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# Synthesis and X-ray crystal structure of salts of the bis(1,2-dimethyldicarbadodecarborane)aurate(III) anion

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## Abstract

The reaction of $Tl_2(1,2\text{-}Me_2C_2B_9H_9)$ with gold(I) ($PPh_3Me[AuBr_2]$ or AuX(ylide)) or gold(III) complexes $[AuCl_3(SC_4H_8)]$ gives $Q[Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ ($Q = PPh_3Me$, $[Au(ylide)_2]$ or $N(PPh_3)_2$). The structure of $[N(PPh_3)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ has been established by X-ray crystallography. It crystallizes in *Pnma* with $a = 25.792(8)$, $b = 12.810(3)$, $c = 10.994(3)$ Å (at −95 °C), $Z = 4$, $R = 0.027$, $R_w = 0.029$. The gold atom is coordinated by the boron atoms of each C2B3 face, with Au–B = 2.193–2.277 Å.

## Introduction

The 1,2-dicarbollide ion $[(B_9C_2H_{11})^{2-}]$ has been shown [1, 2] to form 'sandwich-bonded' complexes with gold(III) and gold(II), but no gold(I) derivatives have been described of the 1,2-dimethyl-substituted dicarbollide $[(Me_2C_2B_9H_9)^{2-}]$. Here we report some attempts to prepare gold(I) complexes by reacting $PPh_3Me[AuBr_2]$ or AuX(ylide) (X = Cl or Br; ylide = $CH_2PPh_3$, $CH_2PPh_2Me$ or $CH_2PPhMe_2$) with $Tl_2(1,2\text{-}Me_2C_2B_9H_9)$. Oxidation to gold(III) occurs and $Q[Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ ($Q = PPh_3Me$ or $[Au(ylide)_2]$) is obtained, instead of the desired products.

## Experimental

Instrumentation and general experimental techniques were as described earlier [3]. Nuclear magnetic resonance spectra were recorded on a Varian XL 200 spectrometer in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ ($^1H$) and 85% $H_3PO_4$ (external, $^{31}P$). The yields and C, H and N analyses of the novel complexes are listed in Table 1.

### *Preparation of the complexes*

*$(PPh_3Me)[Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ (1)*

To a solution of $(PPh_3Me)[AuBr_2]$ (0.127 g, 0.2 mmol) in 30 ml of dichloromethane was added $Tl_2(1,2\text{-}Me_2C_2B_9H_9)$ [4] (0.114 g, 0.2 mmol) and the mixture was stirred for 3 h at room temperature. The dark precipitate was filtered off. The red solution was concentrated to 2 ml. Addition of diethyl ether (20 ml) gave complex **1** as a red solid. $^1H$ NMR 7.8–7.5 (m, 15H, Ph), 3.25 [d, 3H, PMe, *J*(PH) 13.4 Hz] and 2.17 (s, 12H, CMe) ppm.

*$[Au(ylide)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$*
*(ylide = $CH_2PPh_3$ (2), $CH_2PPh_2Me$ (3) or*
*$CH_2PPhMe_2$ (4))*

A mixture of AuX(ylide) [3] (0.1 mmol) (X = Cl or Br; ylide = $CH_2PPh_3$, $CH_2PPh_2Me$ or $CH_2PPhMe_2$) and $Tl_2(1,2\text{-}Me_2C_2B_9H_9)$ [4] (0.059 g, 0.1 mmol) in 30 ml of dichloromethane was stirred for 3 h at room temperature. The precipitate containing TlX was filtered off and the red solution was concentrated to *c.* 2 ml. Addition of n-hexane (20 ml) precipitated complexes **2**–**4** as red solids. $^1H$ NMR $\delta$, **2**: 7.65–7.4 (m, 30H, Ph), 2.20 (s, 12H, CMe) and 1.69 [d, 4H, $CH_2$, *J*(PH) 12.6 Hz] ppm; **3**: 7.65–7.5 (m, 20H, Ph), 2.21 (s, 12H, CMe) and 2.0 [d, 6H, PMe, *J*(PH) 12.9 Hz] and 1.42 [d, 4H, $CH_2$, *J*(PH) 12.7 Hz] ppm; **4**: 7.6–7.4 (m, 10H, Ph), 2.22 (s, 12H, CMe) and 1.91 [d, 12H, PMe, *J*(PH) 13.1 Hz] and 1.20 [d, 4H, $CH_2$,

