Aerosol-assisted chemical vapour deposition (AACVD) of silver films from triorganophosphine adducts of silver carboxylates, including the structure of [Ag(O$_2$CC$_3$F$_7$)(PPh$_3$)$_2$]

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Abstract

Silver carboxylates [Ag(O$_2$CR): R = Me, ^{t}Bu, 2,4,6-Me$_3$C$_6$H$_2$], fluorocarboxlyates [Ag(O$_2$CR$_f$): R$_f$ = C$_3$F$_7$, C$_6$F$_{13}$, C$_7$F$_{15}$] and their phosphine adducts [Ag(O$_2$CR)·nPR$'_3$: R = Me, ^{t}Bu, 2,4,6-Me$_3$C$_6$H$_2$, R$'$ = Me, Ph, n = 2; R = Me, R$'$ = Me, n = 3; Ag(O$_2$CR$_f$).2PPh$_3$, R$_f$ = C$_3$F$_7$, C$_6$F$_{13}$, C$_7$F$_{15}$] have been synthesised, characterised spectroscopically and used as precursors in the aerosol-assisted chemical vapour deposition of silver films. All the phosphine adducts produced films, though in general PMe$_3$ adducts, proved more successful than PPh$_3$ analogues. The fluoro-carboxylates and their PPh$_3$ adducts all generated silver films, though the growth rate for the adducts was lower. All these latter films showed carbon impurities while fluorine was also evident in most cases. The X-ray structure of AgO$_2$CC$_3$F$_7$·2PPh$_3$ is also reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silver; Carboxylate; Phosphine; Thin film; AACVD; X-ray

1. Introduction

Silver films have a wide variety of technological applications including contacts in microelectronic circuitry [1], components of high T_c superconductors [2] and bactericidal coatings [3], and thus there is a continuing interest in methodology for their deposition. Two issues are central to this process; precursor design; and delivery method. The thermal instability and general involatility of most silver precursors examined to date has dictated that only low-pressure CVD experiments have consistently been successful in depositing films, though more recently we and others have shown aerosol-assisted CVD to be equally effective. Furthermore, although a number of precursor systems have been reported, the overwhelming majority are based on adducts of β-diketonates, viz: Ag(hfac)(L) with L = cod [4], Me$_3$P (1; 1:2) [4–6], Et$_3$P [5,6], MeCN [7], Et$_2$S [8], Et$_3$SiCH=CH$_2$ [9], Me$_3$SiC≡CSiMe$_3$ [10] or Ag(fod)·(L),

with L=Me$_3$P [6], Et$_3$P [6,11]. We have recently reported the use of a variety of Ph$_3$P adducts of both silver β-diketonates and β-ketoiminates, Ag(hfacNhex)(PPh$_3$) being a particularly effective precursor [12]. In addition to these, brief reports on the use of AgF [13], AgI [14], [CF$_3$(F)C=C(CF$_3$)]Ag [15,16] and C$_5$H$_5$Ag(PR$_3$) [17] have also been made.

Silver carboxylates constitute an alternative class of precursors for silver CVD which, until very recently, appear to have been largely overlooked, though the use of Ag(O$_2$CCF$_3$) has been reported [18,19]. Other silver fluorocarboxylates Ag(O$_2$CR$_f$) [R$_f$ = CF$_3$(CF$_2$)$_2$, CF$_3$(CF$_2$)$_6$, CF$_3$(CF$_2$)$_8$, C$_6$F$_5$, C$_6$F$_5$CH$_2$] and representative 1:1 adducts Ag(O$_2$CR$_f$)(PPh$_3$) (R = C$_2$F$_5$, C$_3$F$_7$, C$_7$F$_{15}$, C$_9$F$_{19}$, C$_6$F$_5$, C$_6$F$_5$CH$_2$) have since been prepared and their thermal stabilities assessed [20,21]. A more detailed examination of AgO$_2$CC$_2$F$_5$ [22] and the adducts Ag(O$_2$CR$_f$)(PMe$_3$) (R$_f$ = C$_2$F$_5$, C$_3$F$_7$, C$_8$F$_{17}$) [22,23] has recently been published, while the use of Ag(CO$_2$C$_4$H$_9^t$)(PBu$_3$) has also recently been communicated [24].

Like β-diketonates, the carboxylates groups are potentially bidentate allowing for greater stability and

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coordinative saturation around the metal. Silver carboxylates are known to be thermally stable at temperatures below several hundred degrees Centigrade and are thought to decompose like many metal carboxylates via a decarboxylation mechanism [25].

$$AgO_2CR \xrightarrow{\Delta} RAg + CO_2$$
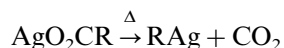
Decarboxylation has been implicated in both thermal decomposition [26,27], and mass spectrometry studies of silver carboxylates [28–30]. The Hunsdieker reaction, in which AgO_2CR and bromine react to give RBr, $AgBr$ and CO_2, essentially involves the thermal decarboxylation of a silver carboxylate in the presence of a catalyst. Such a decomposition mechanism yields unstable organometallic species in situ, thus silver carboxylates could effectively be considered as 'masked' organosilver precursors. Silver fluorocarboxylates are also thought to decompose via decarboxylation [25] on the basis of mass spectrometry [28,30], thermal [20,21,26,27,31] and photochemical decomposition [26] studies. It has, however, been suggested that the decomposition pathway may differ mechanistically from that of non-fluorinated carboxylates [27], as up to 80% yields of coupling products, R–R, are also produced in the reaction:

$$2AgO_2C(CF_2)_nCF_3 \xrightarrow{\Delta} CF_3(CF_2)_{2n} + CF_3 + 2CO_2 + 2Ag$$
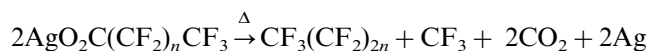
In this paper we report the use of phosphine adducts of AgO_2CR as precursors for the deposition of silver films by aerosol-assisted chemical vapour decomposition (AACVD) methodology.

2. Experimental

2.1. General

IR spectra were recorded as Nujol or hexachlorobutadiene mulls between KBr plates using a Nicolet 510P Fourier transform spectrometer within the range $4000–400$ cm^{-1} with a medium slit width and a peak resolution of 4.0 cm^{-1}; data are quoted only for the region $1800–1200$ cm^{-1}. Carbon, hydrogen and nitrogen were determined using a Carlo–Erba Strumentazione E.A. model 1106 microanalyser operating at 500 °C. Results were calibrated against an acetanilide standard. ^1H and ^{13}C NMR spectra were recorded using either JEOL JNM-GX-270FT (270 MHz) or JEOL EX-400 (400 MHz) Fourier transform spectrometers using $SiMe_4$ as an internal reference. ^{19}F, ^{31}P and ^{109}Ag NMR spectra were recorded on a JEOL EX-400 (400 MHz) spectrometer; chemical shifts are relative to $CFCl_3$ $[\delta(^{19}F)]$, 85% H_3PO_4 $[\delta(^{31}P)]$ and 1 M $AgNO_3$ $[\delta(^{109}Ag)]$. ^{109}Ag spectra were recorded as DEPT experiments at an observational frequency of 18.45 MHz. A pulse width

of 25 μs was used with an acquisition time of 0.744 s and a pulse delay of 10.0 s. Observable resonances were typically detected after 500–1000 scans.

Thermal analysis experiments were carried out using Dupont 951 TGA module and Dupont 910 DSC cell-base with a TA Instruments 2100 controller, at atmospheric pressure in either air-, nitrogen- or helium-purged atmospheres, from room temperature (r.t.) to 850 °C at a ramp rate of 25 °C min^{-1}. Samples were examined by SEM using a JEOL 6310 scanning electron microscope operating at accelerating voltages of 5, 10 or 15 kV. Coatings under investigation were not sputter coated, although, a path to ground was provided by means of silver dag or electrically conducting putty. Film thickness estimates using EDXS techniques were performed on a JEOL Superprobe instrument operating at an accelerating voltage of 5 kV with a beam current of 5×10^{-8} A. Sheet resistance was measured over a 25 mm square. Silver 'dag' busbar contacts were painted on the sample and resistance measured using a digital voltmeter. Reflectance spectra at near-normal incidence were measured on a Hitachi U-3410 spectrophotometer over the range 295–2600 nm in 5 nm steps. Calibration was against rhodium standard mirrors. Reflectance data are quoted at $\lambda = 550$ nm for both the coated surface and the film/glass interface (as observed through the glass). The assessment area (corresponding to the beam size) was a rectangle of approximately 11×4 mm.

Details of our apparatus and experimental methodology for the AACVD of silver films are given elsewhere [12]. Typically, 0.4–0.8 g of sample was dissolved in 25–40 cm^3 of THF, experimental growth times were dependent on N_2 (carrier) flow rates (typically 0.7–1.2 l min^{-1}) and varied between 10 and 30 min.

2.2. Synthesis

2.2.1. Silver(I) acetate, $Ag(O_2CCH_3)$ (1)

A solution of silver nitrate (3.7 g, 21.8 mmol) in 20 cm^3 of distilled water was added to a solution of sodium acetate (1.7 g, 21.1 mmol) in 20 cm^3 of distilled water. The precipitate was filtered immediately in air, washed with distilled water, ethanol and diethyl ether, and dried in vacuo. Yield 2.26 g, 64%. *Anal.* Found (Calc. for $C_2H_3O_2Ag$) C, 14.3(14.4); H, 1.76(1.81); Ag, 66.7 (64.6)%. IR: 1345w, 1422sh, 1514b. ^1H NMR (DMSO-d^6): 1.8 (s, CH_3). ^{13}C NMR (DMSO-d^6): 174.8 (O_2C), 22.2 (CH_3).

