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Journal of Organometallic Chemistry 561 (1998) 1–6

Journal of Organometallic Chemistry

Gold(I) complexes with the ligand 1-thiolate-1,2-dicarba-*closo*-dodecaborate. Crystal structure of $[Au_2(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})_2(\mu\text{-dppe})]$

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Received 12 May 1997; received in revised form 11 February 1998

Abstract

Neutral and anionic gold(I) mononuclear derivatives with the 1-thiolate-1,2-dicarba-*closo*-dodecaborate ligand of stoichiometries $[Au(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})L]$ and $[Au(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})_2]^-$ have been synthesised. The complex $[Au(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})(AsPh_3)]$ is a good starting material for the synthesis of the dinuclear gold(I) derivative $[Au_2(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})_2(\mu\text{-PP})]$, where PP is a diphosphine. The compound $[Au_2(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})(PPh_3)_2]BF_4$ has also been prepared. The structure of the neutral complex $[Au_2(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})_2(\mu\text{-dppe})]$ is confirmed by single-crystal X-ray diffraction. There are no short gold–gold interactions. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Gold(I); *o*-Carborane; Thiolate

1. Introduction

Thiolate compounds enjoy increasing interest because of their varied chemistry; worthwhile topics for study include the potential of complexes with respect to S–C bond cleavage reactions and desulphurisation [1], the novel structures of some coordination complexes [2] and the possibility of stabilisation of unusual oxidation states. Applications in the study of biological systems [3] and use in medicine as antiarthritric or cancerostatic drugs [4] also contribute to the growing interest in these compounds. Our recent work has focused on the preparation of thiolate gold complexes with carborane ligands [5] because of their potential applications, the result of the specific properties of carborane clusters, in the following fields: synthesis of polymers [6], homogenous catalysis [7], boron neutron capture therapy [8].

As a continuation of our investigations of the synthesis and reactivity of gold and silver derivatives with carborane ligands [9], our attention is now centred on the chemistry arising from monosubstituted ligands based on *o*-carborane. Their preparation is not an easy task because of the great tendency of the monolithiated carborane derivative to disproportionate. Recently, Hawthorne et al. prepared monosubstituted compounds [10] by blocking one position using the bulky group $SiMe_2^tBu$ to form the monolithiated derivative. Teixidor et al. [11] prevented dilithiation by using dimethoxyethane as solvent and prepared $[1\text{-}(PPh_2)\text{-}1,2\text{-}C_2B_{10}H_{11}]$ and $[1\text{-}(SH)\text{-}1,2\text{-}C_2B_{10}H_{11}]$, but no chemistry of these ligands has been reported to the best of our knowledge.

Here we present the first results in the study of the reactivity of the monothiolate $[1\text{-}(SH)\text{-}1,2\text{-}C_2B_{10}H_{11}]$ ligand.

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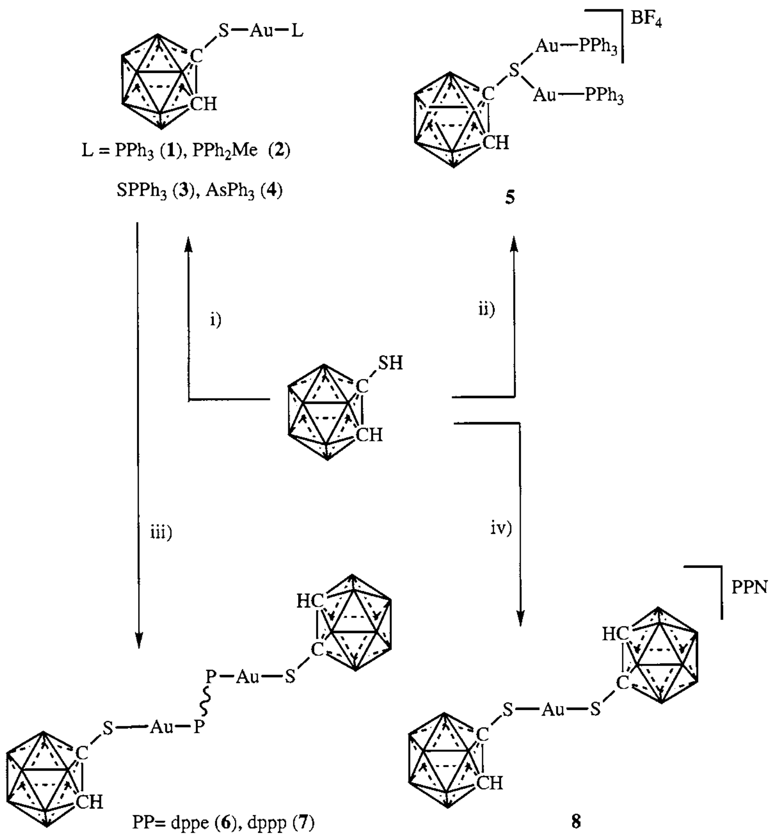
PII S0022-328X(98)00500-2



