ Å, $\beta = 93{\cdot}22(4)°$, $U = 1718{\cdot}4(1)$ Å$^3$, $D_c = 1{\cdot}844$ g cm$^{-3}$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 87{\cdot}46$ cm$^{-1}$. $R$ is currently 0·040 for 1962 independent observed reflections.
*Crystal data* (II): $[(Et_2NCS_2)_2Au]^+[(1,2\text{-}C_2B_9H_{11})_2Au]^-$, $M = 954{\cdot}6$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}3786(9)$, $b = 20{\cdot}6068(22)$, $c = 10{\cdot}0656(11)$ Å, $\beta = 105{\cdot}346(8)°$, $U = 1675{\cdot}9(1)$ Å$^3$, $D_c = 1{\cdot}891$ g cm$^{-3}$, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 89{\cdot}7$ cm$^{-1}$. The final $R$-index is 0·022 for 1486 independent observed reflections.

Table

Bond lengths (Å) and angles (°) for $C_2B_3$ faces and for metal–cage interactions. Estimated standard deviations are given in parentheses.

| | C–C | B–C(av) | B–B′(av)[a] | C–M(av) | B–M(av) | B′–M[a] | B–B′–B[a] | $B_3$–$C_2B_2$ dihedral angle |
|---|---|---|---|---|---|---|---|---|
| (I) | 1·46(2) | 1·82(2) | 1·81(2) | 2·78(1) | 2·22(1) | 2·20(1) | 98 | 163 |
| (II) | 1·50(1) | 1·75(1) | 1·82(1) | 2·77(1) | 2·26(1) | 2·20(1) | 98 | 166 |
| $(1,2\text{-}C_2B_9H_{11})Re(CO)_3^-$ [b] | 1·61(2) | 1·71(2) | 1·78(2) | 2·31(1) | 2·33(1) | 2·35(1) | 106 | 180 |

[a] B′ refers to the unique boron atom of the $C_2B_3$ face. [b] Ref. 6.

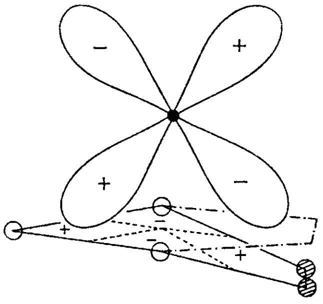

Figure 2. Overlap of filled $d_{xz}$ (metal) orbital with vacant $e_2$ (cage) orbital.

The position of the gold atom with respect to the $C_2B_3$ face is similar in (I) and (II). It should be pointed out that the accuracy of structures (I) and (II) and the cage distortions revealed, particularly the distinct non-planarity of the $C_2B_3$ face, suggest that a conventional description in terms of a simple movement of the metal atom between positions related to a least-squares plane through the $C_2B_3$ face is not easily justified. In (I) and (II) the 'slip' is predominantly due to a lengthening of the B–C bonds and a bending of the $C_2B_3$ plane, since the position of the gold atom with respect to the face $B_3$ fragment is similar to that expected for a symmetrically bonded complex. Relevant bond lengths and angles are given in the Table together with corresponding values for the symmetrically bonded complex $(1,2\text{-}C_2B_9H_{11})\text{-}Re(CO)_3^-$.[6] The $^{11}$B n.m.r. data show that the observed structures of (I) and (II)[3] persist in solution [*e.g.* (I) in $CH_2Cl_2$/25 °C at 28·9 MHz shows doublets at $\delta + 24{\cdot}6$ (relative intensity 1), $+5{\cdot}8(2)$, $+1{\cdot}9(1)$, $-6{\cdot}5(2)$ $-11{\cdot}7(2)$, and $-21{\cdot}7(1)$; shifts relative to $BF_3.Et_2O$ = 0 p.p.m., downfield shifts +ve] both spectra showing a low-field resonance characteristic of the 'slipped' structure.[3]

In the light of these results we have prepared the 18e system $(1,2\text{-}C_2B_9H_{11})Pt(PPh_3)_2$, by the action of $Tl_2C_2B_9H_{11}$ on *cis*-$(Ph_3P)_2$ $PtCl_2$. The $^{11}$B n.m.r. spectrum of this compound also contains a low-field doublet, and indeed the entire spectrum [doublets at $\delta + 15{\cdot}8(1)$, $+8{\cdot}2(5)$, and $-21{\cdot}4(3)$ p.p.m.] strongly resembles that of the 'slipped' 20e complex $(1,2\text{-}C_2B_9H_{11})_2Pd^{2-}$.[3] It is interesting to note that, when the two carbon atoms in the $C_2B_3$ face are separated by a boron atom in other similar 18e/$d^8$ systems, *e.g.* 3,3-$(Me_2PhP)_2$-1, 7-$Me_2$-3,1,7-$PtC_2B_9H_9$, a symmetrical structure is again preferred.[7]

These results confirm that the *nido*-'slipped' configuration is not confined to 'electron-rich' systems, but appears to be related simply to the presence of a formal $d^8$ or $d^9$ metal ion. On the basis of a donor–acceptor bonding model, one possible rationalisation is that, in a formal $d^6$ ion, both the $d_{xz}$ and $d_{yz}$ orbitals are vacant and can accept electrons from the $C_2B_9$ cage, whereas in a formal $d^8/d^9$ ion one of these orbitals is filled and can thus donate electrons to a vacant cage-antibonding orbital (Figure 2). The asymmetry of such overlap is consistent with the observed distortions (Table). The results also indicate that further examination of the factors which have hitherto been assumed to cause 'slip'-distortion is required, and that such distortions may occur in other 18e compounds, such as $(1,2\text{-}C_2B_9H_{11})Pt(1,5\text{-}C_8H_{12})$, where symmetrical structures have been proposed.[8]

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