Inorganica Chimica Acta, 59 (1982) 203–206

A Reinvestigation of some Triphenylphosphine–Silver Halide Complexes and their Reaction with Stannous Chloride: ^{119m}Sn Mössbauer and ^{31}P FT NMR Studies

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Received September 15, 1981

Silver chloride reacts with triphenylphosphine to form either $Ag(PPh_3)_2Cl$ or $Ag(PPh_3)_3Cl$, depending upon the solvent, whereas silver bromide and iodide afford the tris(triphenylphosphine)silver(I) halides. The reactions of these silver–phosphine–halide complexes with anhydrous stannous halides are investigated and the structures of the isolated complexes, both in the solid state and in solution, are discussed in terms of their ^{31}P NMR and ^{119m}Sn Mössbauer spectra and their molar conductivities.

Introduction

Stannous chloride finds applications in photography as a reduction sensitiser for silver halide emulsions [1, 2]. In the course of our studies into the possible use of other inorganic tin salts in the photographic field, we have investigated the synthesis of compounds containing both silver and tin. Examples of these derivatives in the literature are rare and those previously reported include $Ag(PPh_3)_3SnCl_3$ [3], Ag_2BaSnS_4 [4], $AgInSnS_4$ [5] and the intermetallic compound, Ag_3Sn [6]. In view of the reducing properties of the triphenylphosphine ligand [7], it was of interest to reinvestigate the preparation of $Ag(PPh_3)_3SnCl_3$ [3] and to study the reactions of various triphenylphosphine–silver(I) halide complexes with stannous halides.

Experimental

Chlorobis(triphenylphosphine)silver(I)

Freshly prepared silver chloride (1.43 g, 10 mmol) was suspended in chloroform (150 ml), and, with stirring, a solution of triphenylphosphine (10.97 g, 40 mmol) in the same solvent was added dropwise. The mixture was stirred for 1 h at room temperature, followed by filtration and addition of pentane to the filtrate until the solution turned cloudy. On cooling, the product separated as white crystals, which were filtered off, washed with pentane and dried *in vacuo*.

Chlorotris(triphenylphosphine)silver(I)

This was prepared using the above procedure, but with dichloromethane employed as solvent. The product was obtained on addition of pentane or hexane as a white, highly crystalline solid.

Tris(triphenylphosphine)trichlorostanniosilver(I)

Anhydrous stannous chloride (0.81 g, 4.3 mmol) was added to a solution of chlorotris(triphenylphosphine)silver(I) (4 g, 4.3 mmol) in dichloromethane (30 ml) and the suspension was stirred for 1 h at room temperature. Acetone (50 ml) was added to the resulting clear solution, which was then concentrated in volume using a rotary evaporator. The product separated as white crystals, and these were dried *in vacuo*.

$Ag(PPh_3)_4^+OH^-\cdot(Cl_3SnOH.\ H_2O)_2$

Chlorobis(triphenylphopshine)silver(I) (0.5 g, 0.75 mmol) was dissolved in hot methanol and, to the resulting clear solution, anhydrous stannous chloride (0.14 g, 0.74 mmol) in methanol was added. A white crystalline precipitate of the product formed immediately and, on cooling, this was filtered off and dried *in vacuo*.

Bromo- and iodo-tris(triphenylphosphine)silver(I)

These complexes were prepared by a route similar to that used to prepare the chloro-analogue and, in

0020-1693/82/0000-0000/$02.75

TABLE I. Analytical and Physical Data for the Complexes.

