Chemical Vapor Deposition of Silver

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The complexes [Ag(hfac)(PR_3)] and [Ag(fod)(PR_3)] (hfac = 1,1,1,5,5,5-hexafluoropentanedionato; fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato; R = CH_3, C_2H_5) have been prepared by displacement of olefin from [Ag(hfac)(alkene)] compounds by the phosphines PR_3 or by direct reaction of silver(I) oxide, PR_3 and the respective β-diketone. The complex [Ag(fod)(PEt_3)] melts at 26–28 °C and so can act as a liquid CVD precursor above this temperature. Unlike several other silver(I) hfac complexes, these phosphine derivatives are monomeric, as shown by an X-ray structure determination of [Ag(hfac)(PMe_3)], and they are volatile. Each complex has been shown to be an excellent precursor for the thermal chemical vapor deposition of silver films at temperatures of 250–350 °C. The resulting films are shown by XPS and EDX analysis to contain silver with some carbon impurity. Pure silver films are formed by CVD from [Ag(fod)(PR_3)] at 300 °C by using moist hydrogen as carrier gas. The SEM image of a film grown from [Ag(hfac)(PMe_3)] at 350 °C shows a rough surface with average grain size of 1–2 μm, but smoother films with grain sizes of 0.1–0.25 μm are formed by CVD from [Ag(fod)(PR_3)] under H_2.

Introduction

The formation of films of the coinage metals by chemical vapor deposition is of great interest, with recent advances made on CVD of copper,[1] gold,[1a,2] and silver.[1a,3–9] An efficient process for CVD of silver has several potential applications.[10] Applications in microelectronics are limited at present due to problems of diffusion into silicon substrates, but there is interest in forming silver as a component of high-temperature superconducting ceramics, as silver mirrors or as bactericidal coatings.[10]

The major problem in developing CVD of silver is the lack of stable, volatile silver complexes which can act as CVD precursors.[1–9,11–13] 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.[3,11] The organosilver complexes [AgC(CF_3)=CF(CF_3)]$_n$ and [Ag(η-C_5H_5)(PR_3)] have been shown to deposit pure Ag films under thermal or plasma enhanced CVD conditions, 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.[3,6,12] There have been reports of silver CVD using the trifluoroacetate, trifluoroacetylacetonate, or hexafluoroacetylacetonate derivatives as precursors,[4] but most of these complexes do not sublime easily and require unconventional vaporization techniques.[3–9] CVD of silver is possible using the silver complexes reported to have the composition [Ag(hfac)(alkene)], where hfac = 1,1,1,5,5,5-hexafluoropentanedionato and alkene = C_6H_{10}, C_7H_{12}, C_8H_{14},

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1995.

(1) (a) Kodas, T. T., Hampden-Smith, M. J., Eds. *The Chemistry of Metal CVD*; VCH: Weinheim, 1994. (b) Shin, H.-K.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M.; Farr, J. D. *J. Mater. Res.* **1991**, *3*, 246. (c) Shin, H.-K.; Chi, K. M.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424. (d) Kumar, R.; Maverick, A. W. *Chem. Mater.* **1993**, *5*, 251. (e) Baum, T. H.; Larson, C. E. *Chem. Mater.* **1992**, *4*, 365.

(2) (a) Puddephatt, R. J. *Polyhedron* **1994**, *13*, 1233. (b) Kodas, T. T.; Baum, T. H.; Comita, P. *J. Cryst. Growth* **1988**, *87*, 378. (c) Puddephatt, R. J.; Treurnicht, I. *J. Organomet. Chem.* **1987**, *319*, 129. (d) Dryden, N. H.; Shapter, J. G.; Coatsworth, L. L.; Norton, P. R.; Puddephatt, R. J. *Chem. Mater.* **1992**, *4*, 979. (e) Messelhauser, J.; Flint, E. B.; Suhr, H. *Appl. Surf. Sci.* **1992**, *54*, 64. (f) Holl, M. M. B.; Seidler, P. F.; Kowalczyk, S. P.; McFeeley, F. R. *Inorg. Chem.* **1994**, *33*, 510.

(3) (a) Oehr, C.; Suhr, H. *Appl. Phys. A* **1989**, *49*, 691. (b) Oehr, C.; Suhr, H. (Schering A.-G.) German Patent DE 3,828,211 (Cl. C23C16/18), Feb 1990, Appl. 16 Aug 1988; *Chem. Abstr. 114*, 28448y.

(4) (a) Anon. *Res. Discuss.* **1986**, *261*, 61. (b) Anon. *Res. Discuss.* **1986**, *263*, 146. Cited in ref 3. (c) Shapiro, M. J.; Lackey, W. J.; Hanigofsky, J. A.; Hill, D. N.; Carter, W. B.; Barefield, E. K. *J. Alloys Comp.* **1992**, *187*, 331. (d) Baum, T. H.; Larson, C. E. U.S. Patent 5,-096,737, Mar 1992. (e) Beach, D. B.; Jasinski, J. M. U.S. Patent 4,-948,623, 1990.

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

(6) Jeffries, P. M.; Wilson, S. R.; Girolami, G. S. *J. Organomet. Chem.* **1993**, *449*, 203.

(7) Lin, W.; Warren, T. H.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 11644.

(8) Xu, C. Y.; Hampden-Smith, M. J.; Kodas, T. T. *Adv. Mater.* **1994**, *6*, 775.

(9) Yuan, Z.; Dryden, N. H.; Li, X.; Vittal, J. J.; Puddephatt, R. J. *J. Mater. Chem.*, in press.

