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Synthesis and Characterization of $[Ag_4(\mu_3\text{-}SC_2B_{10}H_{11})_2(\mu\text{-}O_3SCF_3)_2(PPh_3)_4]$: A Silver Complex with a μ_3-Thiolate Ligand

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Introduction

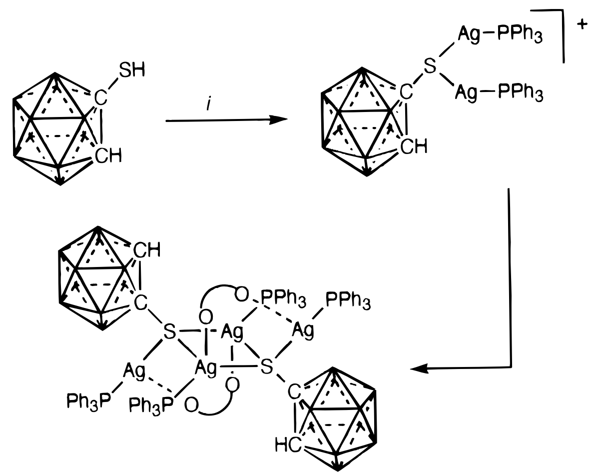
Metal−thiolate coordination chemistry is of fundamental interest in view of the structural diversity displayed and the relevance to the metal sites of a variety of redox-active metalloproteins.[1−3] Despite the fact that silver thiolates have been known for many years, their molecular structures are still of considerable interest mainly because they are incompletely characterized, largely because of difficulties with insolubility and poor crystal quality. One aproach to the problem has been to increase the steric bulk of the substituents,[4−8] which has led to several successful crystal structure determinations. Another reported method is the reaction of silver thiolates with small amounts of bulky and structure-terminating heteroligands, such as tertiary phosphines.[9−11]

Here we report the synthesis of a discrete silver(phosphine) thiolate species synthesized using a double approach, employing (a) the *o*-carborane backbone[12] as a bulky substituent and (b) the complex $[Ag(O_3SCF_3)PPh_3]$ as a source of silver already coordinated by a tertiary phosphine. The resulting thiolate species have a different structure in solution than in the solid state: in solution, the complex is dinuclear, $[Ag_2(SC_2B_{10}H_{11})(CF_3SO_3)(PPh_3)_2]$, with a bridging thiolate ligand, whereas in the solid state, it becomes a tetranuclear derivative with a triply bridging thiolate ligand.

Results and Discussion

The treatment of 1-(SH)-1,2-$C_2B_{10}H_{11}$ with $[Ag(O_3SCF_3)PPh_3]$ and Na_2CO_3 in dichloromethane in 1:1 or 1:2 ratio gives a white solid for which analytical and spectroscopic data indicate the formula $[Ag_2(SC_2B_{10}H_{11})(CF_3SO_3)(PPh_3)_2]$ (see Scheme 1). The IR spectrum displays the υ(B−H) vibrations at 2591 (br, vs) cm^{-1}; the bands arising from the CF_3SO_3 anion appear at $\upsilon(SO_3)$ 1265 (s) cm^{-1}, $\upsilon_{sym}(CF_3)$ 1223 (s) cm^{-1} and $\upsilon_{asym}(CF_3)$ 1159 (s) cm^{-1}.

Scheme 1[a]



[a] Conditions: (i) $2[Ag(O_3SCF_3)(PPh_3)] + Na_2CO_3$; OO = μ-O_3SCF_3.

The ^{1}H NMR spectrum shows the resonances for the phenyl protons between 7.3 and 7.6 ppm. The resonances of the protons bonded to boron are usually very broad, and only a slight protuberance over the baseline is observed, whereas the CH proton appears as a singlet at 3.82 ppm. Integrated signals indicate that there are two PPh_3 groups for each carborane nucleus. The $^{31}P\{^1H\}$ NMR spectrum recorded at room temperature shows a broad signal that sharpens into two doublets when the experiment is carried out at −55 °C. The two doublets arise from equivalent phosphorus atoms coupled with both ^{107}Ag and ^{109}Ag nuclei.

