

# Synthesis of the first organometallic gold(I) derivatives of *m*-carborane: crystal structure of $[\text{Au}_2(\mu\text{-}1,7\text{-C}_2\text{B}_{10}\text{H}_{10})(\text{PPh}_3)_2] \cdot 1/2\text{CH}_2\text{Cl}_2$

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Received 6 June 1996; revised 19 July 1996

## Abstract

The treatment of 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$  with  $^n\text{BuLi}$  followed by addition of two equivalents of  $[\text{AuCl}(\text{PR}_3)]$  gives the dimetallated species  $[\text{Au}_2(\mu\text{-}1,7\text{-C}_2\text{B}_{10}\text{H}_{10})(\text{PR}_3)_2]$ , where the *m*-carboranyl ligand bridges the two  $\text{AuPR}_3^+$  fragments. The crystal structure of  $[\text{Au}_2(\mu\text{-}1,7\text{-C}_2\text{B}_{10}\text{H}_{10})(\text{PPh}_3)_2]$  has been established by X-ray diffraction.

**Keywords:** Gold(I); Organometallic derivatives; *m*-Carborane

## 1. Introduction

The synthesis of carboranyl derivatives has been extensively studied, because in some respects they resemble organic compounds with electron-accepting groups [1–4]. During the past decade investigations in the field of C-substituted carboranes have involved the creation of new models to be used in theoretical investigations [5], the preparation of organic and organometallic carboranyl compounds for the production of polymeric materials [6–8], and biological and medical investigations [9]. These compounds have proved particularly useful in boron neutron capture therapy (BNCT) for cancer [10–13].

Although a few transition metal complexes containing the carboranyl group have been described, examples of *closo*-carboranes bonded to gold by 2c–2e  $\sigma$ -bonds are relatively rare (as opposed to the more widely studied *nido*-carborane derivatives interacting with gold via cluster bonding) [14–18]. The first report was made by Mitchell and Stone [19], who prepared the complexes  $[\text{Au}(2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})(\text{PPh}_3)]$  (R = H, Me, Ph), one of which has been structurally characterized [20]. Since then two more reports have dealt with  $\sigma$ -bonded gold carborane derivatives, one by Reid and Welch [21] who prepared the complexes  $[\text{Au}(2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})\text{L}]$

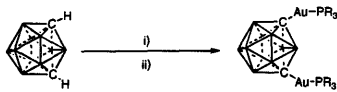
(R =  $\text{CH}_2\text{OCH}_3$ , Ph; L =  $\text{PPh}_3$ ,  $\text{P}(o\text{-tol})_3$ ,  $\text{PCy}_3$ ,  $\text{PEt}_3$ ,  $\text{AsPh}_3$ ) and the recently published work by Hawthorne and coworkers [22] where the dimetallated species of the *o*-carborane and bis(*o*-carborane) are synthesized. However, no studies have dealt with the *m*-carborane. Therefore, as part of our studies with carborane derivatives [23–27], we report on the synthesis of organometallic gold(I) derivatives of *m*-carborane.

## 2. Results and discussion

The reaction of 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$  with  $^n\text{BuLi}$  in diethyl ether at 0°C followed by the addition of two equivalents of  $[\text{AuCl}(\text{PR}_3)]$  leads, after work-up, to the doubly metallated species  $[\text{Au}_2(\mu\text{-}1,7\text{-C}_2\text{B}_{10}\text{H}_{10})(\text{PR}_3)_2]$  [ $\text{PR}_3 = \text{PPh}_3$  (1),  $\text{PPh}_2\text{Me}$  (2),  $\text{PPh}_2(p\text{-tol})$  (3)] (Scheme 1).