(10) (a) Galvan, D. H.; Avalosborja, M.; Farias, M. H.; Cotaaraiza, L.; Reyes, A.; Cruzreyes, J.; Early, E. A.; Nieva, G.; Deandrade, M.; Maple, M. B. *J. Mater. Sci.* **1994**, *29*, 2713. (b) Yun, J.; Harmer, M. P.; Chou, Y. T. *J. Mater. Res.* **1994**, *9*, 1342. (c) Sen, S.; In-Gann, C.; Chen, C. H.; Sefanescu, D. M. *Appl. Phys. Lett.* **1988**, *54*, 766. (d) Mimura, M.; Kumakura, H.; Togano, K.; Maeda, H. *Appl. Phys. Lett.* **1989**, *54*, 1582. (e) Imanaka, N.; Saito, F.; Imai, H.; Adachi, G. *Jpn. J. Appl. Phys.* **1989**, *28*, L580. (f) Osamura, K.; Takayama, T.; Ochiai, S. *Appl. Phys. Lett.* **1989**, *55*, 396. (g) Matsuoka, Y.; Ban, E.; Ogawa, H. *J. Phys. D* **1989**, *22*, 564. (h) Miller, J. H.; Holder, S. L.; Hunn, J. D.; Holder, G. N. *Appl. Phys. Lett.* **1989**, *54*, 2256. (i) Ekin, J. W.; Larson, T. M.; Bergren, N. F.; Nelson, A. J.; Swartzlander, A. B.; Kazmerski, L. L.; Panson, A. J.; Blakenship, B. A. *Appl. Phys. Lett.* **1988**, *52*, 1819. (j) Liedberg, H.; Lundeberg, T. *Urol. Res.* **1989**, *17*, 359.

(11) (a) Van Koten, G.; Noltes, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, pp 709–763. (b) Beverwijk, C. D. M.; Van Der Kerk, J. M.; Leusink, A. J.; Noltes, J. G. *Organomet. Chem. Rev.* **1970**, *5*, 215.

(12) (a) Bailey, A.; Corbitt, T. S.; Hampden-Smith, M. J.; Duesler, E. N.; Kodas, T. T. *Polyhedron* **1993**, *12*, 1785. (b) Xu, C.; Corbitt, T. S.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *J. Chem. Soc., Dalton Trans.* **1994**, 2841.

(13) Yuan, Z.; Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Can. J. Chem.* **1994**, *72*, 1605.

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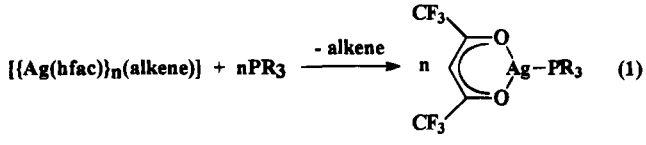
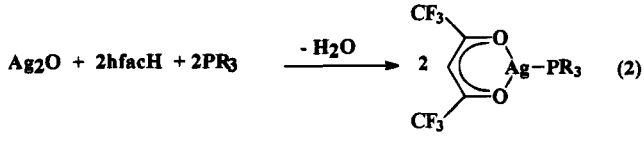
C_8H_{12}, C_8H_8, or $CH_2{=}CHSiMe_3$,[4d,13,14] but sublimation is accompanied by much decomposition. The problem is that these complexes lose alkene at or below the sublimation temperature with formation of $[Ag(hfac)]_n$, which is insufficiently volatile for CVD; transport in the vapor phase is therefore inefficient. Many such compounds are actually more complex than indicated by the formula [Ag(hfac)(alkene)].[14] For example, the complex with alkene = 1,5-cyclooctadiene is properly formulated as $[Ag_2(COD)_2(\mu\text{-hfac})_2]$ and with norbornadiene it is $[Ag_4(NBD)_2(\mu\text{-hfac})_4]$.[12] Recently, the use of aerosol vaporization methods has allowed efficient CVD from related complexes [Ag(hfac)L], with L = R_2S for example,[8] and the complexes [Ag(β-diketonate)(C≡NMe)] have also been reported as CVD precursors.[9] This paper reports precursors for CVD of silver of formula [Ag(β-diketonate)(PR_3)] 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. A preliminary account of part of this work has been published,[5] and similar, independent results have also been published.[7] Surface science studies using these precursors have been published recently.[15]

Results

Synthesis and Characterization of the Precursors. 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], which might then volatilize before ligand dissociation occurred. When L = PPh_3, complexes of this type are known but are involatile,[14] 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 initial aim was to prepare the complexes, [Ag(hfac)(PR_3)], **1a**, R = Me; **1b**, R = Et, which contain more volatile phosphines than PPh_3.[14] A convenient route is to displace the alkene in [{Ag(hfac)}$_n$(alkene)], n = 1 or 2 depending on the alkene, by PR_3 (eq 1). The alkene complex can





be isolated or it can be generated in situ from Ag_2O, hfacH, and alkene and immediately reacted with phosphine. Alternatively, the complexes could be prepared by direct reaction of Ag_2O, hfacH, and PR_3 (eq 2). A similar method is to treat Ag_2O with hfacH in tetrahydrofuran to give a complex tentatively identified as [{Ag(hfac)}$_2$(THF)] (note that the similar reaction in ether yields [{Ag(hfac)}$_2$(H_2O)][12]) and to treat this with PR_3

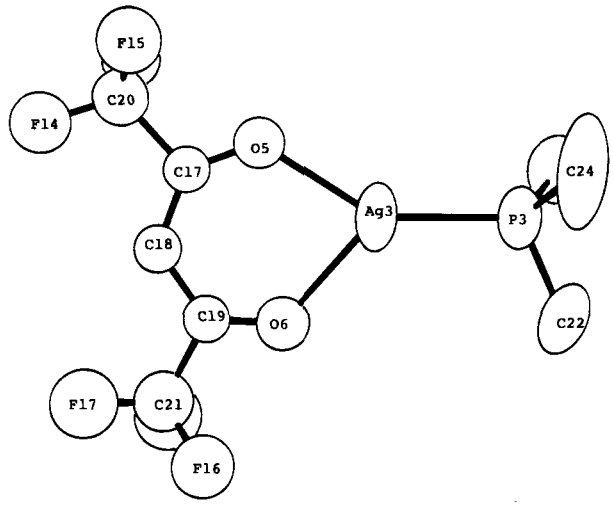


Figure 1. View of the molecular structure of one of the three independent molecules of [Ag(hfac)(PMe_3)].