Scheme 1: i) [AuClL], ii) [O{Au(PPh$_3$)}$_3$]BF$_4$, iii) 1/2 PP (L = AsPh$_3$), iv) 1/2 PPN[AuCl$_2$]

Scheme 1.

2. Results and discussion

The reaction of 1-thiol-1,2-dicarba-*closo*-dodecaborane with [AuClL] in dichloromethane and in the presence of Na_2CO_3 affords the thiolate gold(I) complexes [Au(1-S-1,2-$C_2B_{10}H_{11}$)L] [L = PPh$_3$ (**1**), PPh$_2$Me (**2**), SPPh$_3$ (**3**), AsPh$_3$ (**4**)] (see Scheme 1). Complexes **1**–**4** behave as non-conductors in acetone solutions and are moisture- and air-stable. Their IR spectra show a broad absorption centred between 2572 and 2602 cm^{-1} (vs, br) arising from the B–H stretching modes of the *o*-carborane nucleus [12].

In the ^{1}H-NMR spectra of these complexes, a signal for the CH proton is observed at about 3.8 ppm ($\Delta\delta$ on comparing different complexes is < 0.3 ppm); the signal from the phenylic protons in complexes **1**–**4** and the doublet from the methylene protons in compound **2** are also present.

The ^{31}P{^{1}H}-NMR spectra of complexes **1**–**3** show a singlet for the phosphorus atom shifted downfield from the starting materials.

In the positive ion mass spectra (FAB$^+$) of these derivatives the most intense peaks are assigned to the fragments [AuL]$^+$ and [AuL$_2$]$^+$. The molecular peak [M]$^+$ is only present in the spectrum of complexes **2** and **4** [$m/z = 572$ (5%) (**2**), 679 (17%) (**4**)]. However, the peak assigned to [M + AuL]$^+$ [1094 (8%) (**1**), 970 (10%) (**2**), 1157 (7%) (**3**), 1181 (17%) (**4**)] is always observed, which implies a considerable stability for such dinuclear complexes. Thus, we attempted the reaction of 1-(SH)-1,2-$C_2B_{10}H_{11}$ with [O{Au(PPh$_3$)}$_3$]BF$_4$. This reaction affords the dinuclear cationic complex [Au$_2$(1-S-1,2-$C_2B_{10}H_{11}$)(PPh$_3$)$_2$]BF$_4$ (**5**) (see Scheme 1).

In the IR spectrum of **5**, the absorption corresponding to the B–H stretching band of the carborane moiety is observed at 2585 cm^{-1}. The absorptions ν_d(BF) and ν_d(FBF) of the anion BF$_4$ are at 1068 and 537 cm^{-1}, respectively [13].

The ^{31}P{^{1}H}-NMR spectrum presents a singlet for the two equivalent phosphorus atoms at 35.6 ppm (s), shifted downfield from compound **1**.

Complex **5** exhibits the cation/ion molecular peak in the positive ion fast atom spectrum at $m/z = 1094$

