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Synthesis of gold(III) complexes with the 1,2-dithiolate-*o*-carborane ligand.
Crystal structures of [N(PPh$_3$)$_2$][AuCl$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)] and [AuCl(S$_2$C$_2$B$_{10}$H$_{10}$)(CH$_2$PPh$_3$)]

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Abstract

The reaction of 1,2-dithiol-*o*-carborane, under basic conditions, with *trans*-NBu$_4$[AuCl$_2$R$_2$] or [N(PPh$_3$)$_2$][AuCl$_4$] results in the formation of the anionic gold(III) derivatives NBu$_4$[(AuR$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)] [R = C$_6$F$_5$ (1), C$_6$F$_3$H$_2$ (2)] or [N(PPh$_3$)$_2$][AuCl$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)] (3). Neutral gold(III) species are synthesized from suitable starting materials such as [AuCl$_3$L] or [AuCl$_2$X(PPh$_3$)], leading to the complexes [AuCl(S$_2$C$_2$B$_{10}$H$_{10}$)L] [L = CH$_2$PPh$_3$ (4), CH$_2$PPh$_2$Me (5)] or [AuX(S$_2$C$_2$B$_{10}$H$_{10}$X(PPh$_3$)] [X = Cl (6), C$_6$F$_5$ (7)]. Complexes 3 and 4 were characterized by X-ray diffraction studies. © 1997 Elsevier Science S.A.

Keywords: Gold(III); Dithiolate complexes; *o*-carborane; X-ray structure

1. Introduction

There is continuing interest in complexes of thiolate ligands with transition metals, particularly gold, for several reasons. Among these are the relevance to biological systems [1–4], the potential of the chemistry relating to S–C bond cleavage reactions and desulfurization [5,6], the novel structure of such complexes [7–9] and possible applications in organosulfur chemistry. The majority of the dithiolate gold(III) complexes described in the literature are homoleptic anions, e.g. [Au(S–S)$_2$]$^-$ {S–S=S(CN)C=C(CN)S (maleonitriledithiolate) [10]; S$_2$C=C(CN)$_2$ (isomaleonitriledithiolate) [11]; 1,2-S$_2$C$_6$H$_4$ (1,2-benzenedithiolate) [12]; 3,4-S$_2$C$_6$H$_3$Me (dimercaptoluene) [13–16]; C$_3$S$_5$ (1,3-dithiol-2-thione-4,5-dithiolate, dmit) [17]; C$_4$H$_4$S$_4$ (5,6-di-hydro-1,4-dithiino-2,3-dithiolate) [18,19]}. Heterolep-

tic dithiolate gold(III) derivatives are far less common and only the complexes {Au(mnt)(S$_2$CNR$_2$)] [10,20], [Au(S–S)X$_2$]$^-$, (Au(S–S)XL] [S–S = maleonitriledithiolate, dmit, S$_2$C$_6$H$_4$] have been previously described [21,22].

We are currently studying 1,2-dithiol-*o*-carborane and its derivatives and have recently reported some gold(I) complexes [23,24] as well as the synthesis of the homoleptic dithiolate gold(III) species [25], and further studies of the partial degradation of one or the two carborane cages. Here we report on the synthesis of heteroleptic dithiolate gold(III) complexes with 1,2-dimercapto-*o*-carborane. This ligand has been scarcely studied; apart from our own studies only a few complexes of Co(II) and Ni(II) have been previously described [26,27]. Furthermore, complexes incorporating an *o*-carborane backbone are receiving much attention for potential use in tumor-seeking drugs for boron neutron capture therapy [28,29], also for the synthesis of high temperature polymers [30] or for potential applications as novel catalysts [31].