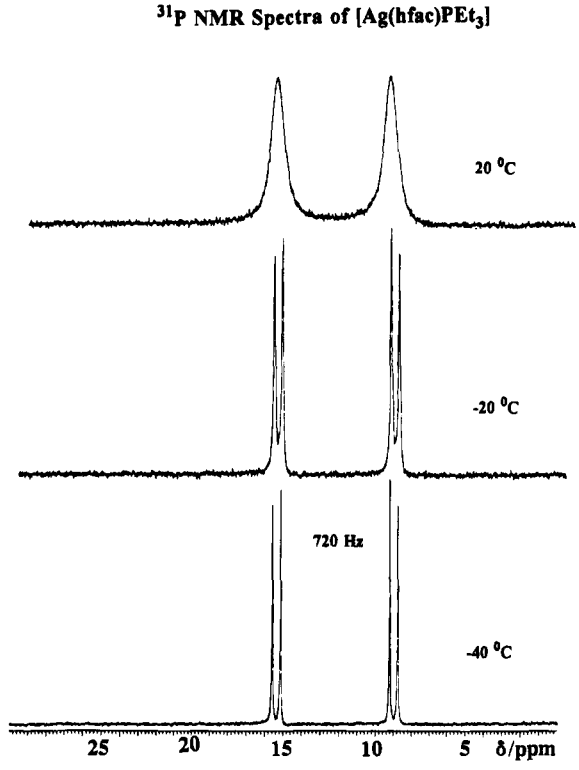


Figure 2. ^{31}P NMR spectra of [Ag(hfac)(PEt_3)] as a function of temperature. The broadness at higher temperatures is indicative of ligand exchange.

with displacement of the weakly coordinated solvent molecule. The complexes [Ag(fod)(PR_3)], **2a**, R = Me; **2b**, R = Et, were prepared similarly, and details are given in the Experimental Section.

The new complexes **1** and **2** are white or very pale yellow solids (MP: **1a**, 142–143 °C; **1b**, 45–46 °C; **2a**, 88–90 °C; **2b**, 26–28 °C) which are stable to air, moisture, and ambient light (it is presumed that, like many silver compounds, they would be decomposed by long exposure to UV light). The complexes with L = PEt_3 are initially isolated as oils, but the pure compounds obtained by vacuum sublimation are low melting solids. Since **2b** melts at 26–28 °C, it could easily be used as a liquid precursor in CVD experiments. All of the complexes could be sublimed under vacuum at 50–80 °C without decomposition and are therefore pre-

(14) (a) Partenheimer, W.; Johnson, E. H. *Inorg. Synth.* **1976**, *16*, 117. (b) Doyle, G.; Eriksen, K. A.; Van Engen, D. *Organometallics* **1985**, *4*, 830. (c) Gibson, D.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 367.

(15) Serghini-Monim, S.; Yuan, Z.; Griffiths, K.; Norton, P. R.; Puddephatt, R. J. *J. Am. Chem. Soc.*, in press.

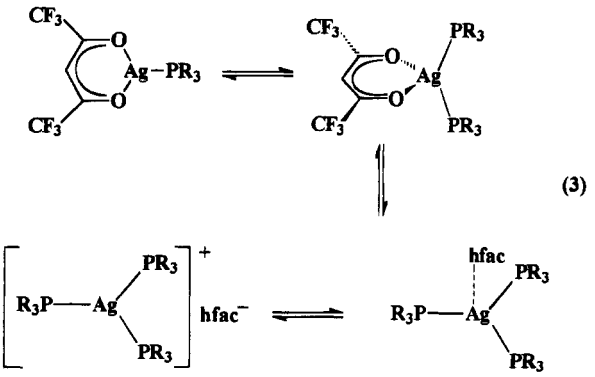
Table 1. Selected Bond Distances (Å) and Angles (deg)

molecule 1		molecule 2		molecule 3	
Ag(1)−P(1)	2.311(3)	Ag(2)−P(2)	2.325(4)	Ag(3)−P(3)	2.326(4)
Ag(1)−O(1)	2.285(8)	Ag(2)−O(3)	2.292(8)	Ag(3)−O(5)	2.268(8)
Ag(1)−O(2)	2.299(8)	Ag(2)−O(4)	2.297(8)	Ag(3)−O(6)	2.309(8)
O(1)Ag(1)P(1)	141.5(2)	O(3)Ag(2)P(2)	144.1(3)	O(5)Ag(3)P(3)	147.7(2)
O(2)Ag(1)P(1)	138.4(2)	O(4)Ag(2)P(2)	135.9(3)	O(6)Ag(3)P(3)	131.5(2)
O(2)Ag(1)O(1)	80.1(3)	O(4)Ag(2)O(3)	80.0(3)	O(6)Ag(3)O(5)	80.7(3)

sumed to be monomeric, as proved for the highest melting complex **1a** by an X-ray structure determination.

The structure of **1a** is shown in Figure 1, and selected bond distances and angles are in Table 1. There are three independent molecules in the unit cell, each with somewhat different bond parameters, and the crystal is isomorphous with the copper analogue.[1c] Ranges of bond parameters are 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), and O−Ag−O = 80.0(3)−80.7(3)° and indicate significant distortion from the optimum symmetry as seen most clearly in the large range of angles O−Ag−P. Nevertheless, the molecules have distorted trigonal planar stereochemistry, and there is no evidence for intermolecular association of the type observed in some related complexes.[12] This is, of course, a positive feature in terms of volatility and suitability as a CVD precursor. All evidence indicates that the structure established for **1a** is common to all complexes **1** and **2**.

The complexes **1** and **2** have also been characterized by their spectroscopic properties. The ^{1}H NMR spectra require little comment except that integration confirmed the stoichiometry of the compounds. However, the ^{31}P NMR spectra are of some interest since they indicate that exchange of ligands occurs easily. An R_3P−Ag group is expected to give rise to two superimposed doublets due to the couplings $^1J(^{107}AgP)$ and $^1J(^{109}AgP)$ [^{107}Ag and ^{109}Ag each have nuclear spin $I = 1/2$ and have natural abundances of 52 and 48%, respectively]. This pattern was observed in the low temperature ^{31}P NMR spectra, but at room temperature, the resonances appeared as either a broad doublet (**1b**, **2b**) or a broad singlet (**1a**, **2a**). Typical spectra are shown in Figure 2. The loss or partial loss of coupling $^1J(AgP)$ indicates that phosphine exchange can occur easily. The limiting values of $^1J(^{107}AgP)$ for **1a**, **1b**, **2a**, and **2b** are 760, 720, 728, and 702 Hz, respectively, in the range expected if silver uses mostly its 5s orbital in bonding to the phosphine and 5p orbitals in bonding to the β-diketonate.[16] The exchange becomes faster in the presence of excess phosphine ligand in the case of **1b** with PEt_3 as judged by the lower temperature needed to give well resolved AgP couplings. Addition of 1 mol of PEt_3 gave [Ag(hfac)(PEt_3)$_2$] (eq 3) with $^1J(^{107}AgP)$ = 468 Hz, in the range expected for sp hybridization at silver(I), and addition of 2 equiv gave [Ag(hfac)(PEt_3)$_3$] with $^1J(^{107}AgP)$ = 303 Hz, in the range expected for sp^2 hybridized silver(I).[16] In the last case, a conductivity experiment indicated a small degree of ionization to [Ag(PEt_3)$_3$]$^+$(hfac)$^-$, and it is not clear how the hfac ligand binds in the covalent form. Because the loss of extra phosphine ligands to regenerate **1b** is relatively easy and the Ag-hfac bonding appears to become more



ionic when extra phosphine ligands are present,[13] the use of the more phosphine-rich compounds as CVD precursors is unfavorable. The mechanism of phosphine exchange in **1** or **2** is not clear. These complexes are stable to phosphine dissociation in the solid or liquid state up to 100 °C, so a dissociative mechanism is unlikely.

