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Inorganica Chimica Acta 308 (2000) 37-44

Inorganica Chimica Acta

Synthesis of (phosphine)silver(I) trifluoromethanesulfonate complexes and the molecular structure of di-µ-trifluoromethylsulfonate-(tetrakis-triphenylphosphine)disilver(I)

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Abstract

Reactions of silver trifluoromethanesulfonate (triflate) and equimolar amounts of triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, bis(diphenylphosphino)methane, or 1,1-bis(diphenylphosphino)ethane in either DME or CH_2Cl_2 solution produced the corresponding 1:1 complexes [(L)Ag(I)(SO₃CF₃)] (2–5) in > 80% yields. A related 2:1 complex [(Ph₃P)₂Ag(I)(SO₃CF₃)] (1) was also obtained using 2 equiv. of Ph₃Ph. Both ³¹P NMR variable temperature solution spectra as well as solid state spectra were recorded for the new complexes, and were generally helpful in structural assignments. An X-ray crystallographic study of 1 shows this to be a dimeric complex with bridging triflate ions; the silver atoms having distorted tetrahedral coordination. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Silver complexes; Phosphine complexes; Triflate complexes

1. Introduction

Recent studies in our laboratory have been concerned with the formation and structure of thermally stable organosilver compounds of the type (η - C_3H_4R)Ag(L), where L = a triorganophosphine and R = an electron-withdrawing substituent [1]. (Phosphine)-silver(I) trifluoromethanesulfonate complexes were found to be highly useful intermediates in the formation of these organosilver derivatives. In this paper, we describe the synthesis of a series of new complexes of the type [(L)Ag(I)(SO_3CF_3)], where L = mono- or bidentate phosphine ligands, together with an X-ray structural investigation of the related complex [(Ph₃P)₂Ag(I)(SO₃CF₃)] (1).

2. Experimental

2.1. Materials and general procedures

All operations were carried out under an argon atmosphere using standard Schlenk, vacuum or glovebox techniques. The argon was dried with H_2SO_4 , P_2O_5 , and molecular sieves, and trace oxygen was removed with activated BTS catalyst. Dimethoxyethane (DME) was predried over sodium wire, and both dimethoxyethane and pentane were distilled under argon from Na/K alloy. Dichloromethane (CH₂Cl₂) was dried and distilled under argon from CaH₂. Silver(I) trifluoromethanesulfonate, triphenylphosphine, bis-(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane and 1,1-bis(diphenylphosphino)ethane were purchased from Aldrich Chemical Co.

Proton (¹H) NMR spectra were obtained on Bruker AC-80 or 200 MHz spectrometers, or on Varian XL-200 or XL-300 spectrometers, and were referenced to tetramethylsilane as an internal standard. Solution phosphorus (³¹P) NMR spectra were obtained on either Bruker AC-80, Varian XL-200 or MSL-300 spectrome-

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ters and are referenced to 85% H₃PO₄ in D₂O as an external standard. Solid state ³¹P NMR spectra were obtained on an IBM 200 MHz spectrometer and are referenced to CaHPO₄. Melting points were obtained on a Mel-Temp apparatus from Laboratory Devices, Inc., and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

2.2. Preparation of mono(triphenylphosphine)silver(I) trifluoromethanesulfonate (2)

In a 100 ml round-bottom Schlenk flask were placed silver(I) trifluoromethanesulfonate (1.0 g, 3.9 mmol) and triphenylphosphine (1.0 g, 3.9 mmol). Ca. 40 ml of CH₂Cl₂ was added to the combined solids and the reaction was allowed to stir at 25°C for 12 h. The clear solution was concentrated to half of its original volume under reduced pressure and then ca. 15 ml of pentane was added. The solution was cooled to -20° C to yield 1.8 g (89%) of mono(triphenylphosphine)silver(I) trifluoromethanesulfonate as a white, crystalline air-stable solid, m.p. 148-149°C. ¹H NMR (CDCl₃): δ 7.35-7.62 (m, C₆H₅). ³¹P NMR (75% CH₂Cl₂, 25% CDCl₃, -73° C): δ 15.23 (d, ${}^{1}J(Ag-P) = 774$ Hz). Solid state ³¹P NMR: δ 12.14 (d, ¹*J*(Ag–P) = 793 Hz). Anal. Calc. for 2 C₁₉H₁₅AgF₃O₃PS: C, 43.95; H, 2.91; Ag, 20.78. Found: C, 43.73; H, 2.86; Ag, 20.92%.

