Synthesis and characterization of organophosphine/phosphite stabilized silver(I) methanesulfonates: Crystal structures of [Ph$_3$PAgO$_3$SCH$_3$] and [(Ph$_3$P)$_2$AgO$_3$SCH$_3$]

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ABSTRACT

Six organophosphine/phosphite stabilized silver(I) methanesulfonates of type [L$_n$AgO$_3$SCH$_3$] (L = Ph$_3$P, n = 1, **2a**; n = 2, **2b**; n = 3, **2c**; L = (EtO)$_3$P; n = 1, **2d**; n = 2, **2e**; n = 3, **2f**) were synthesized by the reaction of silver methanesulfonates with triphenylphosphine or triethylphosphite in dichloromethane under nitrogen atmosphere. These complexes were obtained in high yields and characterized by elemental analysis, ^{1}H-, ^{13}C{H} NMR, IR spectroscopy and thermogravimetric analysis (TGA), respectively. X-ray single crystal analysis reveals that complex **2a** is a tetramer [Ph$_3$PAgO$_3$SCH$_3$]$_4$ and complex **2b** is a monomer. The thermal stability of **2a** has been studied by applying thermogravimetric analysis. It starts to decompose between 50 and 440 °C in a three-step process. The final residue (Ag) is about 20.50%.

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1. Introduction

Silver(I) complexes have been widely studied because they have shown a great tendency to form rich structure characteristics [1–6], potential application in catalysis [7] and material science [8,9]. Lewis-base stabilized silver(I) complexes have recently attracted renewed interests, mostly because of their application as precursors in the growth of silver thin films via chemical vapor deposition (CVD) techniques, which could be used as new interconnect material for the future generations of deep submicro integrated circuits because of the lower resistivity and superior electromigration resistance [10–15].

The key to achieve success for CVD, however, is the selection of suitable precursors. As the precursor for CVD, the complexes should have: (i) suitable vapor pressure for transporting it from bubbler to CVD reactor; (ii) suitable thermal decomposition mechanism, (iii) suitable thermal stability which means that it could not decompose during the transportation but decompose easily in the reactor [16,17]. Several organic molecules have been often used as ligands to synthesize the silver complexes, such as β-diketonate and its analogous as the main ligands [18,19], and phosphines as ancillary ligands [20,21]. For example, [(CH$_3$)$_3$CCOCHCOC$_3$F$_7$Ag-PEt$_3$] [22], [(fod)$_3$Ag(PPh$_3$)$_5$] [23] were reported to be successfully used as precursors for the silver film deposition. Lewis-base stabilized silver carboxylates such as [Ph$_3$PAgO$_2$CR] [24], [(Ph$_3$P)$_2$AgO$_2$CC$_3$F$_7$] [25] are another kind of precursors for silver deposition due to the higher utility of silver (100%) according to

the radical decomposition mechanism. But to the best of our knowledge, Lewis-base stabilized silver methanesulfonates have not been reported until now. In order to search for the new kind of silver precursor used in CVD technique, a series of organophosphine stabilized silver(I) sulfonates, [L$_n$AgO$_3$SCH$_3$] (L = Ph$_3$P, n = 1, **2a**; n = 2, **2b**; n = 3, **2c**; L = (EtO)$_3$P; n = 1, **2d**; n = 2, **2e**; n = 3, **2f**), were synthesized and characterized. The single crystal structures of **2a** and **2b** were determined and discussed. The thermal stability of **2a** has been studied by applying thermogravimetric analysis (TGA) has been studied as well.

2. Experimental

2.1. General procedure

All operations were carried out under an atmosphere of purified nitrogen with standard Schlenk techniques. The solvent dichloromethane (CH$_2$Cl$_2$) was purified by distillation from P$_2$O$_5$ under N$_2$. The AgO$_3$SCH$_3$ was synthesized by reacting CH$_3$SO$_3$H with excessive Ag$_2$CO$_3$ in water. ^{1}H NMR were recorded on a Bruker Avance 300 spectrometer operating at 300.130 MHz in the Fourier transform mode; ^{13}C{H} NMR spectra were recorded at 75.467 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane (δ = 0.0 ppm) with the solvent as the reference signal (^{1}H NMR, CDCl$_3$ δ = 7.26; ^{13}C{H} NMR, CDCl$_3$ δ = 77.55). Infrared spectra were collected on Bruker Vector 22 at room temperature. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. Melting points were observed in sealed capillaries and were uncorrected. Thermogravimetric analysis were performed on a American TA2000/2960

