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Silver(I) aryloxide–triphenylphosphine complexes. An assessment of their potential as CVD precursors and the structure of $[Ag(OC_6H_4Me\text{-}2)(PPh_3)_3]\cdot 2\text{-}MeC_6H_4OH\cdot C_6H_5Me$

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Abstract

The silver aryloxide–triphenylphoshine complexes $[Ag(OR)(PPh_3)_2]$ (R = $C_6H_2Cl_3$-2,4,6 (**1**), C_6H_4Me-2 (**2**) or $C_6H_2(CH_2NMe_2)_3$-2,4,6 (**3**)) and $[Ag(OR)(PPh_3)_3]\cdot ROH$ (R = Ph (**4**) or C_6H_4Me-2 (**5**)) have been prepared and characterised. Complexes **1**, **3** and **5** were tested as precursors for the growth of silver films on glass substrates using an aerosol-assisted chemical vapour deposition method. Although films were produced, they were of poor quality compared to those produced from other silver complexes as precursors. A crystal structure determination of **5** as a toluene solvate shows the *o*-cresolato ligand to be monodentate and together with the triphenylphosphine ligands generates a distorted tetrahedral array around the silver. The additional *o*-cresol molecule is hydrogen-bonded to the *o*-cresolato oxygen atom and not directly bonded to silver.

Keywords: Crystal structures; Silver complexes; Aryloxide complexes

1. Introduction

Although metal alkoxides and aryloxides are an extremely well established group of compounds [1], relatively little is known of such compounds of silver(I) reflecting its low affinity for oxygen donor ligands. Some 25 years ago, a study [2] of reactions between silver ions and alkoxide ions illustrated the instability of silver alkoxides. For example, reactions of $AgClO_4$ with LiOR (R = Me or Et) afforded pure silver whereas use of LiOR with R = t-Bu or i-Pr produced a mixture of silver, silver alkoxide and other uncharacterised silver species. However, since then a few isolated reports of silver aryloxides have appeared, two general methods of preparation having been employed [3]. The first involves the reaction of a silver salt and a sodium or lithium aryloxide in the parent alcohol or in tetrahydrofuran. The alternative approach utilises the reaction of silver oxide and an aryl alcohol in aqueous acetone.

Silver aryloxides appear to be polymeric via bridging aryloxide ligands as shown [4] by a structure determination of $[Ag(OC_6H_2Cl_3\text{-}2,4,5)]_n$ in which the silver is bonded to three oxygens from three different aryloxide ligands and to one carbon from another aryl ring which also uses its oxygen to bond to a further silver in the polymer. The geometry around each silver is approximately trigonal pyramidal with respect to the oxygens but a further weak Ag–Cl interaction gives the silver an overall trigonal bipyramidal coordination.

Attempts to generate monomeric silver aryloxides have involved the use of additional ‘soft’ ligands which have a greater affinity for silver(I) than aryloxides. Thus monomeric $[Ag(OC_6H_2Cl_3\text{-}2,4,6)(PPh_3)_2]$ has monodentate aryloxide and triphenylphosphine ligands arranged in a trigonal planar fashion around the metal with again an additional weak intramolecular Ag···Cl interaction [5]. Apart from this phosphine example, the macrocyclic polythiaether ligand 1,4,7,10,13,16-hexathiacyclotetra-

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decane (18S6), has been used [6] to stabilise the picrate $[Ag_2(pic)_2(18S6)]$ and a dimeric quinolinolato complex $[Ag_2(C_9H_6NOH)_3(C_9H_6NO)(PPh_3)_2]^+[CH_3CO_2]^- \cdot H_2O$ containing a N,O-chelating quinolinolato C_9H_6NO ligand [7] is also known. In addition, we have reported the only crystallographically-authenticated example of a silver siloxide, viz $\{[Ag(PPh_3)_2(\mu_4\text{-}OMe_2SiOSiMe_2O)\}_2$ [8].

We have already reported [9] that good quality silver films can be produced by the aerosol-assisted chemical vapour deposition technique (AACVD) using silver carboxylate, fluorocarboxylate, β-ketoenolate or β-ketoiminate-trimethyl- or triphenyl-phosphine complexes as precursors. It was also felt worthwhile to attempt the synthesis of some silver aryloxide–phosphine complexes containing analogous weak Ag–O and strong Ag–P interactions and subject them to AACVD to assess the possibility of producing coherent silver films with desirable features such as high reflectivity and hardness. Alkoxides and aryloxides of several metals e.g., Zr, Sn, Nb have been used as precursors for either sol–gel or CVD production of metal oxide films, but, given the thermal instability of silver oxide above approximately 160 °C, a metal film would be expected from the AACVD of silver aryloxide complexes. Indeed, analogous copper metal films have been deposited by CVD of $[Cu(OBu^t)]_4$ [10] and the adduct $[Cu(OBu^t)(PMe_3)]$ [11].

