Synthesis of Silver(I) Complexes with the Bis(diphenylphosphanyl)-*o*-carborane Ligand. Crystal Structure of $[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ and $[Ag\{(SPPh_2)_2CH_2\}\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4 \cdot CH_2Cl_2$

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Silver(I) perchlorate or nitrate react readily with bis(diphenylphosphanyl)-*o*-carborane to give the complexes $[AgX\{(PPh_2)_2C_2B_{10}H_{10}\}]$ [X = ClO_4 (**1**), NO_3 (**2**)]. The perchlorate ligand is weakly bound to the silver atom and thus can be displaced by other ligands affording the three-coordinated complexes $[AgL\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ [L = PPh_3 (**3**), PPh_2Me (**4**), $AsPh_3$ (**5**), C_5H_4NCOOH (**6**), C_9H_6NCOOH (**7**), $SPPh_3$ (**8**)]. Compounds **3** and **4** can also be obtained by reaction of $[Ag(OClO_3)PR_3]$ with the diphosphane. Treatment of complex **1** with bidentate ligands leads to the cationic four-coordinated $[Ag(L-L)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ [L–L = $(PPh_2)_2C_2B_{10}H_{10}$ (**9**), bipy (**10**), phen (**11**), $(SPPh_2)_2CH_2$ (**12**)] or to the neutral $[Ag(S_2CNR_2)\{(PPh_2)_2C_2B_{10}H_{10}\}]$ [NR_2 = NEt_2 (**13**), NC_4H_8 (**14**)]. The crystal structures of **11** and **12** have been established by X-ray crystallography. In both complexes the silver(I) atoms exhibit tetrahedral coordination by two phosphorus and two nitrogen or two sulfur atoms, respectively.

Most diphosphane complexes of silver are of the type $AgXP_2$, where X is halide and P_2 is a diphosphane[1-5]. In general, they adopt dimeric structures in the solid state, with the exception of the silver chloride complex of 2,11-bis[(diphenylphosphanyl)methyl]benzo[*c*]phenanthrene, which is monomeric[6]. Complexes of the type $[Ag(P_2)_2]^+$ or $[Ag(P_2)(L-L)]^+$ are not common. The previously reported bisphosphanesilver(I) complexes were prepared by Sadler et al.[7], who studied by $^{109}Ag\{^{31}P\}$ INEPT pulse sequences the complexes $[Ag(P_2)_2]^+$ with P_2 = $Et_2P[CH_2]_2PPh_2$, $Ph_2P[CH_2]_2PPh_2$, $Ph_2P[CH_2]_3PPh_2$, and $Ph_2PCH{=}CHPPh_2$. Subsequently the crystal structures of the complexes $[Ag\{(PPh_2)_2(CH_2)_2\}_2]NO_3$ and $[Ag\{(PPh_2)_2(CH{=}CH)\}_2][SnPh_2(NO_3)_2]$ were reported[8,9]. As far as we are aware no mixed four-coordinated or cationic three-coordinated silver(I) complexes have been reported with chelating diphosphane ligands.

In our studies with *o*-carborane derivatives as ligands we have reported on the synthesis of unusual high-coordinated gold(I) complexes with the bis(diphenylphosphanyl)-*o*-carborane ligand[10]. We have now extended our studies to silver(I) complexes and prepared a variety of three- and four-coordinated derivatives where the diphosphine acts as a chelating ligand. The crystal structures of two mixed tetrahedral complexes are described here.

The observation that compounds of the type $[M(dppe)_2]^+$ [M = Au, Ag; dppe = 1,2-bis(diphenylphosphanyl)ethane] have significant antitumour activities has increased interest in these type of complexes[11-13].

Synthesis and Properties of the Complexes

Bis(diphenylphosphanyl)-*o*-carborane reacts with one equivalent of $AgClO_4$ in diethyl ether or with $AgNO_3$ in acetone at room temperature to give the colourless complexes **1** and **2**, respectively (see Scheme 1). In these complexes the rigidity of the *o*-carborane moiety causes the chelating mode of the diphosphane ligand to be preferred to the bridging mode.