Compound	M. Pt. (°C)	Analyses %[a]				
		C	H	P	Hal.	Ag
$Ag\{PPh_3\}_2Cl$	184–186	64.38(64.71)	4.91(4.49)	8.57(9.29)	4.52(5.31)	16.7(16.17)
$Ag\{PPh_3\}_3Cl$	185–187	69.68(69.71)	4.78(4.84)	10.07(10.00)	4.19(3.82)	10.8(11.62)
$Ag\{PPh_3\}_3Br$	158–160	66.25(66.52)	4.79(4.62)	9.52(9.54)	7.70(8.21)	10.9(11.08)
$Ag\{PPh_3\}_3I$	168–169 (168)[b]	63.42(63.80)	4.84(4.40)	9.03(9.13)	12.09(12.43)	10.5(10.57)
$Ag\{PPh_3\}_3SnCl_3$	194–196 (194–6)[d]	58.06(57.88)	4.32(4.02)	7.73(8.30)	8.89(9.51)	9.6(9.64)[c]
$Ag(PPh_3)_4^+OH^-\cdot(Cl_3SnOH\cdot H_2O)_2$	215–218	51.05(51.00)	3.99(3.96)	6.66(7.32)	11.98(12.57)	6.4(6.37)[e]

[a] Calcd. values in parentheses. [b] F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, *95*, 201 (1965). [c] Sn 9.8(10.63). [d] J. A. Dilts and M. P. Johnson, *Inorg. Chem.*, *5*, 2079 (1966). [e] Sn 13.9(14.05).

this case, dichloromethane or chloroform were suitable solvents.

The melting points and analytical data for the complexes are shown in Table I.

Conductivity data were obtained using a Wayne-Kerr bridge for solutions of the compounds in nitromethane or dichloromethane. Mössbauer spectra were obtained at 80 K using a constant acceleration microprocessor Mössbauer spectrometer as described previously [8]. The experimental error in the isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters is ± 0.05 mm s^{-1}.

Proton noise decoupled ^{31}P NMR spectra were recorded at 40.48 MHz, using a deuterium lock to 10–20% internal CD_2Cl_2, on a JEOL PFT-100 spectrometer. ^{31}P chemical shifts, $\delta(^{31}P)$, are reported with respect to external 85% H_3PO_4 and those to high field are negative in sign.

TABLE II. ^{119m}Sn Mössbauer Parameters (mm s^{-1}) for the Complexes.

Complex	δ[a]	ΔE_Q
$Ag(PPh_3)_3SnCl_3$	2.61 (2.54)[b] (2.54)[c] (1.71)[d]	1.67 (1.69)[b] (1.70)[c] d
$Ag(PPh_3)_4^+OH^-\cdot(SnCl_3OH\cdot H_2O)_2$	0.30	0

[a] Relative to $BaSnO_3$. [b] R. V. Parish and P. J. Rowbotham, *J. Chem. Soc. Dalton Trans.*, 37 (1973). [c] M. J. Mays and P. L. Sears, *J. Chem. Soc. Dalton Trans.*, 2254 (1974). [d] P. A. Grutsch, M. V. Zeller and T. P. Fehlner, *Inorg. Chem.*, *12*, 1431 (1973) (ΔE_Q not quoted).

Results and Discussion

$Ag(PPh_3)_3SnCl_3$ was first synthesised by Dilts and Johnson [3] by the reaction of $SnCl_2\cdot 2H_2O$ with $Ag(PPh_3)_3Cl$ in acetone at room temperature, but, in a later paper, Parish and Rowbotham were unable to obtain the complex by this method and achieved its preparation by the reaction of $SnCl_2$ with $Ag(PPh_3)_3Cl$ in dichloromethane [9]. In Dilts' synthesis [3], the $Ag(PPh_3)_3Cl$ starting material was obtained using the method of Cariati and Naldini [10], in which silver chloride was stirred with triphenylphosphine, in a 1:4 molar ratio, in chloroform. However, Muetterties and his co-workers claim [11] that this route [10] gives a chloroform solvate, $Ag(PPh_3)_3Cl\cdot 5/3CHCl_3$, m.p. 178–180°. We find that Cariati and Naldini's method [10] furnishes $Ag(PPh_3)_2Cl$ (Table I), regardless of whether chloroform, toluene, methanol or acetonitrile are used as solvents whereas, in dichloromethane, the tris(triphenylphosphine)silver(I) halide complexes are formed in good yield:

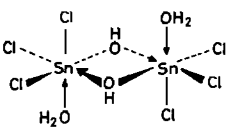
$$AgX + 4PPh_3 \xrightarrow[X\,=\,Cl,\,Br\text{ or }I]{CH_2Cl_2} Ag(PPh_3)_3X + PPh_3$$