2.2.2. Silver pivalate, $Ag(O_2CC_4H_9{}^t)$ (2)

Pivalic acid (5.0 g, 49 mmol) was suspended in 100 cm^3 of distilled water and stirred vigorously with gentle warming. The acid was solubilised with concentrated ammonia solution, then the solution was gently

warmed to remove excess ammonia. The reaction mixture was filtered to remove unreacted acid and impurities found in the acid. Silver nitrate (8.5 g, 50 mmol) was dissolved in 25 cm^3 of distilled water and added to the solution resulting in a thick white precipitate, which was filtered immediately in air. The precipitate was washed with distilled water followed by ethanol and diethyl ether and dried in vacuo for 3 h. Yield 9.2 g, 88%. *Anal*. Found (Calc. for $C_5H_9O_2Ag$) C, 28.6 (28.7); H, 4.35 (4.3)%. IR: 1217, 1352, 1366, 1399,1512, 1526, 1564. ^{1}H NMR (DMSO-d^6): 1.12 (s, CMe$_3$). ^{13}C NMR (DMSO-d^6): 182.0 (O$_2$C), 29.0 (CCH$_3$). ^{109}Ag NMR (20 °C, DMSO-d^6): 303.

Also prepared by the same method as for **2** were.

2.2.3. Silver mesitylate, $Ag(O_2CC_6H_2Me_3)$ (3)

Yield 96%. *Anal*. Found (Calc. for $C_9H_{11}O_2Ag$) C, 44.0 (41.7); H, 4.11 (4.28)%. IR: 1393, 1441, 1557, 1613. ^{1}H NMR (DMSO-d^6): 6.76 (m, 2H, C$_6$H$_2$), 2.23 (m, 6H, *o*-CH$_3$), 2.20 (m, 3H, *m*-CH$_3$). ^{13}C NMR (DMSO-d^6): 174.3 (O$_2$C), 139.0, 135.1, 132.4, 127.5 (C$_6$H$_2$Me$_3$), 20.7 (C$_6$H$_2$CH$_3$), 20.1 (C$_6$H$_2$CH$_3$). ^{109}Ag (20 °C, DMSO-d^6): 266.

2.2.4. Silver perfluoroheptanoate, $Ag(O_2CC_6F_{13})$ (5)

Yield 77%. *Anal*. Found (Calc. for $C_7F_{13}O_2Ag$): C, 17.7 (17.8)%. M.p. 282 °C. IR: 1233, 1366, 1424, 1460, 1578, 1611, 1660. ^{13}C NMR (DMSO-d^6): 159.8 (m, $J = 23.5$ Hz, O$_2$C), 119.1 (m, CF$_n$), 115.3 (m, CF$_n$), 110.6 (m, CF$_n$). ^{19}F NMR (DMSO-d^6): −80.7 (t, $J = 9.9$ Hz, CF$_3$), −115.0 (t, $J = 12.1$ Hz, αCF$_2$), −121.8 (CF$_2$), −122.2 (CF$_2$), −123.0 (CF$_2$), −126.1 (CF$_2$). ^{109}Ag NMR (20 °C, DMSO-d^6): 171.

2.2.5. Silver perfluorooctanoate, $Ag(O_2CC_7F_{15})$ (6)

Yield 53%. *Anal*. Found (Calc. for $C_8F_{15}O_2Ag$): C, 18.2 (18.5)%. M.p. 252–261 °C (by DSC). IR: 1204, 1237, 1296, 1323, 1366, 1420, 1613. ^{13}C NMR (DMSO-d^6): 159.0 (m, $J = 23$ Hz, O$_2$C), 118 (CF$_n$), 115 (CF$_n$), 112 (CF$_n$), 108 (CF$_n$). ^{19}F NMR (DMSO-d^6): −80.9 (t, $J = 8.7$ Hz, CF$_3$), −115.1 (t, $J = 11.2$ Hz, αCF$_2$), −121.8 (CF$_2$), −122.3 (CF$_2$), −122.4 (CF$_2$), −123.1 (CF$_2$), −126.4 (CF$_2$). ^{109}Ag NMR (20 °C, DMSO-d^6): 173.

2.2.6. Silver perfluorobutyrate, $Ag(O_2CC_3F_7)$ (4)

Silver oxide (1.0 g, 4.3 mmol) was added to a stirred solution of perfluorobutyric acid (1.65 g, 7.7 mmol) in distilled water. After stirring for 30 min, the solution was filtered to remove unreacted silver oxide. Solvent and unreacted acid were removed in vacuo over 4 h to leave a dry white solid. Yield 1.67 g, 68%. *Anal*. Found (Calc. for $C_4F_7O_2Ag$): C, 14.9 (14.9)%. M.p. 298 °C (by DSC). IR: 1225, 1287, 1343, 1426, 1609, 1669. C NMR (DMSO-d^6): 135.6 (m, 30 Hz, CO$_2$), 89.9 (qt, 287, $J = 30$ Hz, CF$_n$), 81.0 (m, CF$_n$). ^{19}F NMR

(DMSO-d^6): −81.7 (t, $J = 8.1$ Hz, CF$_3$), −119.2 (q, $J = 8.1$ Hz, αCF$_2$), −128.3 (CF$_2$). ^{109}Ag NMR (20 °C, DMSO-d^6): 173.

2.2.7. O,O′-Acetatobis(trimethylphosphine)silver(I), $Ag(O_2CCH_3)(PMe_3)_2$ (7)

Silver acetate (**1**) (0.4 g, 2.3 mmol) was suspended in benzene (15 cm^3) and stirred. To this was added 3.5 equiv. of trimethylphosphine as a solution in toluene (1 M soln., 8 cm^3, 8 mmol). The solution cleared immediately on addition of the phosphine. The solvent and excess phosphine were removed in vacuo to give a brown precipitate in quantitative yield. On contact with air the compound reverted to a slightly brown clear oil. *Anal*. Found (Calc. for $C_8H_{21}O_2AgP_2$) C, 30.8 (30.1); H, 6.46 (6.63)%. IR: 1261, 1283, 1339, 1404, 1574. ^{1}H NMR (CDCl$_3$): 1.78 (s, 3H, O$_2$CCH$_3$), 1.25 (s, 18H, PCH$_3$). ^{13}C NMR (CDCl$_3$): 180.8 (O$_2$C), 21.0 (CH$_3$) 15.8 (d, $J = 11.1$ Hz, PCH$_3$). ^{31}P NMR (20 °C, CDCl$_3$): −38.4. ^{31}P NMR (−80 °C, CDCl$_3$/CH$_2$Cl$_2$): −43.4 (dd, $J = 268$ Hz), −38.8 (br). ^{109}Ag NMR (−80 °C, CDCl$_3$/CH$_2$Cl$_2$): 772.

Also prepared by the same method as **7** were.

2.2.8. O,O′-Pivalatobis(trimethylphosphine)silver(I), $Ag(O_2CC_4H_9{}^t)(PMe_3)_2$ (8)

Yield 70%. *Anal*. Found (Calc. for $C_{11}H_{27}O_2AgP_2$) C, 34.8 (36.7); H, 7.82 (7.56)%. IR: 1219, 1283, 1304, 1362, 1401, 1422, 1557, 1653. ^{1}H NMR (CDCl$_3$): 1.25 (s, 18H, PCH$_3$), 1.11 (s, 9H, CCH$_3$). ^{13}C NMR (CDCl$_3$): 184.7 (O$_2$C), 39.4 (CCH$_3$), 28.6 (–CCH$_3$), 15.3 (d, $J = 8.3$ Hz, PCH$_3$). ^{31}P NMR (20 °C, CDCl$_3$): −39.1. ^{31}P NMR (−80 °C, CDCl$_3$/CH$_2$Cl$_2$): −38.2 (br).

2.2.9. O,O′-Mesitylatobis(trimethylphosphine)silver(I), $Ag(O_2CC_6H_2Me_3)(PMe_3)_2$ (9)

Yield 97%. *Anal*. Found (Calc. for $C_{15}H_{29}O_2AgP_2$) C, 45.3 (43.8); H, 7.11 (7.11)%. The compound was successfully recrystallised from a heptane–dichloromethane solvent mixture, although analysis results were no closer. *Anal*. Found (Calc. for $C_{15}H_{29}O_2AgP_2$) C, 45.4 (43.8); H, 7.21 (7.11)%. IR: 1287, 1304, 1435, 1564. ^{1}H NMR (CDCl$_3$): 6.66 (m, 2H, C$_6$H$_2$), 2.27 (m, 6H, *o*-CH$_3$), 2.14 (m, 3H, *p*-CH$_3$), 1.30 (s, 18H, PCH$_3$). ^{13}C NMR (CDCl$_3$): 176.5 (O$_2$C), 140.5, 135.1, 132.5, 127.8 (C$_6$H$_2$Me$_3$), 20.9, 20.3 (C$_6$H$_2$CH$_3$), 16.1 (PCH$_3$). ^{31}P NMR (20 °C, CDCl$_3$): −39.6. ^{31}P NMR (−80 °C, CDCl$_3$/CH$_2$Cl$_2$): −38.0 (d, $J \sim 500$ Hz). ^{109}Ag NMR (−80 °C, CDCl$_3$/CH$_2$Cl$_2$): 834.