The reactivity of complex **1** with monodentate ligands has been studied. The reaction of **1** in dichloromethane with tertiary phosphanes leads to the three-coordinated complexes **3** or **4**. These complexes can also be obtained by the reaction of $[Ag(OClO_3)PR_3]$ with the diphosphane ligand. Other monodentate ligands with arsenic, nitrogen, or sulfur donor atoms have been used to synthesize a variety of three-coordinated complexes of silver(I); the ligands used were triphenylarsane, triphenylphosphane sulfide, picolinic and quinoleic acid, whereby the latter act as monodentate ligands and cannot be deprotonated by treating the complexes with Na_2CO_3 (Scheme 1).

The use of bidentate ligands has allowed us to prepare four-coordinated derivatives, and we have again chosen ligands with various donor centres. The reaction of **1** with the bis(diphenylphosphanyl)-*o*-carborane ligand gives the homoleptic diphosphane complex **9**, also obtained by reaction of two equivalents of the ligand with $AgClO_4$; whereas with nitrogen or sulfur donor ligands such as bipy, phen, $(SPPh_2)CH_2$, or dithiocarbamates the mixed four-coordinated complexes **10**–**14** are obtained.

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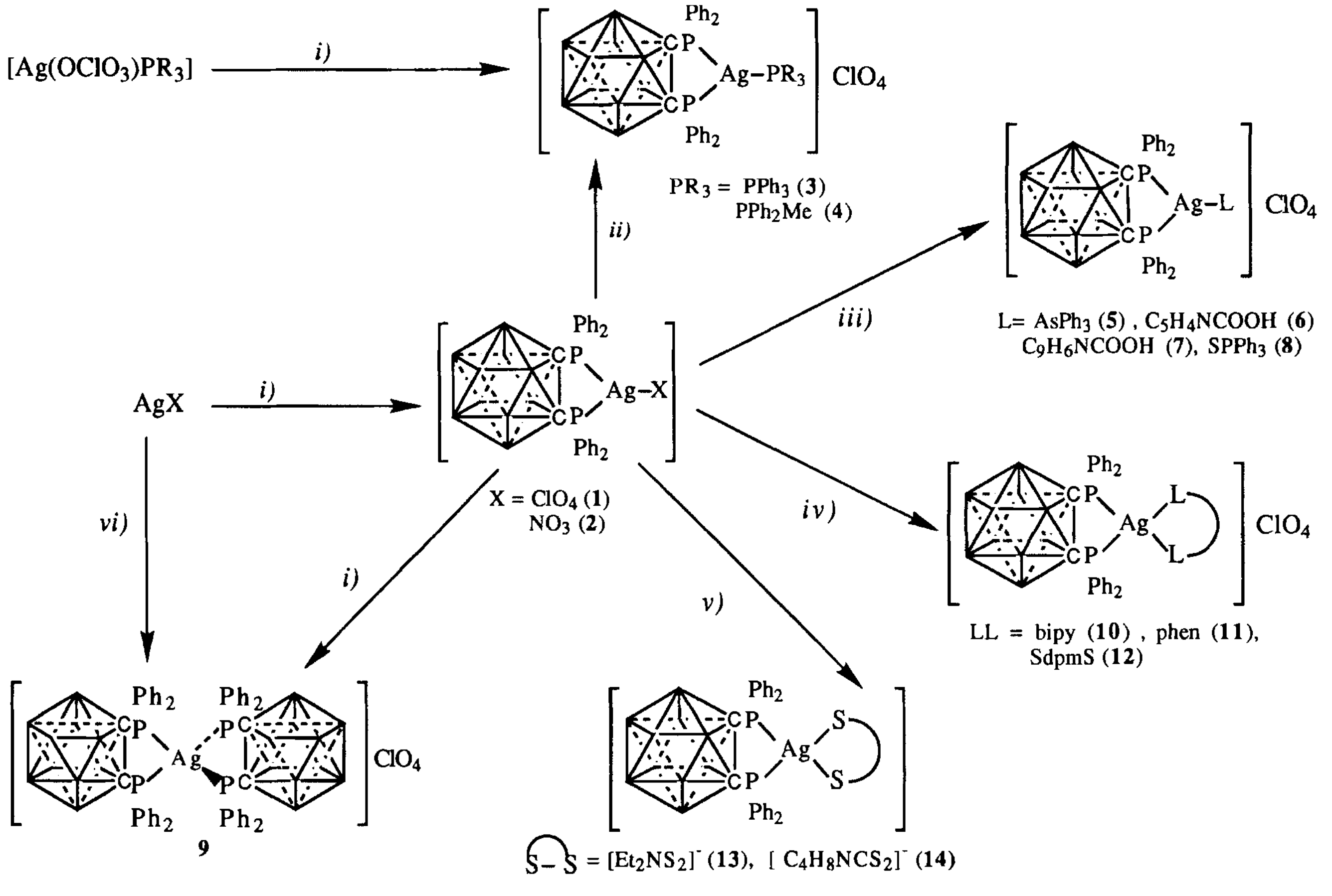
Scheme 1