Complexes 1–3 are white solids readily soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_2\text{O}$  and THF. They are moderately stable in air and in solution; their thermal stability is lower than that of the *o*-carboranyl derivatives mentioned above. They behave as non-conductors in acetone solutions. The IR spectra show absorption bands arising from the carborane moiety; the stretching vibrations of the B–H bonds appear as a broad absorption at ca.  $2590\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra of 1–3 show resonances due to the phenyl protons and complexes 2 and 3 also show singlets arising from the methyl protons. The hydrogens attached to the boron atoms of the carborane

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i) 2 <sup>t</sup>BuLi, ii) 2 [AuCl(PR<sub>3</sub>)]. PR<sub>3</sub> = PPh<sub>3</sub> (1), PPh<sub>2</sub>Me (2), PPh<sub>2</sub>(*p*-tol) (3)

Scheme 1.

cage are usually very broad and appear as a slight protuberance in the baseline between 1 and 3 ppm. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra show only one singlet, because of the equivalence of the phosphorus atoms. There is a displacement in the chemical shift to higher frequency ( $\Delta = 5\text{--}7$  ppm) compared with the chemical shift for the [AuCl(PR<sub>3</sub>)] precursors. The positive-ion mass spectra (FAB) present the molecular peaks for complexes 1 and 2 with coincident experimental and isotopical distribution at  $m/z = 1061$  (17%) and 936 (15%) respectively; this peak does not appear for compound 3. In all cases the most intense peak corresponds to [Au(PR<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.

The molecular structure of 1 has been determined by X-ray diffraction and is shown in Fig. 1. Selected bond lengths and angles are collected in Table 1 and atomic coordinates in Table 2. The molecule possesses two gold(phosphine) units bridged by the carboranyl moiety; each gold atom is bonded to one phosphorus and one carbon atom with angles very close to linearity, 179.3(2) and 174.1(2)°. These values are very similar to those found in the *o*-carborane derivative [Au<sub>2</sub>( $\mu$ -1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(PPh<sub>3</sub>)<sub>2</sub>] [178.9(4) and 174.2(4)°]. The lack of distortion around the gold centres together with a very long Au–Au distance, 5.74 Å, precludes an aurophilic interaction. The Au–C bond lengths are 2.054(7) and 2.047(7) Å, similar to those found in [Au(2-H-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(PPh<sub>3</sub>)] [2.039(8) Å] [20], [Au(2-CH<sub>2</sub>OCH<sub>3</sub>)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(AsPh<sub>3</sub>)] [2.039(8) Å] [21]

Table 1  
Selected bond lengths [Å] and angles [°]

Au(1)–C(1)	2.054(7)	Au(1)–P(1)	2.265(2)
Au(2)–C(7)	2.047(7)	Au(2)–P(2)	2.271(2)
P(1)–C(31)	1.808(4)	P(1)–C(21)	1.812(4)
P(1)–C(11)	1.826(4)	P(2)–C(51)	1.813(4)
P(2)–C(41)	1.813(4)	P(2)–C(61)	1.820(4)
C(1)–Au(1)–P(1)	179.3(2)	C(7)–Au(2)–P(2)	174.1(2)
C(31)–P(1)–C(21)	106.3(2)	C(31)–P(1)–C(11)	105.7(3)
C(21)–P(1)–C(11)	104.9(2)	C(31)–P(1)–Au(1)	112.1(2)
C(21)–P(1)–Au(1)	113.8(2)	C(11)–P(1)–Au(1)	113.3(2)
C(51)–P(2)–C(41)	105.3(2)	C(51)–P(2)–C(61)	107.1(2)
C(41)–P(2)–C(61)	106.2(2)	C(51)–P(2)–Au(2)	117.2(2)
C(41)–P(2)–Au(2)	112.1(2)	C(61)–P(2)–Au(2)	108.4(2)

