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New Precursors for Chemical Vapor Deposition of Silver

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The formation of films of the coinage metals by chemical vapor deposition has been an area of great interest, but the work has been concentrated almost exclusively on copper[1] and gold[2] with very few reports on CVD of silver.[3,4] An efficient process for CVD of silver has several potential applications, for example, in forming silver as a component of high-temperature superconducting ceramics, as contacts in microelectronic devices, or as silver mirrors. Thus, for example, silver has been observed to increase critical current densities[5-9] and T_c,[10] as well as acting as a good material for forming low-resistivity contacts with superconducting ceramic materials[11] and, since the superconducting films are often grown by CVD, the incorporation of silver by CVD has obvious advantages.

The major problem in developing CVD of silver is the lack of stable, volatile silver complexes which can act as CVD precursors.[3,12] Most organosilver compounds are both air and moisture sensitive, along with the added complications of their low thermal stability and light sensitivity, while most inorganic complexes are involatile.[3,12] The organosilver complexes $[AgC(CF_3){=}CF(CF_3)]_n$ and $[Ag(\eta\text{-}C_5H_5)(PR_3)]$ have been shown to deposit pure Ag films under plasma-enhanced CVD conditions,[3] but they and related perfluoroalkyl compounds are not easy to handle owing to their sensitivity to air and moisture and they often decomposed on attempted sublimation. There have been reports of silver CVD using the trifluoroacetate or trifluoroacetylacetonate as precursors,[4] but the complexes do not sublime easily and require unconventional vaporization techniques.[3,4] This paper reports new precursors for CVD of silver which are easily synthesized, which can be stored and handled in air, which are reliably volatile, and which give pure silver films under thermal CVD conditions.

CVD of silver is possible using the known silver complexes [Ag(hfac)(alkene)], where hfac = 1,1,1,5,5,5-hexafluoropentanedionato and alkene = C_6H_{10}, C_7H_{12}, C_8H_{14}, C_8H_{12}, C_8H_8 or $CH_2{=}CHSiMe_3$,[4d,13,14] but sublimation is accompanied by much decomposition. The problem is that these complexes lose alkene at or below the sublimation temperature with formation of $[Ag(hfac)]_n$, which is insufficiently volatile for CVD; transport in the vapor phase is therefore inefficient. It was hypothesized that use of a ligand L with stronger donor ability than an alkene would result in more stable products, [Ag(hfac)L]. When L = PPh_3, complexes of this type are known but are involatile,[15] while analogous copper complexes $[Cu(hfac)(PR_3)]$ with R = Me or Et are volatile and are good precursors for CVD of copper.[1,4d] Hence the new complexes $[Ag(hfac)(PR_3)]$ (**1a**, R = Me; **1b**, R = Et), which contain more volatile phosphines than PPh_3, were synthesized.[16] A convenient route is to displace the alkene in [Ag(hfac)(alkene)] by PR_3, but other methods are also applicable.[15,16] These new complexes are stable to air, moisture and light. Complex **1a** is a white solid, while **1b** is a pale yellow solid which melts at 45 °C. Both complexes have been characterized by their spectroscopic properties,[16] and **1a** was also characterized by X-ray structure determination (Figure 2).[16] Unlike [Ag(hfac)(alkene)], these complexes **1** do not undergo thermolysis with loss of ligand at temperatures below 100 °C, as illustrated by the thermogravimetric analysis of $[Ag(hfac)(PMe_3)]$ shown