2.3. Preparation of bis(triphenylphosphine)silver(I) trifluoromethanesulfonate (1)

Silver(I) trifluoromethanesulfonate (0.51 g, 2.0 mmol) and triphenylphosphine (1.05 g, 4.0 mmol) were added to a 100 ml round bottom Schlenk flask. The flask was cooled to -10° C and ca. 50 ml of DME was added. A white solid immediately precipitated from solution, but the reaction was allowed to stir for 2 h with gradual warming to 25°C. The reaction mixture was filtered and the white solid was extracted with ca. 20 ml of CH₂Cl₂. A small amount of pentane was added to the clear solution and it was cooled to -20° C, producing 1.2 g (77%) of bis(triphenylphosphine)silver(I) trifluoromethanesulfonate as small white air-stable crystals, m.p. 212–214°C. ¹H NMR (CDCl₃): δ 7.20–7.63 (m, C₆H₅). ³¹P NMR (75% CH₂Cl₂, 25% CDCl₃, -73°C): δ 11.64 (dd, ${}^{1}J({}^{107}\text{Ag}-\text{P}) = 487, {}^{1}J({}^{109}\text{Ag}-\text{P}) = 562$ Hz). Solid state ³¹P NMR: δ 10.05 (d, ¹*J*(Ag–P) = 484 Hz). Anal. Calc. for 1 C₃₇H₃₀AgF₃O₃P₂S: C, 56.86; H, 3.87; Ag, 13.80. Found: C, 56.68; H, 4.00; Ag, 13.76%.

2.4. Preparation of [1,2-bis(diphenylphosphino)ethane]silver(I) trifluoromethanesulfonate (3)

In a 100 ml round-bottom Schlenk flask were placed 0.75 g (1.9 mmol) of 1,2-bis(diphenylphosphino)ethane

and 0.49 g (1.9 mmol) of silver(I) trifluoromethanesulfonate. DME (ca. 50 ml) was added to the mixture, and after 30 min of stirring, a white solid precipitated from solution. After filtration, the solid was taken up in ca. 25 ml of CH₂Cl₂ and pentane was then added until the solution turned slightly cloudy. The solution was cooled to -20° C to give 1.1 g (88%) of [1,2-bis(diphenylphosphino)ethane]silver(I) trifluoromethanesulfonate as small white air-stable crystals, m.p 259-261°C. ¹H NMR (CDCl₃): δ 2.64 (4 H, br s, CH₂CH₂), 7.21–7.94 (20 H, m, C₆H₅). ³¹P NMR (75% CH₂Cl₂, 25% CDCl₃, 25°C): δ 6.28 (dd, ${}^{1}J({}^{109}\text{Ag}-\text{P}) = 569, {}^{1}J({}^{107}\text{Ag}-\text{P}) =$ 505 Hz). Solid state ³¹P NMR: δ 9.15 (d, ¹J(Ag-P) = 519 Hz). Anal. Calc. for 3, C₂₇H₂₄AgF₃O₃P₂S: C, 49.48; H, 3.69; Ag, 16.46. Found: C, 49.24; H, 3.69; Ag, 16.43%.

2.5. Preparation of [bis(diphenylphosphino)methane]silver(I) trifluoromethanesulfonate (4)

In a manner similar to the synthesis of 2, bis-(diphenylphosphino)methane (1.0 g, 2.6 mmol), silver(I) trifluoromethanesulfonate (0.67 g, 2.6 mmol) and ca. 40 ml of CH₂Cl₂ were combined in a 100 ml round-bottom Schlenk flask, and the reaction allowed to stir at 25°C for 12 h. Concentration of the clear solution under reduced pressure, addition of ca. 15 ml of pentane and cooling to -20° C produced 1.4 g (84%) of [bis-(diphenylphosphino)methane]silver(I) trifluoromethanesulfonate as a white crystalline solid. The compound was air-stable and had an m.p. of 265-267°C. ¹H NMR (CDCl₃): δ 3.95 (4 H, m, CH₂, ²*J*(¹H-³¹P) = 5 Hz), 7.22-7.62 (40 H, m, C₆H₅). ³¹P NMR (75% CH₂Cl₂, 25% CDCl₃, 25°C): δ 6.86 (m). Solid state ³¹P NMR: δ 1.21 (m). Anal. Calc. for 4, C₂₆H₂₂AgF₃O₃P₂S: C, 48.69; H, 3.46; Ag, 16.82. Found: C, 48.59; H, 3.52; Ag, 16.61%.