2. Experimental

2.1. General

IR spectra were recorded as Nujol or hexachlorobutadiene mulls using a Nicolet 510P FT spectrometer within the range 4000–400 cm^{-1}: only selected data are quoted later in this section. Microanalyses for carbon, hydrogen and nitrogen were carried out using a Carlo-Erba Model 1106 microanalyser. JEOL GX 270 or EX 400 FT spectrometers were used to obtain ^1H, ^{13}C ($SiMe_4$ reference) and ^{31}P (85% H_3PO_4 reference) NMR spectra. FAB (LSIMS) mass spectra were recorded by the EPSRC mass spectrometry service at the University of Wales, Swansea using caesium ion bombardment at 25 kV, the samples being in a 3-nitrobenzyl alcohol matrix, dissolution being assisted by use of dichloromethane co-solvent.

Thermal analysis experiments were carried out at atmospheric pressure in a helium-purged atmosphere from room temperature (r.t.) to 450 °C at a ramp rate of 25 °C min^{-1} using a Dupont 951 TGA module, a Dupont 910 DSC cellbase and a TA Instruments 2100 controller. Details of the apparatus and experimental methodology for the AACVD of films generated from silver compounds as precursors have been given in full elsewhere [9]. Essentially, attempts were made to grow films on scrupulously clean glass substrates under an atmospheric pressure of dinitrogen using a horizontal cold wall CVD reactor. The precursor was delivered to the gas phase as an aerosol generated by nebulising an anhydrous tetrahydrofuran solution, the aerosol being swept into the reactor using dinitrogen as carrier gas. Film quality was estimated by EDXS techniques using a JEOL Superprobe instrument operating at an accelerating voltage of 5 or 10 kV with a beam current of 5×10^{-8} or 5×10^{-9} A.

2.2. Syntheses

As far as possible, syntheses were carried out in the absence of light and under an atmosphere of dintrogen using previously dried solvents.

2.2.1. (2,4,6-Trichlorophenolato)bis(triphenylphosphine)silver(I) (*1*)

This compound was prepared by an adaptation of the literature method [5]. Silver oxide (0.23 g, 1.0 mmol), 2,4,6-trichlorophenol (0.43 g, 2.2 mmol) and triphenylphosphine (1.15 g, 4.4 mmol) were heated together for 2 h in refluxing toluene (75 cm^3). After filtration of the hot mixture, 60–80° boiling range petroleum spirit was added to the filtrate until a precipitate appeared. This colourless solid was filtered, washed with toluene and dried *in vacuo*. Yield 1.34 g, 81%. *Anal.* Found (Calc. for $C_{42}H_{32}AgCl_3OP_2$): C, 60.9 (60.9); H, 3.87 (3.89)%. IR: 1583w, 1558w, 1516w, 1435m, 1244m [ν(CO)]. ^1H NMR ($CDCl_3$): 7.38–7.24 (m, 30H, C_6H_5), 6.97 (s, 2H, $Cl_3C_6H_2O$). ^{13}C NMR ($CDCl_3$): 160.0 (CO), 133.9 (d, $^2J = 16.5$ Hz, PC_6H_5), 132.6 ($Cl_3C_6H_2O$), 132.1 (d, $^1J = 27.0$ Hz, PC_6H_5), 130.1 (PC_6H_5), 128.8 (d, $^3J = 10.0$ Hz, PC_6H_5), 127.1 ($Cl_3C_6H_2O$), 123.7 ($Cl_3C_6H_2O$), 112.7 ($Cl_3C_6H_2O$). ^{31}P NMR (−25 °C, $CDCl_3/CH_2Cl_2$); 9.38 (unresolved d, $^1J(AgP) = 345$ Hz).

2.2.2. (*o*-Cresolato)bis(triphenylphosphine)silver(I) (*2*)

A mixture of silver oxide (1.00 g, 4.3 mmol), *o*-cresol (2-methylphenol) (0.93 g, 8.6 mmol) and triphenylphosphine (4.46 g, 17.0 mmol) was stirred overnight at r.t. in toluene (40 cm^3). The resulting light grey product was filtered and washed with toluene before drying *in vacuo*. Yield 4.77 g, 75%. *Anal.* Found (Calc. for $C_{43}H_{37}AgOP_2$): C, 69.3 (69.8); H, 5.06 (5.04)%. IR: 1622w, 1583m, 1435m, 1294w, 1278m [ν(CO)]. ^1H NMR ($CDCl_3$): 7.40–7.24 (m, 34H, $C_6H_5 + MeC_6H_4O$), 2.21 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 154.1 (CO), 134.0 (d, $^2J = 16.5$ Hz, PC_6H_5), 132.5 (d, $^1J = 25.4$ Hz, PC_6H_5), 130.8 (MeC_6H_4O), 129.9 (PC_6H_5), 128.8 (d, $^3J = 10.0$ Hz, PC_6H_5), 126.9 (MeC_6H_4O), 123.8 (MeC_6H_4O), 120.2 (MeC_6H_4O), 114.9 (MeC_6H_4O), 15.7 (CH_3). ^{31}P NMR (−25 °C, $CDCl_3/CD_2Cl_2$): 6.77.