analyzer with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

2.2. Synthesis

2.2.1. Synthesis of CH$_3$SO$_3$Ag (1)

Methane sulfonic acid (5 g, 0.052 mol) dissolved in 50 mL of H$_2$O was added dropwise into a stirred suspended solution of [Ag$_2$CO$_3$] (8.7 g, 0.031 mol) in 20 mL of H$_2$O at 20 °C. The clear solution was obtained by filtration through a pad of celite after stirring the reaction mixture for 1 h at 20 °C. A white solid product was obtained after removing water in Rotary Evaporator and Vacuum Drying Oven at 50 °C. The product was stored under nitrogen and keep in dark place. Yield: 8.8 g (83%, based on Ag$_2$CO$_3$).

2.2.2. Synthesis of Ph$_3$PAgO$_3$SCH$_3$ (2a)

Triphenylphosphine (0.1318 g, 0.5 mmol) dissolved in 20 mL of CH$_2$Cl$_2$ was added dropwise into a stirred suspended solution of [CH$_3$SO$_3$Ag] (0.1020 g, 0.5 mmol) in 20 mL of CH$_2$Cl$_2$ at 0 °C. The clear solution was obtained by filtration through a pad of celite after stirring the reaction mixture for 6 h at 0 °C. A white solid product was obtained after removing all the volatiles in oil-pump vacuo, yield: 0.21 g (91%, based on CH$_3$SO$_3$Ag). M.p.: 187 °C dec. *Anal.* Calc. for C$_{19}$H$_{18}$O$_3$AgPS: C, 49.05; H, 3.90. Found: C, 48.93; H, 3.85%. ^{1}H NMR (CDCl$_3$): δ 2.8 (s, 3H, CH$_3$–H), 7.4–7.6 (m, 15H, Ph–H). ^{13}C{H} NMR (CDCl$_3$): δ 39.1 (CH$_3$), 134.3 (J_{PC} = 16.0 Hz, C$_6$H$_5$), 132.3 (J_{PC} = 22.4 Hz, C$_6$H$_5$), 131.4 (C$_6$H$_5$), 129.6 (J_{PC} = 10.36 Hz, C$_6$H$_5$). IR (KBr) data (cm^{-1}): 3051 (m), 2962 (m), 1476 (m), 1435 (s), 1388 (m), 1258 (s), 1196 (vs), 1093 (vs), 1023 (vs), 804 (s), 740 (s), 692 (vs), 507 (s).

2.2.3. Synthesis of (Ph$_3$P)$_2$AgO$_3$SCH$_3$ (2b)

Complex **2b** as a white solid was obtained following the above procedure, only using [CH$_3$SO$_3$Ag] (0.1401 g, 0.69 mmol) and triphenylphosphine (0.3621 g, 1.38 mmol) instead. Yield: 0.477 g (95%, based on AgO$_3$SCH$_3$). M.p.: 195 °C dec. *Anal.* Calc. for C$_{37}$H$_{33}$O$_3$AgP$_2$S: C, 61.08; H, 4.57. Found: C, 60.87; H, 4.54. ^{1}H NMR (CDCl$_3$): δ 2.6 (s, 3H, CH$_3$), 7.2–7.4 (m, 30H, Ph). ^{13}C{H} NMR (CDCl$_3$): δ 39.1 (CH$_3$), 134.4 (J_{PC} = 13.3 Hz, C$_6$H$_5$), 132.3 (J_{PC} = 22.3 Hz, C$_6$H$_5$), 130.9 (C$_6$H$_5$), 129.4 (J_{PC} = 10.36 Hz, C$_6$H$_5$). IR (KBr) data (cm^{-1}): 3053 (m), 2959 (m), 1476 (m), 1435 (s), 1392 (m), 1263 (s), 1200 (vs), 1095 (vs), 1039 (vs), 804 (m), 749 (s), 696 (vs), 507 (s).