2.6. Preparation of [1,1-bis(diphenylphosphino)ethane]silver(I) trifluoromethanesulfonate (5)

In a manner similar to the synthesis of **2**, 1,1-bis-(diphenylphosphino)ethane (0.38 g, 0.95 mmol), silver(I) trifluoromethanesulfonate (0.25 g, 0.95 mmol) and ca. 30 ml of CH₂Cl₂ were combined in a 100 ml round-bottom Schlenk flask, and the reaction was allowed to stir at 25°C for 3 h. After filtration through Celite, pentane was added until the clear solution turned slightly cloudy. The solution was cooled to -20°C to yield 0.56 g (88%) of [1,1-bis(diphenylphosphino)ethane]silver(I) trifluoromethanesulfonate as a white crystalline air-stable solid, m.p. 287–293°C. ¹H NMR (CDCl₃): δ 1.55 (3 H, m, CH₃), 4.84 (1 H, m, CH), 7.22–7.82 (20 H, m, C₆H₅). ³¹P NMR (75% CH₂Cl₂, 25% CDCl₃, 25°C): δ 25.77 (m). Solidstate ³¹P NMR: δ 20.81 (m). *Anal.* Calc. for **5**, $C_{27}H_{24}AgF_{3}O_{3}P_{2}S:$ C, 49.48; H, 3.69; Ag, 16.46. Found: C, 49.36; H, 3.76; Ag, 16.30%.

2.7. Crystallographic data collection and refinement of the structure

Tan-colored crystals of $[(Ph_3P)_2Ag(I)(SO_3CF_3)]$ (1) suitable for X-ray analysis were obtained by recrystallization from solutions of the complex in a CH₂Cl₂– pentane mixture. Diffraction data were obtained on an Enraf-Nonius CAD-4 diffractometer at room temperature using graphite monochromated Mo K α radiation. Unit cell dimensions were obtained from 25 accurately centered reflections in the range 24 < 2 θ < 30°. The reflection intensities were monitored with four standard reflections and there was no significant variation in their intensity over the data collection period. An empirical absorption correction based on Ψ scans was applied to the data. Details of cell parameters and refinement results are given in Table 1.

The positions of the silver atom and the two triphenylphosphine groups were determined by direct methods and the positions of the atoms of the trifluoromethylsulfonate ion were then located from subsequent successive difference Fourier syntheses. The

Table 1

Crystal data and structure refinement results for $\{Ag[P(C_6H_5)_3]_2, (CF_3SO_3)\}_2$

Empirical formula	$Ag_2P_4S_2C_{74}H_{60}O_6F_6$
Formula weight	1563.0
Temperature (K)	293(2)
Wavelength (Å)	0.71073 (Mo Kα)
Crystal system	triclinic
Space group	<i>P</i> 1 (no. 2)
Unit cell dimensions	
a (Å)	12.368(5)
$b(\dot{A})$	12.707(7)
c (Å)	13.309(3)
α (°)	71.93(3)
β (°)	62.57(3)
γ (°)	70.59(4)
$V(Å^3)$	1719.9(12)
D_{calc} (g cm ⁻³)	1.509
Z	1
Absorption coefficient (cm^{-1})	7.92
Absorption correction	Based on Ψ scans
Crystal size (mm)	$0.3 \times 0.45 \times 0.50$ mm
Relative transmission factors	0.74-1.00
Data collection	$\omega/2\theta$
2θ Range (°)	3.0-45.0
Independent reflections	4183
Parameters	410
$R_1^{a}, wR_2^{b} [I \ge 2\sigma(I)]$	0.050, 0.130
R_1^{a} , wR_2^{b} (all data)	0.066, 0.145
Goodness-of-fit	1.108