2.2.10. O,O′-Acetatobis(triphenylphosphine)silver(I), $Ag(O_2CCH_3)(PPh_3)_2$ (10)

Yield 85%. *Anal*. Found (Calc. for $C_{38}H_{33}O_2AgP_2$) C,65.9 (66.0); H, 4.78 (4.81)%. IR: 1308, 1331, 1396, 1553. ^{1}H NMR (CDCl$_3$): 7.41–7.22 (m, 30H, C$_6$H$_5$), 2.01 (s, 3H, O$_2$CCH$_3$). ^{13}C NMR (CDCl$_3$): 177.6 (O$_2$C),

133.6 (d, 8.3 Hz, PC_6H_5), 132.4 (d, $J = 11.9$ Hz, PC_6H_5), 129.7 (PC_6H_5), 128.5 (d, $J = 4.6$ Hz, PC_6H_5). ^{31}P NMR (20 °C, $CDCl_3$): 8.01. ^{31}P NMR (-80 °C, $CDCl_3$–CH_2Cl_2): 7.6 (dd, $J = 490$ Hz). ^{109}Ag NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 907 (t, $J = 489$ Hz).

2.2.11. O,O′-Pivalatobis(triphenylphosphine)silver(I), Ag(O_2CC_4H_9 ′)(PPh_3)_2 (11)

Yield 52%. *Anal.* Found (Calc. for $C_{41}H_{39}O_2AgP_2$) C, 66.9 (67.1); H, 5.31(5.36)%. IR: 1225, 1406, 1435, 1477, 1543. ^1H NMR ($CDCl_3$): 7.45–7.22 (m, 30H, C_6H_5), 1.23 (s, 9H, CCH_3). ^{13}C NMR ($CDCl_3$): 185.2 (O_2C), 133.9 (d, $J = 18.4$ Hz, PC_6H_5), 132.5 (d, $J = 27.6$ Hz, PC_6H_5), 129.9 (PC_6H_5), 128.6 (d, $J = 9.2$ Hz, PC_6H_5), 39.4 (CCH_3), 28.7 (CCH_3). ^{31}P NMR (20 °C, $CDCl_3$): 8.51. ^{31}P NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 7.75 (dd, $J = 480$ Hz). Ag NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 931 (t, $J = 484$ Hz).

2.2.12. O,O′-Mesitylatobis(triphenylphosphine)silver(I), Ag(O_2CC_6H_2Me_3)(PPh_3)_2 (12)

Yield 6.5 mmol, 94%. *Anal.* Found (Calc. for $C_{46}H_{42}O_2AgP_2$) C, 68.5 (69.4); H, 5.15 (5.31)%. The compound was satisfactorily recrystallised from a toluene–dichloromethane solvent mixture to give poor quality crystals approximating to the compound as a 1:1 dichloromethane solvate. *Anal.* Found (Calc. for $C_{47}H_{44}O_2AgP_2Cl_2$) C, 64.0 (64.0); H, 4.69 (5.0)%. IR: 1304, 1435, 1479, 1545, 1574. ^1H NMR ($CDCl_3$): 7.35–7.15 (m, 30H, PC_6H_5), 6.65 (m, 2H, $O_2C_6H_2$), 2.16 (m, 6H, o-CH_3), 2.00 (m, 3H, p-CH_3). ^{13}C NMR ($CDCl_3$): 176.9 (O_2C), 139.5, 134.8 ($C_6H_2Me_3$), 133.8 (d, $J = 8.3$ Hz, PC_6H_5, 133.1 (d, $J = 9.2$ Hz, PC_6H_5), 132.6 ($C_6H_2Me_3$), 129.8 (PC_6H_5, 128.7 (d, $J = 4.6$ Hz, PC_6H_5), 127.2 ($C_6H_2Me_3$), 20.9 ($C_6H_2CH_3$), 19.4 ($C_6H_2CH_3$). ^{31}P NMR (20 °C, $CDCl_3$): 5.56. ^{31}P NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 7.98 (dd, $J = 497$ Hz). ^{109}Ag NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 895 (t, $J = 503$ Hz).

2.2.13. O,O′-Acetatotris(triphenylphosphine)silver(I), Ag(O_2CCH_3)(PPh_3)_3 (13)

Silver acetate (**1**) (1.67 g, 10 mmol) was added to a solution of triphenylphosphine (9.18 g, 35 mmol) in 50 cm^3 of toluene and the mixture stirred in the absence of light for 24 h. The pale cream precipitate was filtered in air and dried in vacuo. Yield 7.82 g, 82%. *Anal.* Found (Calc. for $C_{56}H_{48}O_2AgP_3$) C, 68.7 (70.52); H, 4.90 (5.07)%. IR: 1325, 1435, 1563. ^1H NMR ($CDCl_3$): 7.36–7.02 (m, 45H, C_6H_5), 2.00 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 174.8 (O_2C), 133.7 (d, $J = 8.3$ Hz, PC_6H_5), 133.2 (d, $J = 10.1$ Hz, PC_6H_5), 129.6 (PC_6H_5), 128.5 (d, $J = 4.6$ Hz, PC_6H_5), 22.2 (CH_3). ^{31}P NMR (20 °C, $CDCl_3$): 5.79. ^{31}P NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 7.4 (d, $J \sim 450$ Hz), 4.9 (dd, $J = 256$ Hz).

2.2.14. O,O′-Perfluorobutyratobis(triphenylphosphine)silver(I), Ag(O_2CC_3F_7)(PPh_3)_2 (14)

Silver perfluorobutyrate (**11**) (0.4 g, 1.3 mmol) was stirred in toluene (50 cm^3 with an excess of triphenylphosphine (2.0 g, 7.9 mmol). The mixture was stirred in the absence of light for 24 h. The resulting cream precipitate was filtered in air, washed with 2 cm^3 of toluene and dried in vacuo. Yield 0.55 g, 52%. The compound was recrystallised from a toluene–ethanol solvent mixture. *Anal.* Found (Calc. for $C_{40}H_{30}F_7O_2AgP_2$): C, 56.9 (56.8); 3.44 (3.58)%. M.p. 186 °C. IR: 1208, 1229, 1267, 1312, 1343, 1437, 1659. ^{13}C NMR ($CDCl_3$): 133.8 (d, $J = 18.4$ Hz, PC_6H_5), 133.1 (d, $J = 18.3$ Hz, PC_6H_5), 129.8 (PC_6H_5), 128.7 (d, $J = 9.2$ Hz, PC_6H_5). ^{19}F NMR ($CDCl_3$): -81.2 (t, $J = 9.2$ Hz, CF_3), -117.3 (q, $J = 9.3$ Hz, αCF_2), -127.3 (CF_2). ^{31}P NMR (20 °C, $CDCl_3$): 5.7 (br). Ag NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 823 (t, $J = 524$ Hz).

Also prepared by the same method as that of **14** were.

2.2.15. O,O′-Perfluoroheptanoatobis(triphenylphosphine)silver(I), Ag(O_2CC_6F_{13})(PPh_3)_2 (15)

Yield 90%. The product was recrystallised from a toluene–ethanol solvent mixture and dried in vacuo. *Anal.* Found (Calc. for $C_{43}H_{30}F_{13}O_2AgP_2$): C, 51.8 (51.9); 2.94 (3.04)%. M.p. 182 °C. IR: 1200, 1237, 1289, 1310, 1356, 1437, 1480, 1659. ^1H NMR ($CDCl_3$): 7.43–7.36 (m, 20H, PC_6H_5), 7.34–7.28 (m, 10H, PC_6H_5). ^{13}C NMR ($CDCl_3$): 133.8 (PC_6H_5), 131.4 (d, $J = 20$ Hz, PC_6H_5), 130.4 (PC_6H_5), 128.9 (PC_6H_5). ^{19}F NMR ($CDCl_3$): -81.3 (t, $J = 9.7$ Hz, CF_3), -116.4 (t, $J = 12.7$ Hz, αCF_2), -122.3 (CF_2), -122.9 (CF_2), -123.3 (CF_2), -126.6 (CF_2). ^{31}P NMR (20 °C, $CDCl_3$): 10.2 (br). ^{109}Ag NMR (-80 °C, $CDCl_3/CH_2Cl_2$): 823 (t, $J = 523$ Hz).

2.2.16. O,O′-Perfluorooctanoatobis(triphenylphosphine)silver(I), Ag(O_2CC_7F_{15})(PPh_3)_2 (16)

Yield 83%. The compound was recrystallised from an ethanol–toluene solvent mixture. *Anal.* Found (Cal. for $C_{44}H_{30}F_{15}O_2AgP_2$): C, 51.8 (50.6); H, 3.14 (2.89)%. M.p. 133 °C. IR: 1206, 1242, 1310, 1437, 1572, 1586, 1692. ^1H NMR ($CDCl_3$): 7.40–7.30 (m, 20H, PC_6H_5), 7.28–7.22 (m, 10H, PC_6H_5). ^{13}C NMR ($CDCl_3$): 133.8 (d, $J = 16.6$ Hz, PC_6H_5), 131.9 (d, $J = 27.6$ Hz, PC_6H_5), 130.2 (PC_6H_5), 128.8 (d, $J = 9.2$ Hz, PC_6H_5. ^{19}F NMR ($CDCl_3$): -81.3 (t, $J = 9.8$ Hz, CF_3), -116.4 (t, $J = 12.7$ Hz, αCF_2), -122.1 (CF_2), -122.5 (CF_2), -122.8 (CF_2), -123.1 (CF_2), -126.6 (CF_2). ^{31}P NMR (20 °C, $CDCl_3$): 8.9 (br).