In the positive-ion liquid secondary ion mass spectra (LSIMS) the most intense peaks correspond to the fragments $[Ag(PPh_3)_2]^+$ (m/z = 669, 100%) and $[Ag(PPh_3)]^+$ (m/z = 433, 42%). However, the most significant peak appears at m/z = 916 (5%) and is assigned to the fragment $[Ag_2(SC_2B_{10}H_{11})(PPh_3)_2]^+$. Molecular weight data of **1** in $CHCl_3$ (isopiestic method) gives a value of 1075, which agrees with the calculated 1064 for $[Ag_2(SC_2B_{10}H_{11})(CF_3SO_3)(PPh_3)_2]$.

The molecular structure of the complex **1**, as determined by X-ray diffraction studies, is shown in Figure 1. A selection of bond lengths and angles are collected in Table 1. In contrast to the dinuclear formulation inferred from spectroscopic data, the solid-state structure is unambiguously established as the tetranuclear species $[Ag_4(SC_2B_{10}H_{11})_2(\mu\text{-}O_3SCF_3)_2(PPh_3)_4]$. However, we believe that in solution the compound could indeed be dinuclear; the phosphorus atoms in the solid state are only equivalent in pairs, which is not consistent with the $^{31}P\{^1H\}$ NMR spectrum in solution. Furthermore, the mass spectrum does not present either molecular peak or any fragment arising from the tetranuclear complex and the molecular weight corresponds to the dinuclear species.

Complex **1**, which displays crystallographic inversion symmetry, contains two "$[Ag_2(SC_2B_{10}H_{11})(PPh_3)_2]$" units linked through two further Ag−S bonds; the silver atoms are also chelated by triflate oxygens. The center of the molecule consists of a four-membered ring formed by alternating sulfur and silver atoms S1 and Ag2; the other two silver atoms Ag1 are exocyclically bonded to the thiolate, which thus acts as a triply bridging ligand. This structural framework contrasts with that found in gold complexes of the type $[Au_2(\mu\text{-}SR)(PR_3)_2]^+$, whose molecules are associated through weak Au···Au contacts to form

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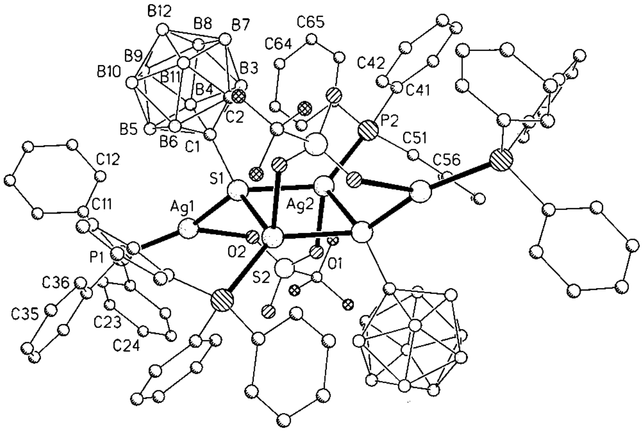

Figure 1. Molecule of complex **1** in the crystal, showing the atom numbering scheme of the asymmetric unit. H atoms are omitted for clarity; radii are arbitrary.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Ag(1)−P(1)	2.3772(13)	Ag(1)−S(1)	2.4252(12)
Ag(1)−O(2)	2.601(4)	Ag(2)−O(1)	2.382(4)
Ag(2)−P(2)	2.3841(14)	Ag(2)−S(1)	2.5467(14)
Ag(2)−S(1) #1	2.6508(14)	S(1)−C(1)	1.796(5)
C(1)−C(2)	1.640(6)	S(2)−O(3)	1.420(5)
S(2)−O(1)	1.421(5)	S(2)−O(2)	1.433(4)