2.2.4. Synthesis of (Ph$_3$P)$_3$AgO$_3$SCH$_3$ (2c)

Complex **2c** was synthesized following the synthesis of **2a** (Section 2.2.1). In this respect, triphenylphosphine (0.4388 g, 1.67 mmol) was reacted with [AgO$_3$SCH$_3$] (0.1132, 0.558 mmol). After appropriate work-up (see Section 2.2.1), complex **2c** was obtained as a white solid. Yield: 0.51 g (93%, based on AgO$_3$SCH$_3$]). M.p.: 215.2 °C dec. *Anal.* Calc. for C$_{55}$H$_{48}$AgO$_3$P$_3$S: C, 66.74; H, 4.89. Found: C, 66.47; H, 4.62%. ^{1}H NMR (CDCl$_3$): δ 2.5 (s, 3H, CH$_3$), 7.2–7.4 (m, 45H, Ph). ^{13}C{H} NMR (CDCl$_3$): δ 39.4 (CH$_3$), 134.2 (J_{PC} = 16.06 Hz, C$_6$H$_5$), 132.3 (J_{PC} = 23.29 Hz, C$_6$H$_5$), 130.7 (C$_6$H$_5$), 129.3 (J_{PC} = 9.24 Hz, C$_6$H$_5$). IR (KBr) data (cm^{-1}): 3051 (m), 2959 (m), 1480 (m), 1435 (s), 1387 (m), 1260 (s), 1196 (vs), 1087 (s), 1035 (vs), 804 (m), 749 (s), 696 (vs), 507 (s).

2.2.5. Synthesis of (EtO)$_3$PAgO$_3$SCH$_3$ (2d)

Complex **2d** was synthesized following the synthesis of **2a** (Section 2.2.1). In this respect, [(EtO)$_3$P] (1.88 g, 11.32 mmol) was reacted with [AgO$_3$SCH$_3$] (2.29 g, 11.32 mmol). After appropriate work-up, complex **2d** can be isolated as a colourless liquid. Yield: 3.77 g (90%, based on AgO$_3$SCH$_3$). *Anal.* Calc. for C$_7$H$_{18}$O$_6$AgPS: C, 22.78; H, 4.92. Found: C, 22.67; H, 4.78%. ^{1}H NMR (CDCl$_3$): δ 1.2 (t, 9 H, CH$_3$/CH$_3$CH$_2$–, J_{HH} = 7.0), 2.8 (s, 3 H), 4.0 (m, 6H, CH$_2$/

CH$_3$CH$_2$–). ^{13}C{H} NMR (CDCl$_3$): δ 39.2 (CH$_3$), 16.6 (J_{PC} = 6.5 Hz, CH$_3$/CH$_3$CH$_2$–), 61.4 (J_{PC} = 3.1 Hz, CH$_2$/CH$_3$CH$_2$–). IR (KBr) data (cm^{-1}): 2981 (s), 2929 (m), 2900 (m), 1477 (m), 1444 (m), 1391 (m), 1244 (s), 1207 (s), 1152 (vs), 1095 (m), 1015 (vs), 942, (vs), 764 (vs), 555 (s).

2.2.6. Synthesis of [(EtO)$_3$P]$_2$AgO$_3$SCH$_3$ (2e)

Complex **2e** was synthesized following the synthesis of **2a** (Section 2.2.1). In this respect, [(EtO)$_3$P] (1.4231 g, 8.57 mmol) was reacted with [AgO$_3$SCH$_3$] (0.8700 g, 4.285 mmol). After appropriate work-up (see Section 2.2.1), complex **2e** was obtained as a colourless liquid. Yield: 2.09 g (91%, based on AgO$_3$SCH$_3$). *Anal.* Calc. for C$_{13}$H$_{33}$O$_9$AgP$_2$S: C, 29.17; H, 6.21. Found: C, 29.03; H, 6.22%. ^{1}H NMR (CDCl$_3$): δ 1.2 (t, 18H, CH$_3$/CH$_3$CH$_2$–, J_{HH} = 7.0), 2.7 (s, 3H), 4.0 (m, 12H, CH$_2$/CH$_3$CH$_2$–). ^{13}C{H} NMR (CDCl$_3$): δ 39.2 (CH$_3$), 16.7 (J_{PC} = 5.6 Hz, CH$_3$/CH$_3$CH$_2$–), 61.3 (J_{PC} = 2.2 Hz, CH$_2$/CH$_3$CH$_2$–). IR (KBr) data (cm^{-1}): 2981 (s), 2934 (m), 2904 (m), 1478 (m), 1444 (s), 1388 (m), 1238 (s), 1208 (s), 1163 (s), 1098 (m), 1020 (vs), 939 (vs), 768 (vs), 531 (s).