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2. Results and discussion

The reaction of 1,2-dithiol-*o*-carborane, 1,2-(SH)$_2$-1,2-C$_2$B$_{10}$H$_{10}$, with *trans*-NBu$_4$[AuCl$_2$R$_2$] in dichloromethane and in the presence of Na$_2$CO$_3$ affords the anionic gold(III) derivatives NBu$_4$[AuR$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)][R = C$_6$F$_5$ (1), C$_6$F$_3$H$_2$ (2)]. Complexes 1 and 2 are pale yellow solids, stable to air and moisture at room temperature. They show conductivities of ca. 110 Ω^{-1}cm^{2}mol^{-1}, typical of 1 : 1 electrolytes, consistent with their formulation.

The IR spectra show the characteristic ν(B–H) stretching frequencies of the carborane nucleus as a broad band around 2600 (s, br) cm^{-1}; they also present the typical absorptions of the mutually *cis* polyhalophenyl groups at 804 (m) and 810 (m) for the C$_6$F$_5$ and 800 (w, br) cm^{-1} for the C$_6$F$_3$H$_2$ group. The ^{19}F NMR spectra show the presence of equivalent C$_6$F$_5$ or C$_6$F$_3$H$_2$ groups; two multiplets and a triplet are observed for the pentafluorophenyl unit and a multiplet and a triplet for the trifluorophenyl group. The negative-ion fast atom bombardment (FAB) spectrum of complex 2 shows the molecular anion peak, [Au(C$_6$F$_3$H$_2$)$_2$-(S$_2$C$_2$B$_{10}$H$_{10}$)]$^-$, at $m/z = 666$ (11%) with coincident experimental and isotopic distribution.

Similarly, the treatment of equivalent amounts of [N(PPh$_3$)$_2$][AuCl$_4$] and (SH)$_2$C$_2$B$_{10}$H$_{10}$ in dichloromethane leads to a mixture of the homo and heteroleptic species [N(PPh$_3$)$_2$][Au(S$_2$C$_2$B$_{10}$H$_{10}$)$_2$] and [N(PPh$_3$)$_2$][AuCl$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)] (3), respectively. The former has been previously reported by us [25] and has a characteristic red color that allows it to be separated
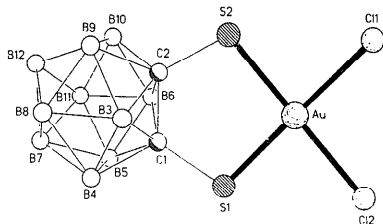

Fig. 1. The anion of complex 3 in the crystal with the atom numbering scheme. H atoms are omitted for clarity; radii are arbitrary.

by hand from the purple crystals of complex 3. This latter complex has been characterized by means of mass spectrometry and X-ray diffraction analysis. In the negative-ion fast atom bombardment spectrum the molecular anion peak, [AuCl$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)]$^-$, appears as the base peak at $m/z = 474$; other fragmentation peaks originate from the loss of one or two chlorine atoms and appear at $m/z = 439$ (44%) and 404 (11%), respectively.

Scheme 1 shows i) Q[AuCl$_2$R$_2$], ii) [N(PPh$_3$)$_2$][AuCl$_4$], iii) [AuCl$_3$L], iv) [AuCl$_2$X(PPh$_3$)].

The structure of the anion of complex 3 is shown in Fig. 1. Atomic coordinates are found in Table 1 and selected bond lengths and angles in Table 2. The gold center has a square-planar geometry (mean deviation of 5 atoms from best plane: 0.016 Å), being chelated by

R = C$_6$F$_5$(1), C$_6$F$_3$H$_2$(2)

(3)

X = Cl (6), C$_6$F$_5$ (7)

L = CH$_2$PPh$_3$ (4), CH$_2$PPh$_2$Me (5)
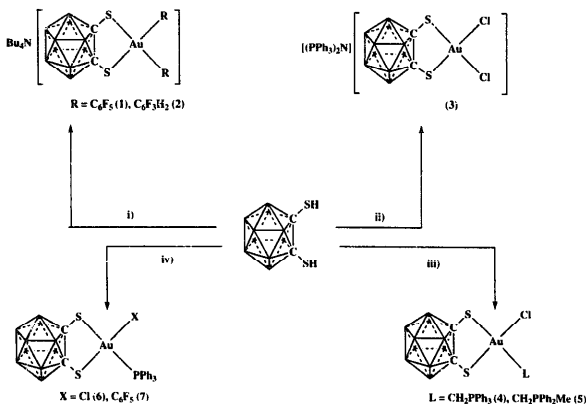
Scheme 1. i) Q[AuCl$_2$R$_2$], ii) [N(PPh$_3$)$_2$][AuCl$_4$], iii) [AuCl$_3$L], iv) [AuCl$_2$X(PPh$_3$)].