2.3. X-ray crystallography

Crystallographic quality crystals of $Ag(O_2CC_3F_7)$-$(PPh_3)_2$ (**14**) were obtained by slow evaporation at r.t. of a toluene–ethanol solvent mixture. The crystals were found to be light, air and moisture stable. Data (6102

reflections) were collected on a CAD-4 four-circle automatic diffractometer and were corrected for Lorentz and polarization but not for absorption. In the final least-squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. Full experimental details are given in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

Three silver carboxylates [Ag(O$_2$CR), R = CH$_3$ (**1**), ^{t}C$_4$H$_9$ (**2**), 2,4,6-Me$_3$C$_6$H$_2$ (**3**)] have been prepared from reactions of AgNO$_3$ and RCO$_2$M (M = Na, NH$_4$), with yields in the range 64–96%. Fluorinated derivatives have similarly been prepared: Ag(O$_2$CC$_3$F$_7$) (**4**) from Ag$_2$O and the free acid, and Ag(O$_2$CC$_6$F$_{13}$) (**5**) and Ag(O$_2$CC$_7$F$_{15}$) (**6**) from AgNO$_3$ and [R$_f$CO$_2$][NH$_4$] (yields 53–77%). In contrast to the non-fluorinated analogues, these compounds exhibited an increased degree of volatility and solubility in common organic solvents without addition of phosphines.

Addition of excess Me$_3$P to each of the silver non-fluorinated carboxylates yielded only 2:1 adducts, Ag(O$_2$CR)(PMe$_3$)$_2$ [R = Me (**7**), ^{t}Bu (**8**), 2,4,6-Me$_3$C$_6$H$_2$ (**9**)] in high yield (70–96%). With Ph$_3$P as base, AgO$_2$CMe can form either 2:1 (**10**) or 3:1 (**13**) adducts depending on the stoichiometry of the reaction, while the two more hindered silver carboxylates yielded only 2:1 adducts [R = ^{t}Bu (**11**), 2,4,6-Me$_3$C$_6$H$_2$ (**12**)] even when an excess of phosphine was added; preparative yields were similar (52–94%). The silver fluorocarboxylates formed 2:1 adducts with Ph$_3$P when two or more equivalents of phosphine were added [R = C$_3$F$_7$ (**14**), C$_6$F$_{13}$ (**15**), C$_7$F$_{15}$ (**16**); yields: 52–90%]. The triphenylphosphine adducts were easier to purify by recrystallisation, the trimethylphosphine adducts suffering from the lability and volatility of the donor ligand.

While numerous silver carboxylate structures have been determined, the two most common structural motifs are the bridged-dimer (I) and aggregation of this dimer into a ladder arrangement (II); polymeric structures incorporating bridging carboxylates (III) are relatively rare.
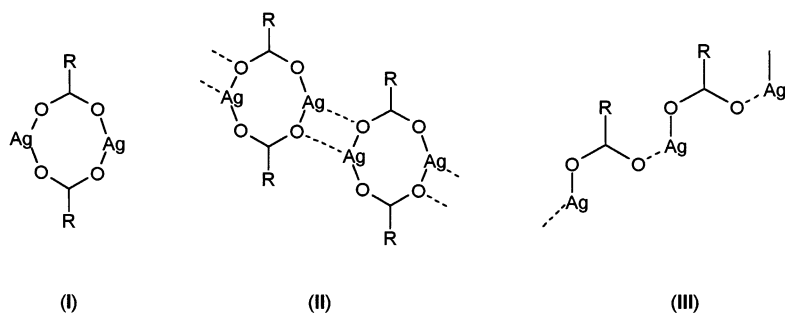
Table 1
Crystal and experimental data for **14**

	14 [a]
Empirical formula	C$_{40}$H$_{30}$AgF$_7$O$_2$P$_2$
Formula weight	845.45
Temperature (K)	293 (2)
Wavelength (Å)	0.71069
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	13.160(5)
b (Å)	13.251(4)
c (Å)	13.613(4)
α (°)	97.29(3)
β (°)	109.15(3)
γ (°)	118.20(2)
V (Å^3)	1859.6(11)
Z	2
Crystal size (mm)	0.2 × 0.2 × 0.1
Absorption coefficient (mm^{-1})	0.697
θ Range	2.03–23.92°
Independent reflections	5814 [R_{int} = 0.0165]
Reflections observed ($>2\sigma$)	4131
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0437$, $R_2 = 0.1145$
R indices (all data)	$R_1 = 0.0840$, $R_2 = 0.1483$
Goodness-of-fit	0.936

[a] Full-matrix least-squares on F^2.

Similarly, silver carboxylates with phosphine donors increase in structural complexity as the number of Lewis bases decreases. For example, Ag(O$_2$CCH$_3$)-(PPh$_3$) is tetranuclear containing both trigonal O$_2$PAg and tetrahedral O$_3$PAg centres [32] while Ag(O$_2$CH)-(PPh$_3$)$_2$ is a monomer with four-coordinate silver [33]. These species are also prone to solvation, as reflected in the structural analyses of Ag(O$_2$CCH$_3$)(PPh$_3$)$_2$ [34], and Ag(O$_2$CCH$_3$)(PPh$_3$)$_2$·H$_2$O. 1.5EtOH [35].

In principle, distinctions between these various structural types can be made on the basis of IR data relating to the carboxylate group, though the unreliability of this approach has been pointed out [36,37]. Tentative assignments have been made for ν_a(CO$_2$), ν_s(CO$_2$) and $\Delta[\nu_a$(CO$_2$) − ν_s(CO$_2$)] (Table 2). The values of $\Delta\nu$ found for silver acetate (**1**: 92 cm^{-1}) and pivalate (**2**: 113 cm^{-1}) are much lower than those of the corresponding sodium salts (143 cm^{-1}, 135 cm^{-1}, respectively) and

(I)   (II)   (III)

Table 2
Selected IR data (cm^{-1}) for silver(I) carboxylates and their adducts

	$v_a(CO_2)$	$v_s(CO_2)$	Δv
$Ag(O_2CCH_3)$ (**1**)	1514	1422	92
$Ag(O_2CBu^t)$ (**2**)	1512	1399	113
$Ag(O_2CC_6H_2Me_3)$ (**3**)	1557	1393	164
$Ag(O_2CC_3F_7)$ [a] (**4**)	1609	1426	183
$Ag(O_2CC_6F_{13})$ (**5**)	1611	1424	187
$Ag(O_2CC_7F_{15})$ [b] (**6**)	1613	1420	193
$Ag(O_2CCH_3)(PMe_3)_2$ (**7**)	1574	1404	170
$Ag(O_2CBu^t)(PMe_3)_2$ (**8**)	1557	1401	156
$Ag(O_2CC_6H_2Me_3)(Pme_3)_2$ (**9**)	1564	1387	177
$Ag(O_2CCH_3)(PPh_3)_2$ (**10**)	1553	1396	157
$Ag(O_2CBu^t)(PPh_3)_2$ (**11**)	1562	1402	160
$Ag(O_2CC_6H_2Me_3)(PPh_3)_2$ (**12**)	1545	1385	160
$Ag(O_2CCH_3)(PPh_3)_3$ (**13**)	1565	1406 [c]	159 [c]
$Ag(O_2CC_3F_7)(PPh_3)_2$ (**14**)	1660	1394	266
$Ag(O_2CC_6F_{13})(PPh_3)_2$ (**15**)	1660	1395	265
$Ag(O_2CC_7F_{15})(PPh_3)_2$ (**16**)	1692	1360	332

[a] Literature values $v_a(CO_2)$ 1678, $v_s(CO_2)$ 1400, Δv 278 cm^{-1}.
[b] Literature values $v_a(CO_2)$ 1658, $v_s(CO_2)$ 1400, Δv 258 cm^{-1}.
[c] Assignment complicated by a nearby peak at 1381 cm^{-1}, assignment of $v_s(CO_2^-)$ to this band would give Δv 184 cm^{-1}.

are consistent with a chelating carboxylate [36,38], although this conflicts with the general structural trend for silver carboxylates which are known to prefer motifs I and II and for which Δv is approximately 145 cm^{-1}. The presence of oxygen–silver bridges between dimeric sub-units (motif II) will effectively lower the C–O bond order and the available IR data for **1**, **2** are thus equally consistent with this structure. In contrast, the IR spectrum of the mesitylate **3** shows a much larger Δv (164 cm^{-1}), more consistent with motif I. Δv for the silver fluorocarboxylates was found to span a narrow range (183–193 cm^{-1}) implying a similar carboxylate bonding mode in compounds **4**–**6**. A low-quality structure determination of **4** shows it to adopt structure I but with two additional intermolecular Ag···O contacts between dimers of approximately 2.6 Å [39]. These results differ, however, from published IR data on several of these compounds. Compounds **4**, **6**, prepared from Ag_2CO_3 and the free acid, are reported as exhibiting Δv of 278 and 258 cm^{-1}, respectively [20], on which basis monodentate bonding of the carboxylates was proposed despite the published structure of (**4**).