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$

^b
$$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}.$$

'triflate' ions were found to be coordinated to the silver ions and to act as bridging ligands to centrosymmetrically related silver atoms. In addition, the ions are statistically disordered in two orientations, such that one half 'triflate' is related to its partner by a non-crystallographic mirror plane passing through the two coordinated oxygen atoms and their two trans-related fluorine atoms of the $-CF_3$ groups. In contrast to some other situations, where the $CF_3SO_3^-$ ion is often crystallographically disordered [2], the disorder in this instance was relatively well-defined and fairly readily modeled. Thus, the sulfur and carbon atoms together with the uncoordinated oxygen and its trans-related fluorine atom of each of the two mirror related ions were given population parameters of 0.5 on the basis of the near equality of their thermal parameters. These populations were not varied in the subsequent refinement.

The structure was refined by full-matrix least squares on F^2 using all 4183 independent reflections, with anisotropic thermal parameters assigned to silver, the atoms of the two phosphine ligands and the two coordinated oxygen atoms. The phenyl group hydrogen atoms were included based on a riding model with C–H = 0.95 Å. Atomic scattering factors for all non-hydrogen atoms were taken from International Tables [3], while that given by Stewart et al. was used for hydrogen [4]. Corrections for anomalous dispersion were included in the calculations [5]. All crystallographic calculations were carried out using the SHELXS-86 and SHELXL-93 program packages [6,7].

3. Results and discussion

3.1. Synthesis and characterization of (phosphine)silver(I) trifluoromethane sulfonate complexes

The synthesis of the (phosphine)silver(I) trifluoromethanesulfonate (triflate) complexes could be accomplished using either of two different reaction conditions. By reaction of equimolar (1:1) mixtures of silver triflate and a triorganophosphine at room temperature in DME as the solvent, the desired 1:1 complexes could readily be obtained. Both reagents were soluble in DME, but upon mixing, a white precipitate appeared within minutes. After the reaction mixture was stirred 30 min to 2 h to insure completion, the solution was filtered in an inert atmosphere. The white solid was taken up in a minimum amount of CH_2Cl_2 , pentane was added, and the solution was cooled to $-20^{\circ}C$ to produce the desired complexes (2–5) in > 80%yields:

AgSO₃CF₃ + L
$$\xrightarrow{\text{DME or}}_{\text{CH}_2\text{Cl}_2}$$
 (L)AgSO₃CF₃
(2) L = Ph₃P
(3) L = Ph₂PCH₂CH₂PPh₂

(4) $L = Ph_2PCH_2PPh_2$

(5) $L = (Ph_2P)_2CHCH_3$

An alternate synthetic procedure utilized CH_2Cl_2 as the solvent. By an analogous method, the reaction was allowed to stir for 3–12 h to form a clear solution. Concentration of the solution, addition of a small amount of pentane or hexane, and subsequent crystallization at $-20^{\circ}C$ afforded 2–5 in comparable yields.

In addition to the 1:1 ratio of phosphine to silver complexes, a 2:1 derivative was also prepared in the case of Ph₃P. In a manner similar to the above procedures, the 2:1 complex (1) was prepared in 77% yield:

$$AgSO_3CF_3 + 2Ph_3P \xrightarrow[CH_2Cl_2]{OH} (Ph_3P)_2AgSO_3CF_3$$

All of the complexes 1-5 were air-stable in solution as well as in the solid state. Exposure of 1-5 to light over several days caused the white complexes to turn yellow, indicating a sensitivity to light. The complexes were very soluble in halogenated solvents such as CH_2Cl_2 and $CHCl_3$, and were moderately soluble in more polar solvents such as tetrahydrofuran and toluene.

3.2. ³¹P NMR spectral analysis

The (phosphine)silver(I) triflate complexes synthesized in this study have also been characterized by ³¹P NMR techniques, including variable temperature solution NMR and solid-state NMR. ³¹P NMR is a valuable tool in this regard, since silver has two NMR-active isotopes. ¹⁰⁷Ag and ¹⁰⁹Ag are both spin 1/2 nuclei with high natural abundances of 52% and 48%, respectively. Ag–P coupling often is very broad in phosphine-silver complexes at ambient temperatures in solution due to rapid ligand exchange on the NMR time scale. However, Ag-P coupling can be observed in the solid state and at low temperatures in solution [8-10]. For chelated phosphine ligands, resolution of this coupling can often be observed at temperatures approaching room temperature. There have been a number of reports concerning Ag-P coupling in solution, but little information is currently available on solid state studies of this unique interaction.