Table 1
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for **3**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Au	8226(1)	1045(1)	7520(1)	30(1)
Cl(1)	8113(2)	−618(2)	8546(1)	50(1)
Cl(2)	8940(2)	2314(2)	8177(1)	40(1)
S(1)	8383(2)	2661(2)	6516(1)	50(1)
S(2)	7512(2)	−209(1)	6888(1)	37(1)
C(1)	7914(5)	2096(5)	5779(3)	32(3)
C(2)	7495(5)	706(5)	5957(3)	30(3)
B(3)	8849(7)	1096(7)	5518(4)	40(2)
B(4)	8609(7)	2559(7)	4943(4)	42(2)
B(5)	7130(6)	3003(7)	5066(4)	39(2)
B(6)	6425(6)	1827(6)	5716(4)	36(2)
B(7)	7528(7)	2482(7)	4292(5)	46(2)
B(8)	8585(8)	1291(8)	4585(5)	52(2)
B(9)	7897(7)	109(7)	5256(5)	45(2)
B(10)	6398(7)	535(7)	5385(4)	42(2)
B(11)	6177(7)	2016(7)	4775(5)	45(2)
B(12)	7087(7)	941(8)	4487(5)	49(2)
P(1)	6093(1)	7070(1)	1688(1)	22(1)
P(2)	7387(1)	5022(1)	1431(1)	20(1)
N	7189(4)	6356(4)	1482(2)	24(2)
C(11)	5132(4)	6205(5)	2400(3)	27(2)
C(12)	4017(5)	5839(5)	2254(3)	34(2)
C(13)	3335(5)	5139(6)	2819(4)	42(2)
C(14)	3763(5)	4794(6)	3527(3)	48(2)
C(15)	4869(6)	5140(6)	3678(5)	43(3)
C(16)	5557(5)	5840(5)	3116(3)	37(3)
C(21)	5226(4)	7793(5)	895(3)	26(2)
C(22)	5659(5)	7860(5)	193(3)	32(2)
C(23)	5026(5)	8456(5)	−422(3)	36(2)
C(24)	3952(5)	8979(5)	−345(3)	37(2)
C(25)	3513(5)	8925(5)	348(3)	37(2)
C(26)	4152(5)	8351(5)	965(3)	33(2)
C(31)	6664(4)	8255(5)	2043(3)	30(2)
C(32)	7841(5)	8563(5)	1951(3)	35(2)
C(33)	8263(5)	9508(5)	2199(4)	41(2)
C(34)	7504(4)	10112(5)	2580(4)	40(2)
C(35)	6326(5)	9808(5)	2646(3)	37(2)
C(36)	5906(5)	8871(5)	2391(3)	34(2)
C(41)	6088(5)	4109(4)	1618(2)	26(2)
C(42)	5877(4)	3299(4)	2301(3)	27(2)
C(43)	4794(5)	2737(5)	2454(3)	37(2)
C(44)	3948(5)	2935(5)	1916(3)	33(2)
C(45)	4150(4)	3734(5)	1237(3)	34(2)
C(46)	5218(4)	4328(5)	1085(3)	28(2)
C(51)	7893(4)	5038(4)	521(3)	26(2)
C(52)	7742(5)	4048(5)	242(3)	29(3)
C(53)	8188(5)	4077(5)	−448(3)	33(3)
C(54)	8777(5)	5081(4)	−863(3)	34(3)
C(55)	8926(5)	6060(5)	−591(3)	33(3)
C(56)	8496(4)	6043(5)	101(3)	27(2)
C(61)	8531(4)	4307(4)	2055(3)	26(2)
C(62)	8936(4)	3148(5)	2068(3)	30(2)
C(63)	9849(5)	2623(5)	2526(3)	35(2)
C(64)	10370(5)	3246(5)	2966(3)	37(3)
C(65)	9982(5)	4382(5)	2960(3)	33(2)
C(66)	9061(5)	4921(5)	2511(3)	30(2)
Cl(3)	6744(2)	7453(2)	4532(1)	72(1)
Cl(4)	8567(2)	5973(3)	4164(2)	106(1)
C(3)	8150(8)	7409(7)	4161(6)	73(5)
Cl(5)	9407(4)	1236(5)	294(3)	88(3)
Cl(5')	9373(10)	70(11)	345(6)	181(4)