Thermal Properties of the Precursors. Many of the complexes [Ag(hfac)L] sublime at about 80−100 °C under vacuum and so it is important that loss of L with formation of oligomeric, involatile [{Ag(hfac)}] does not occur below 100 °C. The complexes [{Ag(hfac)}$_n$(alkene)] or [Ag(hfac)(SR_2)][12] do decompose at least partially before sublimation. However, the complexes **1** and **2** do not undergo thermolysis with loss of ligand at temperatures below 100 °C, and so they can be sublimed without decomposition. The thermal stabilities were tested by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The complexes **1** decomposed over the temperature range 140−280 °C to leave a residue of metallic silver, whereas the onset of thermolysis for the alkene complexes was typically 70−100 °C (Figure 3). The residual weight for **1a** at 440 °C corresponds to 25% of the original weight of the complex which compares well with the calculated silver content of 27%. The small discrepancy is probably due to some weight loss from sublimation of the precursor prior to thermolysis, but it is clear that the complexes do not sublime at atmospheric pressure, though they do sublime under vacuum leaving no silver residue. The complexes **2** sublime more easily and TGA traces are shown in Figure 4. The residual weights are 4% and 1% for **2a** and **2b**, respectively, between 140 and 280 °C, while the calculated silver contents are 22.5 and 20.7%; clearly they undergo almost quantitative sublimation (really evaporation since both are liquids in the temperature range where weight loss occurs) at atmospheric pressure. Thus complexes **2** are somewhat more thermally stable and are at least as volatile as the corresponding complexes **1**, and this improves their performance as CVD precursors, as outlined below.

CVD Experiments. Films of silver were grown from the precursors **1** by using a low-pressure vertical CVD

(16) (a) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386. (b) Lancashire, R. J. In *Comprehensive Coordination Chemistry;* Pergamon: Oxford, UK, 1987, Vol. 5, Chapter 54.

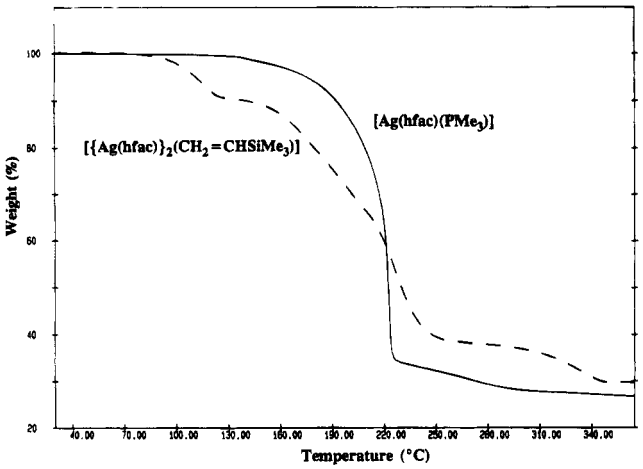


Figure 3. Thermogravimetric analysis (TGA, weight, %) for $[Ag_2(hfac)_2(CH_2{=}CHSiMe_3)]$ and $[Ag(hfac)(PMe_3)]$ under N_2. In each case, the heating rate was 20 °C/min. The weight loss for $[Ag_2(hfac)_2(CH_2{=}CHSiMe_3)]$ at 150 °C was 13.0% whereas the calculated alkene content is 13.7%.

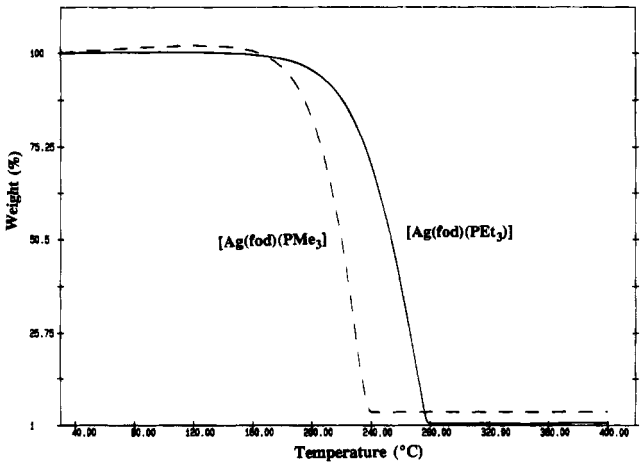


Figure 4. Thermogravimetric analysis (TGA, weight, %) for $[Ag(fod)(PMe_3)]$ and $[Ag(fod)(PEt_3)]$ under N_2. In each case, the heating rate was 20 °C/min. Note the low residual masses, indicating almost quantitative sublimation (compare Figure 3).

reactor which has been described elsewhere[17] 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 a period of 30–60 min onto glass, silicon, or copper 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 (faster growth gives a more coarse grained film). A typical growth rate for $[Ag(hfac)(PMe_3)]$ with precursor at 95 °C and glass substrate at 310 °C was 2 μ h^{-1}. In an independent study, it was not found possible to deposit silver films on glass, silicon, or silver substrates from the precursor **1a** at temperatures from 200–425 °C.[7] In our own work, there were sometimes problems in initiating deposition, but coherent films could be grown on glass, silicon, or copper, without using special methods of treating the surfaces. The induction periods observed in growing films on glass or silicon are presumed to be due to slow nucleation, the growth being

(17) Dryden, N. H.; Kumar, R.; Ou, E.; Rashidi, M.; Roy, S.; Norton, P. R.; Puddephatt, R. J.; Scott, J. D. *Chem. Mater.* **1991**, *3*, 677.