For complexes 1 and 2, both variable temperature solution and solid state ³¹P studies were conducted. In the case of 2, the ³¹P NMR solution spectrum at 25°C consisted of a broad singlet, but at -73°C appeared as a doublet with a ¹J(Ag–P) coupling of 774 Hz centered at 15.23 ppm. The solid-state ³¹P NMR spectrum also occurred as a doublet due to ¹J(Ag–P) coupling with a

magnitude of 793 Hz centered at 12.14 ppm. The coupling and chemical shift values were close but not the same as the solution values, since solid state spectra have increased line widths due to dipolar coupling which are not averaged by molecular tumbling [11]. Coupling in these complexes is due to spin–spin coupling between ³¹P and the ¹⁰⁹Ag and ¹⁰⁷Ag isotopes. Individual resolution of phosphine–silver isotope coupling is not apparent in the ³¹P NMR spectra of **2**, and an averaged doublet is therefore observed.

In the case of the 2:1 complex **1**, two doublets were observed in the ³¹P NMR solution spectrum at -73° C. The two doublets were due to the ³¹P resonance being split by each Ag isotope. The magnitude of the coupling was ¹J(¹⁰⁹Ag-P) = 562 and ¹J(¹⁰⁷Ag-P) = 487 Hz, and the pattern was centered at 11.64 ppm. The ratio of these two couplings should be equal to their magnetogyric ratios [11]. For $J(^{109}Ag-^{31}P)/J(^{107}Ag-^{31}P)$, this ratio is 1.15. Experimental results match with theory in this case, since the ratio of 562/487 = 1.15. In the ³¹P solid-state spectrum of **1**, one doublet was observed at 10.05 ppm with ¹J(Ag-P) = 484 Hz. In the solid state, it is often not possible to observe individual resolved ¹⁰⁹Ag-³¹P and ¹⁰⁷Ag-³¹P scalar couplings, since the line widths are so broad.

For complex 3, the spin-spin splitting due to coupling of phosphorus to the individual silver isotopes was observable even at room temperature in the solution spectrum. This result might be anticipated for a chelating ligand such as 1,2-(diphenylphosphino)ethane and in turn suggests that this ligand chelates to a single metal center [12]. The pattern in the ³¹P NMR solution spectrum of 3 was centered at 6.28 ppm, with ¹J(¹⁰⁹Ag-P) = 569 and ¹J(¹⁰⁷Ag-P) = 505 Hz. This ratio of 1.13 is approximately equal to the theoretical value. In the solid-state ³¹P NMR spectrum of 3, one doublet was observed at 9.15 ppm with ¹J(Ag-P) = 519 Hz.

The ³¹P NMR solution spectral patterns for 4 and 5 at 25°C were considerably more complicated than patterns for 1-3 discussed above. This is no doubt due to additional phosphorus-silver couplings, and suggest that 4 and 5 are dimeric or tetrameric in solution. The solid-state ³¹P NMR spectra for both 4 and 5 likewise appeared as broad multiplets.

3.3. Crystallographic study of [(Ph₃P)₂Ag(I)(SO₃CF₃)] (1)

Fig. 1 gives an ORTEP plot of the structure of the complex $[(Ph_3P)_2Ag_2 (SO_3CF_3)_2]$, together with the atom labeling for the asymmetric unit, while Table 2 lists the bond distance and angle data for the coordination geometry about the silver atom. Fig. 2 gives two views of the central portion of the molecule and as may be seen, two triflate anions act as bridging ligands, linking two bis-triphenylphosphine silver units to form



Fig. 1. Perspective drawing of the structure of $\{[(C_6H_5)_3P]_2Ag(CF_3SO_3)\}_2$ (1), giving the atomic labeling scheme. Atoms are represented by thermal ellipsoids at the 50% probability level.

a centrosymmetric dimer of which this central portion forms a quasi-planar eight-membered ring. Fig. 2(B) illustrates the relative conformations of the two 'half' disordered triflate anions. Although these anions might be termed bidentate, the bridging is quite asymmetric, the two silver-oxygen distances differing by 0.2 Å with the angles around the oxygens also differing significantly. Likewise, although the geometry around the silver atom may be thought of as being approximately tetrahedral, the angular deviations from a tetrahedral geometry, together with the differing silver-oxygen distances are rather large. The silver atom is, in fact, fairly close to being coplanar with the two phosphorus atoms and oxygen atom O(1); the sum of the three angles, being 353.4°, so that the geometry is better described as being trigonal pyramidal.

