Journal of Organometallic Chemistry, 81 (1974) 271–280

THE CRYSTAL STRUCTURE OF TRIS(TRIPHENYLPHOSPHINE)GOLD(I)-[DODECAHYDRIDO-6-THIA-*nido*-DECABORATE(1—)]

LLOYD J. GUGGENBERGER

Central Research Department, E.I. du Pont de Nemours and Company. Experimental Station, Wilmington, Delaware 19898 (U.S.A.) *

(Received May 29th, 1974)

Summary

The crystal structure of tris(triphenylphosphine)gold(I)[dodecahydrido-6-thia-*nido*-decaborate(1—)], $[(C_6H_5)_3P]_3AuB_9H_{12}S$, has been determined using X-ray techniques and counter data. The compound is a salt consisting of $[(C_6H_5)_3P]_3Au^+$ cations and $B_9H_{12}S^-$ anions. The cation is trigonal and nearly planar with Au—P distances of 2.382(5) Å and P—Au—P angles of 119.3(36)°. The $B_9H_{12}S^-$ thiaborane anion is an open icosahedral fragment with the S atom in the 6 position, on the periphery of the decaborane polyhedron. The structure is the same as that found in solution for the isoelectronic $B_{10}H_{14}^{2-}$ anion. Crystals are triclinic, space group $P\bar{1}$, with $a = 13.086(12)$, $b = 19.635(32)$, $c = 11.180(8)$ Å, $\alpha = 103.60(16)$, $\beta = 72.10(9)$, and $\gamma = 94.76(15)$°. The structure was refined by least squares to a conventional R of 0.077.

Introduction

Reactions of simple salts of copper(II), silver(I) and gold(II) with $CsB_9H_{12}S$ in aqueous ethanol solutions containing excess triphenylphosphine give the compounds $[(C_6H_5)_3P]_3MB_9H_{12}S$ [M = Cu, Ag, Au] [1]. We were particularly interested in these compounds because we initially thought they incorporated M—borane or M—H—borane interactions based on their infrared spectra. This turns out not to be the case, however, and as this structure illustrates, they are instead 1/1 salts of $[(C_6H_5)_3P]_3Au^+$ cations and $B_9H_{12}S^-$ anions. The structures of both components of the salt are of interest in their own right since (a) there is very little structural chemistry on Au^I species, and (b) $B_9H_{12}S^-$ is isoelectronic with $B_{10}H_{14}^{2-}$, a known borane with several acceptable topological structures whose molecular structure has only recently been established in solution by ^{11}B NMR [2]. The preparation and chemistry of $B_9H_{12}S^-$ complexes as well as a preliminary account of the structural studies were reported earlier [1, 3].

---

* Contribution No. 2115.

Experimental

The copper and gold $[(C_6H_5)_3P]_3MB_9H_{12}S$ complexes were shown to be isomorphous in the solid state. The structure work was initiated on the copper complex in order to minimize the heavy atom contribution to the X-ray diffraction. The copper complex, however, decomposed quite rapidly during our data collection. We then proceeded to the gold complex for the rest of the X-ray work. No decomposition was observed with crystals of the gold complex; this is consistent with the observed hydrolytic and oxidative stability for these complexes where the order of stability is $Au > Ag > Cu$ [1].

Crystals of $[(C_6H_5)_3P]_3AuB_9H_{12}S$ are triclinic with cell parameters of $a = 13.086(12)$, $b = 19.635(32)$, $c = 11.180(8)$ Å, $\alpha = 103.60(16)$, $\beta = 72.10(9)$, and $\gamma = 94.76(15)°$. The observed and calculated densities for two formula units per cell are 1.41 and 1.42 g cm^{-3}, respectively. The space group is $P\bar{1}$ which imposes no special symmetry on either the cation or anion.

A prismatic crystal of dimensions 0.08 × 0.11 × 0.18 mm was used in the data collection. Data were measured on a Picker four-circle automatic diffractometer using Zr-filtered Mo radiation (λ 0.7107). The $\theta-2\theta$ scan technique was used with a scan range of 1.75° (1°/min) plus the $K_{\alpha_1}-K_{\alpha_2}$ separation. Backgrounds of 20 sec were taken before and after each reflection. A total of 3591 reflections was measured out to 35° in 2θ; this included standards and duplicates in the $h0l$ zone which were averaged.

An absorption correction was applied to the data in addition to the usual Lorentz and polarization corrections *. The linear absorption correction for Mo radiation is 30.2 cm^{-1}. The crystal shape was approximated by six plane faces for the absorption correction; the minimum and maximum calculated transmission factors were 0.60 and 0.76, respectively. The structure factor errors were estimated as described earlier [4]. Those data with $F_o < 2\sigma(F_o)$ were considered "unobserved".