2.2.7. Synthesis of [(EtO)$_3$P]$_3$AgO$_3$SCH$_3$ (2f)

Complex **2f** was synthesized following the synthesis of **2a** (Section 2.2.1). In this respect, [(EtO)$_3$P] (1.5644 g, 9.4 mmol) was reacted with [AgO$_3$SCH$_3$] (0.6337 g, 3.1 mmol). After appropriate work-up, complex **2f** can be isolated as a colourless liquid. Yield: 2.06 g (93%, based on AgO$_3$SCH$_3$). *Anal.* Calc. for C$_{19}$H$_{48}$O$_{12}$AgP$_3$S: C, 32.53; H, 6.90. Found: C, 32.33; H, 6.72%. ^{1}H NMR (CDCl$_3$): δ 1.2 (t, 27H, CH$_3$/CH$_3$CH$_2$–, J_{HH} = 7.0), 2.6 (s, 3H), 4.0 (m, 18H, CH$_2$/CH$_3$CH$_2$–). ^{13}C{H} NMR (CDCl$_3$): δ 39.2 (CH$_3$), 16.6 (J_{PC} = 5.8 Hz, CH$_3$/CH$_3$CH$_2$–), 60.8 (J_{PC} = 3.4 Hz, CH$_2$/CH$_3$CH$_2$–). IR (KBr) data (cm^{-1}): 2982 (vs), 2934 (s), 2902 (m), 1477 (m), 1444 (m), 1391(s), 1241 (s), 1209 (s), 1161 (s), 1098 (m), 1022 (vs), 941 (vs), 764 (vs), 531 (s).

2.3. Single crystal structures of Ph$_3$PAgO$_3$SCH$_3$ (2a) and (Ph$_3$P)$_2$AgO$_3$SCH$_3$ (2b)

Single crystals of **2a** and **2b** could be obtained by cooling a saturated dichloromethane solution to −30 °C. Suitable crystals for X-ray determination were placed in glue under N$_2$ for they are sensitive to moisture and oxygen. The crystal structure data collection was done on a BRUKER SMART APEX CCD diffractometer using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) at room temperature. The program SMART [26] was used for determination of the unit cell. Data reduction and integration was carried out with SAINT [26] and absorption corrections were applied using the program SADABS [27]. The structure was solved using direct methods and refined by full-matrix least-squares procedures on F^2 (SHELX-97 [28]). All of the non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data and details on refinement are presented in Table 1. The crystal structures of **2a** and **2b** are drawn using ORTEP [29].

3. Results and discussion

3.1. Synthesis

The phosphine/phosphite stabilized silver(I) methanesulfonates (L = Ph$_3$P, n = 1, **2a**; n = 2, **2b**; n = 3, **2c**; L = (EtO)$_3$P; n = 1, **2d**; n = 2, **2e**; n = 3, **2f**) were prepared by using Ph$_3$P/(EtO)$_3$P reacting with solver(I) methanesulfonate in dichloromethane in stoichiometry at 0 °C under nitrogen atmosphere in high yield (Scheme 1). The complexes were isolated as white solids (**2a–2c**) or colourless liquids (**2d–2f**). They are very sensitive to temperature, moisture, oxygen as well as light. The complexes are insoluble in cold
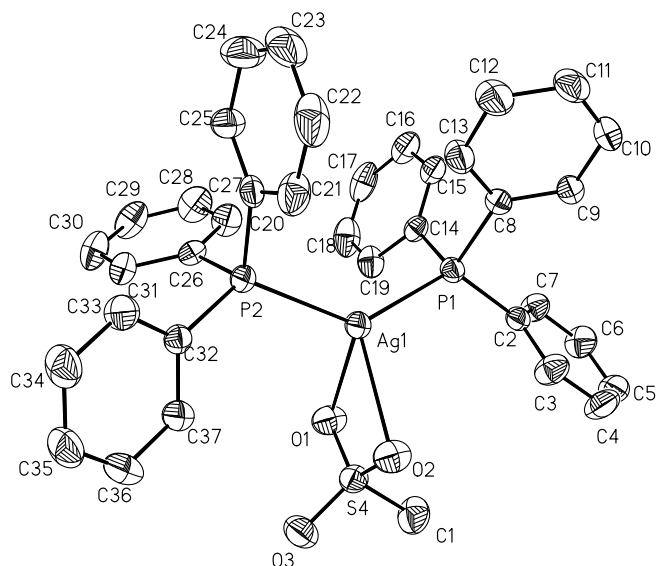
Table 1
Crystallographic data and structure refinement details for **2a** and **2b**