Table 2
Selected bond lengths [Å] and angles [deg] for **3**

Bond lengths

Au–S(1)	2.271(2)	Au–S(2)	2.278(2)
Au–Cl(2)	2.324(2)	Au–Cl(1)	2.325(2)
S(1)–C(1)	1.782(6)	S(2)–C(2)	1.785(6)
C(1)–C(2)	1.622(8)		

Angles

S(1)–Au–S(2)	94.89(6)	S(1)–Au–Cl(2)	85.69(6)
S(2)–Au–Cl(2)	179.29(6)	S(1)–Au–Cl(1)	178.65(8)
S(2)–Au–Cl(1)	85.31(6)	Cl(2)–Au–Cl(1)	94.13(6)
C(1)–S(1)–Au	103.6(2)	C(2)–S(2)–Au	103.5(2)

the dithiolate ligand and bonded to the two chlorine atoms. The bite angle S(1)–Au–S(2) of 94.89(6)° is wider than those found in homoleptic dithiolate gold(III) derivatives, such as [N(PPh$_3$)$_2$][Au(dmit)$_2$] [91.88(5), 91.76(5)°] [32], [Au(PPh$_2$Me)$_2$][Au(3,4-S$_2$C$_6$H$_3$Me)$_2$] [90.02(12)°] [16], or NBu$_4$[Au(S$_2$C$_2$B$_{10}$H$_{10}$)$_2$] [87.37(6), 87.41(6)°] [24].

The Au–S bond distances, 2.271(2) and 2.278(2) Å, are amongst the shortest found in this type of derivatives; however the Au–Cl bond lengths are longer than usual, 2.324(2) and 2.325(2) Å. In the complex [AuCl$_3$(PPh$_3$)] these distances are 2.273(4) and 2.282(4) Å for the mutually *trans* chlorine atoms, and 2.347(4) Å for the chlorine atom *trans* to the triphenylphosphine, showing the high *trans* influence of the phosphine [33]. In complex **3** the Au–Cl distances are slightly shorter but show the higher *trans* influence of the sulfur atoms of the dithiolate ligand compared to the chlorine atoms. The C–S, 1.782(6), 1.785(6) Å and the C–C, 1.622(8) Å, bond lengths in the carborane cage are similar to those in the homoleptic derivative NBu$_4$[Au(S$_2$C$_2$B$_{10}$-H$_{10}$)$_2$].

The reaction of (SH)$_2$C$_2$B$_{10}$H$_{10}$ with [AuCl$_3$L] (molar ratio 1:1) in the same conditions (dichloromethane, Na$_2$CO$_3$) gives the neutral derivatives [AuCl(S$_2$C$_2$B$_{10}$H$_{10}$)L] [L = CH$_2$PPh$_3$ (**4**), CH$_2$PPh$_2$Me (**5**)]. Complexes **4** and **5** are yellow or orange solids, respectively, stable to moisture and air, and they are non-conducting in acetone. Their IR spectra show the presence of ν(B–H) at ca. 2602 (s, br), ν(Au–S) at ca. 330 (m) and ν(Au–C) bands at ca. 582 (m) cm^{-1}. The ^{1}H NMR spectra indicate the presence of the ylide ligand and thus a doublet appears for **4** and two doublets for **5**. The ^{31}P{^{1}H} NMR spectra show one singlet for the phosphorus atom of the ylide ligand. The positive-ion fast atom bombardment (FAB) mass spectra present the molecular peak only for complex **4** with coincident experimental and isotopical distribution at $m/z = 714$ (9%).