i) $B_{10}H_{10}C_2(PPh_2)_2$, *ii)* PR_3, *iii)* L, *vi)* L-L, *v)* S-S, *vi)* 2 $B_{10}H_{10}C_2(PPh_2)_2$

Compounds **1**–**14** are air- and moisture-stable solids; all of them are conducting in acetone solution (1:1 electrolytes)[14] with the exception of **13** and **14**, which are neutral.

The complexes **1**–**14** have been characterized by means of elemental analysis, IR and NMR spectroscopy, and by FAB$^+$ mass spectrometry. The NMR-spectroscopic and analytical data are summarized in Tables 1 and 2, respectively.

The IR spectra of all the complexes show bands due to the diphosphane and particularly the normal B–H stretching modes of the *o*-carborane nucleus between 2551 and 2642 cm^{-1} (vs, br). In the complexes **3**–**14** the bands around 1100 (vs, br) and 620 cm^{-1} (s) arise from the ClO_4^- anion (T_d)[15]. Compound **1** shows a coordinated perchlorate anion (C_{3v}) with bands at 1108 (vs, br), 1160 (vs, br), 920 (w), 618 (s), and 615 cm^{-1} (s), while complex

Table 1. $^{31}P\{^1H\}$ NMR data for the complexes[a]

Complexes	δ(P P)	J(Ag-P)[b]	δ(L)	J(Ag-P)	J(PA-PX)
1 $[Ag(OClO_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	17.5(dd)	401.6, 350.6			
2 $[Ag(ONO_2)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	16.0(dm)	359.6			
3 $[Ag(PPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$[c]	21.6(ddd)	279.9, 243.7	13.6(ddt)	549.0, 474.9	63.4
4 $[Ag(PPh_2Me)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$[c]	20.1(ddd)	282.3, 244.5	-3.6(ddt)	558.1, 483.2	64.2
5 $[Ag(AsPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	22.6(dd)	309.8, 267.4			
6 $[Ag(C_5H_4NCOOH)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	20.0(dd)	378.4, 328.4			
7 $[Ag(C_9H_6NCOOH)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	19.7(dd)	368.4, 324.5			
8 $[Ag(SPPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	17.9(dd)	339.3, 293.0	46.5(s)		
9 $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}_2]ClO_4$	12.2(dd)	335.5, 291.8			
10 $[Ag(bipy)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	24.7(dd)	354.2, 317.4			
11 $[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	21.2(dd)	354.2, 307,6			
12 $[Ag\{(SPPh_2)_2CH_2\}\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	15.0(dd)	300.6, 260.3	38.5(s)		
13 $[Ag(S_2CNEt_2)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	15.2(s, br)				
14 $[Ag(S_2CNC_4H_8)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	5.0(s, br)				

[a] Recorded in $[D_6]$acetone; s = singlet, dd = doublet of doublets, ddd = doublet of doublets of doublets, ddt = doublet of doublets of triplets, dm = doublet of multiplets, br = broad. – [b] Coupling constants in Hz, $J(^{109}Ag,P)$ and $J(^{107}Ag,P)$. – [c] Recorded in $CDCl_3$.

2 possesses vibrations at 1400 (vs, br), 1304 (vs, br), and 999 cm^{-1} (s) for $\nu(NO_2)$ (symmetric and asymmetric) and $\nu(NO)$, respectively. The separation of the highest-frequency bands is 96 cm^{-1} which is in agreement with the assignment of the NO_3 as a unidentate ligand[16,17]. For complex **12** there also appears a band at 580 cm^{-1} (s) for the vibration $\nu(P{=}S)$ (cf. 605 cm^{-1} in the free ligand).