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TABLE 1. Analytical data of complexes

| Complex | | Yield (%) | Analysis: found (calc.) (%) | | | $\Lambda_M$[a] |
|---|---|---|---|---|---|---|
| | | | C | H | N | |
| **1** | $(PPh_3Me)[Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ | 42 | 41.1<br>(40.8) | 5.8<br>(6.1) | | 128 |
| **2** | $[Au(CH_2PPh_3)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ | 72 | 43.2<br>(43.6) | 4.95<br>(5.1) | | 120 |
| **3** | $[Au(CH_2PPh_2Me)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ | 68 | 38.05<br>(37.8) | 5.4<br>(5.3) | | 114 |
| **4** | $[Au(CH_2PPhMe_2)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ | 65 | 30.8<br>(30.65) | 5.65<br>(5.55) | | 145 |
| **5** | $[N(PPh_3)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ | 65 | 49.8<br>(50.0) | 5.65<br>(5.7) | 1.45<br>(1.3) | 134 |
| **6** | $[N(PPh_3)_2][Au(1,2\text{-}Me_2,3\text{-}ClC_2B_9H_8)_2]$ | 76 | 47.15<br>(46.95) | 5.2<br>(5.2) | 1.3<br>(1.25) | 140 |

[a] In acetone, $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

$J$(PH) 12.8 Hz} ppm. $^{31}$P NMR δ, **2**: 32.1; **3**: 28.1; **4**: 27.5 ppm.

### *$[N(PPh_3)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ (5)*

To a solution of $AuCl_3(SC_4H_8)$ (0.040 g, 0.1 mmol) and $[N(PPh_3)_2]Cl$ [5] (0.057 g, 0.1 mmol) in 30 ml of dichloromethane was added $Tl_2(1,2\text{-}Me_2C_2B_9H_9)$ (0.114 g, 0.2 mmol) and the mixture was stirred for 2 h at room temperature. The precipitate was filtered off and the solution was concentrated to *c*. 2 ml. Addition of diethyl ether (10 ml) gave red crystals of **5** which were recrystallized from dichloromethane–diethyl ether. $^1$H NMR δ: 7.4–7.3 (m, 30H, Ph) and 2.20 (s, 12H, CMe) ppm. $^{31}$P NMR δ: 21.7 ppm. When $Tl_2(1,2\text{-}C_2B_9H_{11})$ was used, the complex $[N(PPh_3)_2][Au(1,2\text{-}C_2B_9H_{11})_2]$ was obtained.

### *$[N(PPh_3)_2][Au(1,2\text{-}Me_2,3\text{-}ClC_2B_9H_8)_2]$ (6)*

To a solution of **5** (0.105 g, 0.1 mmol) in 30 ml of dichloromethane was added an excess of $Cl_2$ (0.5 ml of a 1 M $CCl_4$ solution, 0.5 mmol) and immediately the solution turned violet. The solution was concentrated to *c*. 2 ml and addition of diethyl ether gave complex **6** as a violet solid. $^1$H NMR δ: 7.7–7.2 (m, 30H, Ph) and 2.41–2.26 (complex signal, carborane cage H protons and Me groups) ppm. $^{31}$P NMR δ: 21.7 ppm.