Compound	2a	2b
Formula	$C_{80}H_{80}Ag_4Cl_8O_{12}P_4S_4$	$C_{38}H_{35}AgCl_2O_3P_2S$
Formula weight	2200.64	812.43
Crystal dimensions (mm)	$0.4 \times 0.5 \times 0.6$	$0.5 \times 0.5 \times 0.6$
Crystal system	tetragonal	monoclinic
Space group	$I4_1/a$	$P2_1/c$
a (Å)	23.993(1)	9.381(1)
b (Å)	23.993(1)	20.165(1)
c (Å)	15.702(1)	19.653(1)
α (°)	90.00	90.00
β (°)	90.00	92.58
γ (°)	90.00	90.00
V [Å^3]	9039.2(8)	3714.1(4)
Z value	4	4
D_{calc} (g/cm^3)	1.617	1.453
Index ranges	$-26 \leqslant h \leqslant 30$,	$-10 \leqslant h \leqslant 11$,
	$-30 \leqslant k \leqslant 30$,	$-13 \leqslant k \leqslant 25$,
	$-17 \leqslant l \leqslant 19$	$-24 \leqslant l \leqslant 24$
$F(000)$	4416	1656
μ(Mo Kα) (mm^{-1})	1.309	0.864
λ (Mo Kα) (Å)	0.71073	0.71073
Temperature (K)	293	293
$2\theta_{max}$ (°)	54	54
Number of reflections measured	4934	7992
Independent reflections observed $[I > 2\sigma(I)]$	4568	6687
Number of refined parameters	254	433
R_1 $[I > 2\sigma(\theta)]^a$	0.0901	0.0624
wR_2 $[I > 2\sigma(\theta)]^b$	0.1592	0.1472
Goodness-of-fit^c	1.068	1.168
$\Delta\rho_{max}$ (e Å^{-3})	1.01	0.71
$\Delta\rho_{min}$ (e Å^{-3})	-0.61	-0.51

^{a} $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$.
^{b} $w_{2a} = 1/[\sigma^2(F_o^2) + (0.0038P)^2 + 166.3623P]$, $P = (F_o^2 + 2F_c^2)/3$. $w_{2b} = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 3.1225P]$, $P = (F_o^2 + 2F_c^2)/3$.
^{c} $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$, n = number of reflections, p = parameters used.

$$CH_3SO_3Ag + nL \xrightarrow{CH_2Cl_2} L_nAgO_3SCH_3$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2a - 2f}$$

L = Ph$_3$P;	n = 1 (2a)
	n = 2 (2b)
	n = 3 (2c)
L = (EtO)$_3$P;	n = 1 (2d)
	n = 2 (2e)
	n = 3 (2f)

Scheme 1. Synthesis of complexes **2a–2f**.

non-polar solvent like petroleum, whereas they are highly soluble in polar or unsaturated hydrocarbons such as methylenechloride, benzene. All the obtained products gave satisfactory elemental analysis results, which were characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C{H} NMR, respectively.

As we know, the typical group vibration of sulfonates shows in the range of 1350–1050 cm^{-1} [30,31]. When the R–SO$_3^-$ anion is "free", that is to say, non-coordinated, it shows local C_{3v}-symmetry with two v_{so} bands for the symmetrical. Upon coordination to a metal, the C_{3v}-symmetry is broken and for a C_s-symmetrical R–SO$_2$–O–M moiety and three v_{SO} bands are observed (v^{as}(SO$_2$); v^s(SO$_2$); v(S–O)). In the case of lithium and sodium salt of the methanesulfonate anion (CH$_3$SO$_3^-$), the v^{as}(SO$_2$); v^s(SO$_2$) are observed at 1233 and 1060 cm^{-1}, respectively (for the NaO$_3$SCH$_3$) and $v^{as}_{(SO2)}$ (1244 cm^{-1}); $v^s_{(SO2)}$ (1185 cm^{-1}); $v_{(S-O)}$ (1050 cm^{-1}) for LiO$_3$SCH$_3$ [32]. In the IR spectra of **2a–2f** it shows prominent absorptions in v_{SO3} region. The absorptions in the range of 1238–1268 cm^{-1}

and 1180–1200 cm^{-1} can be interpreted as the asymmetric and symmetric vibration of SO$_2$, which is the similar as previous reported [33–37]. The absorptions around 1030 cm^{-1} can be assigned as vibration of S–O; which is similar to the reported value [33–37].