The $^{31}P\{^1H\}$-NMR spectra of complexes **1**, **2**, **5**–**14** consist of a doublet of doublets because of the coupling of the equivalent diphosphane phosphorus atoms with both ^{107}Ag and ^{109}Ag nuclei. For some of the complexes (**1**, **6**, **7**, **9**–**12**) the coupling with both nuclei is observed at room temperature, whereas for the others signals with an average coupling constant or a broad singlet appear. For these complexes the spectra were recorded at low temperature. Lability of phosphorus ligands in silver phosphane complexes has previously been discussed[18]. The dithiocarbamate derivatives **13** and **14** show a broad singlet even at −80°C. The absence of ^{31}P-$^{107,109}Ag$ spin-spin coupling indicates rapid ligand exchange even at low temperature. In complexes **8** and **12** the resonances for the phosphorus of the $SPPh_3$ and $(SPPh_2)_2CH_2$ ligands also appear as singlets.

Two different phosphorus environments are also present in compounds **3** and **4**, but now with mutual coupling. An AX_2 system appears for the phosphorus atoms with coupling of A and X with the ^{107}Ag and ^{109}Ag nuclei; thus a doublet of doublets of doublets (see Figure 1) is observed for the X_2 part (diphosphane phosphorus) and a doublet of doublets of triplets for the A part (phosphane phosphorus). The coupling constants of the PR_3 phosphorus with both silver nuclei are bigger than those to the diphosphane phosphorus, the latter being the smallest values in the three- and four-coordinate complexes.

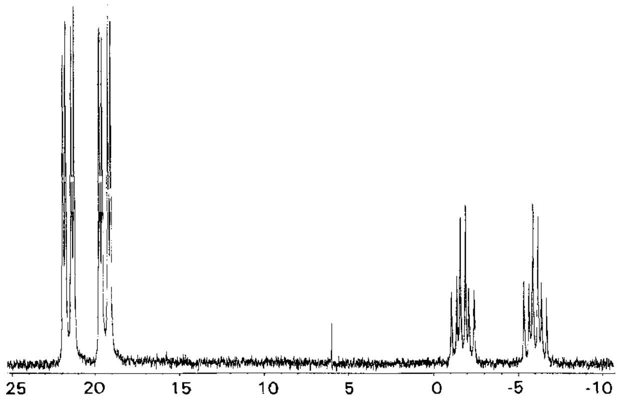


Figure 1. $^{31}P\{^{31}H\}$ NMR spectrum of complex **4** at −55°C

Table 1 shows the ^{31}P-^{109}Ag and ^{31}P-^{107}Ag spin-spin coupling for the complexes. Although the values in tertiary phosphane silver complexes usually increase with decreasing coordination number, not many studies have dealt with bis(tertiary) phosphane complexes. It seems that the coupling constants increase with decreasing Ag−P distance and increasing P−Ag−P angle[6]. In our complexes the values for the three-coordinated compounds are similar to those reported for $[AgXP_2]$ (X = Cl, $SnCl_3$, ClO_4, NO_3; P_2 = 2,11-bis[(diphenylphosphanyl)methyl]benzo[*c*]phenanthrene)[6]. However, the coupling constants in the four-coordinated derivatives are larger than those published for $[Ag\{(PPh_2)_2(CH_2)_2\}_2]^+$ [$^1J_{av}(AgP)$ 248 Hz][7]. Comparison with Ag−P distances and P−Ag−P angles can be only made with compounds **11** and **12**, for which crystal structures have been established. $[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ (**11**) with short Ag−P distances (see X-ray comments below) and a wide P−Ag−P angle possesses a larger coupling constant than complex **12** [$^1J_{av}(AgP)$ 331 vs. 280.4].

The $^2J(PP)$ values are 63.4 and 64.2 Hz for complexes **3** and **4**, respectively. No comparison can be made with other three-coordinated silver complexes but the values are smaller than those in the related gold(I) complexes $[Au(PR_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ [R_3 = Ph_3, Ph_2Me: $^2J(PP)$ = 136.3 Hz][10].