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(16) The starting materials, [Ag(hfac)(cyclohexane)] and [Ag(hfac)(1,5-cyclooctadiene)], were synthesized by literature methods.[13,14] The synthesis of **1a** is given as an example. A solution of [Ag(hfac)(1,5-cyclooctadiene)] (1.29 g, 3.05 mmol) in THF (20 mL) was prepared in a 100-mL Schlenk flask. PMe_3 (3.05 mL, 1.0 M solution in THF, Aldrich) was then added to the stirred solution via syringe and the solution was stirred for 30 min. The solvent was evaporated from the final pale yellow reaction mixture in vacuo to yield a yellow-brown solid residue. The product **1a** was isolated by sublimation (0.05 mmHg/80–100 °C) onto a dry ice/acetone cooled probe to yield a white solid (0.95 g, 2.42 mmol, 79%). Spectroscopic data: FT-IR (KBr pellet) 2980 (m), 2913 (m), 1671 (s), 1559 (m, sh), 1520 (vs), 1425 (m), 1255 (s), 1194 (s), 1140 (s), 952 (s), 850 (m), 787 (s), 754 (m), 738 (s), 661 (s), 575 (s), 524 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.47 (d, 9H, $P(CH_3)_3$), $^2J_{HP}$ = 8.2 Hz), 5.88 (s, ^1H, acac-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 177.39 (q, $C{=}O$, $^2J_{CF}$ = 32.4 Hz), 117.76 (q, CF_3, $^1J_{CF}$ = 289.0 Hz) 87.65 (s, *C*H), 15.8 (d, $P(CH_3)_3$, $^2J_{PC}$ = 23.8 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) −39.64 (s, $P(CH_3)_3$). LRMS (EI, 70 eV) *m/e* (rel int): 390, 392 (10.7, 9.6) $[Ag(Hfac)(PMe_3)]^+$; 314,316 (1.3, 1.3) $[Ag(hfac)]^+$; 259, 261 (0.7, 0.6) $[Ag(PMe_3)_2)]^+$; 245, 247 (5.0, 4.5) $[Ag(hfac) - CF_3]^+$; 183, 185 (100, 92) $[Ag(PMe_3)]^+$. Crystal data: triclinic, space $P\bar{1}$, $a = 12.662(3)$, $b = 15.112(4)$, $c = 11.052(1)$ Å, $\alpha = 102.42(2)$, $\beta = 94.82(1)$, $\gamma = 93.98(2)°$, $Z = 6$, $R = 0.0619$, $R_w = 0.0621$. The complex **1b** was prepared similarly from [Ag(hfac)(cyclohexene)], isolated as a viscous yellow oil by removal of solvent in vacuo at room temperature, and purified by vacuum distillation (0.05 mmHg, 50–80 °C) onto a dry ice/acetone cooled probe. Spectroscopic data: FT-IR (KBr pellet): 2969 (m), 2936 (m), 2909 (m), 2880 (m), 1674 (s), 1566 (m), 1526 (vs), 1461 (m), 1252 (s), 1195 (s), 1141 (vs), 1038 (m), 789 (m), 768 (m), 755 (m), 660 (s), 575 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.76 (s, 1H, C*H*), 1.66 (dq, 6H, CH_2, $^3J_{HH}$ = 7.7 Hz, $^2J_{PH}$ = 7.7 Hz), 1.13 (dt, 9H, CH_3, $^3J_{HH}$ = 7.7 Hz, $^3J_{PH}$ = 17.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 176.43 (q, $C{=}O$, $^2J_{CF}$ = 31.7 Hz), 117.88 (q, CF_3, $^1J_{CF}$ = 289.4 Hz), 86.70 (s, *C*H), 17.42 (d, PCH_2, $^2J_{PC}$ = 18.9 Hz), 9.06 (d, P–C–CH_3, $^3J_{PC}$ = 4.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 6.63 (s, $P(C_2H_5)_3$). LRMS (EI, 70 eV) *m/e* (rel int): 432, 434 (3.5, 3.1) $[Ag(hfac)(PEt_3)]^+$, 343, 345 (0.8, 0.7) $[Ag(PEt_3)_2]^+$, 314, 316 (0.6, 0.55) $[Ag(hfac)]^+$, 225, 227 (100, 91) $[Ag(PEt_3)]^+$.

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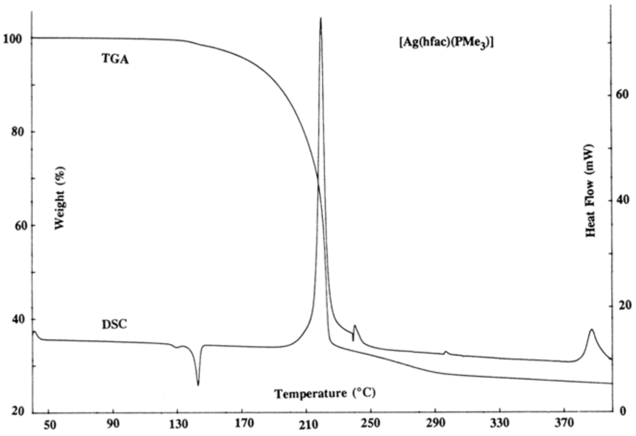


Figure 1. Thermogravimetric analysis (TGA, weight, %) and differential scanning calorimetry (DSC, heat flow, mW) traces for the thermolysis of [Ag(hfac)(PMe_3)]. In each case, the heating rate was 20 °C/min.