The NMR spectra (^{1}H and ^{13}C{H}) were recorded for all six complexes (see Section 2) at room temperature, In ^{1}H NMR, the proton spectra were consistent with the stoichiometries of the complexes. The protons of complexes **2a–2c** in the aryl proton region of the ^{1}H NMR spectra were in the range of 7.2–7.6 ppm. The complexes (**2d–2f**) are easily distinguished because the resonances of the protons show only two groups. The proton of CH$_3$ – in CH$_3$SO$_3$ – appeared at 2.6–2.8 ppm, which agrees with previous reported [23]. In the ^{13}C{H} NMR spectra of **2a–2c** the triphenylphosphine carbon resonances are easily distinguished (in the range of 129.6–134.2 ppm). The carbon resonance of CH$_3$ – on CH$_3$SO$_3$ – shows in the lower field (39.1–39.4 ppm) comparing to that of [(EtO)$_3$P] (ca. 16.7 ppm).

3.2. Single crystal structure of 2a and 2b

The X-ray single crystal analysis results indicate that the molecular formula of complex **2a** is [(Ph$_3$PAgO$_3$SCH$_3$)$_4$ · 4CH$_2$Cl$_2$] and complex **2b** is [(Ph$_3$P)$_2$AgO$_3$SCH$_3$ · CH$_2$ Cl$_2$]. Because of different molar ratio of triphenylphosphine with silver methylsulfonate, complex **2b** is a monomer with each silver atom coordinated by two PPh$_3$ groups. Complex **2a**, however, is a tetramer with the silver atom coordinated by one PPh$_3$ group. The molecular structure of **2a** and **2b** are depicted in Fig. 1 and Fig. 2, and selected bond distances (Å) and bond angles (°) are given in Table 2.

Complex **2a** crystallizes in the tetragonal with space group $I4_1/a$, which is composed of a tetramer [Ph$_3$PAgO$_3$SCH$_3$]$_4$ and four molecules of dichloromethane, as shown in Fig. 1. This is different from the reported complex [Ph$_3$PAgO$_3$SCF$_3$] which exists as a trimer [38]. In the tetramer complex, the Ag$_4$O$_4$ core of the molecule is regarded as a "cubane-like" framework, with the alternate corners of the cube occupied by the silver atoms and the methanesulfonic oxygen atoms. The phosphorous atoms are approximately apical,

Fig. 1. ORTEP drawing of **2a**, showing 30% probability displacement ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity.

Fig. 2. ORTEP drawing of **2b**, showing 30% probability displacement ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for **2a** and **2b**

*Complex **2a***			
Ag(1)–P(1)	2.348(2)	Ag(1)–O(1)	2.389(5)
Ag(1)–O(1)[b]	2.465(5)	Ag(1)–O(1)[c]	2.449(5)
P(1)–Ag(1)–O(1)	135.5(1)	P(1)–Ag(1)–O(1)[b]	133.0(1)
P(1)–Ag(1)–O(1)[c]	130.8(1)	O(1)–Ag(1)–O(1)[b]	79.5(2)
O(1)–Ag(1)–O(1)[c]	78.5(2)	O(1)[b]–Ag(1)–O(1)[c]	77.1(2)
Ag(1)–O(1)–Ag(1)[a]	102.5(2)	Ag(1)[a]–O(1)–Ag(1)[b]	100.3(2)
Ag(1)–O(1)–Ag(1)[b]	98.7(2)		
Complex 2b			
Ag(1)–P(1)	2.434(1)	Ag(1)–P(2)	2.422(1)
Ag(1)–O(1)	2.501(3)	Ag(1)–O(2)	2.552(3)
P(1)–Ag(1)–P(2)	132.4(4)	P(1)–Ag(1)–O(1)	104.0(8)
P(1)–Ag(1)–O(2)	108.9(8)	P(2)–Ag(1)–O(1)	106.6(8)
P(2)–Ag(1)–O(2)	118.3(8)	O(1)–Ag(1)–O(2)	56.5(1)

Symmetry code: a = 5/4 − y, 1/4 + x, 9/4 − z; b = 1 − x, 3/2 − y, z; c = −1/4 + y, 5/4 − x, 9/4 − z.

coordinating to the silver atom, thereby completing a distorted tetrahedral coordination arrangement of the silver atom. The angles of O–Ag–O [79.5(2)°, 77.1(2)°, 78.5(2)°] and Ag–O–Ag [100.7(2)°, 102.5(2)°, 98.7(2)°] are close to 90°, but the former are smaller than the latter, which confirms the deformation of the "cubane" just like other "cubane-like" complexes [39,40]. The P–Ag distance (2.348(2) Å) is close to the sum of covalent radio of P and Ag atoms (2.44 Å) [39] and slightly shorter than other complexes [(Ph₃P)₂Ag (O₂CC₃F₇)] 2.406(1) Å [24], [(Ph₃P)₃Ag(OPhMe₂)], 2.539(2) Å [41].