The complexes show the molecular cation/ion peaks in the FAB^+ mass spectra at *m/z* (%) 620 (**1**, 100), 620 (**2**, 100), 882 (**3**, 100), 820 (**4**, 82), 914 (**8**, 83), 1133 (**9**, 20), 776 (**10**, 22), 800 (**11**, 72), 1069 (**12**, 10), 767 (**13**, 37), and 769 (**14**, 11). In the spectra of compounds **5**–**7** the highest peak corresponds to the $[Ag\{(PPh_2)_2C_2B_{10}H_{10})\}]^+$ fragment, which is also present with high intensity in all the complexes.

Crystal Structure Determinations

$[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ (**11**): The molecular structure of the cation of complex **11** is shown in Figure 2. The silver atom is chelated by one diphosphane and one phenanthroline ligand, thus presenting a somewhat distorted tetrahedral geometry. The distortions arise from the restricted bite of the diphosphane [P(1)−Ag−P(2) 89.38(6)°] and the phenanthroline [N(1)−Ag−N(10) 72.7(2)°]. These values compare well with others found in related complexes with bis(diphenylphosphanyl)-*o*-carborane acting as a chelating ligand, e.g. $[Au(PPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ 90.2(1)°[10], and also with those found in the tetrahedral complex $[Ag(dppe)_2]NO_3$[9] with bite angles of 84.5(1) and 83.8(1)°. The dihedral angle between the AgP(1)P(2) and AgN(1)N(2) planes is 79.2°, close to the ideal value of 90°.

The Ag−P bond distances are Ag−P(1) 2.463(2) and Ag−P(2) 2.479(2) Å and may be compared to those in other four-coordinated silver complexes $[Ag(PPh_3)_4]X$ (four independent crystal structure determinations)[19–23] and $[Ag(dppe)_2]NO_3$. The Ag−P bonds in the latter compounds are all longer than the Ag−P bonds in **11**. In $[Ag(PPh_3)_4]X$, with the cation situated on a crystallographic three-fold axis (i.e. two unique Ag−P bond distances), there are one short and three longer Ag−P bonds, X = ClO_4 [1 × 2.650(2), 3 × 2.668(5) Å]. The same trend is observed for $[Ag(dppe)_2]NO_3$ where the Ag−P distances fall in the range 2.488(3)−2.527(3).

The Ag−N bond distances are 2.312(5) and 2.333(5) Å and are of the same order than those found in other tetrahedrally coordinated silver(I) with macrocycles as ligands[23,24].

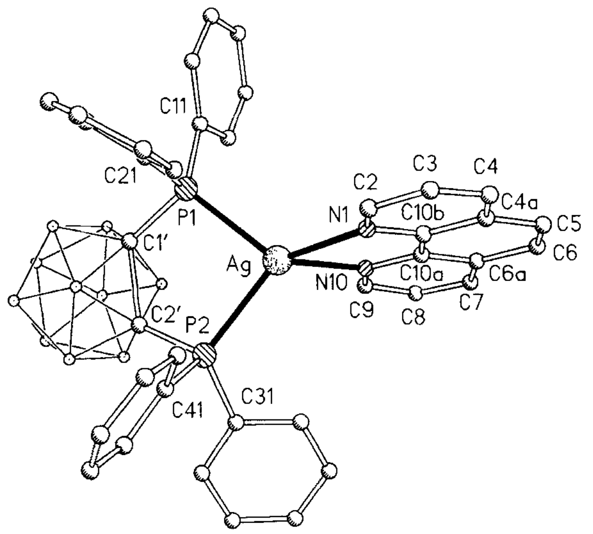


Figure 2. Structure of the cation of **11** in the crystal. H atoms are omitted for clarity. Radii are arbitrary. Selected bond lengths and angles: Ag–N(1) 2.312(5), Ag–N(10) 2.333(5), Ag–P(1) 2.463(2), Ag–P(2) 2.479(2), P(1)–C(1') 1.888(7), P(2)–C(2') 1.884(6) Å; N(1)–Ag–N(10) 72.7(2), N(1)–Ag–P(1) 122.47(1), N(10)–Ag–P(1) 126.21(13), N(1)–Ag–P(2) 134.64(13), N(10)–Ag–P(2) 116.17(14), P(1)–Ag–P(2) 89.38(6)°