Structure solution and refinement

The structure was solved stepwise using heavy atom techniques. The R value $(\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ was 0.28 for the 2100 largest reflections with the Au atom only in the model. The phenyl rings were treated as rigid bodies in the refinement (C—C = 1.397 Å, C—H = 1.0 Å). The R and R_w, $[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, for an isotropic refinement with all nonhydrogen atoms in the model and group temperature factors for the phenyl rings are 0.069 for R and 0.085 for R_w (1796 largest reflections used). At this point the nonring atoms were given anisotropic temperature factors and the ring carbon atoms individual isotropic temperature factors. Hydrogen atoms were located on an electron density difference map for the thiaborane cage (0.2 to 0.5 e^- $Å^{-3}$) these hydrogen positional parameters were refined, but not the thermal param-

---

* The absorption program used was Prewitt's ACACA. Other programs used were the Busing—Levy error function program ORFFE, the least-squares program ORFLS (a copy of which was received from Dr. G.D. Stucky), the Johnson plotting program ORTEP, and the Fourier program FOUR (a local version of a program written by Dr. C.J. Fritchie, Jr.).

eters (6.0 Å^2). Hydrogen atoms were placed at their calculated positions on the phenyl rings with fixed isotropic temperature factors of 6.0 Å^2. The refinement continued including all observed reflections and refining the position and thermal parameters in two groups: (a) the Au, P, and nine rigid group atoms, and (b) the Au, P, B, and borane H atoms. The final R values for 3094 observed reflections were 0.077 for R and 0.071 for R_w; the R values for all the data (3900 reflections) are 0.095 for R and 0.089 for R_w. A final electron density difference map showed no unusual peaks except for two of 1.4 and 1.5 e$^-$ Å^{-3} in the immediate vicinity of the Au and P atoms.

Neutral atom form factors were used [5]; the Au atom was corrected for the real and imaginary part of the anomalous scattering effect [6]. The function $\Sigma w(|F_o|-|F_c|)^2$ was minimized in the refinement. A list of observed and calculated structure factors (× 5 in electrons) is available *.

The final positional and thermal parameters for the nonring atoms are given in Table 1; the phenyl ring atom parameters are listed in Table 2.

Results and discussion

The crystal structure of $[(C_6H_5)_3P]_3AuB_9H_{12}S$ consists of the packing of discrete $[(C_6H_5)_3P]_3Au^+$ cations and $B_9H_{12}S^-$ anions. The overall structure of the anion is shown in Fig. 1. The thiaborane framework is that of an open icosahedral fragment. The labeling here is the conventional polyhedral labeling up to B(5); S is in the polyhedral 6-position, B(6) in the polyhedral 7-position, etc. The hydrogen atoms are labeled according to the B atoms to which they are bonded, except for H(8) through H(12) where the H and B atom correspondence is given in Table 1. It is significant, although not too surprising, that the S atom is on the periphery of the polyhedral cage; this was predicted earlier [3]. All hydrogen atoms are terminal except for H(11) and H(12) which bridge B(5) — B(9) and B(6) — B(7), respectively, on the periphery of the polyhedron. There is no crystallographically imposed symmetry, but the $B_9H_{12}S^-$ anion has idealized $C_s(m)$ point symmetry where the idealized mirror plane contains the atoms S, B(2), H(2), B(4), H(4), B(8), H(8) and H(9).

A list of interatomic distances and angles is given in Table 3. Individual distances for the thiaborane cage are shown in Fig. 2 which also shows an idealized planar view of the anion; mean thiaborane distances and all pertinent angles are given in Table 3. The B—B and B—H distances are in the range frequently found for similar geometries in other compounds. The distances are consistent with the idealized $C_s(m)$ point symmetry when the estimated errors are taken into account. The relatively large σ values here probably result primarily from the overwhelming dominance of the scattering by the $[(C_6H_5)_3P]_3Au^+$ cation. The average B—S distance of 1.89(3) Å is consistent with difference in radii of B and S. A value of 2.02(5) Å was found in $[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$ where the S atom is also incorporated in the polyhedral framework [7], but