and [Au<sub>2</sub>(1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(PPh<sub>3</sub>)<sub>2</sub>] [2.055(14), 2.033(15) Å] [22]. It has been shown that the Au–C distances depend on the hybridisation state of the carbon atom, e.g. for C(sp<sup>3</sup>) the range is 2.09–2.13 Å, for C(sp<sup>2</sup>) 2.05–2.09 Å, and finally for C(sp) 1.97–2.01 Å. The distances found in the *o*-carboranyl and *m*-carboranyl derivatives described by us are clearly characteristic values of a carbon with sp<sup>2</sup> hybridisation, as was pointed out from the study of the IR and <sup>13</sup>C NMR spectroscopic data of carboranes [20]. These short Au–C bond distances suggest that this bond is stronger than other gold–carbon  $\sigma$ -bonds, which supports Stone's observations that the unusual stability of auracarboranes is attributed to the electron-withdrawing influence of the carboranyl cage. Similar stability has been observed in gold–perfluoroalkyl complexes, and the Au–C distances are only slightly longer than those commented on here, but still in the range for a carbon with sp<sup>2</sup> hybridisation [28–31]. However, it is Welch's belief that the shortness of the Au–C bond is due to efficient  $\sigma$ -donor properties of the carborane and that the carborane does not function as an electron-withdrawing group.

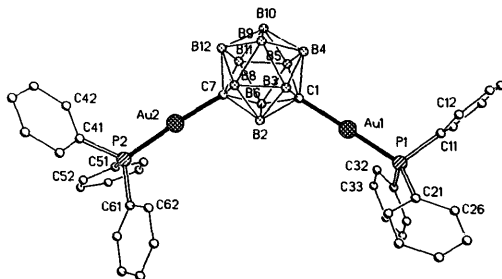


Fig. 1. Molecular structure of the complex [Au<sub>2</sub>(1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(PPh<sub>3</sub>)<sub>2</sub>] in the crystal showing the atom numbering scheme. Radii are arbitrary; H atoms are omitted for clarity.

Table 2

Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ]

Atom	x	y	z	$U_{\text{eq}}$
Au(1)	2187.3(3)	4972.2(2)	6685.9(2)	34.2(1)
Au(2)	2287.7(3)	1922.5(2)	3783.8(2)	32.2(1)
P(1)	2744(2)	6301(2)	6932.2(14)	32.8(4)
P(2)	3139(2)	1298(2)	2197.2(12)	30.8(4)
C(11)	1841(5)	7011(4)	8124(3)	38(2)
C(12)	2008(5)	6435(4)	8963(4)	56(2)
C(13)	1301(6)	6921(5)	9890(3)	71(3)
C(14)	427(5)	7984(5)	9978(3)	67(3)
C(15)	260(5)	8561(4)	9139(4)	62(2)
C(16)	967(5)	8074(4)	8212(3)	49(2)
C(21)	4311(3)	5802(4)	6899(4)	32(2)
C(22)	5148(4)	4855(4)	6349(4)	47(2)
C(23)	6368(4)	4472(4)	6271(4)	51(2)
C(24)	6751(3)	5036(4)	6743(4)	49(2)
C(25)	5914(4)	5983(4)	7293(4)	50(2)
C(26)	4693(4)	6367(3)	7371(3)	45(2)
C(31)	2577(5)	7356(4)	6020(4)	37(2)
C(32)	1524(4)	7733(5)	5769(4)	50(2)
C(33)	1332(4)	8568(5)	5095(4)	65(3)
C(34)	2193(6)	9027(4)	4673(4)	71(3)
C(35)	3247(5)	8651(5)	4924(4)	67(3)
C(36)	3439(4)	7815(5)	5597(4)	48(2)
C(41)	3150(4)	-45(3)	2086(4)	33(2)
C(42)	2035(4)	-101(3)	2235(4)	40(2)
C(43)	1960(4)	-115(4)	2256(4)	52(2)
C(44)	3000(5)	-2072(3)	2128(4)	56(2)
C(45)	411(4)	-2015(3)	1979(4)	57(2)
C(46)	4189(3)	-1001(4)	1958(4)	48(2)
C(51)	2454(5)	2137(4)	1315(3)	35(2)
C(52)	2718(4)	1741(3)	383(3)	40(2)
C(53)	2258(5)	2443(4)	-300(3)	48(2)
C(54)	1533(6)	3541(4)	-51(4)	69(3)
C(55)	1269(5)	3938(3)	881(4)	77(3)
C(56)	1730(5)	3236(4)	1564(3)	55(2)
C(61)	4728(3)	1133(4)	1761(3)	31(2)
C(62)	5341(4)	796(4)	2442(3)	43(2)
C(63)	6562(4)	636(5)	2153(3)	49(2)
C(64)	7170(3)	812(5)	1184(4)	53(2)
C(65)	6557(4)	1148(5)	502(3)	54(2)
C(66)	5336(4)	1308(4)	791(3)	41(2)
C(1)	1690(6)	3757(6)	6475(5)	29.6(15)
B(2)	2644(7)	2789(7)	5577(6)	30(2)
B(3)	2383(8)	2456(7)	6834(6)	36(2)
B(4)	860(7)	3253(7)	7493(6)	32(2)
B(5)	180(7)	4086(7)	6627(6)	31(2)
B(6)	1293(7)	3779(7)	5455(6)	28(2)
C(7)	1697(6)	2424(6)	5220(5)	29.7(15)
B(8)	2389(8)	1593(8)	6011(16)	39(2)
B(9)	1262(8)	1869(7)	7201(16)	37(2)
B(10)	-78(8)	2879(7)	7071(16)	34(2)
B(11)	191(7)	3200(7)	5809(16)	30(2)
B(12)	867(8)	1841(7)	6163(16)	33(2)
C1	5573(7)	5695(4)	43(4)	203(3)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_i$  tensor.

