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Notes

Synthesis and ^{109}Ag NMR Studies of Homoleptic Silver(I) Stibines

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Introduction

We recently reported the synthesis and properties of a range of homoleptic copper(I) stibine complexes,[1] in which variable-temperature NMR studies mainly utilizing the ^{63}Cu nucleus were used to confirm the presence of tetrahedral $[Cu(SbR_3)_4]^+$ or $[Cu(L\text{-}L)_2]^+$ (L-L = $R_2Sb(CH_2)_3SbR_2$, R = Me or Ph, etc.) cations in solution. A comparison with related phosphine and arsine complexes $[CuL_4]^+$ (L = PR_3, AsR_3) showed that the tendency to dissociate ligand in solution decreased in the order $PR_3 > AsR_3 > SbR_3$.[1] Here we report our studies of some silver(I) stibines using ^{109}Ag NMR spectroscopy as the major solution probe. Few reports of homoleptic silver(I) stibines have been published,[2,3] although phosphine and arsine analogues are well-known and the tetrahedral cations $[Ag(PPh_3)_4]^+$ and $[Ag(AsPh_3)_4]^+$ have been structurally characterized.[4,5]

Experimental Section

Physical measurements were made as described elsewhere.[1] Silver-109 NMR spectra were recorded at 16.75 MHz[6] and copper-63 NMR at 95.5 MHz on a Bruker AM360 and referenced to 9.1 mol dm^{-3} $AgNO_3$ in D_2O (+47 ppm from the Ag^+ resonance at infinite dilution)[7] and $[Cu(MeCN)_4]^+$ (0 ppm) in MeCN at 300 K, respectively. Molar conductivities are reported for 10^{-3} mol dm^{-3} solutions.

Complexes were made under a dinitrogen atmosphere and the silver(I) complexes stored in sealed containers wrapped in aluminum foil in a freezer.

$[Ag(SbMe_3)_4]BF_4$. A solution of $AgBF_4$ (0.195 g, 1.0 mmol) in acetone (5 mL) was added in the dark to an ice-cold solution of $SbMe_3$ (*ca.* 6 mmol) in diethyl ether (60 mL). The solution was filtered, the solvent removed *in vacuo*, and the white solid placed immediately in the freezer. (0.45 g, 53%). Anal. Calcd for $C_{12}H_{36}AgBF_4Sb_4$: C, 16.7; H, 4.2. Found: C, 16.2; H, 4.2. ^{1}H NMR ($CDCl_3$): δ 1.1 (s). Λ_m (CH_2Cl_2) = 26 Ω^{-1} cm^2 mol^{-1}.

$[Ag(SbEt_3)_4]BF_4$. A solution of $AgBF_4$ (0.194 g, 1.0 mmol) in acetone (5 mL) was added in the dark to ice-cold Et_3Sb (0.84 g, 4.0 mmol) in acetone (15 mL). The solution was stirred for 1 h before removing the solvents *in vacuo*. The white oily solid was washed several times with pentane, and the washings were discarded. The oil was dissolved in dichloromethane (10 mL), and pentane was added until the solution turned cloudy, whereupon the solution was stoppered and placed in the freezer. A white solid formed, which was isolated by filtration and dried *in vacuo*. (0.46 g, 45%). Anal. Calcd for $C_{24}H_{60}AgBF_4Sb_4$: C, 26.2; H, 5.5. Found: C, 26.6; H, 6.0. ^{1}H NMR ($CDCl_3$): δ 1.3 (br). Λ_m (CH_2Cl_2) = 27 Ω^{-1} cm^2 mol^{-1}.

The other complexes were prepared by the method described below.

$[Ag(Me_2Sb(CH_2)_3SbMe_2)_2]BF_4$. A solution of $AgBF_4$ (0.194 g, 1.0 mmol) in acetone (5 mL) was added in the dark to ice-cold $Me_2Sb(CH_2)_3SbMe_2$ (0.7 g, 2.0 mmol) in acetone (10 mL). The solution was stirred for 1 h and filtered before removing the solvent *in vacuo*. The solid was washed with pentane, dried *in vacuo*, and placed immediately in the freezer (0.6 g, 68%). Anal. Calcd for $C_{14}H_{36}AgBF_4Sb_4$: C, 19.0; H, 4.1. Found: C, 18.7; H, 3.7. ^{1}H NMR ($CDCl_3$): δ 1.1 (s) [2H] 1.3−1.7 (m) [H]. FAB mass spectrum (3-NOBA), *m/z*: found M$^+$ 992, 798, 453; calculated for $[Ag_2(L\text{-}L)_2BF_4]^+$ 992, $[Ag(L\text{-}L)_2]^+$ 797, $[Ag(L\text{-}L)]^+$ 453 (based upon ^{109}Ag, ^{121}Sb, ^{10}B).