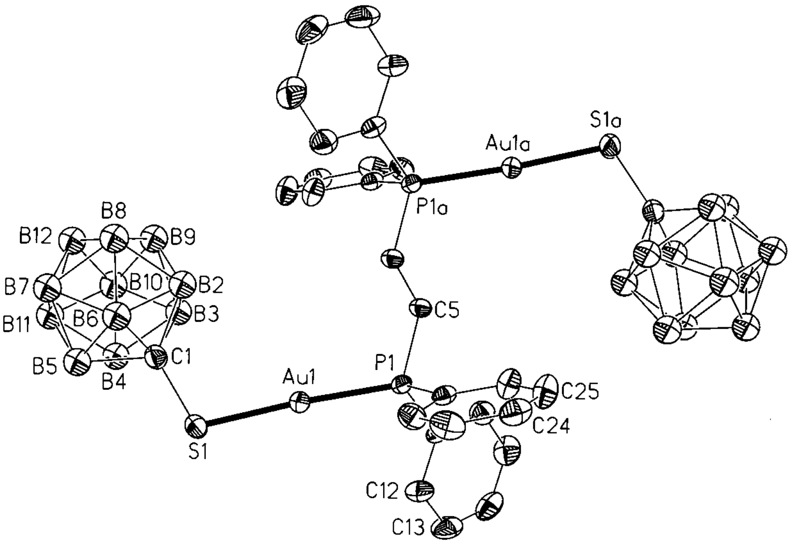


Fig. 1. Molecule of complex **6** in the crystal with the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

(20%), although the most intense peak is assigned to $[Au(PPh_3)]^+$ ($m/z = 459$).

The complex $[Au(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_1)(AsPh_3)]$ (**4**) reacts with diphosphines in the molar ratio 2:1 to afford the dinuclear compounds $[Au_2(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_1)_2(\mu\text{-}PP)]$ [PP: dppe = 1,2-bis(diphenylphosphino)ethane (**6**), dppp = 1,3-bis(diphenylphosphino)propane (**7**)] which are moisture- and air-stable.

The presence in these compounds of the carborane moiety is shown by a broad absorption at 2579 (**6**) and 2596 (**7**) cm^{-1} in their IR spectra, and a signal in their ^1H-NMR spectra at about 3.8 ppm, assigned to the CH proton. The signals corresponding to the methylene and phenylic protons in these compounds are also present.

The two phosphorus atoms in the molecules are equivalent, as only one signal is present in their $^{31}P\{^1H\}$-NMR spectra.

Although the molecular peaks $[M]^+$ appear in the positive ion mass spectra (FAB^+) of complexes **6** and **7** [$m/z = 1142$ (6%) (**6**), 1178 (4%) (**7**)], the most intense are those corresponding to $[M\text{-}(SC_2B_{10}H_1)]^+$ [968 (**6**), 882 (**7**)].

Table 1
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths (Å)			
Au(1)–P(1)	2.2621(9)	Au(1)–S(1)	2.3071(11)
P(1)–C(11)	1.811(4)	P(1)–C(21)	1.816(3)
P(1)–C(5)	1.825(3)	S(1)–C(1)	1.787(4)
Bond angles (°)			
P(1)–Au(1)–S(1)	176.06(3)	C(5)–P(1)–Au(1)	114.32(12)
C(1)–S(1)–Au(1)	106.49(13)		

The structure of complex **6** has been established by X-ray diffraction and is shown in Fig. 1, with selected bond lengths and angles in Table 1, and atomic coordinates in Table 2. The molecule possesses crystallographic inversion symmetry. The gold atoms display an essentially linear geometry, with P–Au–S 176.06(3)°. The gold centres are bridged by one diphosphine ligand with Au–P distances of 2.2621(9) Å, similar to those observed in complexes containing the analogous dithiolate: $[Au_2(\mu\text{-}1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10})(PPh_3)_2]$, $[Au_2(\mu\text{-}1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10})(\mu\text{-dppey})]$ ([5]a) [dppey = *o*-phenylenebis(diphenylphosphino)] or in other dithiolate complexes: $[Au_2(\mu\text{-}1,2\text{-}S_2C_6H_4)(PPh_3)_2]$ [14], $[Au_2(\mu\text{-}3,4\text{-}S_2C_6H_3Me)(PPh_3)_2]$ [15], $[Au_2(\mu\text{-MNT})(PPh_3)_2]$ [MNT = 1,2-dicyanoethene-1,2-dithiolate] [16].

The Au–S distance, 2.3071(11) Å, is of the same order as that found in complexes mentioned above or in $[Au_2\{\mu\text{-}1,2\text{-}S_2(CH_2)_3\}(\mu\text{-dppm})]$ [15] [μ-dppm = bis(diphenylphosphinomethane)] and $[Au_2(\mu\text{-MNT})(\mu\text{-dppey})_2]$ [17], which contain related bridging ligands.