*2.2.3. [2,4,6-Tris(dimethylaminomethyl)phenolato]bis(triphenylphosphine)silver(I) (**3**)*

A mixture of silver oxide (1.00 g, 4.3 mmol), 2,4,6-tris(dimethylaminomethyl)phenol (2.28 g, 8.6 mmol) and triphenylphosphine (4.46 g, 17.0 mmol) was stirred in toluene (40 cm^3) overnight at r.t. Filtration of the resulting darkly coloured mixture gave a clear filtrate which deposited a very light grey solid on standing at r.t. This product was filtered, washed with toluene and dried *in vacuo.* Yield 5.09 g, 66%. *Anal.* Found (Calc. for $C_{51}H_{56}AgN_3OP_2$): C, 67.6 (68.3); H, 6.19 (6.29); N, 4.45 (4.69)%. IR: 1604m, 1435w, 1311s, 1229m [ν(CO)], 1170w [ν(CN)], 1142w [ν(CN)]. ^{1}H NMR ($CDCl_3$): 7.43–7.23 (m, 30H, C_6H_5), 6.94 [s, 2H, $(Me_2NCH_2)_3C_6H_2O$], 3.52 (s, 4H, CH_2N), 3.29 (s, 2H, CH_2N), 2.28 [s, 12H, $(CH_3)_2N$], 2.21 [s, 6H, $(CH_3)_2N$]. ^{13}C NMR ($CDCl_3$): 155.5 (CO), 134.0 (d, $^2J = 16.5$ Hz, PC_6H_5), 132.5 (d, $^1J = 26.4$ Hz, PC_6H_5), 130.0 (PC_6H_5), 128.7 (d, $^3J = 8.9$ Hz, PC_6H_5), 128.3 [$(Me_2NCH_2)_3C_6H_2O$], 123.0 [$(Me_2NCH_2)_3C_6H_2O$], 63.8 (CH_2N), 60.3 (CH_2N), 45.1 [$(CH_3)_2N$], 44.8 [$(CH_3)_2N$]. ^{31}P (−25 °C, $CDCl_3/CD_2Cl_2$): 7.32.

*2.2.4. (Phenolato)tris(triphenylphosphine)silver(I)·phenol (**4**)*

This compound was prepared in a similar manner to the copper(I) analogue [12]. A mixture of silver oxide (2.32 g, 10.0 mmol), phenol (1.88 g, 20.0 mmol) and triphenylphosphine (10.49 g, 40.0 mmol) was heated in toluene (80 cm^3) at 75 °C for 10 h. The pale brown solution was filtered while still hot and the filtrate cooled to r.t. After standing overnight in the dark, the product precipitated as a light beige solid which was filtered, washed with toluene and dried *in vacuo*. Yield 7.79 g, 72% (based on phenol as limiting reagent). *Anal.* Found (Calc. for $C_{66}H_{56}AgO_2P_3$): C, 73.0 (73.2); H, 5.45 (5.18)%. IR: 3368w,br, 3184w [ν(OH)], 1622m, 1606w, 1585w, 1435s, 1248m [ν(CO)].

^{1}H NMR ($CDCl_3$): 7.31–6.71 (m, 55H, $PC_6H_5 + C_6H_5O + C_6H_5OH$), 6.40 (s, 1H, OH), ^{13}C NMR ($CDCl_3$): 160.5 (CO), 133.7 (d, $^2J = 15.4$ Hz, PC_6H_5), 132.4 (d, $^1J = 17.6$ Hz, PC_6H_5), 130.1 (PC_6H_5), 128.9 (d, $^3J = 8.8$ Hz, PC_6H_5), 128.1 (C_6H_5O), 116.8 (C_6H_5O), 116.6 (C_6H_5O). ^{31}P NMR (−25 °C, $CDCl_3/CD_2Cl_2$): 5.08.