---

* This table is deposited as NAPS Document, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1. FINAL POSITIONAL AND THERMAL PARAMETERS (× 10^4) FOR $[(C_6H_5)_3P]_3AuB_9H_{12}S$ [a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au	0.20600(8)	0.26567(5)	0.22635(9)	51.7(8)	16.7(3)	69.3(12)	−1.1(4)	−0.4(7)	13.8(5)
P(1)	0.11694(49)	0.30673(31)	0.10063(56)	64.2(60)	19.0(24)	71.7(79)	1.0(30)	5.0(58)	5.7(36)
P(2)	0.18646(51)	0.14186(31)	0.20754(56)	81.9(65)	15.8(23)	73.5(80)	−0.2(31)	−16.0(50)	11.8(35)
P(3)	0.26175(47)	0.34270(31)	0.38906(54)	54.3(57)	23.5(25)	69.4(78)	−4.3(30)	−18.6(55)	16.7(36)
S	0.3599(6)	0.8372(4)	0.3055(7)	123(8)	50(3)	129(10)	5(4)	−34(7)	36(5)
B(1)	0.2744(35)	0.7342(25)	0.1153(32)	204(56)	100(26)	83(48)	−37(31)	40(42)	64(31)
B(2)	0.2548(25)	0.8109(20)	0.2223(29)	86(33)	73(18)	101(44)	−1(20)	−45(32)	28(25)
B(3)	0.3109(26)	0.8134(18)	0.0511(32)	109(36)	50(16)	155(50)	3(20)	−5(35)	68(25)
B(4)	0.3066(31)	0.7362(18)	−0.0192(27)	187(48)	47(17)	66(40)	−25(23)	−11(36)	21(21)
B(5)	0.3127(18)	0.7407(14)	0.2524(22)	36(22)	41(11)	65(33)	−22(13)	−30(23)	11(15)
B(6)	0.3753(28)	0.8694(16)	0.1560(35)	93(33)	27(14)	169(51)	9(18)	−44(35)	15(25)
B(7)	0.4549(21)	0.8192(16)	0.0020(26)	50(27)	50(15)	109(42)	−2(16)	−3(28)	36(21)
B(8)	0.5190(20)	0.7408(13)	0.0107(23)	49(25)	29(11)	75(34)	10(13)	−42(24)	22(16)
B(9)	0.3957(27)	0.6905(17)	0.0933(30)	95(34)	47(15)	147(49)	0(18)	−38(33)	25(22)
H(1)	0.254(25)	0.737(17)	0.053(29)	6.0					
H(2)	0.176(19)	0.850(12)	0.275(22)	6.0					
H(3)	0.297(22)	0.833(15)	0.000(26)	6.0					
H(4)	0.395(18)	0.720(12)	−0.121(22)	6.0					
H(5)	0.226(17)	0.704(12)	0.257(22)	6.0					
H(6)	0.354(21)	0.914(13)	0.160(25)	6.0					
H(7)	0.470(17)	0.831(11)	−0.104(20)	6.0					
H(8)B(3)	0.555(19)	0.713(12)	−0.104(23)	6.0					
H(9)B(3)	0.544(28)	0.769(19)	0.102(30)	6.0					
H(10)B(9)	0.381(18)	0.629(13)	0.050(22)	6.0					
H(11)B(5)B(9)	0.400(21)	0.730(14)	0.204(27)	6.0					
H(12)B(6)B(7)	0.489(21)	0.850(13)	0.112(24)	6.0					

Group [b]	x_c	y_c	z_c	ϕ	θ	ζ
Ring 1	0.0766(7)	0.1895(5)	−0.1407(10)	5.656(9)	0.349(8)	4.512(9)
Ring 2	0.2337(8)	0.4350(5)	−0.0305(8)	1.278(9)	−0.112(8)	3.542(8)
Ring 3	−0.1226(8)	0.3578(4)	0.2802(10)	1.412(8)	0.129(8)	1.626(8)
Ring 4	0.2565(8)	0.0681(5)	0.3986(9)	2.231(9)	0.098(9)	0.620(8)
Ring 5	0.3194(7)	0.0648(5)	−0.0706(10)	3.508(9)	0.413(8)	4.913(9)
Ring 6	−0.0671(9)	0.1096(5)	0.2609(9)	3.158(13)	−0.779(8)	2.864(12)
Ring 7	0.3588(8)	0.4917(5)	0.3281(7)	4.533(9)	0.290(8)	6.060(8)
Ring 8	0.0525(7)	0.3766(5)	0.6362(9)	6.207(8)	0.076(8)	0.899(7)
Ring 9	0.4416(8)	0.2860(5)	0.4853(10)	4.248(12)	0.795(9)	1.596(11)

[a] Estimated standard deviations here and in other tables are given in parentheses. The anisotropic temperature factor is of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] x_c, y_c, z_c are the group centers in fractional coordinates and ϕ, θ, ζ are the orientation angles for the groups in radians.