The Au–P distances, 2.265(2) and 2.271(2) Å, are of the same order as those in organogold complexes of the type  $[\text{AuR}(\text{PPh}_3)]$  and as that in the carboranyl deriva-

tive [2.271(2) Å]. There are no interactions with the boron or hydrogen atoms of the carborane cage.

### 3. Experimental

Infrared spectra were recorded in the range 4000–200  $\text{cm}^{-1}$  on a Perkin–Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca.  $5 \times 10^{-4}$  mol dm $^{-3}$  solution with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded on a VG autospec, with the FAB technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian 300 Unity and Bruker ARX 300 spectrometer in  $\text{CDCl}_3$ . Chemical shifts are cited relative to 85%  $\text{H}_3\text{PO}_4$  (external,  $^{31}\text{P}$ ) and  $\text{SiMe}_4$  (external,  $^1\text{H}$ ).  $[\text{AuCl}(\text{PR}_3)]$  was prepared following literature procedures [32] and 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$  was purchased from Dexcel Corporation.

#### 3.1. $[\text{Au}_2(\mu\text{-}1,7\text{-C}_2\text{B}_{10}\text{H}_{10})(\text{PR}_3)_2] [\text{PR}_3 = \text{PPh}_3 (1), \text{PPh}_2\text{Me} (2), \text{PPh}_2(p\text{-tol}) (3)]$