*2.2.5. (o-Cresolato)tris(triphenylphosphine)silver(I)·o-cresol·toluene solvate (**5**)*

This compound was prepared by the same method as **2** using the same ratio of silver oxide (1), triphenylphosphine (4) and *o*-cresol (2) in toluene. After removing the insoluble **2** which precipitates from solution, crystals of **5** are formed on standing. *Anal.* Found (Calc. for $C_{75}H_{68}AgO_2P_3$): C, 74.9 (74.9); H, 5.65 (5.70)%. IR: 1581w, 1435m, 1244m [ν(CO)]. ^{1}H NMR ($CDCl_3$): 7.35–7.25 (m, 58H, $PC_6H_5 + MeC_6H_4O + MeC_6H_4OH + C_6H_5CH_3$), 2.35 (s, 3H, $C_6H_5CH_3$), 2.24 (s, 6H, $CH_3C_6H_4O + CH_3C_6H_4OH$). ^{13}C NMR ($CDCl_3$): 156.3 (CO), 136.4 ($C_6H_5CH_3$), 133.9 (d, $^2J = 16.5$ Hz, PC_6H_5), 133.3 (d, $^1J = 17.6$ Hz, PC_6H_5), 132.6 (MeC_6H_4O), 132.1 (MeC_6H_4O), 132.0 (MeC_6H_5O), 130.4 (MeC_6H_4OH), 129.7 (PC_6H_5), 129.0 ($C_6H_5CH_3$), 128.7 (d, $^3J = 8.8$ Hz, PC_6H_5), 128.4 ($C_6H_5CH_3$), 128.2 (MeC_6H_4O), 126.7 (MeC_6H_4OH), 125.2 (MeC_6H_4O), 124.3 (MeC_6H_4OH), 118.6 (MeC_6H_4OH), 115.5 (MeC_6H_4OH), 21.4 ($CH_3C_6H_5$), 16.2 ($CH_3C_6H_4O + CH_3C_6H_4OH$). ^{31}P NMR: (−25 °C, $CDCl_3/CD_2Cl_2$), 4.51.

2.3. X-ray crystallography

Crystallographic quality crystals of **5** were obtained from a toluene solution cooled in a refrigerator. Crystal data: $C_{75}H_{68}AgO_2P_3$, $M = 1202.07$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.347(2)$, $b = 14.991(2)$, $c = 18.012(3)$ Å, $\alpha = 81.65(2)$, $\beta = 74.42(2)$, $\gamma = 65.27(2)°$, $V = 3150.9$ Å^3, $Z = 2$, $D_{calc} = 1.267$ g cm^{-3}, $\mu = 0.442$ mm^{-1}, $F(000) = 1252$. Data were collected at 293(2) K on a CAD-4 automatic four-circle diffractometer in the range $2.30 < \theta < 23.92°$ using Mo Kα (0.71069 Å) radiation. A crystal of dimensions $0.35 \times 0.35 \times 0.30$ mm was used for data collection. The index ranges were $0 \leq h \leq 15$, $-15 \leq k \leq 17$ and $-19 \leq l \leq 20$. A total of 10 336 reflections were measured of which 9853 were unique, [$R_{int} = 0.0412$].

The diffraction intensities were corrected for Lp but not for absorption. The solution of the structure and refinement (SHELX) converged to a conventional [i.e. based on 5532 reflections with $F_o > 4\sigma(F_o)$] R_1 of 0.0693 and wR_2 of 0.1457 for a weighting scheme of $w = 1/[\sigma^2(F_o)^2 + (0.0907P)^2 + 1.9303P]$ where $P = (F_o^2 + 2F_c^2)/3$. The goodness-of-fit was 1.066, with maximum and minimum residual densities of 0.833 and −0.564 e Å^{-3}, respectively.

The asymmetric unit contains one molecule of the silver aryloxide complex, one molecule of *o*-cresol and one disordered toluene molecule. The disorder was extreme, the most satisfactory refinement being achieved by placing the toluene electron density as two rigid phenyl groups in the occupancy ratio of 52:48 for partial carbons C(69)–C(74) and C(75)–C(80), respectively. The partial methyl carbons of the toluene could not be convincingly located. In the final least-squares cycle all atoms were allowed to vibrate anisotropically except for the partial carbons C(69)–C(80) in the solvent region of the electron density map. Phenyl rings were treated as rigid hexagons throughout and hydrogen atoms were included at calculated positions where relevant in the *o*-cresolato and *o*-cresol moieties except for H2(A) of the *o*-cresol which is involved in hydrogen bonding to the *o*-cresolato oxygen atom O(1). This hydrogen was located

Table 1
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths (Å)			
Ag(1)–O(1)	2.386(5)	Ag(1)–P(1)	2.577(2)
Ag(1)–P(2)	2.539(2)	Ag(1)–P(3)	2.540(2)
O(1)–O(2)	2.565(9)	O(1)–H(2A)	1.59(4)
O(2)–H(2A)	0.98(4)	O(1)–C(55)	1.297(8)
O(2)–C(62)	1.354(8)		
Bond angles (°)			
O(1)–Ag(1)–P(1)	98.36(14)	O(1)–Ag(1)–P(2)	105.2(2)
O(1)–Ag(1)–P(3)	107.8(2)	P(1)–Ag(1)–P(2)	111.08(7)
P(1)–Ag(1)–P(3)	115.73(6)	P(2)–Ag(1)–P(3)	116.41(7)
O(1)–H(2A)–O(2)	170(10)	C(55)–O(1)–Ag(1)	116.4(4)

in a difference Fourier map based on low Bragg data and refined at a distance of 0.98 Å from O(2).