The molecular structure of complex **4** has been established by an X-ray diffraction study. Atomic coordinates are collected in Table 3 and selected bond lengths

Table 3
Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for **4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Au	6440(1)	5197(1)	5846(1)	21(1)
Cl	5553(1)	6241(1)	4928(1)	31(1)
S(1)	6908(1)	5053(1)	4053(1)	27(1)
S(2)	7323(1)	4192(1)	6818(1)	28(1)
C(1)	7724(3)	4278(2)	4397(3)	23(1)
C(2)	7916(3)	3854(2)	5733(3)	21(1)
B(3)	7174(4)	3421(3)	4414(4)	24(1)
B(4)	7737(4)	3666(3)	3259(4)	24(1)
B(5)	8780(4)	4254(3)	3933(4)	26(1)
B(6)	8884(4)	4376(3)	5509(4)	24(1)
B(7)	9116(4)	3507(3)	6253(4)	26(1)
B(8)	8078(4)	2925(3)	5581(4)	24(1)
B(9)	7981(4)	2780(3)	3984(4)	26(1)
B(10)	8974(4)	3300(3)	3682(4)	28(1)
B(11)	9684(4)	3751(3)	5085(4)	28(1)
B(12)	9193(4)	2841(3)	5146(4)	29(1)
C(3)	5930(4)	5368(2)	7380(3)	25(1)
P	6695(1)	5895(1)	8641(1)	21(1)
C(11)	7258(3)	6692(2)	8171(4)	25(1)
C(12)	7868(4)	6604(3)	7395(4)	32(1)
C(13)	8335(4)	7205(3)	7069(4)	37(1)
C(14)	8226(4)	7898(3)	7522(4)	39(1)
C(15)	7649(4)	7986(3)	8301(5)	38(1)
C(16)	7164(4)	7387(2)	8633(4)	29(1)
C(21)	5895(3)	6207(2)	9530(3)	25(1)
C(22)	5094(4)	6671(3)	8953(4)	31(1)
C(23)	4484(4)	6941(3)	9609(4)	36(1)
C(24)	4650(4)	6740(3)	10841(4)	34(1)
C(25)	5427(4)	6266(3)	11399(4)	34(1)
C(26)	6058(4)	6001(3)	10760(4)	30(1)
C(31)	7701(4)	5349(2)	9606(4)	25(1)
C(32)	7558(4)	4595(2)	9799(4)	31(1)
C(33)	8343(4)	4186(3)	10530(4)	36(1)
C(34)	9247(4)	4509(3)	11094(4)	36(1)
C(35)	9398(4)	5248(3)	10944(4)	31(1)
C(36)	8624(4)	5671(2)	10191(3)	26(1)

and angles in Table 4. The molecule is shown in Fig. 2. The gold atom exhibits a square-planar geometry (mean deviation of 5 atoms: 0.022 Å) with angles S(1)–Au–

Table 4
Selected bond lengths [Å] and angles [deg] for **4**

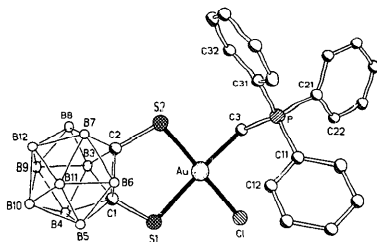| Bond lengths			
Au–C(3)	2.086(4)	Au–S(2)	2.2803(12)
Au–Cl	2.3223(12)	Au–S(1)	2.3245(13)
S(1)–C(1)	1.772(4)	S(2)–C(2)	1.782(4)
C(1)–C(2)	1.643(5)	C(3)–P	1.779(4)
P–C(11)	1.793(5)	P–C(31)	1.793(5)
P–C(21)	1.801(4)		
Angles			
C(3)–Au–S(2)	89.15(13)	C(3)–Au–Cl	89.09(13)
S(2)–Au–Cl	177.86(4)	C(3)–Au–S(1)	175.88(13)
S(2)–Au–S(1)	94.63(4)	Cl–Au–S(1)	87.17(4)
C(1)–S(1)–Au	103.03(13)	C(2)–S(2)–Au	103.59(13)

Fig. 2. Molecular structure of complex **4** in the crystal with the atom labeling scheme. Hydrogen atoms are omitted for clarity; radii are arbitrary.