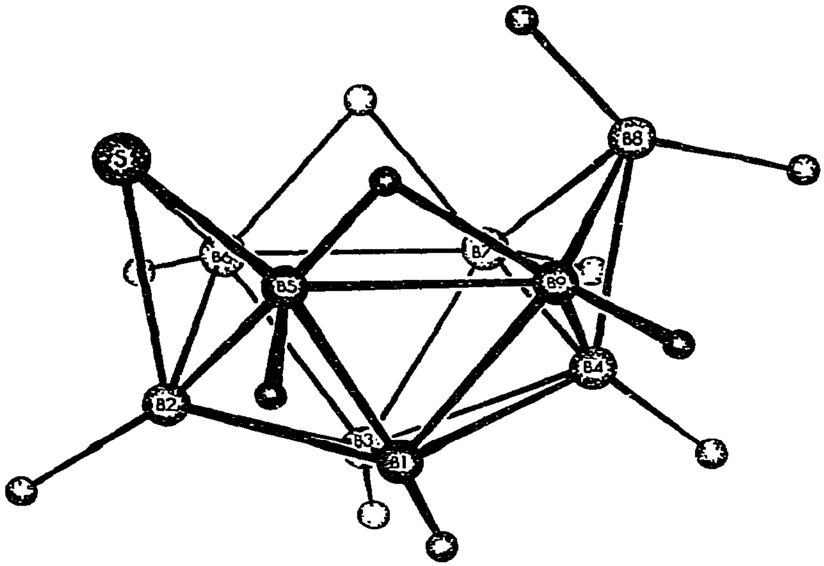

Fig. 1. Structure of the $B_9H_{12}S^-$ anion.

there the S is also bound directly to the Pt metal. A B—S distance of 1.92(1) Å was observed in $B_{10}H_{12}[S(CH_3)_2]_2$ where S is exterior to the polyhedral cage [8].

The structure of the $[(C_6H_5)_3P]_3Au^+$ cation is shown in Fig. 3. There are three triphenylphosphine ligands trigonally disposed about the Au atom. The resultant Au-phosphine geometry is essentially planar; the Au atom is 0.20 Å out of the least-squares plane through the P atoms ($0.7294x + 0.0433y - 0.6827z - 0.881 = 0$). The cation point symmetry is approximately $C_3(3)$ as illustrated in Fig. 3. The following dihedral angles were found between the planes identified by the first label digit in Table 2 and shown on Fig. 3:

1-2, 94.1°; 4-5, 84.0°; 7-8, 68.3°;
1-3, 121.2°; 4-6, 97.5°; 7-9, 81.0°;
2-3, 69.5°; 5-6, 95.3°; 8-9, 75.5°.

Individual distances and angles for the cation are given in Table 3. There are no closely related structures with Au^I—P bonds for comparison; however, observed Au^I—P distances for two-coordinate, linear Au geometries are 2.19 Å in Cl_3PAuCl [9], 2.23(2) in $(C_6H_5)_3PAuCo(CO)_4$ [10], 2.25(1) in $(C_6H_5)_3PAu(CO)_3WC_5H_5$ [11], 2.251(3) in $(C_6H_5)_3PAuSSCN(C_2H_5)_2$ [12], 2.28(1) in $[(C_6H_5)_3PAuC(CF_3)]_2$ [13], and 2.33(1) Å in $(C_6H_5)_3PAuMn(CO)_4$-$P(OC_6H_5)_3$ [14]. In fact, the Au—P distance of 2.382(5) Å found here is among the longest observed for any gold geometry or oxidation state. The 2.5 Å distance in $(CH_3)_3PAuBr_3$ is discounted because the determination is not as accurate as the afore cited structures [15]. Au^I—P single bonds have been estimated at about 2.42 Å [13, 14]. The fact that the Au—P distance here is so long and close to the expected single bond value is somewhat surprising and suggestive perhaps that the gold—phosphorus π bonding is minimal.

(continued on p. 279)

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR THE RIGID GROUPS[a]