$[Ag(SbPh_3)_4]BF_4$. Yield: 70%. Anal. Calcd for $C_{72}H_{60}AgBF_4Sb_4$: C, 53.3; H, 3.7. Found: C, 53.3; H, 3.7. Λ_m ($MeNO_2$) = 71 Ω^{-1} cm^2 mol^{-1}.

$[Ag(SbPh_2Me)_4]BF_4$. Yield: 70%. Anal. Calcd for $C_{52}H_{52}AgBF_4Sb_4$: C, 45.9; H, 3.8. Found: C, 45.8; H, 3.1. ^{1}H NMR ($CDCl_3$): δ 1.3 (s) [3H], 7.2−7.6 (m) [10H]. Λ_m ($MeNO_2$) = 74 Ω^{-1} cm^2 mol^{-1}.

$[Ag(SbPhMe_2)_4]BF_4$. Yield: 65%. Anal. Calcd for $C_{32}H_{44}AgBF_4Sb_4$: C, 34.6; H, 4.0. Found: C, 34.6; H, 4.1. ^{1}H NMR ($CDCl_3$): δ 1.1 (s) [6H], 7.2−7.6 (m) [5H]. Λ_m ($MeNO_2$) = 76 Ω^{-1} cm^2 mol^{-1}.

$[Ag\{SbMe_2(o\text{-}C_6H_4Br)\}_4]BF_4$. Yield: 70%. Anal. Calcd for $C_{32}H_{40}AgBBr_4F_4Sb_4$: C, 26.9; H, 2.7. Found: C, 26.8; H, 2.7. ^{1}H NMR (CD_2Cl_2): δ 1.1 (s) [3H], 7.1−7.5 (m) [2H].

$[Ag(Ph_2Sb(CH_2)_3SbPh_2)_2]BF_4$. Yield: 72%. Anal. Calcd for $C_{54}H_{52}AgBF_4Sb_4$: C, 46.9; H, 3.8. Found: C, 47.0; H, 3.7. ^{1}H NMR ($CDCl_3$): δ 2.2 (m) [3H], 7.2−7.4 (m) [10H]. Λ_m ($MeNO_2$) = 72 Ω^{-1} cm^2 mol^{-1}. FAB mass spectrum (3-NOBA), *m/z*: found M$^+$ 1293, 701; calculated for $[Ag(L\text{-}L)_2]^+$ 1293, $[Ag(L\text{-}L)]^+$ 701.

$[Cu(SbPhMe_2)_4]PF_6$. A solution of ligand (0.69 g, 3.0 mmol) in dichloromethane (10 mL) was added to a solution of $[Cu(MeCN)_4]PF_6$ (0.38 g, 0.75 mmol) in dichloromethane (10 mL). The mixture was refluxed for 20 min and cooled, and diethyl ether (50 mL) was added. The solution was reduced in volume to approximately 20 mL. The off-white precipitate formed was isolated by filtration, dried *in vacuo*, and recrystallized from dichloromethane−diethyl ether. Yield: 59%. Anal. Calcd for $C_{32}H_{44}CuF_6PSb_4$: C, 34.1; H, 3.7. Found: C, 34.1; H, 3.9. ^{1}H NMR ($CDCl_3$): δ 1.15 (s) [6H], 7.3−7.4 (m) [5H].

$[Cu(SbPh_2Me)_4]PF_6.CH_2Cl_2$. Yield: 60% Anal. Calcd for $C_{53}H_{54}Cl_2CuF_6PSb_4$: C, 43.7; H, 3.7. Found: C, 44.1; H, 4.0. ^{1}H NMR ($CDCl_3$): δ 1.3 (s) [6H], 5.3 (s) [H], 7.25−7.4 (m) [20H].