S(2) 94.63(4)°, very similar to that in complex **3** and again wider than those in other dithiolate gold(III) complexes, Cl–Au–S(1) 87.17(4)°, C(3)–Au–S(2) 89.15(13)°. The gold atom lies 0.042 Å out of the plane formed by the four donor atoms. The Au–S bond lengths, 2.2803(12) and 2.3245(13) Å, are very dissimilar and the longer belongs to the sulfur atom *trans* to the ylide ligand, showing its higher *trans* influence compared to the chlorine ligand. The Au–C(3) bond distance of 2.086(4) Å is slightly shorter than others found in ylide gold(III) complexes such as [Au(C_6F_5)$_3$-(CH_2PPh_2Me)] (2.109(6) Å) [34], [Au(SCN)$_3$(CH_2-PPh$_3$)] (2.111(17) Å) [35] or [AuMe$_3$(CH_2PPh_3)] (2.149(13) Å) [36]. The molecules are linked in pairs across inversion centers, with Au...Au′ 3.96, Au...Cl′ 3.71 Å.

In a similar manner the reaction of the gold(III) complexes [AuCl$_2$X(PPh$_3$)] with (SH)$_2C_2B_{10}H_{10}$ in dichloromethane with Na$_2$CO$_3$ leads to the neutral species [AuX(S$_2$C$_2$B$_{10}$H$_{10}$)(PPh$_3$)] [X = Cl (**6**), C$_5$F$_5$ (**7**)]. They are orange (**6**) or yellow (**7**) solids stable to air and moisture and are non-conducting in acetone. The IR spectra show the ν(B–H) absorptions around 2500 (br, s) cm^{-1}; complex **6** presents the ν(AuCl) band at 331 (s) cm^{-1} and **7** the bands arising at the pentafluorophenyl group at 798 (m), 930 (m) and 1503 (m) cm^{-1}.

In the ^{31}P{^{1}H} NMR spectra of **6** and **7** one singlet appears for the phosphorus atom of the triphenylphosphine and in the ^{19}F NMR spectrum of **7** the typical pattern of a C_6F_5 group appears. The mass spectra (FAB +) show the molecular peak only for complex **7** at m/z = 883 (13%).

3. Experimental details

Infrared 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, H and N 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 Unity 300 spectrometer in CDCl$_3$. Chemical shifts are cited relative to SiMe$_4$ (^{1}H, external), 85% H$_3$PO$_4$ (^{31}P, external) and CFCl$_3$ (^{19}F, external). The starting materials (SH)$_2$C$_2$B$_{10}$H$_{10}$ [37], trans-NBu$_4$[AuCl$_2$R$_2$][38,39], [AuCl$_3$L] [35] were prepared by published procedures.

3.1. Synthesis of NBu$_4$[AuR$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)] [R = C$_6$F$_5$ (1), C$_6$F$_3$H$_2$ (2)]