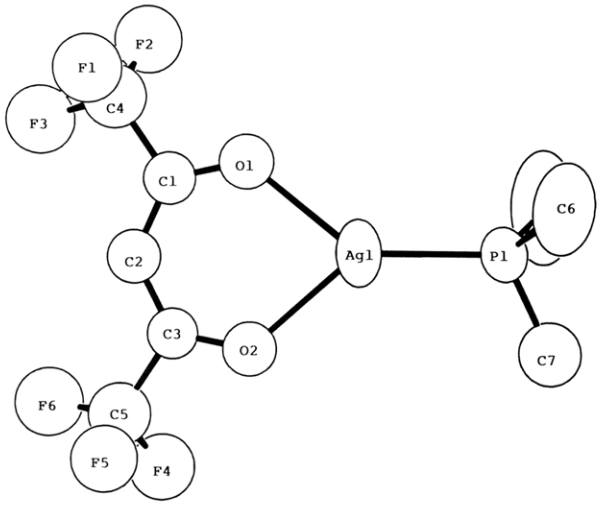
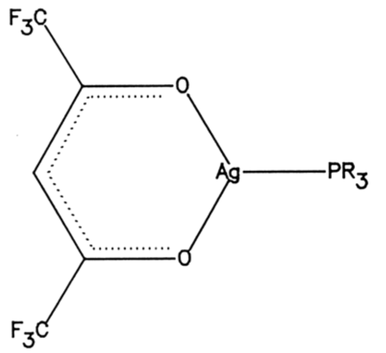


Figure 2. View of the molecular structure of [Ag(hfac)(PMe_3)]. There are three independent molecules in the unit cell, with Ag–P = 2.311(3)–2.326(4), Ag–O = 2.268(8)–2.309(8) Å, O–Ag–P = 131.5(2)–147.7(2), O–Ag–O = 80.0(3)–80.7(3)°.



1a, R = Me; **1b**, R = Et

in Figure 1, but thermolysis occurs mostly over the temperature range 140–280 °C to leave a residue of metallic silver. The residual weight at 440 °C corresponds to 25% of the original weight of the complex which compares well with the calculated silver content of 27%.[17] The small discrepancy is probably due to some weight loss from sublimation of the precursor prior to thermolysis. Under vacuum, the complexes sublime quantitatively, leaving no silver residue.

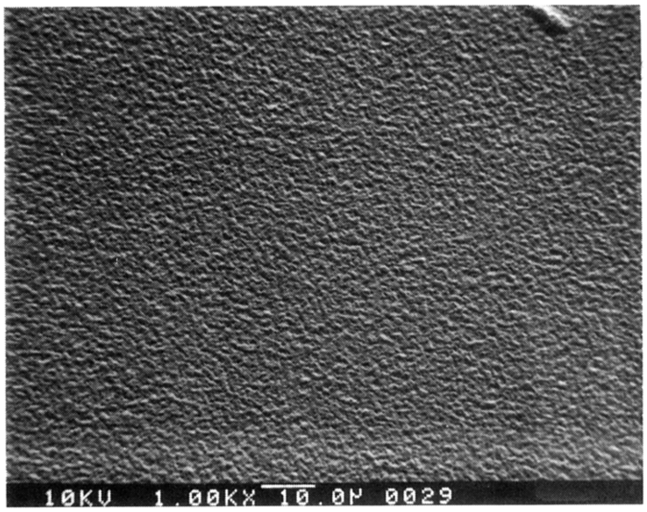


Figure 3. SEM image of a silver film grown from [Ag(hfac)(PMe_3)] on a glass substrate at 350 °C.

Thin films of silver were grown by using a low-pressure vertical CVD reactor which has been described elsewhere[18] with no carrier gas. The precursors were heated to increase their volatility (**1a** at 80–100 °C, **1b** at 50–70 °C) and the films were grown over 30–60 min onto glass substrates heated to 250–350 °C at a pressure of 5×10^{-2} Torr. The resulting films had either a matte finish or a smooth mirrorlike appearance, depending on the conditions of growth. A typical growth rate for [Ag(hfac)(PMe_3)] with precursor at 95 °C and substrate at 310 °C was 2 μm h^{-1}. The compositions of these films were established by XPS and EDX analysis, revealing that they are composed of silver with some carbon present (5–10%). No impurities of oxygen, fluorine, phosphorus, or sulfur were detectable in the films. A typical matte film growth from **1a** has been investigated by SEM, Figure 3, which shows a rough texture with grain sizes of 1–2 μm in diameter. The films adhered well to glass or silicon as indicated by the adhesive tape test. The electrical resistivity of a film of thickness 1.1 μm on glass was 6.5 μΩ cm, which can be compared to the value for pure silver of 1.59 μΩ cm.

It is clear from the above results that the complexes **1** are far superior to any known precursors for the CVD of silver films. The advantages of these compounds are the ease of synthesis and handling, the good volatility and absence of thermolysis prior to sublimation, and the formation of pure silver films by thermal CVD. Complex **1b** melts at 45 °C, and so above this temperature it can act as the first known liquid precursor for CVD of silver.

Acknowledgment. We thank the Ontario Centre for Materials Research and NSERC (Canada) for financial support.

Supplementary Material Available: X-ray structure determination: tables of crystal data, atomic positional and thermal parameters, bond distances and angles, anisotropic thermal parameters, H-atom positions, least squares planes and dihedral angles, and torsion angles (11 pages); list of structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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