A rather similar '3 + 1' distorted trigonal pyramidal geometry is found for the silver atom in the 1:1 complex of silver nitrate with triphenylphosphine [13], where the nitrate ion acts both as an asymmetrically bonded bidentate ligand to one silver and as an almost

symmetrically bonded bridging ligand between neighboring silver ions, so that the structure is based on polymeric Ag-NO₃-Ag chains. In this complex the trigonal plane is formed by the silver and phosphorus atoms and the two shorter silver-oxygen bridge bonds, the sum of the in-plane angles being 359.8°. The silver-phosphorus distances, averaging 2.430(2) Å are marginally longer than the distances of 2.340(4) to 2.370(5) Å found in the 1:1 phosphine adducts that have been characterized [13-15]. However, together with the angle P(1)-Ag-P(2), they are very comparable to the Ag-P distances found in the stoichiometrically equivalent trimethylphosphite complex, {[P(OMe)₃]₄- $Ag_2(NO_3)_2$, [16], in which the nitrate ions form symmetrical bridges to the silver atoms, each through a single oxygen atom.

The geometries of the two 'half' triflate ligands are as expected, apart from the angles involving the coordinated oxygen atoms, O(1)-S(1)-O(2) and O(1)-S(1)'-O(2), which at 120.1(5) and 123.1(5)°, respectively, are much larger than expected and signifi-

Table 2

Selected bond distances and angles for $[Ag(CF_3SO_3)(P(C_6H_5)_3)_2]_2$

Ag-P(1)	2.429(2)
Ag-P(2)	2.431(2)
Ag-O(1)	2.387(6)
Ag–O(2)	2.584(5)
S(1)-O(1)	1.383(7)
S(1)–O(2)	1.389(7)
S(1)'-O(1)	1.369(7)
S(1)'-O(2)	1.363(7)
P(1)-Ag-P(2)	130.4(1)
O(1)-Ag-O(2)	92.8(2)
P(1)-Ag-O(1)	115.9(2)
P(1)-Ag-O(2)	104.6(2)
P(2)-Ag-O(1)	106.1(2)
P(2)-Ag-O(2)	98.2(2)
Ag-O(1)-S(1)	136.1(4)
Ag-O(2)-S(1)	151.9(5)
Ag-O(1)-S(1)'	138.1(4)
Ag–O(2)–S(1)'	179.3(5)
O(1)-S(1)-O(2)	120.1(5)
O(1)–S(1)′–O(2)	123.1(5)

cantly larger than the remaining four O–S–O angles. However as noted earlier, the refinement model treated the two half anions as sharing atoms O(1) and O(2), so that it is quite possible that the refined positions for these two atoms are the average for two unresolved sites having a rather small positional separation. The rather large *U*-tensor values obtained for these atoms supports this conclusion. Because of large least squares correlation effects it was not possible to refine the positions of two separate sites for each oxygen atom.

Although this disorder possibility introduces additional uncertainty into the observed Ag–O distances, the short bond at 2.387(6) Å falls in the range of values of 2.35–2.46 Å, [13,14,16], which are normally observed, while the longer bond at 2.584(5) Å is nearly identical with that observed for a unidentate triflate ion ligand in the polymeric complex $[Ag_2(triflate)_2-(NCC_6H_4CN)_2(H_2O)]_n$, [17].

For the 1:1 complex with triphenylphosphine, i.e. 2, we also propose a dimeric structure, $[Ph_3P-Ag-(CF_3SO_3)-Ag-PPh_3]$ with double triflate bridges, and in which the silver atoms are three coordinate, or distorted four coordinate, if the triflate ion ligand adopt both a bidentate chelating and a bridging role similar to that found for the nitrate analogue noted above [13].