To a solution trans-NBu$_4$[AuCl$_2$R$_2$] (0.1 mmol: 0.084 g, R = C$_6$F$_5$; 0.079 g, R = C$_6$F$_3$H$_2$) in dichloromethane (30 cm^3) was added (SH)$_2$C$_2$B$_{10}$H$_{10}$ (0.1 mmol, 0.029 g) and an excess of Na$_2$CO$_3$. The suspension was stirred for 30 min and the sodium carbonate then filtered off. The solution was concentrated in vacuo to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave complexes 1 or 2 as pale yellow solids. 1, yield 75%. Anal. Calcd for C$_{30}$H$_{46}$AuB$_{10}$F$_{10}$NS$_2$: C, 36.8; H, 4.75; N, 1.4. Found: C, 36.9; H, 4.75; N, 1.4. Λ_M 102 Ω^{-1}cm^{2}mol^{-1}. ^{19}F NMR, δ: -120.7 (m, o-F), -158.3 [t, p-F, J(FF) 19.6 Hz], -162.4 (m, m-F). 2, yield 48%. Anal. Calcd for C$_{30}$H$_{50}$AuB$_{10}$F$_6$N$_5$2: C, 39.7; H, 5.55; N, 1.55. Found: C, 39.85; H, 5.35; N, 1.75. Λ_M 116 Ω^{-1}cm^{2}mol^{-1}. ^{19}F NMR, δ: -116.2 (m, o-F), -173.7 [t, p-F, J(FF) 5.5 Hz].

3.2. Synthesis of [N(PPh$_3$)$_2$] [AuCl$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)] (3)

To a solution [N(PPh$_3$)$_2$][AuCl$_4$] (0.1 mmol, 0.087 g) in dichloromethane (30 cm^3) was added (SH)$_2$C$_2$B$_{10}$H$_{10}$ (0.1 mmol, 0.029 g) and an excess of Na$_2$CO$_3$. The suspension was stirred for 30 min and the sodium carbonate then filtered off. The solution was concentrated in vacuo to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave a mixture of complex 3 and [N(PPh$_3$)$_2$][Au(S$_2$C$_2$B$_{10}$H$_{10}$)$_2$]. Crystallization of the mixture by slow diffusion of hexane into a dichloromethane solution gave purple crystals of 3.

3.3. Synthesis of [AuCl(S$_2$C$_2$B$_{10}$H$_{10}$)L] [L = CH$_2$PPh$_3$ (4), CH$_2$PPh$_2$Me (5)]

To a dichloromethane solution (30 cm^3) of [AuCl$_3$(CH$_2$PPh$_3$)] (0.1 mmol, 0.057 g) or [AuCl$_3$(CH$_2$PPh$_2$Me)] (0.1 mmol, 0.051 g) was added (SH)$_2$C$_2$B$_{10}$H$_{10}$ (0.1 mmol, 0.029 g) and an excess of Na$_2$CO$_3$. The suspension was stirred for 30 min and the sodium carbonate was then filtered off. The solvent was

evaporated in vacuo to ca. 5 cm^3 and addition of hexane (10 cm^3) afforded complexes 4 and 5 as yellow or orange solids, respectively. 4, yield 64%. Anal. Calcd for C$_{21}$H$_{27}$AuB$_{10}$ClPS$_2$: C, 35.25; H, 3.80. Found: C, 35.40; H, 4.1. Λ_M 10 Ω^{-1}cm^{2}mol^{-1}. ^{1}H NMR, δ: 2.51 (d, CH$_2$, J(PH) 10.25 Hz]. ^{31}P{^{1}H} NMR, δ: 28.6 (s). 5, yield 56%. Anal. Calcd for C$_{16}$H$_{25}$AuB$_{10}$ClPS$_2$: C, 29.45; H, 3.85; N. Found: C, 29.15; H, 3.60. Λ_M 6 Ω^{-1}cm^{2}mol^{-1}. ^{1}H NMR, δ: 1.90 [d, Me, J(HP) 10.98 Hz], 2.22 [d, CH$_2$, J(HP) 13.43 Hz]. ^{31}P{^{1}H} NMR, δ: 24.1(s).