The asymmetric unit, omitting the disordered solvent molecule, produced using ORTEX [13], is shown together with the labelling scheme in Fig. 1. Selected bond lengths and angles are given in Table 1.

3. Results and discussion

Five silver aryloxide–triphenylphosphine complexes have been prepared from the reactions in toluene of silver oxide and the appropriate aryl alcohol in the presence of the phosphine. Yields were in the range 66–82%. The products were of two types, the bis-phosphine complexes $[Ag(OR)(PPh_3)_2]$ with R = 2,4,6-$Cl_3C_6H_2$ (**1**), 2-MeC_6H_4 (**2**) or 2,4,6-$(Me_2NCH_2)_3C_6H_2$ (**3**), and the tris-phosphine complexes which also contained an additional molecule of the aryl alcohol $[Ag(OR)(PPh_3)_3]\cdot ROH$ with R = Ph (**4**) or 2-MeC_6H_4 (**5**). Complex **5** was actually isolated as a toluene solvate and its structure confirmed by a single crystal structure determination (*loc. cit.*). Syntheses were carried out in the absence of light as the products were found to be somewhat light-sensitive turning grey or pale brown on standing. Under normal laboratory conditions, attempted recrystallisations of compounds **2**, **3** and **4** from anhydrous toluene invariably produced silver films on the surfaces of the glass equipment. All five compounds also tended to decompose when heated above 80 °C and reacted slowly with chlorinated solvents e.g. $CHCl_3$ to form $[AgCl(PPh_3)_n]$ ($n = 2$ or 3). However, compound **5** could be recrystallised from toluene.

We have previously discussed [9] the value of IR spectroscopy in providing evidence to support specific co-ordination modes for carboxylate ligands in silver carboxylates, perfluorocarboxylates and their bis- and tris-phosphine complexes. Unfortunately, IR spectroscopy is of less significance for these silver aryloxide complexes, although bands can be assigned to C–O stretching vibrations (see Section 2). These are in a similar region to the analogous modes of copper(I) and gold(I) aryloxides [12,14] but provide no information which can be related to co-ordination type.

NMR spectra (^1H, ^{13}C and ^{31}P) were recorded for all five compounds (see Section 2), the proton and carbon spectra confirming the stoichiometries but are otherwise unexceptional. In the aryl proton region of the ^1H NMR spectra of complexes **2**, **4** and **5**, the triphenylphosphine, aryloxide and aryl alcohol (and for **5** additionally the toluene) resonances all extensively overlap. Conversely, for complexes **1** and **3** the resonances of the triphenylphosphine protons are clearly differentiated from those of the aryl protons of the trichlorophenoxo or tris(dimethylaminomethyl)phenoxo ligands. The *ortho*- and *para*-dimethylaminomethyl protons in **3** are magnetically inequivalent, both the methyl and methylene protons displaying the expected 2:1 ratios. This is in contrast with the situation found for dimeric $[GaCl_2\{OC_6H_2(2,4,6\text{-}CH_2NMe_2)_3\}]_2$ [15] in which the *ortho*- and *para*-dimethylaminomethyl protons are apparently magnetically equivalent. In the ^{13}C NMR spectra, all aryloxide C–O resonances are found in the 154–160 ppm range, values similar to those of the free aryl alcohols. Generally, the triphenylphosphine carbon resonances are easily distinguishable from those of the aryloxide or aryl alcohol because of the presence of carbon–phosphorus couplings with characteristic J_{CP} coupling constants. The magnetic inequivalence of the methyl and methylene carbons of **3** is again evident. The ^{13}C NMR spectrum of **5** was difficult to assign convincingly, resonances associated with the *o*-cresol, *o*-cresolato and toluene moieties overlapping considerably.