P(1)−Ag(1)−S(1)	157.18(5)	P(1)−Ag(1)−O(2)	109.15(9)
S(1)−Ag(1)−O(2)	93.48(9)	O(1)−Ag(2)−P(2)	111.1(2)
O(1)−Ag(2)−S(1)	91.6(2)	P(2)−Ag(2)−S(1)	133.14(5)
O(1)−Ag(2)−S(1) #1	94.15(12)	P(2)−Ag(2)−S(1) #1	118.72(5)
S(1)−Ag(2)−S(1) #1	98.84(4)	C(1)−S(1)−Ag(1)	103.7(2)
C(1)−S(1)−Ag(2)	114.6(2)	Ag(1)−S(1)−Ag(2)	117.38(5)
C(1)−S(1)−Ag(2) #1	119.0(2)	Ag(1)−S(1)−Ag(2) #1	120.65(5)
Ag(2)−S(1)−Ag(2) #1	81.16(4)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y + 1, -z + 1$.

loose dimers with square Au_4 units.[13−15] It is also different from the dinuclear copper thiolate derivatives reported thus far which have the following stoichiometries $[Cu_2(SR)_2L_4]$ or $[Cu_2(SR)_2(L-L)_2]$;[16−20] as far as we are aware no dinuclear silver thiolate complexes with auxiliary donor ligands have been reported.

The silver centers Ag2 are characterized by a highly distorted tetrahedral geometry, being bonded to two thiolate sulfur atoms S1, one phosphorus P2 (of PPh_3) and one triflate oxygen O1. The angles around Ag2 range from 91.6(2) to 133.14(5)°; the dihedral angle between the planes formed by P2, Ag2, O1 and S1, Ag2, S1# is 87.7°. The other silver atoms Ag1 display a very distorted trigonal planar geometry, being bonded to a thiolate sulfur S1, phosphorus P1 (of PPh_3), and triflate oxygen O2; Ag lies 0.05 Å out of the plane formed by the other three atoms. There are no interactions between the silver atoms linked to the same sulfur atom, the shortest such distance being Ag2−Ag2# 3.382 Å.

The independent Ag−S distances, 2.4252(12), 2.5467(14), and 2.6508(14) Å, are very dissimilar, presumably because of the different geometry found for the two types of silver atoms, trigonal and tetrahedral. The shortest corresponds to the trigonal silver atoms and compares well with those in other related derivatives such as $[Ag_2\{S_2C_2(CN)_2(PPh_3)_4]$,[21] 2.478(7) Å or the shortest distances in $[Ag_6(SC_6H_4Cl)_6(PPh_3)_5]$,[9] 2.407(5)−2.484(4) Å. The other Ag−S bond lengths, 2.5467(14) and 2.6508(14) Å, are similar to those found in tetrahedral silver complexes such as $[AgBr(18S_6)]$[22] ($18S_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) (2.514(1)−2.636(1) Å), $[Ag\{(SPPh_2)_2CH_2\}\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$[23] (2.540(2), 2.588(2) Å), and $[Ag_2\{S_2C_2(CN)_2\}(PPh_3)_4]$[21] (2.568(7), 2.653(7) Å for the silver atom in a tetrahedral geometry) or the shortest found in the related compound $[Ag_6(SC_6H_4Cl)_6(PPh_3)_5]$[9] with triply bridging thiolate ligands ($Ag^{tetra}-S$ distances from 2.593(4) to 2.838(4) Å). It is worth mentioning that the longest Ag−S distance, 2.6508(14) Å, corresponds to the Ag−S bond generated by symmetry. If this is the weakest Ag−S bond, it could explain the ^{31}P NMR results indicating that **1** is dinuclear in solution.

The Ag−P bond distances differ slightly, as the bonds involving the four-coordinate silver atoms are longer, 2.3841(14) Å, than those of the three-coordinate ones, 2.3772(13) Å. Both distances are similar to those found in $[Ag_4Cl_4(PPh_3)_4]$[24] (average 2.379 Å) where silver atoms are tetracoordinated or $[Ag_4Cl_4(dppm)_2]$[25] (2.366(2) Å for Ag tricoordinated, 2.379(2) Å for Ag tetracoordinated), but they are shorter than those found in other silver complexes such as $[Ag(dppf)(PPh_3)]ClO_4$[26] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) (2.4386(13)−2.4870(12) Å) with a trigonal silver center or in tetrahedral silver complexes such as $[Ag(PPh_3)_4]ClO_4$[27] (1 × 2.650(2), 3 × 2.668(5) Å) or $[Ag(dppe)_2]NO_3$[28] (range 2.488(3)−2.527(3) Å) or $[Ag(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$[23] (2.463(2), 2.479(2) Å). This suggests that in **1** the Ag−P bonds are relatively strong.