Complex **2b** crystallizes in the tetragonal with space group P 2₁/c and exists as a monomer with a molecule of dichloromethane in crystal structure (show in Fig. 2). The silver atom is coordinated by two phosphorus atoms of triphenylphosphine and two methanesulfonic oxygen atoms at the same time. This coordination mode is similar to the reported complex [(MePh₂P)₂AgO₃SCF₃] [42] and several silver(I) carboxylates such as [(Ph₃P)₂Ag (O₂CCH=CHCH₂CH₂CH₃)] [24] and [(Ph₃P)₂Ag(CO₂CF₃)], but different from the reported complex [(Ph₃P)₂AgO₃SCF₃] [42] which exists as a dimmer. The distances of Ag–P [2.422(1), 2.434(1) Å] are longer than that of [(R₃P)₂AgO₃SCF₃] [2.385(8), 2.389(8) Å] and complex **2a** [2.348(2) Å]. The Ag–O distances [2.501(3),
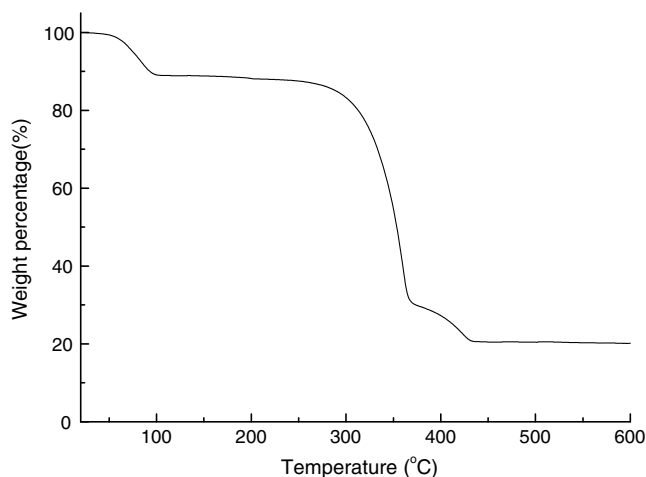

Fig. 3. TG trace of **2a** (heating rate of 10 °C min⁻¹, nitrogen atmosphere).

2.552(3) Å] are much shorter than those [2.775(2), 2.854(2) Å] of [(MePh₂P)₂AgO₃SCF₃] [42] and much longer than those in complex **2a** [2.389(5), 2.449(5), 2.465(5) Å]. The P–Ag–P angle [132.4(4)°] is much smaller than that [156.2(3)°] of [(MePh₂P)₂AgO₃SCF₃] [42], respectively.

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (Fig. 3) was carried-out to determine the relative volatility and evaluate the suitability of complex as possible CVD precursors. These studies are also required to optimize the temperature at which the respective single silver precursor should be maintained during the CVD experiments. Complex **2a**, for example, decomposes between 50 and 440 °C in a three-step process. The first step takes place between 50 and 105 °C with the 10.97% weight loss, the second step is observed in the range of 105–370 °C with the 58.43% weight loss, and the third step is between 370–440 °C with the 10.10% weight loss. The total weight loss is 79.50%. These data show that the percentage of the residue is 20.50% (Ag), which is close to the theoretical value of silver (23.18%) in complex **2a**. The real thermal decomposition mechanism of complex **2a** and other complexes would be studied in the further research.