[Ag{(SPPh$_2$)$_2$CH$_2$}{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ (**12**): The cation of **12** is shown in Figure 3. The chelating ligands now involve two phosphorus and two sulfur atoms, respectively. The geometry at the silver atom is again slightly distorted tetrahedral, with ligand bite angles P(4)–Ag–P(3) 84.56(5) and S(2)–Ag–S(1) 99.20(5)° that are similar to those in **11**. The dihedral angle between planes AgP(3)P(4) and AgS(1)S(2) is 85.1°.

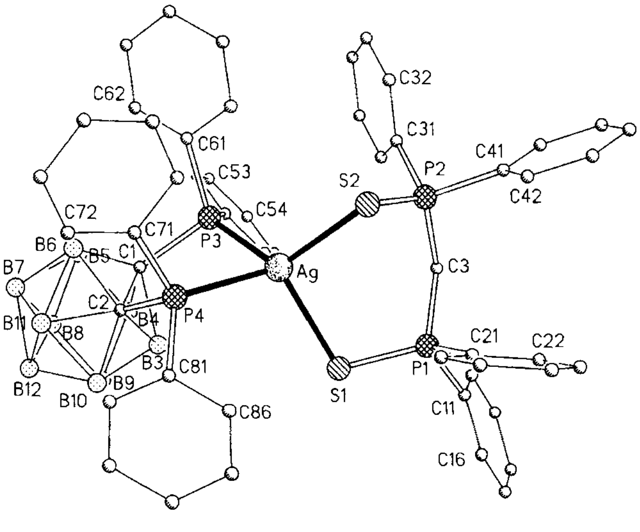


Figure 3. Structure of the cation of **12** in the crystal. H atoms are omitted for clarity. Radii are arbitrary. Selected bond lengths and angles: Ag–P(4) 2.526(2), Ag–P(3) 2.532(2), Ag–S(2) 2.540(2), Ag–S(1) 2.588(2), P(1)–S(1) 1.980(2), P(2)–S(2) 1.983(2), P(1)–C(3) 1.826(5), P(2)–C(3) 1.828(5) Å; P(4)–Ag–P(3) 84.56(5), P(4)–Ag–S(2) 121.10(5), P(3)–Ag–S(2) 122.29(5), P(4)–Ag–S(1) 109.77(5), P(3)–Ag–S(1) 120.74(5), S(2)–Ag–S(1) 99.20(5)°

The Ag–P distances, 2.526(2) and 2.532(2) Å, are longer than in complex **11** and are more similar to those in [Ag(dppe)$_2$]$^+$. The Ag–S bond lengths, 2.540(2) and 2.588(2) Å, can be compared with the values in the complex [Ag$_2${S$_2$C$_2$(CN)$_2$}(PPh$_3$)$_2$] for the silver atom in a tetrahedral geometry, 2.653 and 2.568 Å[25].

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Experimental

IR: Range 4000–200 cm^{-1}, Perkin-Elmer 883, Nujols mulls between polyethylene sheets. – Conductivities: ca. $5 \cdot 10^{-4}$ mol dm^{-3} solutions, Phillips 9509 conductimeter, Λ in Ω^{-1} cm^2 mol^{-1}. – C, H, and N analyses: Perkin-Elmer 240C microanalyser (Table 2). – NMR: Varian XL200 and Varian XL300 Unity spectrometers in CDCl$_3$ or [D$_6$]acetone. Chemical shifts are cited relative to SiMe$_4$ (^{1}H), 85% H$_3$PO$_4$ (external, ^{31}P). – All reactions were carried out at room temperature. Bis(diphenylphosphanyl)-*o*-carborane[26], bis(diphenylphosphanyl)methane disulfide[27], and perchlorato(triphenylphosphane)silver(I)[28] were prepared as described, (methyldiphenylphosphane)perchloratosilver(I) in a similar manner. All other reagents were obtained commercially.