	x	y	z	$B(\text{Å}^2)$		x	y	z	$B(\text{Å}^2)$
C(11)	0.0062	0.1934	−0.0167	4.3(5)	C(61) *	0.0436	0.1213	0.2346	3.9(5)
C(12)	−0.0056	0.1396	−0.1186	6.0(6)	C(62)	−0.0276	0.1693	0.3207	4.8(6)
C(13)	0.0647	0.1357	−0.2426	6.0(6)	C(63)	−0.1383	0.1576	0.3559	5.9(6)
C(14)	0.1468	0.1856	−0.2647	5.2(6)	C(64)	−0.1777	0.0079	0.2871	7.1(7)
C(15)	0.1586	0.2394	−0.1628	3.1(5)	C(65)	−0.1065	0.0499	0.1921	6.7(7)
C(16) *	0.0883	0.2433	−0.0388	3.6(5)	C(66)	0.0042	0.0616	0.1659	5.4(6)
H(11)	−0.0441	0.1961	0.0721	6.0	H(62)	0.0007	0.2120	0.3789	6.0
H(12)	−0.0644	0.1038	−0.1027	6.0	H(63)	−0.1892	0.1919	0.4239	6.0
H(13)	0.0562	0.0972	−0.3156	6.0	H(64)	−0.2570	0.0895	0.3059	6.0
H(14)	0.1971	0.1820	−0.3534	6.0	H(65)	−0.1348	0.0072	0.1428	6.0
H(15)	0.2173	0.2752	−0.1786	6.0	H(66)	0.0551	0.0272	0.0978	6.0
C(21) *	0.1803	0.3792	0.0216	3.4(5)	C(71) *	0.3181	0.4275	0.3567	3.9(5)
C(22)	0.2895	0.3910	0.0086	4.8(6)	C(72)	0.2609	0.4661	0.3090	4.6(6)
C(23)	0.3430	0.4168	−0.0436	5.7(6)	C(73)	0.3016	0.5304	0.2804	4.8(6)
C(24)	0.2871	0.4008	−0.0827	6.4(7)	C(74)	0.3996	0.5560	0.2996	4.6(6)
C(25)	0.1779	0.4791	−0.0696	5.6(6)	C(75)	0.4568	0.5173	0.3472	5.5(6)
C(26)	0.1244	0.4233	−0.0174	4.9(6)	C(76)	0.4161	0.4531	0.3758	4.3(5)
H(22)	0.3295	0.3595	0.0366	6.0	H(72)	0.1908	0.4478	0.2953	6.0
H(23)	0.4212	0.4552	−0.0529	6.0	H(73)	0.2607	0.5581	0.2463	6.0
H(24)	0.3254	0.5308	−0.1200	6.0	H(74)	0.4287	0.6020	0.2791	6.0
H(25)	0.1370	0.5106	−0.0976	6.0	H(75)	0.5269	0.5356	0.3609	6.0
H(26)	0.0462	0.4149	−0.0081	6.0	H(76)	0.4570	0.4254	0.4099	6.0
C(31)	−0.1043	0.3393	0.1469	4.0(5)	C(81) *	0.1454	0.3648	0.5312	2.9(5)
C(32) *	−0.0204	0.3371	0.1986	3.4(5)	C(82)	0.0865	0.3081	0.5749	3.9(5)
C(33)	−0.0387	0.3555	0.3319	4.6(6)	C(83)	−0.0064	0.3199	0.6799	5.5(6)
C(34)	−0.1409	0.3762	0.4135	5.1(6)	C(84)	−0.0404	0.3884	0.7413	5.1(6)

C(35)	−0.2248	0.3785	0.3619	5.8(6)
C(36)	−0.2065	0.3601	0.2285	5.1(6)
H(31)	−0.0912	0.3261	0.0515	6.0
H(33)	0.0214	0.3539	0.3689	6.0
H(34)	−0.1539	0.3895	0.5090	6.0
H(35)	−0.2979	0.3933	0.4203	6.0
H(36)	−0.2666	0.3617	0.1915	6.0
C(41) *	0.2221	0.1022	0.3208	3.2(5)
C(42)	0.3190	0.1215	0.3483	5.3(6)
C(43)	0.3524	0.0875	0.4262	6.3(7)
C(44)	0.2889	0.0341	0.4765	6.5(7)
C(45)	0.1920	0.0148	0.4490	6.3(7)
C(46)	0.1586	0.0488	0.3711	5.9(6)
H(42)	0.3645	0.1597	0.3123	6.0
H(43)	0.4218	0.1013	0.4459	6.0
H(44)	0.3127	0.0097	0.5322	6.0
H(45)	0.1465	−0.0235	0.4850	6.0
H(46)	0.0892	0.0350	0.3514	6.0
C(51) *	0.2572	0.0905	0.0503	4.2(5)
C(52)	0.2761	0.1199	−0.0570	3.0(5)
C(53)	0.3383	0.0842	−0.1778	5.1(6)
C(54)	0.3816	0.0191	−0.1914	5.0(6)
C(55)	0.3626	−0.0103	−0.0841	6.5(7)
C(56)	0.3004	0.0254	0.0367	6.0(6)
H(52)	0.2452	0.1664	−0.0472	6.0
H(53)	0.3519	0.1053	−0.2546	6.0
H(54)	0.4261	−0.0064	−0.2779	6.0
H(55)	0.3936	−0.0569	−0.0939	6.0
H(56)	0.2868	0.0043	0.1135	6.0
C(85)	0.0185	0.4450	0.6975	6.6(7)
C(86)	0.1114	0.4332	0.5925	4.5(6)
H(82)	0.1108	0.2591	0.5310	6.0
H(83)	−0.0486	0.2794	0.7112	6.0
H(84)	−0.1069	0.3968	0.8165	6.0
H(85)	−0.0058	0.4940	0.7414	6.0
H(86)	0.1536	0.4737	0.5612	6.0
C(91)	0.5316	0.2534	0.3911	5.9(6)
C(92)	0.4518	0.2791	0.3549	5.0(6)
C(93) *	0.3618	0.3116	0.4492	4.1(5)
C(94)	0.3516	0.3185	0.5796	4.1(5)
C(95)	0.4315	0.2929	0.6157	6.0(7)
C(96)	0.5215	0.2603	0.5214	6.4(7)
H(91)	0.5961	0.2301	0.3236	6.0
H(92)	0.4591	0.2742	0.2616	6.0
H(94)	0.2872	0.3418	0.6470	6.0
H(95)	0.4242	0.2978	0.7090	6.0
H(96)	0.5786	0.2420	0.5473	6.0