To a solution of 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$  (0.014 g, 0.1 mmol) in diethyl ether (20  $\text{cm}^3$ ) at 0°C and under nitrogen atmosphere was added  $^n\text{BuLi}$  (0.32  $\text{cm}^3$ , 0.62 M, 0.2 mmol). After stirring the mixture for 30 min  $[\text{AuCl}(\text{PR}_3)]$  [ $\text{PR}_3 = \text{PPh}_3$ , 0.098 g;  $\text{PPh}_2\text{Me}$ , 0.086 g;  $\text{PPh}_2(p\text{-tol})$ , 0.102 g; 0.2 mmol] was added. The suspension was stirred for 45 min at room temperature and then filtered over Celite. Concentration of the solution to ca. 5  $\text{cm}^3$  and addition of n-hexane (15  $\text{cm}^3$ ) gave complexes 1 (63% yield), 2 (58% yield) or 3 (61% yield) as white solids. 1: Anal. Found: C, 42.55; H, 4.10.  $\text{C}_{38}\text{H}_{40}\text{Au}_2\text{B}_{10}\text{P}_2$ . Calc.: C, 43.0; H, 3.8%.  $\Lambda_{\text{M}}$  4  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . NMR ( $\text{CDCl}_3$ ):  $^{31}\text{P}\{^1\text{H}\}$  (121 MHz)  $\delta$  40.5(s). 2: Anal. Found: C, 36.5; H, 4.05.  $\text{C}_{28}\text{H}_{36}\text{Au}_2\text{B}_{10}\text{P}_2$ . Calc.: C, 35.9; H, 3.9%.  $\Lambda_{\text{M}}$  2  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$  (300 MHz)  $\delta$  2.02 [d, 6H, Me, J(PH) 9.04 Hz], 7.4–7.6 (m, 20H, Ph);  $^{31}\text{P}\{^1\text{H}\}$  (121 MHz)  $\delta$  23.8(s). 3: Anal. Found: C, 43.95; H, 4.15.  $\text{C}_{40}\text{H}_{44}\text{Au}_2\text{B}_{10}\text{P}_2$ . Calc.: C, 44.15; H, 4.1%.  $\Lambda_{\text{M}}$  3  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$  (300 MHz)  $\delta$  2.52 (s, 6H, Me), 7.3–7.6 (m, 28H, Ph);  $^{31}\text{P}\{^1\text{H}\}$  (121 MHz)  $\delta$  38.9(s).

#### 3.2. Crystal structure determination of complex 1

##### 3.2.1. Crystal data

1 · 1/2  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_{38.5}\text{H}_{41}\text{Au}_2\text{B}_{10}\text{ClP}_2$ ,  $M_r = 1103.44$ , triclinic, space group  $P\bar{1}$ ,  $a = 12.725(3)$ ,  $b = 13.348(3)$ ,  $c = 14.496(3)$  Å,  $\alpha = 82.85(2)$ ,  $\beta = 69.46(2)$ ,  $\gamma = 66.08(2)^\circ$ ,  $U = 2107.2(8)$  Å $^3$ ,  $Z = 2$ ,  $D_c = 1.739 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 7.12 \text{ mm}^{-1}$ ,  $F(000) = 1054$ ,  $T = -100^\circ\text{C}$ .

### 3.2.2. Data collection and reduction

Single crystals were obtained by a slow diffusion of n-hexane into a dichloromethane solution of complex 1. An amber prism  $0.40 \times 0.30 \times 0.20 \text{ mm}^3$  was used to collect 8398 intensities to  $2\theta_{\text{max}} 50^\circ$  (Siemens R3 diffractometer, monochromated Mo K $\alpha$  radiation) of which 7437 were independent ( $R_f = 0.019$ ). An absorption correction based on  $\Psi$ -scans was applied with transmission factors 0.5–0.98. Cell constants were refined from setting angles of 50 reflections in the range  $2\theta 20\text{--}23^\circ$ .

### 3.2.3. Structure solution and refinement

The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on  $F^2$  (SHELXL-93) [33]; Au, P, Cl atoms were refined anisotropically, others isotropically with idealised phenyl groups; borane H atoms were included using a riding model. The complex crystallizes with half a molecule of dichloromethane disordered over a symmetry centre and poorly resolved; only the chlorine atom was refined. Refinement proceeded to  $wR(F^2)$  0.086 for 7437 reflections and 166 parameters, conventional  $R(F)$  0.034,  $S(F^2) = 1.021$ , maximum  $\Delta\rho 1.78 \text{ e \AA}^{-3}$ .

## 4. Supplementary material available

Full details of the structure determination (complete bond lengths and angles, H-atom coordinates, thermal parameters, structure factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD-404772.

## Acknowledgements

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

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