No short contacts are observed between gold atoms, probably because of the bulky nature of the two carborane groups.

We have also carried out the reaction of 1-(SH)-1,2-$C_2B_{10}H_{11}$ with $[N(PPh_3)_2][AuCl_2]$ and excess of Na_2CO_3 in the molar ratio 2:1, obtaining the anionic compound $[N(PPh_3)_2][Au(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})_2]$ (see Scheme 1). The IR spectrum of this compound shows the bands from the B–H stretching modes of the *o*-carborane nucleus at 2591 cm^{-1}.

The ^1H-NMR spectrum of this derivative shows the singlet assigned to the CH proton, and also the broad signal due to the phenylic protons.

In the FAB-MS spectrum, the most intense peak is assigned to the molecular anion $[M]^-$ ($m/z = 547$).

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6**

	x	y	z	U_{eq}
Au(1)	4334(1)	2742(1)	4608(1)	26(1)
P(1)	4363(1)	1538(1)	5771(1)	20(1)
S(1)	4368(2)	4097(1)	3525(1)	44(1)
C(1)	4354(5)	3230(4)	2268(3)	29(1)
C(5)	4266(5)	−83(3)	5203(3)	23(1)
C(11)	2600(4)	1184(3)	6236(3)	24(1)
C(12)	2095(5)	2178(4)	6449(3)	34(1)
C(13)	804(6)	1982(5)	6854(4)	43(1)
C(14)	1(5)	792(4)	7020(3)	40(1)
C(15)	466(5)	−208(5)	6806(4)	41(1)
C(16)	1775(5)	−14(4)	6412(3)	35(1)
C(21)	6355(4)	2388(3)	7015(3)	22(1)
C(22)	7597(5)	3654(4)	7175(3)	31(1)
C(23)	9139(5)	4292(4)	8125(3)	37(1)
C(24)	9437(5)	3686(4)	8899(3)	35(1)
C(25)	8186(5)	2436(4)	8748(3)	39(1)
C(26)	6645(5)	1786(4)	7805(3)	33(1)
B(2)	5316(6)	2193(5)	2201(4)	36(1)
B(3)	3042(6)	1566(5)	1587(4)	35(1)
B(4)	2628(7)	2749(5)	1083(4)	36(1)
B(5)	4559(6)	4106(5)	1384(4)	36(1)
B(6)	6217(6)	3763(5)	2043(4)	37(1)
B(7)	5642(7)	3592(5)	646(4)	37(1)
B(8)	6111(7)	2385(5)	1149(4)	39(1)
B(9)	4112(6)	998(5)	861(4)	39(1)
B(10)	2405(7)	1352(5)	162(4)	40(1)
B(11)	3360(7)	2950(5)	44(4)	39(1)
B(12)	4301(6)	1870(5)	−112(4)	37(1)
C(99)	−621(24)	4663(20)	5102(17)	118(6)
Cl(1)	354(6)	3923(4)	4359(4)	101(1)
Cl(3)	389(7)	6348(4)	4969(5)	120(2)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

3. Experimental

IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin-Elmer 2400 microanalyser. MS spectra were recorded on a VG autospec, with the FAB technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external) and 85% H_3PO_4 (^{31}P, external).

1-(SH)-1,2-$C_2B_{10}H_{11}$ was synthesised from *o*-carborane [11] (Desxil Chemical), dppe, dppp were Aldrich analytical reagent grade and were used as-given. The starting materials [AuClL] [18], $[N(PPh_3)_2][AuCl_2]$ [19] and $[O\{Au(PPh_3)\}_3]BF_4$ [20] were prepared by published procedures.

3.1. Syntheses

3.1.1. *[Au(1-S-1,2-$C_2B_{10}H_{11}$)L] [L = PPh_3 (**1**), PPh_2Me (**2**), $SPPh_3$ (**3**), $AsPh_3$ (**4**)]*