## *X-ray structure determination of compound 1*

### *Crystal data*

$C_{27}H_{48}B_{18}PAu$, $M_r = 795.2$, orthorhombic, space group *Pnma*, $a = 25.792(8)$, $b = 12.810(3)$, $c = 10.994(3)$ Å, $U = 3632$ Å$^3$, $Z = 4$, $D_x = 1.454$ Mg m$^{-3}$, $F(000) = 1576$, $\lambda$(Mo K$\alpha$) = 0.71069 Å, $\mu = 4.1$ mm$^{-1}$, $T = -95$ °C.

### *Data collection and reduction*

A red prism 0.45×0.35×0.2 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens R3 diffractometer, LT-2 low temperature attachment, monochromated Mo K$\alpha$ radiation). A total of 8521 intensities was measured to $2\theta_{max}$ 50°. An absorption correction was applied using the program DIFABS, with transmission factors 0.93–1.23. Merging equivalents gave 3347 unique reflections ($R_{int}$ 0.019), of which 2680 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS). Cell constants were refined from setting angles of 46 reflections in the $2\theta$ range 20–24°.

### *Structure solution and refinement*

The Au atom was located from the Patterson function and other atoms (including all H atoms) in subsequent difference syntheses. Borane H were shifted along the B–H vector to an idealized B–H bond length of 1 Å and then fixed; the other H were included in the refinement using a riding model. Anisotropic full-matrix refinement on $F$ proceeded to $R$ 0.027, $R_w$ 0.029 for 181 parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. $S$ 1.2; max. $\Delta/\sigma$ 0.001; max. $\Delta\rho$ 1.3 e Å$^{-3}$.

Final atomic coordinates are given in Table 2, See also 'Supplementary material'.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$)

| | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Au | 5643.3(1) | 7500 | 6404.6(2) | 178(1) |
| P(1) | 2740.0(6) | 7500 | 5724(2) | 214(5) |
| C(11) | 2360(1) | 6335(3) | 5520(4) | 225(13) |
| C(12) | 2282(2) | 5657(3) | 6482(4) | 297(14) |
| C(13) | 1986(2) | 4764(4) | 6323(5) | 391(16) |
| C(14) | 1765(2) | 4557(4) | 5212(5) | 366(16) |
| C(15) | 1839(2) | 5230(3) | 4253(5) | 337(15) |
| C(16) | 2142(2) | 6111(3) | 4392(4) | 291(14) |
| C(17) | 3258(2) | 7500 | 4640(5) | 193(17) |
| C(18) | 3474(2) | 6560(3) | 4248(4) | 284(14) |
| C(19) | 3892(2) | 6568(4) | 3445(4) | 341(15) |
| C(20) | 4088(2) | 7500 | 3038(6) | 288(21) |
| C(21) | 2997(2) | 7500 | 7238(6) | 291(21) |
| B(1) | 4304(3) | 7500 | 8824(7) | 321(18) |
| B(2) | 4722(2) | 8592(5) | 8779(5) | 387(14) |
| B(3) | 4869(3) | 7500 | 9671(9) | 454(22) |
| B(6) | 4389(2) | 8183(4) | 7442(5) | 282(11) |
| C(7) | 5314(2) | 8086(4) | 8737(4) | 359(15) |
| B(10) | 4793(3) | 7500 | 6467(7) | 269(16) |
| B(11) | 5068(2) | 8571(4) | 7340(5) | 270(11) |
| C(1) | 5770(2) | 8663(5) | 9281(5) | 596(22) |
| B(1′) | 6972(3) | 7500 | 3930(7) | 302(17) |
| B(3′) | 6395(3) | 7500 | 3110(7) | 300(17) |
| B(4) | 6556(2) | 8597(4) | 4008(5) | 300(12) |
| B(5) | 6894(2) | 8190(4) | 5316(5) | 304(12) |
| C(8) | 5958(2) | 8090(3) | 4072(4) | 242(13) |
| B(9) | 6222(2) | 8567(4) | 5456(4) | 236(11) |
| B(10′) | 6493(3) | 7500 | 6319(7) | 241(15) |
| C(2) | 5504(2) | 8686(4) | 3549(4) | 366(15) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