The Ag2−O1 bond distance of 2.382(4) Å compares well with literature values for tetracoordinate silver complexes;[29−31] the long Ag1−O2 distance of 2.601(4) Å is consistent with a weak bond, as has been found in other silver−triflate species.

Experimental Section

Instrumentation. The infrared spectrum was recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. The conductivity was 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 microanalyzer. The mass spectrum was recorded on a VG Autospec, with the LSIMS

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Table 2. Details of Data Collection and Structure Refinement for Complex **1**

chemical formula	$C_{78}H_{82}Ag_4B_{20}F_6O_6P_4S_4$
crystal habit	colorless tablet
crystal size/mm	0.8 × 0.4 × 0.1
crystal system	triclinic
space group	$P\bar{1}$
a/Å	13.492(2)
b/Å	14.592(3)
c/Å	14.740(3)
α/deg	114.313(10)
β/deg	116.815(10)
γ/deg	90.103(14)
U/Å^3	2296.6(7)
Z	1
D_c/Mg m^{-3}	1.540
M	2129.24
F(000)	1064
T/°C	−100
$2\theta_{max}$/deg	50
μ(Mo $K\alpha$)/mm^{-1}	1.062
no. of reflctns measd	8241
no. of unique reflctns	7671
R_{int}	0.023
R^a (F, $F > 4\sigma(F)$)	0.044
wR^b (F^2, all reflctns)	0.109
no. of reflctns used	7671
no. of params	495
no. of restraints	127
S^c	1.035
max $\Delta\rho$/e Å^{-3}	2.52

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

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) or 85% H_3PO_4 (^{31}P, external).

Materials. The starting material 1-(SH)-1,2-$C_2B_{10}H_{11}$ was prepared by published procedures.[32] [Ag(O_3SCF_3)(PPh_3)] was obtained by reaction of Ag(CF_3SO_3) with PPh_3 in dichloromethane.

Syntheses. [$Ag_4(\mu_3$-$SC_2B_{10}H_{11})_2(\mu$-$O_3SCF_3)_2(PPh_3)_4$]. To a solution of 1-(SH)-1,2-$C_2B_{10}H_{11}$ (0.1 mmol, 0.017 g) in dichloromethane (20 mL) were added [Ag(O_3SCF_3)(PPh_3)] (0.2 mmol, 0.104 g) and excess of Na_2CO_3. The mixture was stirred for 30 min and the excess of sodium carbonate filtered off. The resulting solution was concentrated in vacuo to ca. 5 mL, and the addition of hexane (10 mL) gave complex **1** as a white solid. Yield: 68%. Anal. Calcd for $C_{39}H_{40}Ag_2B_{10}F_3O_3P_2S_2$: C, 44.05; H, 3.8. Found: C, 43.95; H, 3.75. Λ_M 125 Ω^{-1} cm^2 mol^{-1}. NMR ^{31}P{^{1}H} $CDCl_3$, −55 °C (121 MHz, H_3PO_4): 13.7 ppm (2 d, J(^{109}AgP) 701.5, J(^{107}AgP) 607.8 Hz).

Crystal Structure Determination of Complex 1. A colorless tablet of 0.80 × 0.40 × 0.10 mm was mounted in inert oil on a glass fiber and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with a LT-2 attachment. Data were registered using monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å, scan mode ω). Cell constants were refined from setting angles of 61 reflections in the range $2\theta = 7-25°$. An absorption correction based on ψ scans was applied. The structure was solved by Patterson analysis and refined anisotropically (except B and H atoms) on F^2 using the program SHELXL-93.[33] H atoms were included using a riding model. The significant residual electron density is in the heavy atom region. Further details are given in Table 2.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for [$Ag_4(\mu_3$-$SC_2B_{10}H_{11})_2(\mu$-$O_3SCF_3)_2(PPh_3)_4$] is available on the Internet only. Access information is given on any current masthead page.

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