$[Cu\{SbMe_2(o\text{-}C_6H_4Br)\}_4]PF_6$. Yield: 65%. Anal. Calcd for $C_{32}H_{40}Br_4CuF_6PSb_4$: C, 26.7; H, 2.8. Found: C, 26.7; H, 3.0. ^{1}H NMR (CD_2Cl_2): δ 1.15 (s) [3H], 7.1−7.5 (m) [2H]

X-ray Structure Determination of $[Ag(SbPh_3)_4]BF_4\cdot CH_2Cl_2$. Suitable air-stable colorless crystals were obtained from CH_2Cl_2−diethyl ether mixtures and mounted directly from the mother liquor in a cold dinitrogen gas stream (150 K) on a Rigaku AFC7S diffractometer. Selected experimental parameters are given in Table 1. Cell dimensions were obtained from 25 carefully centered reflections ($43.1 < 2\theta < 44.9°$). A total of 9555 reflections were recorded ($4 \le 2\theta \le 45°$) using Mo Kα X-rays and a graphite monochromator, and during the data processing, intensities were corrected for decay (1%) using the check reflections and for absorption using ψ-scan data. The structure was solved by direct methods[8] to locate non-H atoms, and at a later stage

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Table 1. Crystallographic Data for $[\text{Ag(SbPh}_3)_4]\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$

mol formula	$C_{72}H_{60}AgBF_4Sb_4\cdot CH_2Cl_2$	T, K	150
fw	1606.94 + 84.93	d(calcd), g cm^{-3}	1.678
space group	$P2_1/c$ (No. 14)	Z	4
a, Å	12.134(2)	λ(Mo Kα), Å	0.710 69
b, Å	23.374(2)	μ, cm^{-1}	20.10
c, Å	23.602(2)	R^a	0.029
β, deg	90.67(1)	$R_w{}^b$	0.027
V, Å^3	6693(1)		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$.

Table 2. ^{109}Ag and ^{63}Cu NMR Data

complex	$\delta(^{109}\text{Ag})^a$	comments
$[\text{Ag(SbMe}_3)_4]\text{BF}_4$	1085	
$[\text{Ag(SbEt}_3)_4]\text{BF}_4$	1031	
$[\text{Ag(SbMe}_2\text{Ph)}_4]\text{BF}_4$	1113	1188 at 180 K
$[\text{Ag(SbMePh}_2)_4]\text{BF}_4$	1119	1185 at 180 K
$[\text{Ag\{SbMe}_2(o\text{-C}_6\text{H}_4\text{Br)\}}_4]\text{BF}_4$	1082	
$[\text{Ag(SbPh}_3)_4]\text{BF}_4$	1166	1193 at 180 K
$[\text{Ag\{Me}_2\text{Sb(CH}_2)_3\text{SbMe}_2\}_2]\text{BF}_4$	1120	
$[\text{Ag(AsPh}_3)_4]\text{BF}_4$	1056	
$[\text{Ag(PPh}_3)_4]\text{BF}_4{}^b$	1124	
$[\text{Cu(SbMe}_2\text{Ph)}_4]\text{PF}_6$	−202 (600)^c	−194 at 185 K
$[\text{Cu(SbMePh}_2)_4]\text{PF}_6$	−242 (1000)^c	−232 at 185 K
$[\text{Cu\{SbMe}_2(o\text{-C}_6\text{H}_4\text{Br)\}}_4]\text{PF}_6$	−190 (2400)^c	−164 (550) at 185 K

[a] In CH_2Cl_2−10% CD_2Cl_2 at 300 K all resonances are singlets. Shifts relative to 9.1 M $AgNO_3$ in H_2O. [b] ^{31}P{^{1}H} NMR: at 300 K, $\delta = +5$ (s); at 180 K, $\delta = +5.75$, two doublets, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 260$ Hz, $^1J(^{107}\text{Ag}-^{31}\text{P}) = 230$ Hz. [c] $\delta(^{63}\text{Cu})$ relative to $[\text{Cu(MeCN)}_4]\text{BF}_4$ in MeCN at 300 K, $w_{1/2}$ in parentheses/Hz.

the methylene chloride of solvation became apparent. Hydrogen atoms were introduced in calculated positions with $B(\text{H}) = 1.2B_{eq}(\text{C})$ where C is the bonded C atom. Full-matrix least squares[8] using 6435 reflections ($I > 3\sigma(I)$) and 766 refined parameters converged to $R = 0.029$. Full listings of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles are given in the Supporting Information.