[AgX{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}] [X = ClO$_4$ (**1**), NO$_3$ (**2**)]: To a solution of AgClO$_4$ (0.021 g, 0.1 mmol) in 20 ml of diethyl ether or AgNO$_3$ (0.017 g, 0.1 mmol) in 20 ml of acetone was added (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$ (0.051 g, 0.1 mmol). Upon stirring for 1 h, complex **1** precipitated as a white solid. For complex **2** the solution was concentrated to 10 ml, and addition of 15 ml of diethyl ether yielded a white solid of **2**.

[AgL{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ [L = PPh$_3$ (**3**), PPh$_2$Me (**4**), AsPh$_3$ (**5**), C$_5$H$_4$NCOOH (**6**), C$_9$H$_6$NCOOH (**7**), SPPh$_3$ (**8**)]: To a solution of **1** (0.071 g, 0.1 mmol) in dichloromethane (25 ml) was added PPh$_3$ (0.026 g, 0.1 mmol) or PPh$_2$Me (0.020 g, 0.1 mmol) or AsPh$_3$ (0.030 g, 0.1 mmol) or C$_5$H$_4$NCOOH (0.013 g, 0.1 mmol) or C$_9$H$_6$NCOOH (0.017 g, 0.1 mmol) or SPPh$_3$ (0.029 g, 0.1 mmol) and the reaction mixture stirred for 1 h. The solution was concentrated to ca. 5 ml, and addition of diethyl ether (15 ml) gave complexes **3**–**8** as white or yellow solids.

Complexes **3** and **4** were also prepared by another procedure: To a solution of [Ag(OClO$_3$)PPh$_3$] (0.047 g, 0.1 mmol) or [Ag(OClO$_3$)PPh$_2$Me] (0.041 g, 0.1 mmol) in 20 ml of dichloromethane was added (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$ (0.051 g, 0.1 mmol). The reaction mixture was stirred for 1 h, concentrated to ca. 5 ml, and addition of diethyl ether led to white solids of complexes **3** or **4**.

[Ag(L–L){(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ [L–L = (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$ (**9**), bipy (**10**), phen (**11**), (SPPh$_2$)$_2$CH$_2$ (**12**)]: To a solution of **1** (0.071 g, 0.1 mmol) in 20 ml of dichloromethane was added (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$ (0.051 g, 0.1 mmol) or bipy (0.016 g, 0.1 mmol) or phen (0.018 g, 0.1 mmol) or (SPPh$_2$)$_2$CH$_2$ (0.044 g, 0.1 mmol) and the mixture stirred for 1 h. Concentration of solvent to ca. 5 ml of addition of diethyl ether (15 ml) gave complexes **9**–**12** as white or yellow solids.

Complex **9** was also synthesized by reaction of AgClO$_4$ (0.021 g, 0.1 mmol) and (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$ (0.102 g, 0.2 mmol) in dichloromethane (25 ml) for 1 h.

[Ag(S$_2$CNR$_2$){(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}] [NR$_2$ = NEt$_2$ (**13**), NC$_4$H$_8$ (**14**)]: To a solution of **1** (0.071 g, 0.1 mmol) in dichloromethane (25 ml) was added a solution of NaS$_2$CNEt$_2$ (0.017 g, 0.1 mmol) or NaS$_2$CNC$_4$H$_8$ (0.017 g, 0.1 mmol) in water (10 ml). Separation of the organic layer, evaporation and addition of diethyl ether afforded complexes **13** or **14** as yellow solids.

Crystal Structure Determination of Complex **11**: Crystal data: C$_{38}$H$_{38}$AgB$_{10}$ClN$_2$O$_4$P$_2$, M_r = 900.1, orthorhombic, space group