---

[a] Asterisks mark the point of ring attachment to the phosphorus atoms. The first number in each label identifies the ring. Each carbon atom was varied isotropically, but hydrogen atom temperature factors were fixed.

TABLE 3

INTERATOMIC DISTANCES AND ANGLES FOR $[(C_6H_5)_3P]_3AuB_9H_{12}S$ [a]

Distances (Å)

Au—P(1)	2.384(7)
Au—P(2)	2.389(6)
Au—P(3)	2.373(14)
av.	2.382(5)
B—S av. of 3	1.89(3)
B—B av. of 18	1.80(1)
B—H terminal av. of 10	1.10(6)
B—H bridge av. of 4	1.34(8)

P(1)—C(16)	1.87(1)
P(1)—C(21)	1 85(1)
P(1)—C(32)	1.86(1)
P(2)—C(41)	1.82(1)
P(2)—C(51)	1.81(1)
P(2)—C(61)	1.83(1)
P(3)—C(71)	1.84(1)
P(3)—C(81)	1.82(1)
P(3)—C(93)	1.84(1)
av.	1.84(1)

Angles (°)

P(1)—Au—P(2)	112.3(2)
P(1)—Au—P(3)	121.5(2)
P(2)—Au—P(3)	124.1(2)
av	119.3(36)
Au—P(1)—C(16)	118.6(4)
Au—P(1)—C(21)	118.4(5)
Au—P(1)—C(32)	111.0(5)
Au—P(2)—C(41)	119.5(4)
Au—P(2)—C(51)	114.2(4)
Au—P(2)—C(61)	106.8(4)
Au—P(3)—C(71)	116.6(4)
Au—P(3)—C(81)	108.4(4)
Au—P(3)—C(93)	118.0(4)
av.	114.6(16)
C(16)—P(1)—C(21)	100.1(5)
C(16)—P(1)—C(32)	101.1(6)
C(21)—P(1)—C(32)	105.4(5)
C(41)—P(2)—C(51)	104.4(5)
C(41)—P(2)—C(61)	103.7(6)
C(51)—P(2)—C(61)	107.2(6)
C(71)—P(3)—C(81)	104.8(5)
C(71)—P(3)—C(93)	102.9(5)
C(81)—P(3)—C(93)	104.8(6)
av.	103.8(7)
P(1)—C(16)—C(11)	119.8(8)
P(1)—C(16)—C(15)	119.6(8)
P(1)—C(21)—C(22)	115.9(8)
P(1)—C(21)—C(26)	124.1(9)
P(1)—C(32)—C(31)	123.9(9)
P(1)—C(32)—C(33)	116.0(9)
P(2)—C(41)—C(42)	119.0(9)
P(2)—C(41)—C(46)	120.7(9)
P(2)—C(51)—C(52)	118 6(7)
P(2)—C(51)—C(56)	121.2(7)
P(2)—C(61)—C(62)	116.4(9)
P(2)—C(61)—C(66)	123.6(9)
P(3)—C(71)—C(72)	118.1(8)
P(3)—C(71)—C(76)	121.9(8)
P(3)—C(81)—C(82)	115.9(7)
P(3)—C(81)—C(86)	124.0(7)
P(3)—C(93)—C(92)	116.0(9)
P(3)—C(93)—C(94)	124.0(9)
av.	119.9(7)