Results and Discussion

$[\text{AgL}_4]\text{BF}_4$ (L = $SbMe_3$, $SbEt_3$, $SbMe_2Ph$, $SbMePh_2$, $SbPh_3$, $\text{SbMe}_2(o\text{-C}_6\text{H}_4\text{Br})$) and $[\text{Ag\{R}_2\text{Sb(CH}_2)_3\text{SbR}_2\}_2]\text{BF}_4$ (R = Me, Ph) (Table 2) were obtained by reaction of anhydrous $AgBF_4$ with the appropriate ligand in acetone or dichloromethane. All are air-stable white solids, soluble in chlorocarbons, MeCN, and $MeNO_2$. Several of the complexes are light sensitive, darkening slowly in the solid state and more rapidly in solution when exposed to fluorescent laboratory lighting. For the $[\text{Ag(SbR}_3)_4]^+$ cations, FAB mass spectra (3-NOBA matrix) revealed $[\text{Ag(SbR}_3)_n]^+$ (n = 1, 2, 3) but no tetrakis(stibine) ions, similar to the results with the corresponding copper(I) complexes.[1] The FAB spectrum of $[\text{Ag\{Ph}_2\text{Sb(CH}_2)_3\text{SbPh}_2\}_2]\text{BF}_4$ showed $[\text{Ag(L-L)}_n]^+$ (n = 1, 2) ions, while that of $[\text{Ag\{Me}_2\text{Sb(CH}_2)_3\text{SbMe}_2\}_2]\text{BF}_4$ showed similar fragment ions and a significant feature corresponding to $[\text{Ag}_2\text{(L-L)}_2\text{BF}_4]^+$. The presence of the latter suggests that these distibine complexes may be polymeric.

The structure of $[\text{Ag(SbPh}_3)_4]\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$ consists of discrete cations containing the tetrahedrally coordinated Ag ion (Figure 1) as well as the BF_4^- anion and solvate molecule. There is no crystallographic symmetry imposed on the cation, but inspection of the Ag−Sb distances and Sb−Ag−Sb angles (Table 3) shows values close to ideal. The only other Ag−Sb distances reported[9] (2.679(1), 2.711(1) Å) are found in a carborane species and are a little shorter than those in the present compound. Several examples of structurally characterized $[\text{Ag(EPh}_3)_4]^+$ cations (E = P,[4] As[5]) have been reported. The corresponding gold(I) cation $[\text{Au(SbPh}_3)_4]^+$ is known[10] (Au−Sb = 2.647(1)−2.655(1) Å), and the closest copper analogue appears to be $[\text{Cu(SbR}_3)_4]^+$ (R = $p\text{-C}_6\text{H}_4\text{F}$)[3] (Cu−Sb = 2.547(1), 2.556(1) Å).[3]

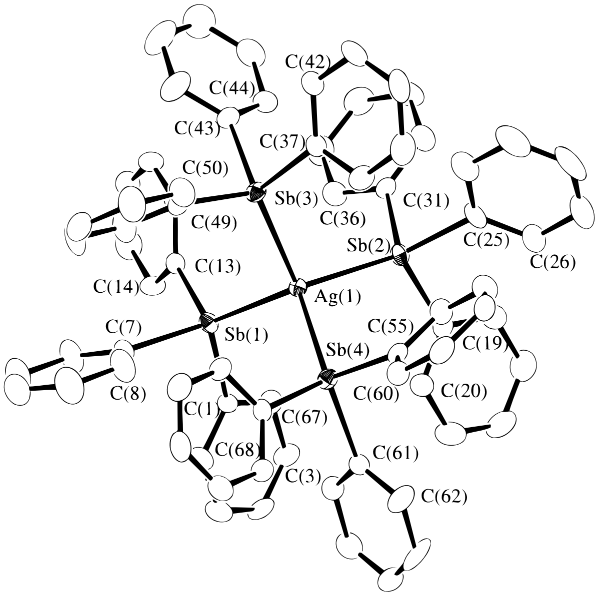

Figure 1. View of the cation in $[\text{Ag(SbPh}_3)_4]\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$ showing the atom-numbering scheme. H atoms have been omitted for clarity, and the thermal ellipsoids are drawn at the 40% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg)