Table 2. CVD Conditions and XPS Analysis of Silver Films

precursor	carrier	P/T^a (torr/ °C)	XPS analysis (atom %) Ag	C	other
$[Ag(hfac)(PMe_3)]$		10^{-2}/350	91	9	
$[Ag(hfac)(PEt_3)]$		10^{-2}/310	95	5	
$[Ag(fod)(PMe_3)]$		10^{-4}/370	60	34	O, 5; F, 1
$[Ag(fod)(PEt_3)]$		10^{-4}/380	78	16	O, 4; P, 2[b]
$[Ag(fod)(PMe_3)]$	H_2	10^{-1}/290	91	9	
$[Ag(fod)(PEt_3)]$	H_2	10^{-1}/260	99	1	
$[Ag(fod)(PMe_3)]$	H_2/H_2O^a	10^{-1}/300	100	0	
$[Ag(fod)(PEt_3)]$	H_2/H_2O^a	10^{-1}/230	99	0	O, 1
$[Ag(fod)(PEt_3)]$	H_2/H_2O^a	10^{-1}/320	95	0	O, 5

[a] The hydrogen gas was passed through a water bubbler before entering the CVD chamber. [b] The presence of P impurity when L = PEt_3 but not PMe_3 could be due to some β-elimination to give ethylene, hydrogen, and phosphido groups, which cannot be desorbed and so ultimately led to phosphide.

Table 3. Crystal Data and Experimental Details

compound, formula weight	$C_8H_{10}F_6O_2P_1Ag_1$, 390.997
crystal system, space group	triclinic
cell dimensions	a = 12.662(3) Å, b = 15.112(4) Å, c = 11.052(1) Å, α = 102.42(2)°, β = 94.82(1)°, γ = 93.98(2)°
temp, °C	23
cell volume (Å^3), Z	2049.6(7), 6
density, g cm^{-3} obsd, calcd	1.90(4), 1.901
F(000)	1140
diffractometer, monochromator	Enraf-Nonius CAD4F; graphite
radiation, wavelength (Å)	Mo Kα, 0.710 73
abs coeff (cm^{-1})	15.0
no. of observ, variables	3294 ($I \geq 2.5\sigma(I)$), 357
final model; R and R_w	0.0619, 0.0621

faster on silver substrate. The compositions of these films were established by XPS and EDX analysis (Table 2), revealing that they are composed of silver with some carbon present (5–10%). No impurities of oxygen, fluorine, phosphorus, or sulfur were detectable (i.e., less than 1% present) in the films. A typical matte film grown from **1a** has a rough texture with grain sizes of 1–2 μm in diameter. The films adhered well to glass or silicon as indicated by the Scotch tape test. The electrical resistivity of a film of thickness 1.1 μm on glass was 6.5 $\mu\Omega$ cm, which can be compared to the value for pure silver of 1.59 $\mu\Omega$ cm. A common method to reduce carbon impurities in CVD metallic films is to use hydrogen as carrier gas. Unfortunately, this method was unsuccessful for the precursors **1** since hydrogen caused premature decomposition in the precursor reservoir. An attempt using a nitrogen carrier gas but combining with hydrogen near the substrate was also unsuccessful. Nevertheless, precursors **1** are far superior to the alkene complexes in contrast to the case of copper CVD from [Cu(hfac)L], where the complex with L = $Me_3SiCH{=}CH_2$ is the most widely used precursor. Figure 3 indicates that the silver complex is oligomeric (perhaps similar to the norbornadiene complex)[12] and decomposes relatively easily by loss of alkene.

In the absence of a reactive carrier gas, the precursors **2** required temperatures of 370–380 °C to give efficient CVD. At these high temperatures, the decomposition was not selective and higher impurities of carbon were observed as well as some impurities of oxygen, phosphorus and fluorine in some cases (Table 2). However, the higher stability of **2** compared to **1** did allow the use of a hydrogen carrier gas and, under these conditions, CVD could be carried out at 230–300 °C and pure

Table 4. Atomic Positional (×10⁴) and Thermal (×10³) Parameters[a]