Monomeric $Ag(O_2CCH_3)(PBu^t_3)$ is reported to have Δv of 164 cm^{-1} [40] and chelating acetate groups of related species have shown a Δv of 162 cm^{-1} [41]. Single crystal X-ray diffraction studies of **10** [34] have revealed a chelating acetate group and for which Δv is 157 cm^{-1}. On this basis, the data of Table 2 suggest that the remaining bis-phosphine adducts also incorporate chelating carboxylates around a four-coordinate

silver. A final point worthy of note is the lack of a much larger Δv for (**13**) which might be expected to involve a unidentate carboxylate group due to the presence of 3 equiv. of phosphine. The data are, however, consistent with previously published IR data for this compound, the authors suggesting values of Δv of 185 cm^{-1} [42] or 190 cm^{-1} [43] support the presence of unidentate bonding. For the silver fluorocarboxylates, Δv increases on adduct formation (**14**: 266; **15**: 265 cm^{-1}) and this is consistent with the data for adducts of alkyl or aryl carboxylates which also increase Δv by approximately 80 cm^{-1} on formation of $Ag(O_2CR)(PR'_3)_2$. Furthermore, this is confirmed by a single crystal X-ray diffraction study of (**14**) (see below) which has shown that the perfluorobutyrate ligand adopts a symmetrical chelating mode similar to (**10**) [34].

^{1}H and ^{13}C NMR results confirm the stoichiometry of the adducts but are otherwise unexceptional. In the ^{13}C NMR spectra the carbonyl carbon (CO_2Ag) appears at a higher field in the fluorocarboxylates (135.6–159.8 ppm) as compared with **1**–**3** (174.3–185.2 ppm).

Compounds **1**–**16** were also investigated using ^{31}P and ^{109}Ag NMR, both at r.t. and at -80 °C. All r.t. ^{31}P NMR spectra exhibited broad unresolved peaks indicating a degree of Lewis base lability in solution. This is consistent with most such previous NMR studies [42–44], though some spectra have been resolved at r.t. [40]. The shift of the phosphorus resonances in the adducts as compared with uncomplexed PR_3 (R = Me, Ph) ($\Delta\delta$), is largely characteristic of the phosphine and not the carboxylate. $\Delta\delta$ for trimethylphosphine and triphenylphosphine adducts were 22.4–25.6 ppm and 10.8–15.4 ppm downfield, respectively. The tris-adduct $Ag(O_2CCH_3)(PPh_3)_3$ (**13**) did not appear different in this respect. At lower temperatures (-80 °C) the solution dynamics were found to be inhibited and the dissociation of ligands was slowed sufficiently to allow spectral resolution in a number of cases. Bis-triphenylphosphine complexes **10**–**12** exhibited a doublet of doublets at 7.8–8.0 ppm with characteristic ^1J ($^{107, 109}$Ag–^{31}P) coupling in the expected range (480–497 Hz). Similar spectra were observed for **14**–**16**, though ^1J was larger (524 Hz.). For $Ag(X)(PR_3)_n$ (X = O_2CCF_3, R = p-$C_6H_5CH_3$), ^1J (^{109}Ag–^{31}P) has been shown to be highly dependent on n [n: 4, 265; 3, 357; 2, 519 Hz] [45]. The tris-adduct **13** showed ^{31}P resonances at both 4.9 and 7.4 ppm, the latter being close to the value found for **12**.

While we were unsuccessful in observing ^{109}Ag resonances for **1**, **8**, **11** and **16**, both silver pivalate (**2**) and mesitylate (**3**) gave ^{109}Ag resonances (DMSO-d^6) at locations (303 and 266 ppm, respectively) comparable with those of other silver carboxylates resonances [e.g. $Ag(O_2CPh)$: 278; $Ag(O_2CC_6H_4NH_2$-$p)$: 180 ppm] [46].

Although significantly more soluble in organic solvents than **1–3**, the fluorocarboxylates **4–6** also required dissolution in DMSO-d^6 to achieve concentrations suitable for ^{109}Ag NMR. These three compounds gave signals in the narrow range 171–173 ppm.

Resolved ^{109}Ag resonances of bis(triphenylphosphine) adducts **10–12**, **14**, **15** appeared as 1:2:1 triplets in the region 823–931 ppm, which represent shifts downfield by approximately 640 ppm on complexation; measured ^1J (^{31}P–^{103}Ag) couplings were consistent with values found in the corresponding ^{31}P NMR spectra. Resonances for trimethylphosphine adducts were either not detected (**8**) or unresolved (**7**: 772; **9**: 834 ppm), indicating dynamic equilibria still operating at −80 °C.

Mass spectral data can provide useful information on molecular aggregation, which in turn can influence both volatility and decomposition mechanism. No silver fragments were identified in the FAB (LSIMS) mass spectra for the silver carboxylates, presumably either due to their very low volatility or their limited solubility in the LSIMS solution matrix. The mass spectrum of **4**, however, was recordable and included several prominent features. The presence of Ag$_2$(O$_2$CR) and the lack of higher oligomers of this fragment concur with previous studies [28,30]. The structure of this compound has been reported previously [39] and consists of [Ag(O$_2$CC$_3$F$_7$)]$_2$ dimeric rings linked by Ag–O bonds (similar to motif II); the mass spectrometry, therefore, confirms that the Ag–O bonds within the dimeric fragment are significantly stronger than those linking the dimers. Secondly, the observation of Ag$_n$ ($n = 2$, 3) and

Ag$_n$(O$_2$CC$_3$F$_7$) ($n = 3$, 5, 7) fragments indicate the formation of ions containing Ag–Ag bonds. Thirdly, the presence of Ag$_2$F (the most abundant silver-containing fragment) and Ag$_3$F$_2$ indicate that AgF may be a final decomposition product in any CVD process involving silver fluorocarboxylates.

For the trimethylphosphine adducts **7–9** the spectra are dominated by monosilver fragments also incorporating phosphine ligands and in these cases M$^+$ (100%) was Ag(PMe$_3$)$_n$ ($n = 1$, 2). A number of dinuclear species were also identified. The fragments Ag$_2$(O$_2$CR)L$_2$ and Ag$_2$(O$_2$CR)L were common to the spectra of **7–9**, and Ag$_2$(O$_2$CR)(O$_2$C)L$_n$ ($n = 3$, 4) were identified in the spectrum of **7**. Such dinuclear species might be taken to indicate a dimeric based structure, although similar fragments are observed in **10** which is known to take up a monomeric arrangement [34]. Similar results were obtained for the triphenylphosphine adducts, with both mononuclear and dinuclear fragments identified. The bis- and tris-complexes of silver acetate **10** and **13** gave almost identical spectra with no significant differences. This may indicate a shared decomposition pathway between the two, or perhaps that **10** is a rapid decomposition product of **13**.

Mass spectrometric studies on the triphenylphosphine adducts **14–16** gave results markedly different from those of the parent fluorocarboxylates and are dominated by AgL$_n$ and Ag(O)L$_n$ fragments (L = PPh$_3$, $n = 1$, 2); the few fragments containing fluorocarbon in the presence of silver were extremely low in abundance. Furthermore, the absence of Ag(O$_2$CR) species in these spectra suggest that decarboxylation is more readily accomplished in the presence of phosphine ligands than when absent.

Compound **14** adopts a monomeric structure (Fig. 1) similar to that of **10**. The only other report on a phoshine adduct of a silver fluorocarboxylate appears to be Ag(O$_2$CCF$_3$)(PPh$_3$)$_2$ [47]. Ag–O bond lengths are noticeably longer in **14** [2.495(5), 2.532(5) Å] when compared with those in **10** (2.420–2.461 Å) [34] but are comparable with those of Ag(O$_2$CCF$_3$)(PPh$_3$)$_2$ (2.526, 2.542 Å) [47]. This is consistent with electron withdrawal from the oxygens by the electronegative C$_3$F$_7$ group. Lengthening of the Ag–O bond has also been observed where oxygen is hydrogen bonded to other species [33,41]. The Ag–O bond lengths in **14** reflect a symmetrical, chelating carboxylate, comparable to Ag(O$_2$CCF$_3$)(PPh$_3$)$_2$ [47] and one component of **10** [34]. The Ag–P bond lengths [2.430(2), 2.436(2) Å] are well within the known range (2.352–2.521 Å) for triphenylphosphine bound to silver and are comparable with those in **10** [34]. Carbon–oxygen bond lengths [1.201(8), 1.232(8) Å] are also found to be shorter in **14** compared with the analogous bonds in **10**. These data suggest that **14** has more ionic character than **10** consistent with the increased electronegativity of the fluoro-
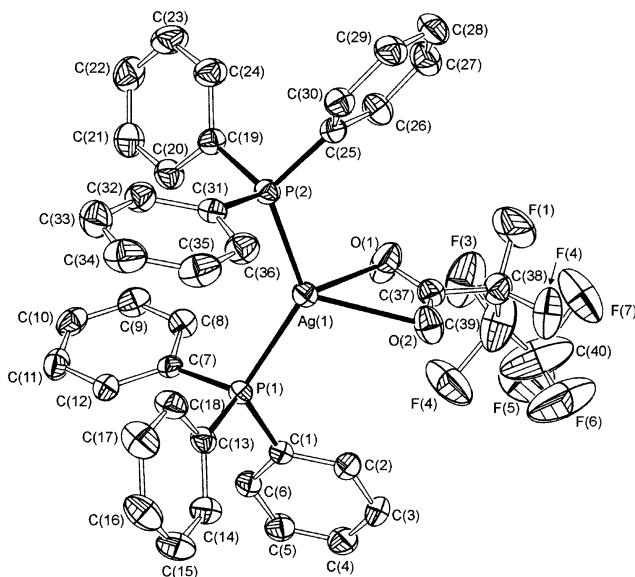

Fig. 1. The asymmetric unit of (**14**) showing the labelling scheme used in the text and Tables; thermal ellipsoids are at the 30% probability level. Selected metrical data: Ag(1)–P(1) 2.436(2), Ag(1)–P(2) 2.430(2), Ag(1)–O(1) 2.495(5), Ag(1)–O(2) 2.532(5), C(37)–O(1) 1.232(8), C(37)–O(2) 1.201(8) Å; P(1)–Ag(1)–P(2) 129.28(5), O(1)–Ag(1)–O(2) 51.3(2), O(1)–C(37)–O(2) 126.9(6)°.