B(2)—S—B(6)	60.0(17)
B(2)—S—B(5)	58.8(12)
av.	59.4(6)
B(2)—B(1)—B(3)	60.7(18)
B(3)—B(1)—B(4)	60.0(19)
B(2)—B(1)—B(5)	64.9(19)
B(4)—B(1)—B(9)	56.1(20)
B(5)—B(1)—B(9)	64.0(21)
B(1)—B(2)—B(3)	61.6(18)
B(1)—B(2)—B(5)	56.7(18)
B(3)—B(2)—B(6)	57.6(20)
B(6)—B(2)—S	60.5(18)
B(5)—B(2)—S	63.3(15)
B(1)—B(3)—B(2)	57.8(16)
B(1)—B(3)—B(4)	60.1(19)
B(2)—B(3)—B(6)	62.6(20)
B(4)—B(3)—B(7)	57.3(19)
B(6)—B(3)—B(7)	61.0(21)
B(1)—B(4)—B(3)	59.9(20)
B(1)—B(4)—B(9)	60.7(22)
B(3)—B(4)—B(7)	60.3(19)
B(7)—B(4)—B(8)	64.4(18)
B(9)—B(4)—B(8)	68.0(23)
B(1)—B(5)—B(2)	58.4(18)
B(1)—B(5)—B(9)	59.6(20)
B(2)—B(5)—S	57.9(13)
B(2)—B(6)—B(3)	59.8(20)
B(2)—B(6)—S	59.5(15)
B(3)—B(6)—B(7)	60.2(20)
B(3)—B(7)—B(6)	58.9(21)
B(3)—B(7)—B(4)	62.4(20)
B(4)—B(7)—B(8)	57.4(17)
B(4)—B(8)—B(7)	58.1(17)
B(4)—B(8)—B(9)	55.5(17)
B(1)—B(9)—B(4)	63.2(22)
B(1)—B(9)—B(5)	56.4(18)
B(4)—B(9)—B(8)	56.5(19)
av.	60.0(5)

---

[a] Individual distances involving boron atoms are given in Fig. 2. The estimated errors of the mean values were calculated according to $[\Sigma(d_i-\bar{d})^2/n(n-1)]^{1/2}$ where d_i and $\bar{d}$ are the function and mean function, respectively.

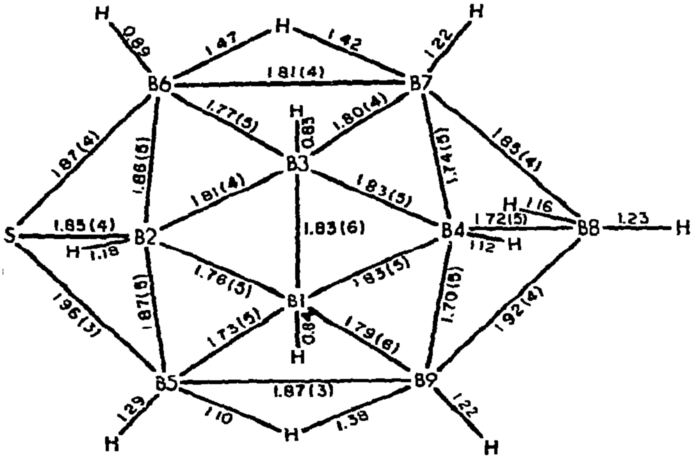

Fig. 2. Interatomic distances in the $B_9H_{12}S^-$ anion.

A stereoview of the crystal structure is shown in Fig. 4. All intermolecular distances were calculated. The shortest contacts between anions and cations were 2.72 Å for the C—(or B—)H type and 1.90 Å for the H—H type (H(8) to H(92)). The shortest interactions involving only the cations were all intramolecular (between phosphines on a given cation) and they are 2.79 Å for C—C, 2.53 Å for C—H, and 2.45 Å for H—H.

The $B_9H_{12}S^-$ anion is isoelectronic with $B_{10}H_{14}^{2-}$ and hence the latter might be expected to have the same structure. Reddy and Lipscomb [16] predicted this earlier based on the anticipated similarity between $B_{10}H_{14}^{2-}$ and $B_{10}H_{12}(CH_3CN)_2$ whose structure is like that of $B_9H_{12}S^-$ except that S and B(8) are replaced by $HBNCCH_3$ groups. The other acceptable topological structure