$Ag(PPh_3)_3Cl$ reacts smoothly with anhydrous stannous chloride in dichloromethane [9] to form $Ag(PPh_3)_3SnCl_3$, but our attempts to prepare the analogous bromo- and iodo-tin complexes by this route were unsuccessful. The reaction of equimolar amounts of $Ag(PPh_3)_2Cl$ and $SnCl_2$ in hot methanol gave a novel crystalline product, $Ag(PPh_3)_4^+OH^-\cdot(Cl_3SnOH, H_2O)_2$, which showed a single peak in the ^{119m}Sn Mössbauer spectrum in the tin(IV) region (Table II). Dimeric species, $(Cl_3SnOH. H_2O)_2$, containing octahedral tin(IV) atoms, as illustrated

TABLE III. ^{31}P NMR Data for the Complexes.[a]

Complex	Chemical shifts, $\delta(^{31}P)$[b]		Coupling Constants[c]	
	Room temp.	–80 °C	$^1J(^{109}Ag–^{31}P)$	$^1J(^{107}Ag–^{31}P)$
$Ag(PPh_3)_2Cl$	3.7	3.3	316	282
$Ag(PPh_3)_3Cl$	3.4	3.0	318	277
$Ag(PPh_3)_3SnCl_3$	8.4	8.3	347[d]	300[d]
		5.9	258[e]	223[e]
$Ag(PPh_3)_4^+OH^- \cdot (SnCl_3OH \cdot H_2O)_2$	8.9	5.9	261[d]	221[d]
		9.7	336[e]	300[e]

[a] In CH_2Cl_2 [b] ±0.1 p.p.m. [c] ±2 Hz. [d] Major species. [e] Minor species.



are likely to be present in aged solutions of stannous chloride and are known to form adducts with Lewis base molecules in which the latter are not directly coordinated to tin [12]. The isomer shift value for $Ag(PPh_3)_4^+OH^- \cdot (Cl_3SnOH.\ H_2O)_2$ falls between that of $Sn(OH)_6^{2-}$ (–0.07 mm s^{-1}) and $SnCl_6^{2-}$ (0.50 mm s^{-1}) [13]. (See Note added in proof).

The Mössbauer parameters for $Ag(PPh_3)_3SnCl_3$ are in good agreement with the literature values (Table II) and indicate that the complex does not contain isolated $SnCl_3^-$ ions [9]. An X-ray study is currently in progress and the results will be reported in a subsequent paper.

Because of the kinetic lability of the silver–phosphorus bond in silver–phosphine complexes, solution studies give no information about structure in solution or composition at ambient temperatures [14]. All silver–phosphine complexes show an averaged ^{31}P chemical shift that is temperature dependent. However, at lower temperatures (*ca.* –60 to –80 °C), exchange processes are significantly reduced and it is possible to study coupling interactions between phosphorus (^{31}P, spin ½) and silver (^{107}Ag and ^{109}Ag, spin ½). It was therefore of interest to study the ^{31}P NMR spectra of the phosphine–silver–tin complexes in solution at low temperatures and to compare them with the related spectra of the starting phosphine-silver halide complexes. The ^{31}P NMR data are presented in Table III.

Consistent with earlier work on tri(*p*-tolyl)phosphine–silver(I) complexes [14], all of the products show a single time-averaged resonance at room temperature, and coupling interactions are absent. Only on cooling to –80 °C does silver–phosphorus coupling become observable. Coupling constant data for the complex $Ag(PPh_3)_3Cl$ indicates that it is dissociated, probably to $Ag(PPh_3)_2Cl$, containing sp^2 hybridised silver (for which the theoretical coupling constant, $^1J(^{107}Ag–^{31}P)$, is 303 Hz [14]) and conductivity measurements at room temperature in dichloromethane suggest that $Ag(PPh_3)_2Cl$ is non-ionic. X-ray studies have shown [15] that, in the solid state, $Ag(PPh_3)_2Cl$ is associated into a dimer, with distorted tetrahedral silver atoms.