Table 3
Thermal stability of silver(I) carboxylates and their adducts from TGA analyses

		Decomposition temperature (°C)			Residue remaining (%)	
		Start [a]	Max [b]	End [c]	Calc. [d]	Found
Ag(O$_2$CC$_3$F$_7$)	(4)	250	367	380	33.6	24.5
Ag(O$_2$CC$_6$F$_{13}$)	(5)	250	351	365	22.9	21.4
Ag(O$_2$CC$_7$F$_{15}$)	(6)	275	361	370	20.7	20.3
Ag(O$_2$CCH$_3$)(PMe$_3$)$_2$	(7)	25	74	148		
		148	221	235	33.8	29.7
Ag(O$_2$CBu^t)(PMe$_3$)$_2$	(8)	70	117	140		
		140	163	186		
		186	233	250	29.8	29.6
Ag(O$_2$CMe$_3$C$_6$H$_2$)(PMe$_3$)$_2$	(9)	76	254	271	26.9	26.3
Ag(O$_2$CCH$_3$)(PPh$_3$)$_2$	(10)	186	193	200	[e]	
		208	288	300	15.6	12.4
Ag(O$_2$CBu^t)(PPh$_3$)$_2$	(11)	200	308	332	14.7	15.6
Ag(O$_2$CMe$_3$C$_6$H$_2$)(PPh$_3$)$_2$·CH$_2$Cl$_2$	(12)	85	120	163	[f]	
		250	280	300	30.9	21.3
Ag(O$_2$CCH$_3$)(PPh$_3$)$_3$	(13)	150	289	300	11.3	13.8
Ag(O$_2$CC$_3$F$_7$)(PPh$_3$)$_2$	(14)	211	243	270	12.8	15.1
Ag(O$_2$CC$_6$F$_{13}$)(PPh$_3$)$_2$	(15)	210	221, 238	267	10.8	7.0
Ag(O$_2$CC$_7$F$_{15}$)(PPh$_3$)$_2$	(16)	160	217, 243	280	10.3	12.1

[a] Temperature corresponding to the onset of decomposition.
[b] Temperature at which the rate of weight loss at a given stage was at a maximum.
[c] Temperature at which decomposition was complete.
[d] Calculated % mass of silver in undecomposed compounds.
[e] Endothermic change with no weight loss.
[f] Probable loss of co-crystallised CH$_2$Cl$_2$ (see Section 2); observed (calculated) weight loss: 13.2 (9.6)%.

carboxylate group, viz: $[(Ph_3P)_2Ag]^{\delta+}[O_2CC_3F_7]^{\delta-}$. Longer Ag–O bonds in **14** compared with **10** have the marginal effect of reducing $<$O–Ag–O [**10**: 52.3, 53.3; **14**: 51.3°], while simultaneously $<$P–Ag–P increases [**10**: 124.1, 129.6; **14**: 129.28°]. Remarkably, the $<$P–Ag–P in Ag(O$_2$CCF$_3$)(PPh$_3$)$_2$ is 142.2° [47].

3.2. Thermal stability

Thermal analyses of **4**–**16** were carried out (Table 3) to give an indication of both the temperatures at which film deposition may be expected to start and also the relative stability of the compounds. The mass of residue remaining at the completion of the experiment is also indicative of volatility and the cleanliness of the decomposition pathway. In general, the trimethylphosphine adducts started to decompose at lower temperatures than triphenylphosphine adducts. For **7**, **8**, decomposition started at 25–70 °C and was complete by 235–250 °C, in a stepwise manner consistent with the loss of phosphine, no doubt due to the high volatility of PMe$_3$. Compound **9** decomposes in a similar temperature window but in a non-sequential manner. For the triphenylphosphine complexes **10**–**12**, decomposition started at higher temperatures but was completed in a narrower temperature range, typically beginning at 186–250 °C and completed by 330 °C. The tris-complex (**13**) started decomposing at a lower temperature

(150 °C) but the characteristics of the weight loss are very similar to those found with the related bis-complex (**10**).

Thermal decompositions of **11**–**16** were investigated under an inert (He) atmosphere (Table 3) to afford comparison with related TGA results for silver fluorocarboxylates [20] and their adducts [21] carried out in an oxygen-containing atmosphere. Under an inert atmosphere, the TGAs of silver fluorocarboxylates **4**–**6** revealed a single-stage decomposition, starting between 250–275 °C and complete by 365–380 °C; maximum rates of decomposition were in the region 350–370 °C. The TGA of **4** and **6** in air are reported to show a two step degradation with 10–15% weight lost between 140–350 °C followed by the remainder of the weight lost between 350–470 °C [20]. Bis(triphenylphosphine) adducts of silver fluorocarboxylates **14**–**16** start to decompose at a lower temperature (160–210 °C), the decompositions being complete by 280 °C. These adducts were found to decompose at lower temperatures (maximum rates of decomposition 217–243 °C) than the analogous adducts of non-fluorinated silver carboxylates (maximum rates of decomposition 280–308 °C). Decomposition temperature ranges were narrower in the case of silver fluorocarboxylate bis(triphenylphosphine) adducts compared with both non-fluorinated adducts and mono(triphenylphosphine) adducts of **4** and **6** (decomposition range 165–400 °C) [21].

The mass of residue remaining at the completion of the experiment was in excellent agreement with silver metal as the single final decomposition product only in the cases of **6**, **8**, **9**. In certain cases [(**5**), (**7**), (**10**), (**15**)], and particularly **4**, **12**, the weight of residue was less than that of silver indicating these to be the most volatile of the compounds studied. For **11**, **13**, **14** and **16** the residual mass was in excess of that calculated for silver, suggesting competing decomposition processes.

3.3. Film growth data

Silver films were grown using AACVD under fixed conditions at 310 °C and 1 bar pressure in a nitrogen atmosphere. Details of our experimental protocol and equipment are given elsewhere [12]. Samples were dissolved in THF, nebulised and passed over the heated glass substrate. The resulting films were found to be soft and although well-adhered to the substrate, could be scratched or damaged relatively easily by touching. Among the non-fluorinated precursors, silver pivalate (**2**) was found not to grow films, either by itself or in the presence of an excess of 1,5-cod which was added to aid solubility. The phosphine adducts all showed an

(a)

(b)

Fig. 2. Scanning electron micrograph at 10 kV of a silver film obtained from the AACVD of $Ag(O_2CBu^t)(PMe_3)_2$ (**8**), (a, top) bar = 10 μm, (b, bottom) bar = 1 μm.

ability to generate films although film thickness and quality was variable between precursors. The trimethylphosphine adducts **7**–**9** produced films of measurable thickness, while the triphenylphosphine adducts, with the exception of **11**, did not. Compounds **7** and **8** produced the thickest films at the highest growth rates (14.4, 13.7 Å min^{-1}) although these films were not reflective on the coating side (1.1 and 0.7%). Compounds **9** and **11** produced thinner coatings at much reduced growth rates (4.1, 5.7 Å min^{-1}) but these were significantly more reflective (46.6, 22.2%), which suggests a correlation between growth rates and reflectance under these conditions. The remaining non-fluorinated precursors generated thin, discontinuous or non-conducting films for which thickness estimates could not be made. Films grown with precursor **13** gave a thin but reflective (49.7%) coating, while the remaining films [from **10**, **12**] were of poor reflectivity (17.5, 17.6%).

Films grown from **7** and **8**, i.e. the thickest films grown at the highest growth rates, appeared to be comprised of a thick mat of crystalline material (Fig. 2). A significant fraction of these coatings appears to be made up of voids and pockets and this no doubt contributes to their poor reflectivity. The films grown from other precursors did not exhibit these surface features, and coatings grown from **11** appeared very uniform in comparison (Fig. 3).

EDXS was used to confirm the presence of silver and also identify the nature of film impurities, although levels were too low to be accurately quantifiable. Carbon impurities were detected in all of the films which were thick or conducting enough for analysis. In addition, trace amounts of phosphorus were detected in films grown from the PMe$_3$ adducts **7**, **8**, which were deposited at the fastest rates. Trace phosphorus impurities have previously been detected in films grown from Et$_3$P adducts of silver β-diketonates, although not Me$_3$P adducts.