Table 2. Analytical data and properties for the complexes

Complexes	Yield (%)	Analysis(%)[a] C	H	N	Λ_M[b]	ν(B-H)[c]
1 $[Ag(OClO_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	82	43.28 (43.38)	4.20 (4.20)		123	2594
2 $[Ag(ONO_2)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	69	45.86 (45.76)	4.78 (4.43)	2.14 (2.05)	2	2614
3 $[Ag(PPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	85	53.55 (53.80)	4.43 (4.61)		134	2616
4 $[Ag(PPh_2Me)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	94	51.19 (50.91)	4.81 (4.71)		126	2605
5 $[Ag(AsPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	88	51.89 (51.49)	4.43 (4.41)		127	2600
6 $[Ag(C_5H_4NCOOH)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	88	45.42 (45.59)	4.12 (4.18)		133	2585
7 $[Ag(C_9H_6NCOOH)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	79	48.03 (48.41)	4.34 (4.17)	1.55 (1.56)	121	2582
8 $[Ag(SPPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	75	51.83 (52.10)	4.21 (4.47)		143	2605
9 $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}_2]ClO_4$	68	50.50 (50.67)	5.16 (4.90)		161	2578
10 $[Ag(bipy)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	64	49.07 (49.35)	4.66 (4.37)	3.39 (3.19)	148	2584
11 $[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	78	50.93 (50.67)	4.50 (4.25)	3.11 (3.11)	174	2597
12 $[Ag\{(SPPh_2)_2CH_2\}\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	58	52.18 (52.42)	4.67 (4.48)		111	2629
13 $[Ag(S_2CNEt_2)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	63	47.98 (48.43)	5.55 (5.24)	1.89 (1.82)	11	2590
14 $[Ag(S_2CNC_4H_8)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	68	48.14 (48.56)	4.67 (4.99)	1.80 (1.82)		2586

[a] Calculated values in parentheses. – [b] In acetone, Ω^{-1} cm^2 mol^{-1}. – [c] cm^{-1}.

*Pna*2$_1$, a = 22.219(4), b = 13.154(3), c = 13.750(3) Å, U = 4019(2) Å^3, Z = 4, D_{calc} = 1.488 Mgm^{-3}, $F(000)$ = 1824, λ(Mo-K_α) = 0.71073 Å, μ = 0.69 mm^{-1}, T = −95°C. – *Data collection and reduction:* Single crystals of **11** in the form of colourless prisms were obtained by diffusion of *n*-hexane into a dichloromethane solution of **11**. A prism 0.14 × 0.16 × 0.26 mm was mounted in inert oil (type RS3000, donated by Riedel-de-Haën), transferred to the cold gas stream of a Siemens R3 diffractometer, and used to collect 6450 unique intensities to $2\Theta_{max}$ 50°, which were used for all calculations. An absorption correction based on Ψ scans was applied, with transmission factors 0.83–0.89. Cell constants were refined from setting angles of 50 reflections in the range 2Θ = 20–23°. – *Structure solution and refinement:* The structure was solved by Patterson analysis followed by tangent expansion and subjected to anisotropic full-matrix least-squares refinement on F^2 (program Siemens SHELXL-93)[29]. H atoms were included by using a riding model. The weighting scheme was of the form $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. Refinement proceeded to $R'(F^2)$ 0.104 with a conventional $R(F)$ of 0.040 for 523 parameters and 417 restraints; S = 1.06; maximum Δρ = 0.78 eÅ^{-3}.

Crystal Structure Determination of Complex **12**: Crystal data: $C_{52}H_{54}AgB_{10}Cl_3O_4P_4S_2$, M_r = 1253.27, monoclinic, space group $P2_1/n$, a = 13.286(6), b = 20.762(9), c = 20.658(9) Å, β = 95.93(4)°, U = 5668(4) Å^3, Z = 4, D_{calcd} = 1.469 Mgm^{-3}, $F(000)$ = 2552, λ(Mo-K_α) = 0.71073 Å, μ = 0.729 mm^{-1}, T = −100°C. – *Data collection and reduction:* A total of 12221 intensities were recorded from a pale-yellow prism of 0.60 × 0.60 × 0.20 mm, obtained from liquid diffusion of petroleum ether into a CH_2Cl_2 solution. An absorption correction based on Ψ scans was applied, with transmission factors 0.59–0.63. Merging equivalents gave 10009 (R_{int} 0.041) unique reflections, of which 10005 were used for all calculations. Other details as for complex **11**. – *Structure solution and refinement:* The structure was solved by direct methods and refined as above. Refinement proceeded to $R'(F^2)$ 0.131, conventional $R(F)$ 0.046 for 680 parameters and 450 restraints. S = 1.05; maximum Δρ = 1.3 eÅ^{-3}.

Further details of the structure determinations 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-400594 (**11**), CSD-400595 (**12**).

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