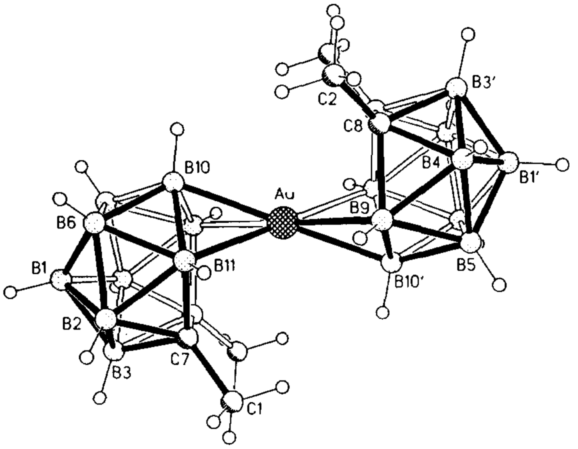

Fig. 1. The anion of complex **1** in the crystal. Radii are arbitrary; the numbering scheme of the asymmetric unit (full bonds) is shown.

## Results and discussion

Addition of solid $Tl_2(1,2\text{-}Me_2C_2B_9H_9)$ to a dichloromethane solution of $(PPh_3Me)[AuBr_2]$ gives a dark precipitate which contains metallic gold. From the filtrate the gold(III) derivative $(PPh_3Me)[Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ (**1**) can easily be isolated.

Oxidation to gold(III) has also been observed starting from AuX(ylide); the complexes $[Au(ylide)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ (ylide = $CH_2PPh_3$ (**2**), $CH_2PPh_2Me$ (**3**) or $CH_2PPhMe_2$ (**4**)) are obtained, which contain the same anion as **1**.

The reaction of $AuCl_3(SC_4H_8)$ with $Tl_2(1,2\text{-}Me_2C_2B_9H_9)_2$ leads to the bis(1,2-dicarbollyl)aurate(III) anion which can be isolated as $[N(PPh_3)_2][Au(1,2\text{-}Me_2C_2B_9H_9)_2]$ (**5**) by addition of $[N(PPh_3)_2]Cl$.

Complex **5** quickly reacts with chlorine to give $[N(PPh_3)_2][Au(1,2\text{-}Me_2,3\text{-}ClC_2B_9H_8)_2]$ (**6**)*, with chlorination of the carborane. The ligand has been chlorinated previously with chlorine but it requires UV radiation [6].

Complexes **1**–**6** are red stable solids at room temperature. Their acetone solutions are conducting with $\Lambda_M = 114\text{–}145\ \Omega^{-1}\ cm^2\ mol^{-1}$ as expected for 1:1 electrolytes.

The structure of complex **1** was determined by X-ray diffraction methods. Single crystals were grown by slow diffusion of diethyl ether into a dichloromethane solution of **1**.

The anion of **1** is shown in Fig. 1; it displays crystallographic mirror symmetry (as does the cation). The mirror plane passes through the atoms Au, B(1), B(3), B(10), B(1′), B(3′) and B(10′). The gold atom is bonded to the three boron atoms of each $C_2B_3$ face open face, with Au–B bond lengths 2.193–2.277 Å; similar values were observed in other Au(III)–dicarbollide species [2].

## Supplementary material

Further details of the structure determination (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Any request for this material should quote a full literature citation and the reference number CSD 55790.

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*The structure of complex **6** was also confirmed by X-ray crystallography; it crystallizes in $C2/c$ with $a = 33.451(9)$, $b = 8.864(3)$, $c = 18.846(5)$ Å, $\beta = 113.14(2)°$ (at −95 °C), $Z = 4$. The anion possesses crystallographic inversion symmetry, and the coordination at gold is similar to that of **1**, with Au–B = 2.22–2.31 Å. Unfortunately the chlorine substituent is disordered over the open face boron atoms adjacent to carbon, so that the refinement is unsatisfactory.

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