To a solution of 1-(SH)-1,2-$C_2B_{10}H_{11}$ (0.017 g, 0.1 mmol) in dichloromethane (30 cm^3) [AuClL] was added (0.1 mmol; 0.049 g L = PPh_3; 0.043 g L = PPh_2Me; 0.054 g L = $SPPh_3$; 0.053 g L = $AsPh_3$) and excess Na_2CO_3. The mixture was stirred for 30 min, excess Na_2CO_3 filtered off and the solution concentrated to ca. 5 cm^3. Addition of diethyl ether (10 cm^3) gave complexes **1**–**4** as white solids. **1**: yield 81%. Anal. Calc. for $C_{20}H_{26}AuB_{10}PS$: C, 37.85; H, 4.1. Found: C, 38.35; H, 4.05. Λ_M 4 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ ppm: 3.87 (s, 1H, CH), 7.3–7.6 (m, br, 15H). $^{31}P\{^1H\}$-NMR, δ ppm: 36.8 (s). **2**: yield 74%. Anal. Calc. for $C_{15}H_{24}AuB_{10}PS$: C, 31.45; H, 4.2. Found: C, 31.7; H, 4.7. Λ_M 2 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ ppm: 3.85 (s, 1H, CH), 2.05 [d, 3H, PMe, J(PH) 9.90 Hz], 7.4–7.7 (m, br, 10H). $^{31}P\{^1H\}$-NMR, δ ppm: 21.4 (s). **3**: yield 74%. Anal. Calc. for $C_{20}H_{26}AuB_{10}PS_2$: C, 36.05; H, 3.95;. Found: C, 36.25; H, 3.8. Λ_M 5 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ ppm: 3.63 (s, 1H, CH), 7.3–7.6 (m, br, 15H). $^{31}P\{^1H\}$-NMR, δ ppm: 43.9 (s). **4**: yield 78%. Anal. Calc. for $C_{20}H_{26}AsAuB_{10}S$: C, 35.4; H, 3.85. Found: C, 35.9; H, 4.1. Λ_M 2 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ ppm: 3.88 (s, 1H, CH), 7.3–7.6 (m, br, 15H).

3.1.2. *[Au_2(1-S-1,2-$C_2B_{10}H_{11}$)$(PPh_3)_2$]BF_4 (**5**)*

To a solution of 1-(SH)-1,2-$C_2B_{10}H_{11}$ (0.017 g, 0.1 mmol) in dichloromethane (30 cm^3) $[O\{Au(PPh_3)\}_3]BF_4$ (0.149 g, 0.1 mmol) was added. The mixture was stirred for 30 min. Concentration of solvent to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) afforded complex **5** as a white solid. Yield 56%. Anal. Calc. for $C_{38}H_{41}Au_2B_{11}F_4P_2S_2$: C, 38.65; H, 3.5. Found: C, 39.1; H, 3.85. Λ_M 138 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ ppm: 3.98 (s, 1H, CH), 7.3–7.5 (m, br, 30H). $^{31}P\{^1H\}$-NMR, δ ppm: 35.6 (s).

3.1.3. *[Au(1-S-1,2-$C_2B_{10}H_{11}$)$_2$(μ-PP)] [PP = dppe (**6**), dppp (**7**)]*

To a dichloromethane solution (20 cm^3) of [Au(1-S-1,2-$C_2B_{10}H_{11}$)($AsPh_3$)] (0.175 g, 0.2 mmol) dppe (0.039 g, 0.1 mmol) or dppp (0.041 g, 0.1 mmol) were added and the solution was stirred for 30 min. The solvent was removed in vacuo and addition of diethyl ether (10 cm^3) gave complexes **6** and **7**, respectively, as white solids. **6**: yield 89%. Anal. Calc. for $C_{30}H_{46}Au_2B_{20}P_2S_2$: C, 31.5; H, 4.05. Found: C, 31.4; H, 3.7. Λ_M 2 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ ppm: 3.90 (s, 1H, CH), 2.62 (br), 7.3–7.6 (m, br, 20H). $^{31}P\{^1H\}$-NMR, δ ppm: 34.4 (s). **7**: yield 81%. Anal. Calc. for $C_{31}H_{48}Au_2B_{20}P_2S_2$: C, 32.2; H, 4.2. Found: C, 31.8; H, 4.2. Λ_M 6 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ ppm: 1.86 [q, 2H, CH_2, J(HH) = 7.5 Hz], 2.73 (m, br), 3.80 (s, 1H, CH), 7.4–7.7 (m, br, 10H). $^{31}P\{^1H\}$-NMR, δ ppm: 32.7 (s).