atom	x	y	z	U_{eq} (Å²)	occu
		Molecule 1			
Ag(1)	3156.0(9)	2447.6(8)	1514.2(10)	86.6(4)	
P(1)	4165(3)	2453(3)	−133(3)	73(1)	
O(1)	3089(7)	1887(6)	3271(8)	79(3)	
O(2)	1646(6)	3047(6)	2227(8)	76(2)	
C(1)	2432(10)	2004(9)	4063(12)	72(4)	
C(2)	1596(10)	2529(9)	4082(12)	75(4)	
C(3)	1261(10)	3004(9)	3226(12)	67(4)	
C(4)	2667(15)	1471(13)	5097(16)	106(5)	
C(5)	306(14)	3585(13)	3463(17)	103(5)	
C(6)	4230(15)	1387(11)	−1164(14)	155(10)	
C(7)	3729(16)	3094(14)	−1172(16)	186(12)	
C(8)	5456(14)	2888(17)	246(17)	220(14)	
F(1)	2178(13)	659(12)	4770(15)	112(5)	0.6
F(2)	3655(15)	1473(12)	5445(16)	122(6)	0.6
F(3)	2192(14)	1912(12)	6158(16)	125(6)	0.6
F(1a)	1938(21)	1432(21)	5778(26)	119(5)	0.4
F(2a)	2885(22)	612(18)	4582(22)	119(5)	0.4
F(3a)	3528(22)	1925(19)	5808(25)	119(5)	0.4
F(4)	459(13)	4395(12)	3120(16)	119(5)	0.6
F(5)	−540(13)	3137(11)	2724(15)	107(5)	0.6
F(6)	41(14)	3749(13)	4565(16)	124(6)	0.6
F(4a)	635(17)	4402(17)	3980(23)	108(7)	0.4
F(5a)	−321(18)	3528(17)	2388(21)	100(7)	0.4
F(6a)	−316(19)	3225(18)	4289(22)	110(8)	0.4
		Molecule 2			
Ag(2)	4997.5(8)	3184.8(8)	4239.5(11)	86.9(5)	
P(2)	6123(3)	2025(3)	4149(5)	98(2)	
O(3)	4262(7)	4151(6)	3137(8)	75(2)	
O(4)	3957(7)	3922(6)	5671(8)	78(3)	
C(9)	3669(9)	4752(8)	3508(11)	63(3)	
C(10)	3262(9)	4996(9)	4633(11)	70(4)	
C(11)	3402(9)	4573(9)	5603(11)	64(3)	
C(12)	3369(16)	5278(14)	2452(17)	112(6)	
C(13)	2803(15)	4895(13)	6761(16)	103(5)	
C(14)	5670(15)	983(12)	3233(21)	211(13)	
C(15)	6456(23)	1704(17)	5545(21)	319(21)	
C(16)	7392(14)	2269(15)	3771(33)	414(34)	
F(7)	2362(14)	5635(13)	2720(16)	104(5)	0.5
F(8)	4004(14)	5987(12)	2585(15)	89(5)	0.5
F(9)	3171(15)	4757(12)	1362(16)	94(5)	0.5
F(7a)	3312(19)	6131(15)	2881(18)	125(7)	0.5
F(8a)	2558(17)	4956(15)	1807(20)	124(7)	0.5
F(9a)	4117(18)	5224(16)	1660(20)	143(7)	0.5
F(10)	3334(17)	4776(14)	7816(20)	121(3)	0.5
F(11)	1876(16)	4497(15)	6611(18)	121(3)	0.5
F(12)	2772(16)	5821(14)	7031(18)	121(3)	0.5
F(10a)	2281(16)	4137(14)	7020(18)	121(3)	0.5
F(11a)	2067(16)	5423(15)	6533(17)	121(3)	0.5
F(12a)	3450(18)	5225(14)	7668(21)	121(3)	0.5
		Molecule 3			
Ag(3)	10445.2(10)	1737.1(8)	10064.5(11)	90.2(5)	
P(3)	9895(3)	2879(3)	9106(4)	82(2)	
O(5)	11715(6)	794(6)	10352(7)	72(2)	
O(6)	9728(6)	1093(6)	11562(8)	79(3)	
C(17)	11690(9)	218(8)	11001(10)	59(3)	
C(18)	10961(9)	29(8)	11782(10)	62(3)	
C(19)	10055(9)	468(8)	12013(11)	60(3)	
C(20)	12664(12)	−366(11)	10860(14)	84(4)	
C(21)	9367(14)	191(13)	12971(16)	99(5)	
C(22)	8645(12)	3272(12)	9531(17)	147(10)	
C(23)	10759(13)	3905(10)	9483(18)	144(9)	
C(24)	9688(18)	2648(12)	7452(14)	184(11)	
F(13)	13541(14)	171(12)	11375(18)	101(6)	0.5
F(14)	12619(13)	−1066(13)	11427(17)	99(5)	0.5
F(15)	12769(14)	−723(13)	9659(16)	105(6)	0.5
F(13a)	13520(14)	75(13)	10597(18)	101(6)	0.5
F(14a)	13001(13)	−537(13)	12017(16)	94(5)	0.5
F(15a)	12428(13)	−1147(12)	10142(17)	98(5)	0.5
F(16)	8334(12)	258(11)	12651(14)	104(5)	0.6
F(17)	9503(14)	−621(12)	13158(16)	124(6)	0.6
F(18)	9568(17)	737(16)	14040(23)	136(8)	0.6
F(16a)	8520(18)	−265(16)	12507(20)	95(5)	0.4
F(17a)	9918(18)	−334(17)	13718(21)	95(5)	0.4
F(18a)	9298(22)	939(19)	13894(26)	95(5)	0.4

[a] The Ag, P, and the methyl carbon atoms were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$.

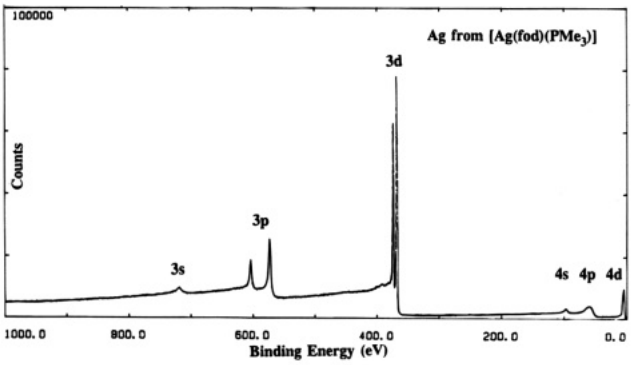


Figure 5. XPS analysis of a silver film formed by CVD from [Ag(fod)(PMe_3)] at 300 °C using H_2/H_2O (0.1 Torr) as carrier gas. The film was sputtered for 1 min with argon ions before analysis, and no impurities are detected.

silver films were obtained (Table 2, Figure 5). The hydrogen could be pure dry H_2 or H_2 saturated with water vapor. In some runs using moist H_2, some oxygen impurity was detected in the silver films. It is possible that these reactions occur by hydrolysis of the Ag−fod linkage to give fodH and R_3PAgOH in the first step. Examination of the films indicated that the morphology depended on the temperature of CVD under H_2. For example, films grown on glass using moist H_2 carrier gas at 320 and 230 °C had surface particle sizes of 1.5−2 and 0.1−0.5 μm, respectively (Figure 6). However, although the surface particle sizes were different, the resistivities of films of thickness of ca. 2 μm were similar at 2.5−3.0 $\mu\Omega$ cm. The higher resistivities compared to bulk metal are probably not due not to impurities in this case but to the presence of poorly connected grains in the silver films (Figure 6).

The main volatile products of CVD were hfacH or fodH and PMe_3 or PEt_3 as determined by trapping and then analysing by GC or NMR. These were the main products in the presence or absence of H_2 carrier gas. CVD under D_2 led to formation of hfacD or fodD as major products determined by MS analysis. No evidence for CVD by disproportionation, as is observed in CVD of copper from analogous precursors,[1] was obtained. This is not surprising since silver(II) is a much less common oxidation state than copper(II). The phosphine ligands present in [$Cu(C_5H_5)(PR_3)$] are known to poison the growth reaction in copper deposition[1] but the phosphines in the silver precursors studied here do not appear to have this effect.