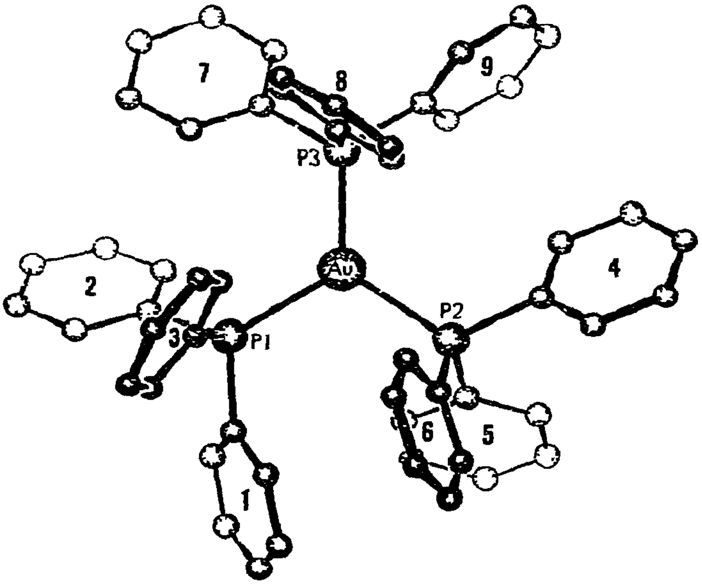

Fig. 3. Structure of the $[(C_6H_5)_3P]_3Au^+$ cation.

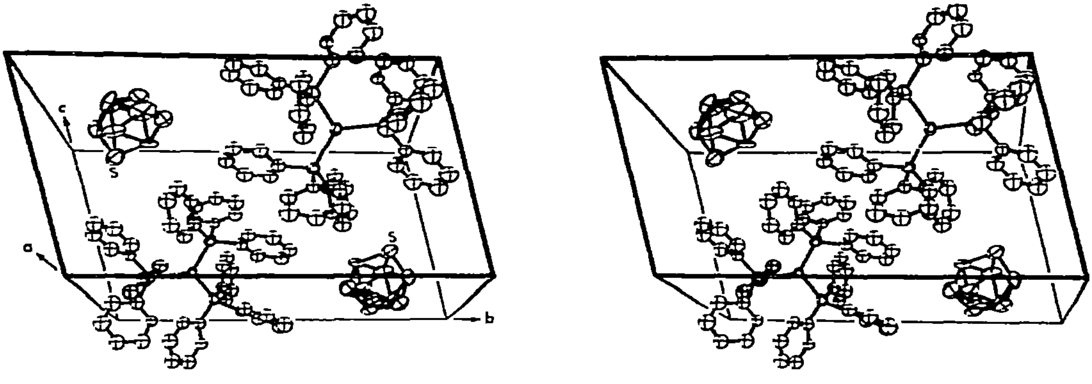

Fig. 4. Stereoview of the crystal structure of $[(C_6H_5)_3P]_3AuB_9H_{12}S$.

for $B_{10}H_{14}^{2-}$ could have four bridging H atoms in the B(8)—B(9) and B(5)—S type positions of Fig. 1. A recent ^{11}B NMR study [2] of $Rb_2B_{10}H_{14}$ shows that it does have the same structure in solution as found here for $B_9H_{12}S^-$. Thus the solution NMR data and the X-ray evidence from an isoelectronic anion are in agreement on the structure of $B_{10}H_{14}^{2-}$.

References

1 F. Klanberg, E.L. Muetterties and L.J. Guggenberger, Inorg. Chem., 7 (1968) 2272.
2 W.N. Lipscomb, R.J. Wiersema and M.F. Hawthorne, Inorg. Chem., 11 (1972) 651.
3 W.R. Hertler, F. Klanberg and E.L. Muetterties, Inorg. Chem., 6 (1967) 1696.
4 L.J. Guggenberger, Inorg. Chem., 7 (1968) 2260.
5 H.P. Hanson, F. Herman, J.D. Lea and S. Skillman, Acta Crystallogr., 17 (1964) 1040.
6 D.H. Templeton, International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1962, p. 215.
7 A.R. Kane, L.J. Guggenberger and E.L. Muetterties, J. Amer. Chem. Soc., 92 (1970) 2571.
8 D.E. Sands and A. Zalkin, Acta Crystallogr., 15 (1962) 410.
9 G.J. Arai, Rec. Trav. Chim., Pays Bas, 81 (1962) 307.
10 T.L. Blundell and H.M. Powell, J. Chem. Soc. A, (1971) 1685.
11 J.B. Wilford and H.M. Powell, J. Chem. Soc. A, (1969) 8.
12 J.G. Wijnhoven, W.P.J.H. Bosman and P.T. Beurskens, J. Cryst. Mol. Struct., 2 (1972) 7.
13 C.J. Gilmore and P. Woodward, Chem. Commun., (1971) 1233.
14 K.A.I.F.M. Mannan, Acta Crystallogr., 23 (1967) 649.
15 M.F. Perutz and O. Weisz, J. Chem. Soc., (1946) 438.
16 J. Reddy and W.N. Lipscomb, J. Chem. Phys., 31 (1959) 610.
17 C. Scheringer, Acta Crystallogr., 16 (1963) 546.
18 R. Eisenberg and J.A. Ibers, Inorg. Chem., 4 (1965) 773.