Sheet resistance measurements over a 25 mm^2 could only be obtained from films grown with precursors **7** and **8** and were measured as 17×10^6 and 168 Ω cm^{-1}, respectively.

Visual inspection of the films grown from the silver fluorocarboxylate precursors indicated that those grown from the adducts appeared more reflective and uniform than those grown from the corresponding compounds without phosphine ligands. In a number of cases, crystalline material was observed embedded into the film, e.g. $Ag(O_2CC_3F_7)$ (**4**) (Fig. 4). It is notable that the adducts **14**–**16** had a significantly reduced growth rates (2.1–3.2 Å min^{-1}) compared with their parents **4**–**6** (3.0–9.0 Å min^{-1}), so a correlation may exist between slower growth rates and superior morphology. The highest estimated growth rate was 9 Å min^{-1} for $Ag(O_2CC_6F_{13})$ (**5**), the lowest (2.1 Å min^{-1}) for $Ag(O_2CC_3F_7)(PPh_3)_2$ (**15**). This apparent order of
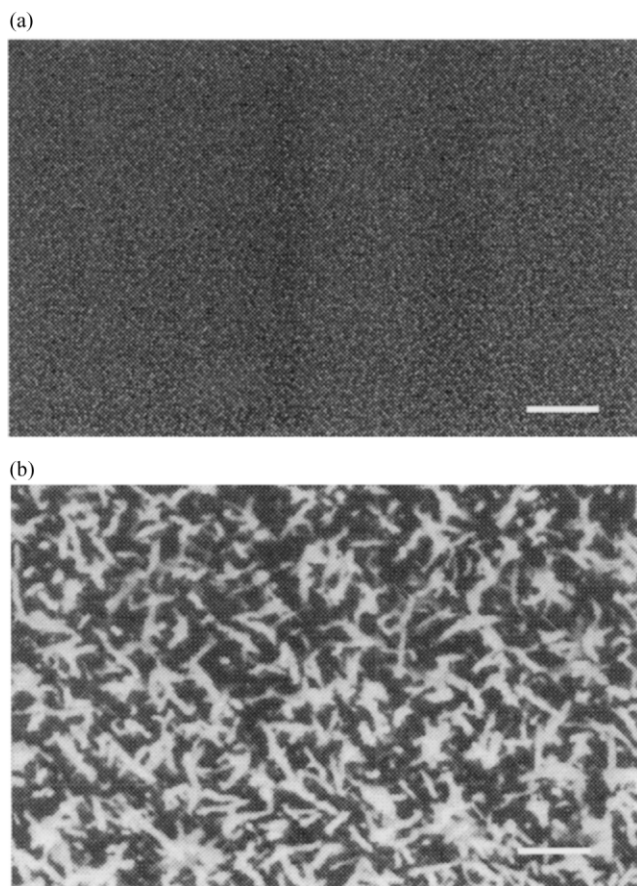
(a)

(b)

Fig. 3. Scanning electron micrograph at 10 kV of a silver film obtained from the AACVD of $Ag(O_2CBu^t)(PPh_3)_2$ (**11**), (a, top) bar = 10 μm, (b, bottom) bar = 1 μm.
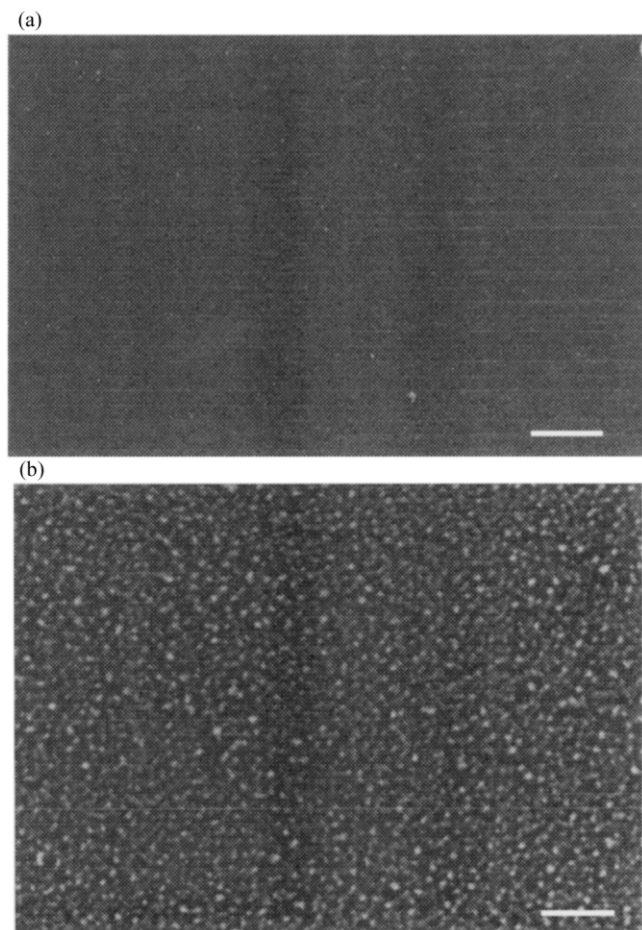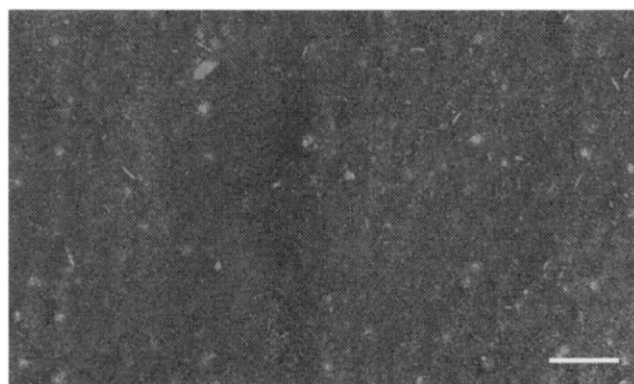

Fig. 4. Scanning electron micrograph at 15 kV of a silver film obtained from the AACVD of $AgO_2CC_3F_7$ (**4**), bar = 10 μm.

growth rate is interesting in view of the fact silver fluorocarboxylate adducts decompose at a lower temperature than the parent silver fluorocarboxylates (Tables 3–5).

EDXS analysis of these films revealed carbon impurities in all of the samples analysed while fluorine contaminants were identified in all of the films except that grown from **4**; phosphorus could not be detected in any of the coatings. Embedded crystalline deposits evident in the film grown from **4** (Fig. 4), could not be identified further; similar but less dramatic crystalline deposits could be seen with films **14–16**, although only at higher magnifications (× 10 000).

Adducts **14–16** produced films with superior reflectance, consistent with the observed surface morphologies. $Ag(O_2CC_6F_{13})(PPh_3)_2$ (**15**) gave the most reflective film. This film was able to reflect 46% of an incident beam of light ($\lambda = 550$ nm), whereas the film grown from its parent fluorocarboxylate **5** was poorly reflect-

Table 4
Appearance of silver films grown from silver(I) carboxylates and their phosphine adducts

		Visual appearance	SEM appearance	Detected impurities
$AgO_2CC_3F_7$	(**4**)	thick white film	very rough surface includes crystalline material in film	C
$AgO_2CC_6F_{13}$	(**5**)	heavy deposition but not reflective, matt in places with white areas	quite rough surface	C, F
$AgO_2CC_7F_{15}$	(**6**)	silver film, whitish, slightly matt appearance	roughish surface	C, F (trace)
$AgO_2CCH_3(PMe_3)_2$	(**7**)	thick greyish film, reflective in places	even film consisting of a thick matt of crystals	C, P (trace)
$AgO_2CBu^t(PMe_3)_2$	(**8**)	thick whitish film, grey in some areas, reflective in others, notably downstream	level film comprised of a thick matt of crystals	C, P (trace)
$AgO_2CC_6H_2Me_3(PMe_3)_2$	(**9**)	silver reflective film on entire substrate	rough undulating surface	C
$AgO_2CCH_3(PPh_3)_2$	(**10**)	transparent dark grey film	non-conducting film	
$AgO_2CBu^t(PPh_3)_2$	(**11**)	silver reflective film, partially transparent	very smooth film	C
$AgO_2CC_6H_2Me_3(PPh_3)_2$	(**12**)	transparent brown film	thin, discontinuous or non-conducting film	C
$AgO_2CCH_3(PPh_3)_3$	(**13**)	transparent but reflective silver film	thin, discontinuous or non-conducting film	
$AgO_2CC_3F_7(PPh_3)_2$	(**14**)	silver film with brown tinge	very smooth surface	C, F (trace)
$AgO_2CC_6F_{13}(PPh_3)_2$	(**15**)	silver film with slight brown tinge	smooth surface	C, F (trace)
$AgO_2CC_7F_{15}(PPh_3)_2$	(**16**)	uniform silver film slightly matt	quite smooth surface	C, F (trace)

Table 5
Properties of silver films grown from silver(I) carboxylates and their phosphine adducts