The ^{31}P NMR spectra of the five complexes were recorded at room temperature and at −25 °C in a $CDCl_3/CD_2Cl_2$ mixed solvent. At room temperature, all resonances were broad singlets in the range δ 5.5–9.5 with no indication of Ag–P coupling, suggesting triphenylphosphine lability in solution as noted in previous similar NMR studies [9,16]. Consequently, in Section 2 we merely report δ values at −25 °C which are in the range δ 4.51–9.38 with $\Delta\delta$ co-ordination shift values (from free triphenylphosphine) of 9.99–14.71. The closely similar $\Delta\delta$ values reflect the nature of the phosphine and are clearly little influenced by change in the type of aryloxide present. The spectra recorded at −25 °C again showed no Ag–P coupling, except for **3** which exhibited a rather broad doublet at δ 9.38 with a $^1J_{AgP}$ of 345 Hz. Resolution of the individual ^{107}Ag and ^{109}Ag components was not achieved.

The FAB (LSIMS) mass spectra of compounds **1**, **3**, **4** and **5** have been recorded and metal-containing fragments identified using the characteristic patterns imposed by the natural abundances of the 107 and 109 isotopes of silver. Only **5** showed a parent ion, albeit of

Table 2
Thermal stabilities of silver aryloxide–triphenylphosphine complexes

	Decomposition temperature (°C)		% Mass loss		
	Start	Finish	Found [a]	Total	Calc. [b]
$[Ag(OC_6H_2Cl_3\text{-}2,4,6)(PPh_3)_2]$ (**1**)	195	320	62.4		
	330	380	17.5	77.9	87.0 [c]
$[Ag(OC_6H_4Me\text{-}2)(PPh_3)_2]$ (**2**)	130	310	75.1	75.1	85.4
$[Ag\{OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6\}(PPh_3)_2]$ (**3**)	55	270	63.1		
	290	315	11.1	74.2	88.0
$[Ag(OC_6H_5)(PPh_3)_3\cdot C_6H_5OH]$ (**4**)	110	180	17.2		
	180	290	68.2	85.4	90.0
$[Ag(OC_6H_4Me\text{-}2)(PPh_3)_3\cdot 2\text{-}MeC_6H_4OH]\cdot C_6H_5CH_3$ (**5**)	110	140	7.1		
	150	300	74.4	81.5	91.0

[a] From TGA plot.
[b] Assuming Ag as final product.
[c] 82.7 for AgCl as residue.

low abundance. Fragments of the type $[Ag(PPh_3)_n]^+$ ($n = 1$ or 2), which have also been identified in the mass spectra of silver carboxylate–triphenylphosphine complexes [9], are again detected in high abundance for all four aryloxides tested, the fragment with $n = 2$ being the most abundant metal-containing ion for **1**, **4** and **5** but $n = 1$ being the most abundant for **3**. The high abundance of these ions reflects the tendency of silver(I) to form linear species in the gas phase [17]. Each compound also shows $[AgO(PPh_3)_2]^+$ fragments, highly abundant for **1** (63% relative to $[Ag(PPh_3)_2]^+$) but only of between 2 and 4% relative abundances for the other aryloxide complexes. This fragment has previously been observed in the mass spectra of $[Ag(C\equiv CPh)(PPh_3)]$ [18] and triphenylphosphine adducts of silver β-ketoenolates and fluorocarboxylates [9]. No fragment ions containing discrete aryloxide groups were detected for any of the compounds. The spectrum of **5** also contains low-abundant di-silver fragment ions such as $[Ag_2(CO)(PPh_3)_2]^+$ and $[Ag_2(OH)(PPh_3)_3]^+$ presumably formed by gas phase reactions in the spectrometer chamber, given that **5** is mononuclear in the solid state.

The mononuclear structure of **5** (Fig. 1) has been established by a single crystal X-ray structure determination. The silver atom is bonded to the oxygen of a monodentate *o*-cresolato ligand and to the phosphorus atoms of three triphenylphosphine ligands to generate a distorted tetrahedral array. The neutral *o*-cresol molecule in the structure is not bonded directly to silver but is hydrogen-bonded via the hydroxyl proton H(2A) to O(1) of the *o*-cresolato group. The proton H(2A) was found during the solution of the structure, the O(1)–O(2) separation and H(2A)–O(1) bond distances of 2.565(9) and 1.59(4) Å, respectively, being similar to those of the *p*-cresolato complex $[Rh(PMe_3)_3(OC_6H_4Me\text{-}4)(HOC_6H_4Me\text{-}4)]$ [19] which has O(1)–O(2) of 2.62 Å and H–O(1) of 1.4(1) Å. In **5**, the O(2)–H(2A)–O(1) system is essentially linear [angle 170(10)°]. The Ag–O bond length of 2.386(5) Å in **5** is quite similar to those found in $[Ag(OC_6H_2Cl_3\text{-}2,4,5]$, [2.317(3)–2.543(3) Å] [4] and in $[Ag(OC_6H_2Cl_3\text{-}2,4,6)(PPh_3)_2]$ [2.255 Å] [5] but shorter than those in the quinolinolato cation [7] $[Ag_2(C_9H_6NO)(C_9H_6NOH)_3(PPh_3)_2]^+$ [2.529(4) and 2.546(4) Å]. The Ag–P bond distances of 2.539(2), 2.540(2) and 2.577(2) Å in **5** are longer than those of $[Ag(OC_6H_2Cl_3\text{-}2,4,6)(PPh_3)_2]$ [2.444(1) and 2.451(1) Å] [5], reflecting the presence of the additional third bulky triphenylphosphine ligand. A comparison with, for example, $[Ag(FBF_3)(PPh_3)_3]$ [20] which has Ag–P bond distances of 2.506(3), 2.543(3) and 2.577(3) Å provides confirmation of this steric effect. The distortion from regular tetrahedral geometry is evident on consideration of the P–Ag–P and P–Ag–O angles (Table 1). The regular tetrahedral angle is exceeded for all three P–Ag–P angles, a feature also found for $[Ag(FBF_3)(PPh_3)_3]$ [20], whereas the P–Ag–O angles are all reduced from the regular tetrahedral angle. As expected, the P–Ag–P angles are smaller than that found [5] for $[Ag(OC_6H_2Cl_3\text{-}2,4,6)(PPh_3)_2]$ [131.1(1)°] where the $AgOP_2$ array is essentially distorted trigonal planar.