A few other silver, [18,19] and mixed silver-platinum complexes [20,21], containing triflate ion ligands have been structurally characterized and apart from the one noted above, the ion generally acts as a μ -2 or μ -3 bridging ligand. For example, in the complex, [Ag(1,4thioxane)₂(CF₃SO₃)], [18], the triflate ion bridges neighboring silver atoms, (Ag–O; 2.59(1) and 2.47(1) Å), while in the complex ion [Ag₆(triphos)₄(CF₃SO₃)₄]²⁺, where 'triphos' is a tridentate tripodal phosphine ligand, the triflate ions adopts a μ -3 bridging mode, sitting above alternate faces of the Ag₆ octahedron [19].



Fig. 2. (A) Perspective view showing the coordination polyhedron of the silver atoms and the conformation of the eight-membered ring in 1. (B) View of the central portion of the structure of 1, showing the two alternative orientations adopted by the disordered triflate ions.

In contrast to the situation for unidentate phosphines, a rather larger number of structures of silver complexes containing bidentate phosphines have been determined, and in the case where the phosphine ligand chelates the silver atom, dimeric complexes of the type [diphos-Ag-X₂-Ag-diphos] in which the two anions, X act as bridging ligands, between the silver phosphine units, are invariably formed [22-25]. Such species have been crystallographically characterized for symmetric phosphines, giving 6-membered, [22], 7-membered, [23], eight-membered, [24] and 9-membered [25] chelate rings, with the anion X, being variously NO_3^- , Cl^- and ClO_4^{-} . On the basis of these structural data, and our ³¹P NMR results, we therefore believe that complex **3**, formed with the symmetric ligand 1.2-bis(diphenylphosphino)ethane, (DPPE), has a similar dimeric structure, [DPPE-Ag-(CF₃SO₃)-Ag-DPPE], with two triflate bridges, and containing four coordinate silver.

With regard to the remaining two complexes, **4** and **5**, containing, respectively, the bidentate phosphine ligands, bis(diphenylphosphino)methane, DPPM, and 1,1-bis(diphenylphosphino)ethane, DPMMe, the more complicated ³¹P NMR spectra on the other hand, suggest oligomeric structures in which the phosphines act as bridging ligands to pairs of silver atoms, so giving more than one type of Ag–P coupling. Both these ligands would give rise to strained 4-membered rings if chelated to one metal center, in contrast to the situation for DPPE, which forms 5-membered chelate rings with one metal center.

Such a ligand bridged structure has been characterized for the dimeric silver nitrate complex, [ONO₂-Ag(DPPM)₂Ag–O₂NO], [26], the phosphines forming a double bridge to the two silver atoms which have a distorted tetrahedral geometry with bidentate nitrate ions, and for the complex of silver bromide with a related phosphine, bis(dimethylphosphino) methane DM-PM, namely [Br-Ag(DMPM)₂Ag-Br] [27]. In addition, DPPM forms a similar ligand bridged structure in the dimeric complex bis(carbomethoxycyclopentadienyl)bis[bis(diphenylphosphino)methane]disilver, (C₅H₄CO- OCH_3)₂(DPPM)₂Ag₂, [28], while in the complex with silver acetate, both DPPM molecules and acetate ions act as bridging ligands to give, in the solid, a tetrameric structure of stoichiometry [Ag₂(CH₃COO)₂DPPM]₂. 2H₂O [29]. Again each silver atom exhibits an irregular four coordinate geometry.

On the basis of these structural results, we therefore believe it most likely that **4** and **5**, [Ag(DPPM)-(CF₃SO₃)] and [Ag(DPMMe)(CF₃SO₃)], also contain similar dimeric phosphine bridged units, Ag₂-(DPPM)₂²⁺ and Ag₂(DPMMe)₂²⁺, and that the triflate ions either function as unidentate, or as bidentate ligands to one silver atom, in each instance giving an overall dimer, [Ag₂(diphos)₂(triflate)₂], or that they act as bridging ligands to link [Ag₂(diphos)₂]²⁺ dimer units into overall tetrameric molecules or perhaps polymeric species with alternating triflate and phosphine double bridges.