3.1.4. $[N(PPh_3)_2][Au(1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})_2]$ (**8**)

To a solution of 1-(SH)-1,2-$C_2B_{10}H_1$ (0.035 g, 0.2 mmol) in dichloromethane (30 cm^3) $[N(PPh_3)_2][AuCl_2]$ (0.081 g, 0.1 mmol) and excess Na_2CO_3 were added. The mixture was stirred for 30 min and excess Na_2CO_3 filtered off. Concentration of the solution to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) afforded complex **8** as a white solid. Yield 77%. Anal. Calc. for $C_{40}H_{52}AuB_{20}NP_2S_2$: C, 44.25; H, 4.8; N, 1.8. Found: C, 44.25; H, 4.8, N, 2.25. Λ_M 136 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR, δ ppm: 3.93 (s, 1H, CH), 7.3–7.5 (m, br, 20H). $^{31}P\{^1H\}$-NMR, δ ppm: 21.7 (s).

3.2. Crystal structure determination of complex **6**

3.2.1. Crystal data

6·CH_2Cl_2, $C_{31}H_{48}Au_2B_{20}Cl_2P_2S_2$, $M_r = 1227.79$, triclinic, space group $P\bar{1}$, $a = 9.0242(12)$, $b = 11.4065(12)$, $c = 13.4348(12)$ Å, $\alpha = 100.563(8)$, $\beta = 107.089(8)$, $\gamma = 111.992(8)°$, $V = 1156.6(2)$ Å^3, $Z = 1$, $D_{calc.} = 1.763$ Mg m^{-3}, $\lambda(\text{Mo–K}_\alpha) = 0.71073$ Å, $\mu = 6.637$ mm^{-1}, $F(000) = 588$, $T = -100$°C.

3.2.2. Data collection and reduction

Single crystals were obtained by a slow diffusion of di-isopropyl ether into a dicloromethane solution of complex **6**. A colourless plate 0.45 × 0.30 × 0.20 mm was used to collect 8391 intensities to $2\theta_{max}$ 55° (Siemens P4 diffractometer, monochromated Mo–K$_\alpha$ radiation) of which 4711 were independent ($R_{int} = 0.0223$). Cell constants were refined from 2θ values of 63 reflections in the range 9–25°. An absorption correction was applied on the basis of Ψ-scans (transmission factors 0.531–1.000).

3.2.3. Structure solution and refinement

The structure was solved by the heavy-atom method and refined on F^2 using the program SHELXL-93 [21]. Au, P, S, Cl and C atoms (except the carbon of the solvent, which is disordered over a symmetry centre) were refined anisotropically. The second C atom of the carborane could not be distinguished from the remaining B atoms; it is probable that there is fivefold disorder, with one C and four B atoms distributed at random. Hydrogen atoms were included using a riding model. $wR(F^2)$ 0.0547 for 4711 reflections, 220 parameters and 40 restraints. Conventional $R(F)$ 0.0235. $S(F^2)$ 0.979. $\Delta\rho = 1.550$ e Å^{-3}.

4. Supplementary material available

Full details of structure determination (except 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-406885.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (No. PB94-0079), the Caja de Ahorros de la Inmaculada (No. CB9/96) and the Fonds der Chemischen Industrie for financial support.

References

[1] (a) F.E. Massoth, Adv. Catal. 27 (1878) 265. (b) M. Nishioka, Energy Fuels 2 (1986) 214.

[2] (a) I.G. Dance, Polyhedron 5 (1986) 1037. (b) P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121. (c) D.W. Stephan, T.T. Nadasdi, Coord. Chem. Rev. 147 (1996) 147.

[3] (a) E.I. Steifel, Prog. Inorg. Chem. 22 (1977) 1. (b) R.L. Robson, R.R. Eady, T.H. Richardson, R.W. Miller, M. Hawkins, J.R. Postage, Nature (Lond.) 322 (1986) 388. (c) K. Kustin, I.G. Macara, Comments Inorg. Chem. 2 (1982) 1. (d) B.J. Hales, E.E. Case, J.E. Morningstar, M.F. Dzeda, L.A. Manterer, Biochemistry 25 (1986) 7251.