Thermal analyses (Table 2) of all five aryloxide complexes were carried out under inert helium atmospheres to obtain information on decomposition temperatures and sequences and on the relative stabilities of the compounds. Such information gives an indication of the viability of these compounds as useful silver film precursors. Under our experimental conditions, two-stage decompositions were evident for all complexes except **2** although the temperature ranges varied widely

Table 3
Conditions for AACVD testing and the nature of the films produced

	$[Ag(OC_6H_2Cl_3\text{-}2,4,6)(PPh_3)_2]$ (**1**)	$[Ag\{OC_6H_2(CH_2NMe_2)_3\}(PPh_3)_2]$ (**3**)	$[Ag(OC_6H_4Me\text{-}2)(PPh_3)_3\cdot 2\text{-}MeC_6H_4OH]\cdot C_6H_5CH_3$ (**5**)
Concentration range (g l^{-1})	50–120	63–65	13–36
Reactor temperature (°C)	300–596	300	250–398
N_2 flow rate (l min^{-1})	0.80–1.05	0.95–1.00	0.50–1.00
Run times (min)	17–88	41–106	20–104
Visual appearance of film [a]	thin, pale grey, not reflective, soft, easily damaged	thick, yellow–brown, not reflective, soft, easily damaged	very thin, yellow–brown, not reflective, soft, easily damaged
Detected impurities [b]	carbon	carbon	carbon

[a] For **1** appearance relates to a film grown at a concentration of 120 g l^{-1}, a reactor temperature of 300 °C and a run time of 88 min; for **3** concentration 65 g l^{-1}; 300 °C; 106 min run time; for **5** concentration 65 g l^{-1}; 300 °C; 75 min run time.

[b] EDXS analysis.

from one compound to another. Complex **2** merely displayed an overall decomposition starting at 130 °C and terminating at 310 °C. The mass loss of 75.1% is not in accord with the final formation of simply silver metal for which a mass loss of 85.4% would be expected. The decomposition of complex **1** started at a higher temperature than all the others with a large first stage mass loss of 62.4% which corresponds to the loss of both triphenylphosphine ligands (calc. mass loss 63.3%). The overall mass loss of 79.9% again suggests that silver metal is not the sole final product (calc. mass loss 87.0%) but is closer to a calculated mass loss of 82.7% if the final product is silver chloride. Indeed, qualitative tests showed the presence of silver chloride in the final residue, the chloride arising from decomposition of the trichlorophenolato ligand and the presence of weak intramolecular Cl···Ag interactions inherent within the structure. Decomposition of complex **3** commenced at