Sb(1)−Ag(1)	2.7297(6)	Sb(3)−Ag(1)	2.7227(6)
Sb(2)−Ag(1)	2.7269(6)	Sb(4)−Ag(1)	2.7200(6)
Sb−C	2.126(6)−2.143(6)	B−F	1.29(1)−1.32(1)
C−C (phenyl)	1.35(1)−1.41(1)		
Sb(1)−Ag(1)−Sb(2)	109.67(2)	Sb(2)−Ag(1)−Sb(3)	110.56(2)
Sb(1)−Ag(1)−Sb(3)	108.76(2)	Sb(2)−Ag(1)−Sb(4)	108.34(2)
Sb(1)−Ag(1)−Sb(4)	110.95(2)	Sb(3)−Ag(1)−Sb(4)	108.56(2)

The ^{109}Ag NMR spectra of the $[\text{Ag(SbR}_3)_4]\text{BF}_4$ complexes in CH_2Cl_2 at 300 K (Table 2) consist of single resonances in the range δ *ca.* 1030−1170. Marked high-frequency shifts of the resonances occur on cooling, an effect observed in other Ag(I) complexes.[6] The resonances were not affected by addition of excess of the corresponding free ligand, showing that dissociation to lower coordination number species was not significant. The complex $[\text{Ag\{Me}_2\text{Sb(CH}_2)_3\text{SbMe}_2\}_2]\text{BF}_4$ had a similar $\delta(^{109}\text{Ag})$ of 1120 consistent with an $AgSb_4$ center, but despite several attempts at different temperatures, a convincing resonance was not observed from CH_2Cl_2 solutions of $[\text{Ag\{Ph}_2\text{Sb(CH}_2)_3\text{SbPh}_2\}_2]\text{BF}_4$. This may be in part due to poor solubility but may also reflect ligand exchange processes (cf. ref 6).

The ^{109}Ag chemical shifts of $[\text{Ag(AsPh}_3)_4]\text{BF}_4$ and $[\text{Ag(PPh}_3)_4]\text{BF}_4$ were unaffected by the presence of excess ligand, although the phosphine complex did not exhibit any $^{107/109}\text{Ag}-^{31}\text{P}$ coupling at room temperature, consistent with fast exchange demonstrated previously by ^{31}P NMR spectroscopy.[11] The ^{1}H NMR spectra at 300 K (Experimental Section) are unexceptional. For complexes of the $\text{SbPh}_n\text{Me}_{3-n}$ (n = 1, 2) ligands, addition of the appropriate free ligand results in a single δ(Me) resonance, consistent with fast exchange. Cooling the solutions to −95 °C failed to resolve separate resonances for bound and

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free ligands, indicating that exchange was fast down to low temperatures. From the ^{1}H and ^{109}Ag NMR results, it seems that while ligand exchange is facile in these d^{10} systems as expected, the equilibrium $[Ag(SbR_3)_4]^+ \rightleftarrows [Ag(SbR_3)_3]^+ + SbR_3$ lies well to the left.

Data on three further examples of $[Cu(SbR_3)_4]PF_6$ complexes are included in Table 2; generally their spectroscopic properties are similar to those reported previously.[1] However, the ^{63}Cu resonance of $[Cu\{SbMe_2(o\text{-}C_6H_4Br)\}_4]PF_6$ was unusually broad at room temperature, but it sharpened both on cooling and in the presence of added stibine. This is the first indication of a tendency to dissociate ligand which is suppressed by excess ligand[1] and may reflect the steric crowding produced by the *o*-bromo substituent. $[Cu(PPh_3)_4]PF_6$ and $[Cu(AsPh_3)_4]PF_6$ both show significant ligand dissociation in solution, in marked contrast both to their silver analogues and to the stibine complexes of both metal ions. This may be attributed largely to steric effects, both the reduced cone angles along the series $PR_3 > AsR_3 > SbR_3$ (fixed R) and the larger radius of Ag(I) compared to Cu(I). However, the weaker donor power of stibine ligands may also reduce the tendency to dissociation from these electron-rich metal centers.[12]

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Supporting Information Available: Listings of complete crystal data and structure determination details (Table S1), non-hydrogen positional and thermal parameters (Tables S2 and S3), hydrogen positional and thermal parameters (Table S4), bond lengths (Table S5), and bond angles (Table S6) (11 pages). Ordering information is given on any current masthead page.

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