[4] (a) W.E. Smith, J. Reglinski, Perspec. Bioinorg. Chem. 1 (1991) 183. (b) R.V. Parish, S.M. Cottrill, Gold Bull. 20 (1987) 3. (c) D.R. Haynes, M.W. Whitehouse, in: K.D. Rainsford, G.P. Velo (Eds.), New Developments in Antirheumatic Therapy, Klawer, Dordrecht, 1989, chapter 8, p. 207. (d) B.M. Sutton, E. McGusty, D.T. Walz, M.J. DiMartino, J. Med. Chem. 15 (1972) 1095. (e) B.M. Sutton, Gold Bull. 19 (1986) 15. (f) T.D. Simon, D.H. Kunishima, D.H. Vibert, A. Lorber, Cancer Res. 41 (1981) 94. (g) C.K. Mirabeli, R.K. Johnson, C.M. Sung, L. Faucette, K. Muirhead, S.T. Crooke, Cancer Res. 45 (1985) 32. (h) T. Okada, B.K. Patterson, S.-Q. Ye, M.E. Gurney, Virology 192 (1993) 631.

[5] (a) O. Crespo, M.C. Gimeno, P.G. Jones, B. Ahrens, A. Laguna, Inorg. Chem. 36 (1997) 495. (b) O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J. Chem. Soc. Dalton Trans. (1992) 1601. (c) O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J. Chem. Soc. Dalton Trans. (1997) 1099. (d) O. Crespo, M.C. Gimeno, P.G. Jones, B. Ahrens, A. Laguna, Inorg. Chem. 36 (1997) 495.

[6] D.A. Brown, H.M. Colquhoun, J.A. Daniels, J.A.H. Macbride, I.R. Stephenson, K. Wade, J. Mater. Chem. 2 (1992) 793.

[7] M.F. Hawthorne, J.F. Liebman, A. Greenberg, R.E. Willians, Advances in Boron and the Boranes, VCH, New York, 1988, p. 225.

[8] (a) R.F. Barth, A.H. Soloway, R.G. Fairchild, Cancer Res. 50 (1990) 1061. (b) M.F. Hawthorne, Pure Appl. Chem. 63 (1991) 327. (c) M.F. Hawthorne, Angew. Chem. 32 (1993) 950.

[9] (a) O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, Inorg. Chem. 33 (1994) 6128. (b) O. Crespo, M.C. Gimeno, P.G. Jones, B. Ahrens, A. Laguna, Inorg. Chem. 35 (1996) 1361. (d) O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J. Chem. Soc. Dalton Trans. (1996) 4583.

[10] (a) F.A. Gomez, S.E. Johnson, M.F. Hawthorne, J. Am. Chem. Soc. 113 (1991) 5915. (b) F.A. Gomez, M.F. Hawthorne, J. Organomet. Chem. 57 (1992) 1384. (c) W. Jiang, I.T. Chizhevsky, M.D. Mortimer, W. Chen, C.B. Knobler, S.E. Johnson, F.A. Gomez, M.F. Hawthorne, Inorg. Chem. 35 (1996) 5417.

[11] C. Viñas, R. Benakki, F. Teixidor, J. Casabó, Inorg. Chem. 34 (1995) 3844.
[12] T.J. Marks, J.R. Kolb, Chem. Rev. 77 (1977) 263.
[13] S. Quist, J.B. Bates, G.E. Boyd, J. Chem. Phys. 54 (1971) 4896.
[14] M. Nakamoto, H. Koijman, M. Paul, W. Hiller, H. Schmidbaur, Z. Anorg. Allg. Chem. 619 (1993) 1341.
[15] M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, R. Terroba, Inorg. Chem. 33 (1994) 3932.
[16] R.M. Dávila, A. Elduque, T. Grant, R.J. Staples, J.P. Fackler Jr., Inorg. Chem. 32 (1993) 1749.
[17] R.M. Dávila, A. Elduque, T. Grant, R.J. Staples, M. Harlass, J.P. Fackler Jr., Inorg. Chim. Acta 217 (1994) 45.
[18] R. Usón, A. Laguna, Inorg. Synth. 21 (1982) 71.
[19] P. Braunstein, R.J.H. Clark, J. Chem. Soc. Dalton Trans. (1973) 1845.
[20] A.N. Nesmeyanow, E.G. Perevalova, Yu.T. Struchkov, M.Yu. Antipin, K.I. Grandberg, V.P. Dyadchenko, J. Organomet. Chem. 201 (1980) 343.
[21] G.M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Gottingen, 1993.