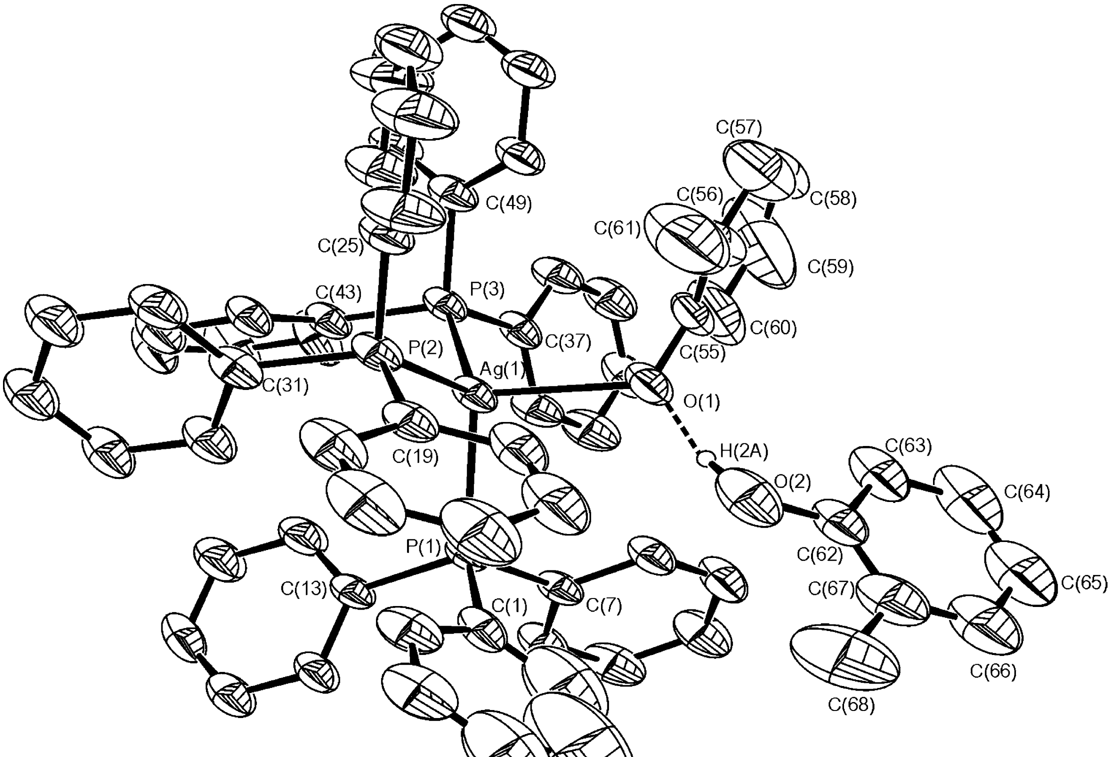

Fig. 1. The asymmetric unit of **5**, showing the labelling scheme used in the text and Table 1. The disordered molecule of toluene solvent has been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

the very low temperature of 55 °C with a large first stage loss of the triphenylphosphine ligands and a smaller second stage loss leading to a final total% mass loss of 74.2%. This is much less than expected if the final residue is silver metal (calc. 88.0%). The decomposition profiles of the two tris-triphenylphosphine complexes **4** and **5** differ from those of the bis-triphenylphosphine complexes in that the first stage involves a small mass loss followed by a much larger second stage mass loss. The overall% mass loss for **4** of 85.4% does not correspond with the final formation of solely silver metal (calc. 90.0%). The first stage in the decomposition of **5** appears to correlate with the% mass loss for the toluene solvate (found 7.1%; calc. 7.7%) but again the overall loss of 81.5% is too low to suggest the final residue is merely silver (calc. 91.0%). These results, therefore, do not support the view that AACVD of the aryloxide complexes should lead to the formation of good quality, pure silver films. Actual AACVD testing confirmed that the aryloxide complexes were unsuitable.

Attempts were made to grow silver films using AACVD under varied conditions but using a constant dinitrogen atmosphere of one bar pressure and the same horizontal cold wall reactor. Details of our experimental protocol and equipment are given elsewhere [9] and results from the use of silver carboxylate, fluorocarboxylate, β-ketoenolate and β-ketoiminate complexes as precursors have already been discussed. Solutions of complexes **1**, **3** and **5** in anhydrous tetrahydrofuran were nebulised and the resulting aerosols passed over heated glass substrates using dinitrogen as carrier gas. Each precursor was tested using differing concentrations, temperatures, dinitrogen carrier gas flow rates and run times (see Table 3) but none of the precursors generated good quality silver films as assessed by their visual appearance, thickness, softness and ease of damage by touch. In the light of the poor quality of the films, their reflectivities and resistivities were not measured and scanning electron micrographs were not obtained, unlike films produced from other silver complexes [9]. However, the films were examined by EDXS which confirmed the presence of silver with trace levels of carbon, oxygen and silicon but the absence of phosphorus. The oxygen and silicon clearly arise from the underlying glass substrates.

4. Conclusions

Some new silver(I) aryloxide complexes containing two or three triphenylphosphine ligands have been prepared and characterised. Very few related complexes have been reported previously. The single-crystal X-ray structure analysis of an *o*-cresolato complex shows it to be mononuclear with a monodentate aryloxide ligand. Three of the complexes have been tested for potential use as precursors for the growth of silver films by AACVD. The results were disappointing, the silver films obtained being vastly inferior to those grown from silver carboxylates, fluorocarboxylates, β-ketoenolates and β-ketoiminates reported earlier [9].

5. Supplementary material

Crystallographic data for structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 190513. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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