It is clear from the above results that the complexes **1** and especially **2** are superior to known precursors for the CVD of silver films, with the possible exception of [$AgC(CF_3)=CF(CF_3)$].[5,7] The advantages of these compounds are the ease of synthesis and handling, the good volatility, and absence of thermolysis prior to vacuum sublimation. In addition, **2** sublime without decomposition in the presence of H_2 and give pure silver films by thermal CVD. Complexes **1b** and **2b** melt at 45−46 and 26−28 °C, respectively, and so, at the normal temperature of 50−80 °C used to evaporate the precursors, they behave as the first known liquid precursors for CVD of silver.

Experimental Section

TGA and DSC data were obtained by using PE TGA7 and DSC7 instruments at atmospheric pressure with a nitrogen purge. NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer and MS by using a Finnegan MAT spectrometer. CVD experiments were carried out using a vertical reactor as described previously,[17] and typical conditions are given in Table 2. The substrates were cleaned before use by washing with distilled water, acetone, and methanol. The silicon substrates were covered with the native oxide, and the glass used was Pyrex.

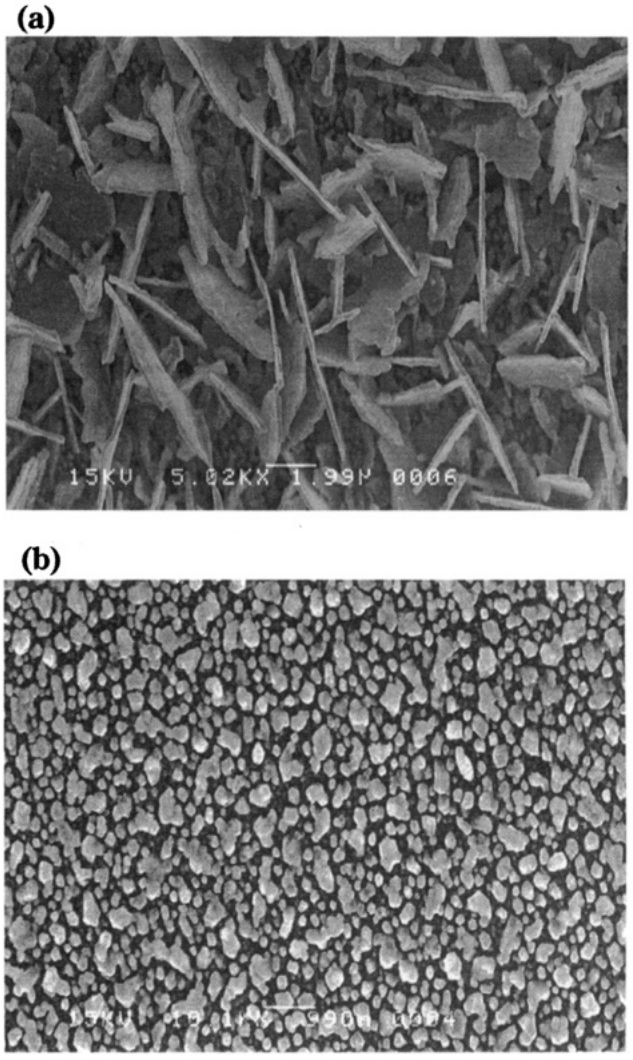


Figure 6. Comparison of the SEM images of a silver films grown from [Ag(fod)(PEt_3)] using H_2/H_2O (0.1 Torr) as carrier gas on a glass substrate: (a) at 320 °C, resistivity 2.6 $\mu\Omega$ cm and (b) at 230 °C, resistivity 2.8 $\mu\Omega$ cm. No thermal annealing was carried out.

The complexes [{Ag(hfac)}$_2$(OH_2)], [{Ag(hfac)}$_2$(cyclohexene)], [{Ag(hfac)}$_2$(t-BuCH=CH_2)], [{Ag(hfac)}$_2$($Me_3SiCH=CH_2$)], and [Ag(hfac)(1,5-cyclooctadiene)] were synthesized by literature methods.[12,14] **Caution**: the phosphine ligands used in this work are toxic and air-sensitive; they were handled in the absence of air using Schlenk techniques in a well-ventilated fume hood.

[Ag(hfac)(PMe_3)]. *Method A.* A solution of PMe_3 in THF (3.05 mL, 1.0 M) was added via syringe to a stirred solution of [Ag(hfac)(1,5-cyclooctadiene)] (1.29 g, 3.05 mmol) in THF (20 mL) 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, ^{1}H, 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) $[Ag(PMe_3)]^+$.

Method B: The complex was also prepared by reaction of $[\{Ag(hfac)\}_2(t\text{-BuCH=CH}_2)]$ (1.5 g) in CH_2Cl_2 (20 mL) with PMe_3 (0.60 mL) for 30 min. The solvent was evaporated under vacuum and the residue was purified by vacuum sublimation, to give product as a white solid; yield 85%.

Method C: To a suspension of Ag_2O (1.06 g) in CH_2Cl_2 (30 mL) cooled to 0 °C was added hfacH (1.30 mL) and the mixture was stirred for 15 min. PMe_3 (0.92 mL) was then added by syringe and the mixture was stirred for 30 min. The solution was filtered, and the solvent was evaporated to give $[Ag(hfac)(PMe_3)]$, which was purified by vacuum sublimation; yield 90%. Anal. Calcd: C, 24.6; H, 2.6. Found: C, 24.5; H, 2.5%.

Crystal data: triclinic, space group $P\bar{1}$, a = 12.662(3), b = 15.112(4), c = 11.052(1) Å, α = 102.42(2), β = 94.82(1), γ = 93.98(2)°, Z = 6, R = 0.0619, R_w = 0.0621.

[Ag(hfac)(PEt$_3$)]. *Method A*: This complex was prepared as in method B above from $[\{Ag(hfac)\}_2(cyclohexene)]$ and PEt_3 and was isolated as a viscous yellow oil by removal of solvent in vacuo at room temperature. It was purified by vacuum distillation (0.05 mmHg, 50−80 °C) onto a dry ice/acetone cooled probe; yield 64%. 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}. ^{1}H 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) $[Ag(PEt_3)]^+$.

Method B: This complex was also prepared by reaction of $[\{Ag(hfac)\}_2(THF)]$ (1.5 g) in CH_2Cl_2 (20 mL) cooled to 0 °C with PEt_3 (0.63 mL) for 30 min. The solvent was evaporated under vacuum and the residue was purified by vacuum sublimation at 100 °C/0.005 Torr to a coldfinger at −78 °C to give $[Ag(hfac)(PEt_3)]$ as a pale yellow solid; yield 75%. Anal. Calcd: C, 30.5; H, 3.7. Found: C, 30.5; H, 3.5%.