		Estimated film thickness (Å) [a]	Deposition time (min)	Estimated deposition rate (Å min^{-1})	% reflectance [b]		Sheet resistance [c] (Ω cm^{-1})
					Coating	Glass	
Ag(O$_2$CC$_3$F$_7$)	**(4)**	90	30	3.0	0.5	42.5	4.2
Ag(O$_2$CC$_6$F$_{13}$)	**(5)**	260	29	9.0	4.9	29.8	14.5
Ag(O$_2$CC$_7$F$_{15}$)	**(6)**	220	46	4.8	18.1	36.5	2.7 × 10^6
Ag(O$_2$CCH$_3$)(PMe$_3$)$_2$	**(7)**	288	20	14.4	1.1	20.7	17 × 10^6
Ag(O$_2$CBu^t)(PMe$_3$)$_2$	**(8)**	273	20	13.7	0.7	42.8	168
Ag(O$_2$CC$_6$H$_2$Me$_3$)(PMe$_3$)$_2$	**(9)**	91	22	4.1	46.6	31.1	∞
Ag(O$_2$CCH$_3$)(PPh$_3$)$_2$	**(10)**		37		17.5	6.5	∞
Ag(O$_2$CBu^t)(PPh$_3$)$_2$	**(11)**	80	14	5.7	22.2	9.7	∞
Ag(O$_2$CC$_6$H$_2$Me$_3$)(PPh$_3$)$_2$	**(12)**		20		17.6	7.3	∞
Ag(O$_2$CCH$_3$)(PPh$_3$)$_3$	**(13)**		23		49.7	30.6	∞
Ag(O$_2$CC$_3$F$_7$)(PPh$_3$)$_2$	**(14)**	65	31	2.1	6.8	8.1	∞
Ag(O$_2$CC$_6$F$_{13}$)(PPh$_3$)$_2$	**(15)**	90	33	2.7	45.9	34.9	∞
Ag(O$_2$CC$_7$F$_{15}$)(PPh$_3$)$_2$	**(16)**	95	30	3.2	20.4	19.8	∞

[a] Film thickness estimated using EDXS.
[b] $\lambda = 550$ nm.
[c] Sheet resistance was measured over a 25-mm square.

ing (4.9%). Of the six films, only three were thick enough to conduct appreciably and hence give a resistance low enough to be measurable. Since films of approximately the same estimated thickness gave very different resistance measurements, [e.g. **4**, **15**], it might assumed that in some cases the conductivity is also dependent on other factors, for example the film grown from **4** also contained appreciable levels of crystalline impurity embedded in the film.

4. Conclusions

Silver films can be grown by AACVD from silver carboxylates, fluoro-carboxylates and their phosphine adducts, with the exception among the compounds examined of silver pivalate. Trimethylphosphine adducts give superior growth rates to triphenylphosphine analogues where comparisons were possible, $AgO_2CR \cdot 2PMe_3$, $R = Me^tBu$ being particularly effective. Silver fluorocarboxylate precursors generated more uniform and reflective coatings than non-fluorinated analogues despite the presence of unidentified crystallites within the film. Superior morphologies were evident from films grown at slower rates, with $AgO_2CC_6F_{13} \cdot 2PPh_3$ being the best of the species examined. Overall, however, the carboxylates and their adducts proved largely inferior as precursors for silver films compared with the silver β-ketoiminates we have reported previously [11].

5. Supplementary material

Crystallographic data for the structure has been deposited with the Cambridge Crystalographic Data Centre, CCDC No. 173588. Copies of this information can 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)

References

[1] R. Gliem, G. Schlamp, Met. Technol. 41 (1987) 34.

[2] D. Lee, X. Chaud, K. Salama, Jpn. J. Appl. Phys. 31 (1992) 2411.

[3] H. Liedberg, T. Lundeberg, Urol. Res. 17 (1989) 359.

[4] T.H. Baum, C.E. Larson, S.K. Reynolds, Ag(hfac)(cod), in: (US, 1992).

[5] N.H. Dryden, J.J. Vittal, R.J. Puddephatt, Chem. Mater. 5 (1993) 765.

[6] Z. Yuan, N.H. Dryden, J.J. Vittal, R.J. Puddephatt, Chem. Mater. 7 (1995) 1696.

[7] Z. Yuan, N.H. Dryden, X. Li, J.J. Vittal, R.J. Puddephatt, J. Mater. Chem. 5 (1995) 303.

[8] C. Xu, M.J. Hampden-Smith, T.T. Kodas, Adv. Mater. 6 (1994) 746.

[9] K.-M. Chi, K.-H. Chen, S.-M. Peng, G.-H. Lee, Organometallics 15 (1996) 2575.

[10] K.-M. Chi, Y.-H. Lu, Chem. Vap. Dep. 7 (2001) 117.

[11] S. Serghini-Monim, Z. Yuan, K. Griffiths, P.R. Norton, R.J. Puddephatt, J. Am. Chem. Soc. 117 (1995) 4030.

[12] D.A. Edwards, R.M. Harker, M.F. Mahon, K.C. Molloy, J. Mater. Chem. 9 (1999) 1771.

[13] R.J.H. Voorhoeve, J.W. Merewether, J. Electrochem. Soc. 119 (1972) 364.

[14] M.J. Shapiro, W.J. Lackey, J.A. Hanigofsky, D.N. Hill, W.B. Carter, E.K. Barefield, J. Alloys Compd. 187 (1992) 331.

[15] C. Oehr, H. Suhr, Appl. Phys. A 49 (1989) 691.

[16] P.M. Jeffries, S.R. Wilson, G.S. Girolami, J. Organomet. Chem. 449 (1993) 203.

[17] C.D.M. Beverwijk, G.J.M. van der Kerk, A.J. Leusink, J. Noltes, J. Organomet. Chem. Rev. 5 (1970) 215.

[18] Anonymous, Res. Discl. 263 (1986) 146.

[19] M.J. Shapiro, W.J. Lackey, J.A. Hanigofsky, D.N. Hill, W.B. Carter, E.K. Barefield, J. Alloys Compd. 187 (1992) 331.

[20] E. Szlyk, I. Lakomska, A. Grodzicki, Thermochim. Acta 223 (1993) 207.

[21] E. Szlyk, I. Lakomska, A. Grodzicki, Pol. J. Chem. 68 (1994) 1529.

[22] E. Szlyk, P. Piszczek, A. Grodzicki, M. Chaberski, A. Golinski, J. Szatkowski, T. Blaszczyk, Chem. Vap. Dep. 7 (2001) 111.

[23] E. Szlyk, P. Piszczek, I. Lakomska, A. Grodzicki, J. Szatkowski, T. Blaszczyk, Chem. Vap. Dep. 6 (2000) 105.

[24] S. Paramonov, S. Samoilenkov, S. Papucha, I. Malkerova, A. Alikhanyan, N. Kuzmina, S.I. Troyanov, A.R. Kaul, J. Phys. IV Fr. 11 (2001) Pr3.

[25] R.C. Mehrotra, R. Bohra, Metal Carboxylates, Academic Press, London, 1983, p. 145.

[26] E.K. Fields, S. Meyerson, J. Org. Chem. 41 (1976) 916.

[27] A.D. Kirschenbaum, A.G. Streng, M. Hauptschein, J. Am. Chem. Soc. 75 (1953) 3141.

[28] S.K. Adams, D.A. Edwards, R. Richards, Inorg. Chim. Acta 12 (1975) 163.

[29] K.L. Busch, R.G. Cooks, R.A. Walton, K.V. Wood, Inorg. Chem. 23 (1984) 4093.

[30] G.D. Roberts, E. White, Org. Mass Spectrom. 16 (1981) 546.

[31] M.J. Ballie, D.H. Brown, K.C. Moss, D.W.A. Sharp, J. Chem. Soc. (A) (1968) 3110.

[32] E.T. Blues, M.G.B. Drew, B. Femi-Onandeko, Acta Crystallogr., Sect. B 33 (1977) 3965.

[33] G.A. Bowmaker, Effendy, J.V. Hanna, P.C. Healy, B.W. Millar, B.W. Skelton, A.H. White, J. Phys. Chem. 99 (1995) 3909.

[34] S.W. Ng, A.H. Othman, Acta Crystallogr., Sect. C 53 (1997) 1393.

[35] J.V. Hanna, S. Ng, Acta Crystallogr., Sect. C 55 (1999) IUC9900031.

[36] A.I. Grigorev, Russ. J. Inorg. Chem. 8 (1963) 409.

[37] D.A. Edwards, R.N. Hayward, Can. J. Chem. 46 (1968) 3443.

[38] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.

[39] A.E. Blakeslee, J.L. Hoard, J. Am. Chem. Soc. 78 (1956) 3029.

[40] R.G. Goel, P. Pilon, Inorg. Chem. 17 (1978) 2876.

[41] S.P. Neo, Z.-Y. Zhou, T.C.W. Mak, K.W.P. Leung, R.-J. Wang, Inorg. Chem. 34 (1992) 520.

[42] D.A. Edwards, M. Longley, J. Inorg. Nucl. Chem. 40 (1978) 1599.

[43] C. Oldham, W.F. Sandford, J. Chem. Soc., Dalton Trans. (1977) 2068.

[44] E.L. Muetterties, C.W. Alegranti, J. Am. Chem. Soc. 92 (1970) 4114.

[45] E.L. Muetterties, W. Alegranti, J. Am. Chem. Soc. 94 (1972) 6386.

[46] R.M. Harker, K.C. Molloy, unpublished results.

[47] S.W. Ng, Acta Crystallogr., Sect. C 54 (1998) 743.