4. Supplementary material

A listing of observed and calculated structure factors (19 pages) and complete tables of crystal data, positional and anisotropic thermal parameters, coordinates for hydrogen atoms, as well as complete tables of bond distances and bond angles are available from one of the authors (J.S.W) on request.

Acknowledgements

The authors thank Dr A. Chandrasekaran for his help with carrying out the crystal structure refinements and Dr Charles Dickinson for his invaluable assistance in obtaining the solid state ³¹P NMR spectra.

References

- L. Lettko, Ph.D. Dissertation, University of Massachusetts, Amherst, 1995.
- [2] J.G. Haasnoot, J. Reedijk, W. Vreugdenhil, J.S. Wood, Inorg. Chem. Acta 167 (1990) 109.
- [3] International Tables for X-ray Crystallography, vol. 4, Kynoch Press, Birmingham, UK, 1974.
- [4] R.F. Stewart, R.F. Davidson, W.T. Simpson, J. Chem. Phys. 42 (1965) 3175.
- [5] D.T. Cromer, D.J. Liberman, J. Chem. Phys. 53 (1970) 1891.
- [6] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
- [7] G.M. Sheldrick, SHELXL-93. Program for crystal structure refinement, University of Göttingen, Germany, 1993.
- [8] S.M. Socal, R.A. Jacobson, J.G. Verkade, Inorg. Chem. 23 (1984) 88.
- [9] E.L. Muetterties, C.W. Alegranti, J. Am. Chem. Soc. 94 (1972) 6386.
- [10] E.C. Alyea, J. Malito, J.H. Nelson, Inorg. Chem. 26 (1987) 4294.
- [11] E.A.V. Ebsworth, D.W.H. Rankin, S. Cradock, Structural Methods in Inorganic Chemistry, 2nd ed., Blackwell Scientific Publications, New York, 1992, p. 97.
- [12] S.J. Berners Price, C. Brevard, A. Pagelot, P.J. Sadler, Inorg. Chem. 24 (1985) 4278.
- [13] R.A. Stein, C. Knobler, Inorg. Chem. 16 (1977) 242.
- [14] A.F.M.J. van der Ploegg, G. van Koten, A.L. Spek, Inorg. Chem. 18 (1979) 1052.
- [15] B.K. Teo, J.C. Calabrese, Inorg. Chem. 15 (1976) 2474.
- [16] J.H. Meiners, J.C. Clardy, J.G. Verkade, Inorg. Chem. 14 (1975) 632.
- [17] D. Venkataraman, S. Lee, J.S. Moore, G.B. Gardner, A.C. Covey, Acta Crystallogr., Sect. C 52 (1996) 2416.
- [18] H.A. Bucholz, G.K. Surya Prakash, J.F.S. Vaughan, R.S. Bau, G.A. Olan, Inorg. Chem. 35 (1996) 4076.
- [19] S.L. James, D.M.P. Mingos, A.J.P. White, D.J. Williams, J. Chem. Soc., Chem. Commun. (1998) 2323.

- [20] T. Yamaguchi, F. Yamazaki, T. Ito, J. Chem. Soc., Dalton Trans. (1999) 273.
- [21] S. Schlecht, K. Dehnicke, J. Magull, D. Fenske, Angew. Chem., Int. Ed. Engl. 36 (1997) 1994.
- [22] E. Tiekink, Acta Crystallogr., Sect. C 46 (1990) 1933.
- [23] F. Caruso, M. Camalli, H. Rimml, L.M. Venanzi, Inorg. Chem. 34 (1995) 673.
- [24] A. Cassel, Acta Crystallogr., Sect. B 32 (1976) 2521.
- [25] S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, M. Munakata, Inorg. Chem. 34 (1995) 1455.
- [26] D.M. Ho, R. Bau, Inorg. Chem. 22 (1983) 4073.
- [27] D. Perreault, M. Drowin, A. Michel, V.M. Miskowski, W.P. Schaefer, Inorg. Chem. 31 (1992) 695.
- [28] L. Lettko, M.D. Rausch, R.O. Day, unpublished results.
- [29] S.P. Neo, Z.-Y. Zhou, T.C.W. Mak, T.S.A. Hor, Inorg. Chem. 34 (1995) 520.