[Ag(fod)(PMe$_3$)]. To a suspension of Ag_2O (0.25 g, 1.08 mmol) in ether (20 mL) was added 1,5-cyclooctadiene (0.27 mL) and fodH (0.50 mL). The mixture was stirred for 5 min and then filtered. To the filtrate was added a solution of PMe_3 in THF (2.16 mL, 1.0 M) and the mixture was stirred for 1 h. The solvent was removed to give the product as a white powder; yield 94%. It was purified by vacuum sublimation at 80 °C/10^{-3} Torr. White crystals could be grown by evaporation of a solution in hexane. Anal. Calcd for $C_{13}H_{19}AgF_7O_2P$: C, 32.6; H, 4.0. Found: C, 33.0; H, 4.1%. NMR in CD_2Cl_2 $\delta(^1H)$ = 1.03 [s, 9H, *t*-Bu]; 1.33 [d, 9H, J(PH) = 18 Hz, PMe_3]; 5.57 [s, 1H, CH]; $\delta(^{31}P)$ = −35.9 [$J(^{107}AgP)$ = 728 Hz at −80 °C]. MS *m/z* = 478 [M$^+$]; 421 [M - C_4H_9]; 183 [M − fod].

[Ag(fod)(PEt$_3$)]. To a mixture of Ag_2O (0.50 g, 2.16 mmol) and Et_3P (0.51 g, 4.32 mmol) in ether (20 mL) was added fodH (1.28 g, 4.32 mmol). The mixture was stirred for 10 min and filtered, and the solvent evaporated to give the product as a pale yellow oil; yield 95%. It was purified by vacuum sublimation at 80 °C/10^{-3} Torr, to give a pale yellow solid, mp 26−28 °C. Anal. Calcd for $C_{16}H_{25}AgF_7O_2P$: C, 36.9; H, 4.8. Found: C, 36.9; H, 4.9%. NMR in CD_2Cl_2: $\delta(^1H)$ = 1.14 [s, 9H, *t*-Bu]; 1.19 [m, 9H, *J*(PH) = 17 Hz, *J*(HH) = 7, *Me*CH_2P]; 1.72 [m, 6H, Me*CH_2*P]; $\delta(^{31}P)$ = 11.8 [$J(^{107}AgP)$ = 702 Hz at −40 °C]. MS *m/z* = 520 [M$^+$]; 463 [M − C_4H_9]; 225 [M − fod].

X-ray Structure Determination. A suitable single crystal (with dimensions of 0.38 × 0.15 × 0.15 mm, with 9 crystal faces {1−10}, {−101}, {0−11}, {110}, and (−100)) was wedged inside a capillary tube to prevent sublimation. Preliminary investigations and the data collection were done on an Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo Kα radiation[18] at 23 °C. Photo and automatic indexing routines, followed by least squares fits of 21 accurately centered reflections (22.6 ≤ 2θ ≤ 25.5°), gave cell constants and an orientation matrix. The Niggli matrix suggested the triclinic system. The crystal density measured by neutral buoyancy method using a mixture of carbon tetrachloride and hexane to be 1.90(4). The number of molecules per unit cell, Z = 6. Intensity data were recorded in the ω−2θ mode, at variable scan speeds (0.82−4.12° min^{-1}) and a scan width of 0.70 + 0.35 tan θ, with a maximum time per datum of 60 s. Static background measurements were made at the end points of the width 0.80 + 0.35 tan θ. Three standard reflections were monitored every 120 min of X-ray exposure time. There were 6170 reflections in the 2θ range 0−46° (−13 ≤ h ≤ 13, −16 ≤ k ≤ 1, −12 ≤ l ≤ 12) and 55 repetitions of the standards were recorded. Corrections were made for Lorentz, monochromator and crystal polarization, background radiation effects, and decay using the NRCVAX crystal structure programs[19] running on a SUN 3/80 workstation. The data were corrected for absorption with the use of an empirical method[20] based on psi scans (ψ = 0−360° every 10°) for χ values near 90°. Nine sets of reflections with θ ranging from 6.2 to 14.7° gave the correction factors minimum and maximum values 0.8244 and 0.9987. The absorption coefficient, μ = 15 cm^{-1}. The equivalent reflection were averaged (R_{int} = 0.019) accordingly. The structure was solved by SHELXS-86 program and subsequent difference Fourier methods.[21] The structure refinements were done by full-matrix least-squares techniques on F with a SHELX-76 program.[22] Anisotropic thermal parameters were assigned for the Ag, P, and the methyl carbon atoms and were refined. All the fluorine atoms were found to be disordered. Two disorder components for each fluorine atom were resolved successfully, and their occupancy factors were determined based on their relative electron densities in the difference Fourier syntheses. All the hydrogen atoms were placed in ideal positions (C−H = 0.95 Å) and their thermal parameters were fixed at U = 0.12. In the final cycles, the refinement of 357 parameters and 3294 ($I \geq 2.5\sigma(I)$) observations, the model converged at R_f = 0.0619, R_w = 0.0621. In the final difference Fourier synthesis ranges 0.807 to −0.514 e A^{-3} where the top 10 peaks were associated with the F atoms. The largest Δ/σ = 0.246 on y of F1a. The experimental details and crystal data, the positional and B_{iso} thermal parameters, tables of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, weighted least-squares planes and dihedral angles, selected torsional angles, and the structures factors have been included in the supporting information.

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Supporting Information 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 (19 pages); tables of structure factor amplitudes (20 pages). Ordering information (9 pages); is given on any current masthead page.

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(18) *CAD4 Diffractometer Manual*; Enraf-Nonius: Delft, The Netherlands, 1988.
(19) Gabe, E. J.; Le Page, Y; Charland, J.-P.; Lee, F. C. *J. Appl. Cryst.* **1989**, *22*, 384.
(20) North, A. C. T.; Phillips, D. C.; Mathews, R. S. *Acta. Crystallogr. A* **1968**, *24*, 351.
(21) Sheldrick, G. M. *SHELXS-86*; University of Gottingen: Gottingen, West Germany, 1986.
(22) Sheldrick, G. M. *SHELX-76*; University of Cambridge, Cambridge, England, 1976.