3.4. Synthesis of [AuX(S$_2$C$_2$B$_{10}$H$_{10}$)(PPh$_3$)] [X = Cl (6), C$_6$F$_5$ (7)]

To a dichloromethane solution (30 cm^3) of [AuCl$_3$(PPh$_3$)] (0.1 mmol, 0.056 g) or

Table 5
Details of data collection and structure refinement for the complexes 3 and 4

Compound	3·1.5 CH$_2$Cl$_2$	4
Chemical formula	C$_{39.50}$H$_{43}$AuB$_{10}$-Cl$_5$NP$_2$S$_2$	C$_{21}$H$_{27}$AuB$_{10}$ClPS$_2$
Crystal habit	purple tablet	yellow tablet
Crystal size [mm]	$0.50 \times 0.40 \times 0.10$	$0.70 \times 0.60 \times 0.25$
Crystal system	triclinic	monoclinic
Space group	P$\bar{1}$	P2$_1$/c
a [Å]	11.352(3)	13.938(5)
b [Å]	11.555(3)	18.051(5)
c [Å]	18.905(4)	11.316(4)
α [deg]	73.90(2)	90
β [deg]	89.39(3)	107.42(3)
γ [deg]	89.45(3)	90
$U / Å^3$	2382.4(10)	2717(2)
Z	2	4
D_c [Mg m^{-3}]	1.589	1.748
M	1140.13	715.03
$F(000)$	1126	1384
T [°C]	-100	-130
$2\theta_{max}$ [deg]	50	55
μ(Mo-$K\alpha$) [mm^{-1}]	3.55	5.74
Transmission	0.61–1.0	0.429–0.974
No. of reflections measured	8428	12487
No. of unique reflections	8428	6255
R_{int}	–	0.048
R(F, $F > 4\sigma(F)$)^a	0.039	0.031
wR(F^2, all refl.)^b	0.101	0.071
No. of parameters	495	275
No. of restraints	367	175
S^c	1.038	1.050
Max. $\Delta \rho$ [e Å^{-3}]	1.72	1.701

^{a}R(F) = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.
^{b}wR(F^2) = $[\Sigma\{w(F_o^2 - F_c^2)2\}/\Sigma(w(F_o^2)^2)]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.
^{c}S = $[\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

$[Au(C_6F_5)Cl_2(PPh_3)]$ (0.1 mmol, 0.069 g) was added $(SH)_2C_2B_{10}H_{10}$ (0.1 mmol, 0.029 g) and an excess of Na_2CO_3. The suspension was stirred for 30 min and the sodium carbonate was then filtered off. The solvent was evaporated in vacuo to ca. 5 cm^3 and addition of hexane (10 cm^3) afforded complexes **6** or **7** as yellow or orange solids, respectively. **6**, yield 76%. Anal. Calcd for $C_{20}H_{25}AuB_{10}ClPS_2$: C, 34.25; H, 3.6; N. Found: C, 34.3; H, 3.3. Λ_M 6 $\Omega^{-1}cm^2mol^{-1}$. $^{31}P\{^1H\}$ NMR, δ: 41.2 (s). **7**, yield 55%. Anal. Calcd for $C_{26}H_{25}AuB_5F_5PS_2$: C, 37.5; H, 3.0. Found: C, 37.6; H, 2.95. Λ_M 3 $\Omega^{-1}cm^2mol^{-1}$. ^{19}F NMR, δ: -121.7 (m, *o*-F), -156.0 [t, *p*-F, J(FF) 19.3 Hz], -160.1 (m, *m*-F). $^{31}P\{^1H\}$ NMR, δ: 31.9 (s).

3.5. X-ray structure determinations of complexes 3 and 4

The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Siemens R3 (**3**) or Stoe STADI-4 (**4**) diffractometer with a Siemens LT-2 low temperature attachment. Data were collected using monochromated MoKα radiation ($\lambda = 0.71073$ Å). Scan type ω (**3**), ω/θ (**4**). Cell constants were refined from setting angles (**3**) or $\pm\omega$ angles (**4**) of ca. 50 reflections in the range $2\theta = 20–23°$. Absorption corrections were applied on the basis of Ψ-scans. Structures were solved by the heavy-atom method and refined on F^2 using the program SHELXL-93 [40]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details are given in Table 5. Special details: for **3** one dichloromethane molecule is severely disordered over an inversion center.

4. Supplementary material available

Full details of the structure determinations (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 numbers 405999 and 406000.

Acknowledgements

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