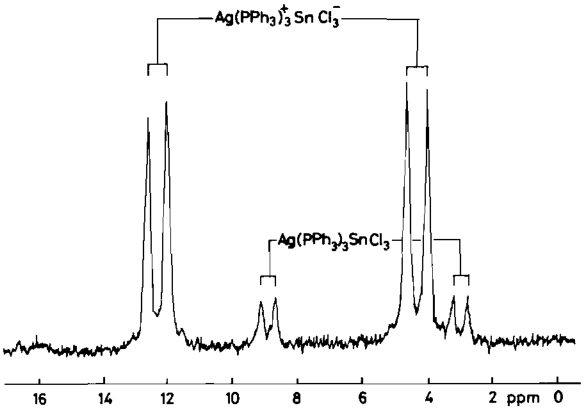


Fig. 1. ^{31}P NMR spectrum of $Ag(PPh_3)_3SnCl_3$ in CH_2Cl_2 at –80 °C.

The ^{31}P NMR spectrum of the complex $Ag(PPh_3)_3SnCl_3$ is also a singlet at room temperature but, at –80 °C, shows the presence of two components, one of which predominates (Fig. 1).

Neither component exhibits phosphorus–silver–tin coupling at this temperature. The coupling constant, $^1J(^{107}Ag–^{31}P)$ (30 Hz), of the major component is slightly greater than that observed in the spectra of $Ag(PPh_3)_nCl$ (n = 2 or 3), but is still in the range expected [14] for an sp^2 hybridised silver atom. It is probable, therefore, that this species in $Ag(PPh_3)_3^+SnCl_3^-$, since the conductivity data in nitromethane solution at room temperature indicate a molar conductivity approaching that of a 1:1 electrolyte (Λ_M = 56.9 S cm^2 mol^{-1}). X-ray studies on a related phosphine–gold–tin compound, Au(PMe$_2$Ph)$_2$SnCl$_3$, suggest that the metal–metal bond is relatively weak [16].

The ^{107}Ag–^{31}P coupling constant for the minor component (223 Hz) indicates an sp^3 hybridised silver atom, which would be consistent with a neutral Ag(PPh$_3$)$_3$SnCl$_3$ species in solution at –80 °C. However, it is thought more likely that this component is due to an ionic complex, $Ag(PPh_3)_4^+SnCl_3^-$, which could be formed by disproportionation of $Ag(PPh_3)_3^+$-$SnCl_3^-$.

The ^{31}P spectrum of $Ag(PPh_3)_4^+OH^-\cdot(SnCl_3OH\cdot H_2O)_2$ also shows only a singlet at room temperature. On cooling to –80 °C, a very complex spectrum results, indicating the presence of at least two phosphine–silver species. The predominant species in solution has $^1J(^{107}Ag–^{31}P)$ = 221 Hz, indicating sp^3 hybridised silver, and the parameters are similar to those of the minor component in the solution of Ag(PPh$_3$)$_3$SnCl$_3$. An additional set of signals with coupling constants very similar to those of the major component in the Ag(PPh$_3$)$_3$SnCl$_3$ solution could be discerned and these could correspond to the species, $Ag(PPh_3)_3^+OH^-\cdot(Cl_3SnOH\cdot H_2O)_2$. Again, a solution of the complex in nitromethane has a high molar conductivity at room temperature, approaching that of a 1:1 electrolyte (Λ_M = 32 S cm^2 mol^{-1}).

Acknowledgements

We wish to thank the International Tin Research Council, London, for permission to publish this paper. We are also grateful to Professor J. D. Donaldson, City University, London, for help and encouragement, Mr. P. A. Cusack and Dr. S. J. Blunden for discussions on the manuscript and Miss A. H. Chapman for silver and tin analyses.

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Note added in proof (March 8, 1982):

The Mössbauer parameters for this complex are identical to those of the similar dimeric molecules [12, 17], $(Cl_3SnOH\cdot H_2O)_2\cdot 4H_2O$ and $(Cl_3SnOEt\cdot EtOH)_2$, for which δ = 0.30, ΔE_Q = 0 [18] and δ = 0.33, ΔE_Q = 0 [19] mm s^{-1} respectively.