4. Supplementary data

CCDC 656251 and 666194 contain the supplementary crystallographic data for **2a** and **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] M. Dennehy, O.V. Quinzani, M. Jennings, J. Mol. Struct. 841 (2007) 110.
[2] I.G. Dance, Polyhedron 5 (1986) 1037.
[3] B. Krebs, G. Henkel, Angew. Chem., Int. Ed. Engl. 30 (1991) 769.
[4] C. Housecroft, Coord. Chem. Rev. 115 (1992) 141.
[5] R.H. Holm, P. Kennepohl, E.I. Solomon, Chem. Rev. 96 (1996) 2239.
[6] M.C. Hong, W.P. Su, R. Cao, W.J. Zhang, J.X. Lu, Inorg. Chem. 38 (1999) 600.
[7] F. Colombo, R. Annunziata, M. Benaglia, Tetrahedron Lett. 48 (2007) 2687.
[8] K. Ozawa, F. Iso, Y. Nakao, Z.X. Cheng, H. Fujii, M. Hase, H. Yamaguchi, J. Eur. Ceram. Soc. 27 (2007) 2665.
[9] H. Schmidt, Y. Shen, M. Leschke, Th. Haase, K. Hohse-Hoeinghaus, H. Lang, J. Organomet. Chem. 669 (2003) 25.
[10] W. Partenheimer, E.H. Johnson, Inorg. Chem. (11) (1972) 2840.
[11] W. Partenheimer, E.H. Johnson, Inorg. Chem. (12) (1973) 1274.
[12] H.K. Hofstee, J. Boersma, G.J.M. van der Kerk, J. Organomet. Chem. 120 (1976) 313.
[13] W.T. Miller, R.H. Sinder, R.J. Hummel, J. Am. Chem. Soc. 91 (1969) 6532.
[14] Y. Zheng, N.H. Dryden, J.J. Vittal, R.J. Puddephatt, Chem. Mater. 7 (1995) 1696.
[15] M. Wen, M. Munakata, Y.Z. Li, Y. Suenaga, T. Kuroda-Sowa, M. Maekawa, M. Anahata, Polyhedron 26 (2007) 2455.
[16] J. Rickerby, J.H.G. Steinke, Chem. Rev. 102 (2002) 1525.
[17] H.K. Shin, K.M. Chi, J. Farkas, M.J. Hampden-Smith, T.T. Kodas, E.N. Duesler, Inorg. Chem. 31 (1992) 424.
[18] A. Bailey, T.S. Corbitt, M.J. Hampden-Smith, E.N. Duesler, T.T. Kodas, Polyhedron 12 (1993) 1785.
[19] D.A. Edwards, M. Longley, J. Inorg. Nucl. Chem. 40 (1978) 1599.
[20] G. Doyle, K.A. Erickson, D. Van Engen, Organometallics 4 (1985) 830.
[21] D. Gibson, B.F.G. Johnson, J. Lewis, J. Chem. Soc. A. (1970) 367.
[22] S.S. Monim, Z. Yuan, K. Griffiths, P.R. Norton, R.J. Puddephatt, J. Am. Chem. Soc. 117 (1995) 4030.
[23] D.A. Edwards, R.M. Harker, M.F. Mahon, K.C. Molloy, J. Mater. Chem. 9 (1999) 1771.
[24] J.L. Han, Y.Z. Shen, C.X. Li, Y.Z. Li, Y. Pan, Inorg. Chim. Acta 358 (2005) 4417.
[25] D.A. Edwards, R.M. Harker, M.F. Mahon, K.C. Molloy, Inorg. Chim. Acta 328 (2002) 134.
[26] Bruker AXS Inc., SAINT, Area Detector Control and Data Integration and Reduction Software, Madison, WI, USA, 1997.
[27] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Germany, 1997.
[28] G.M. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis (Release 97-2), University of Gottingen, Germany, 1997.
[29] L. Zsolnai, G. Huttner, ORTEP, University of Heidelberg, Germany, 1994.
[30] L.J. Bellamy, The Infrared Spectra of Complexes Molecules, vol. 1, Chapman and Hall, London, 1975.
[31] M.G. Miles, G. Doyle, R.P. Cooney, R.S. Tobis, Spectrochim. Acta A 25 (1960) 1515.
[32] R.J. Capwell, K.H. Rhee, K.S. Seshadri, Spectrochim. Acta A 24 (1968) 955.
[33] S.M. Chackalackal, F.E. Stafford, J. Am. Chem. Soc. 88 (1966) 4815.
[34] R. Bala, R.P. Sharma, A.D. Bond, J. Mol. Struct. 830 (2007) 198.
[35] C.Y. Panicker, H.T. Varghese, D. Philip, H.I.S. Nogueira, Spectrochim. Acta A 64 (2006) 744.
[36] D. Philip, A. Eapen, G. Aruldhas, J. Solid State Chem. 116 (1995) 217.
[37] D. Jamro, Y. Marechal, J. Phys. Chem. B. 109 (2005) 19664.
[38] R. Terroba, M.B. Hursthouse, M. Lagunab, A. Mendia, Polyhedron 18 (1999) 807.
[39] B.K. Teo, J.C. Calabrese, Inorg. Chem. 15 (1976) 2467.
[40] M.R. Churchill, K.L. Kalra, Inorg. Chem. 13 (1974) 1065.
[41] D.A. Edwards, M.F. Mahon, K.C. Molloy, V. Ogrodnik, Inorg. Chim. Acta 349 (2003) 37.
[42] M. Bardají, O. Crespo, A. Laguna, A.K. Fischer, Inorg. Chim. Acta 304 (2000) 7.