Allyl(β-diketonato)palladium(II) Complexes, Including Liquid Precursors, for Chemical Vapor Deposition of Palladium

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The synthesis, characterization, and application as chemical vapor deposition (CVD) precursors of several new complexes of the type η^3-allyl(β-diketonato)palladium(II) are reported. Some of these include the first liquid precursors for CVD of thin films of pure palladium. The CVD can be conducted at 170−315 °C, and the purest films are obtained using oxygen as the carrier gas, either at atmospheric pressure or under partial vacuum. Some observations with respect to the mechanism of the CVD process are also described.

Introduction

Thin films of palladium have important applications as electrical contacts (replacing gold), multilayer magnetooptical data storage materials, gas or infrared sensors, multilayer chip capacitors, electrode coating materials,[1] catalysts,[2] and membrane materials for either catalysis or gas separation.[3] At present, physical vapor deposition (PVD) techniques, such as vacuum sputtering, and electroplating are used in industry to prepare palladium films. These techniques are certainly effective but, as line-of-sight methods, they can suffer from shadow effects when used to coat uneven substrates,[1] so there has been much interest in developing chemical vapor deposition (CVD) techniques for palladium thin films.[4] The known precursors for palladium include [Pd(η^3-allyl)$_2$] and derivatives such as [Pd(η^3-$CH_2CHCHMe)_2$], which has a low melting point of 20−23 °C with decomposition; these are excellent precursors for high-purity palladium thin films by thermal CVD, but they have low thermal stability and are sensitive to both oxygen and water so are not easily stored or handled.[5] The complexes [Pd(η^5-C_5H_5)(η^3-allyl)] have similar physical properties but have higher thermal stability, but they give palladium films containing carbon impurities when used as precursors in thermal or plasma-enhanced CVD.[5,6] These precursors give films of palladium(II) oxide when decomposed in an oxygen plasma, and such films can be reduced to metallic palladium with hydrogen.[6] Dimethylpalladium complexes, *cis*-[$PdMe_2L_2$], L = PMe_3 or PEt_3, also give either carbon or phosphorus impurities in the palladium films arising from thermal CVD.[7] The most widely used precursors for palladium films are the β-diketonato complexes [Pd{OC(R)CHC(R)O}$_2$], R = Me or CF_3. These can give an unusual redox mechanism of CVD on metal substrates such as copper to yield palladium metal and [Cu{OC(R)CHC(R)O}$_2$], but thermal CVD on inactive substrates using hydrogen as carrier gas gives pure palladium and the β-diketone $RC(=O)CH_2C(=O)R$.[8] A patent claims CVD of palladium from [Pd(η^5-$C_5H_5)_2$],[8a] but the synthesis of the complex has not been reported.[9] The complexes [Pd(allyl)(β-diketonate)] have been shown to give pure palladium films under mild conditions by thermal CVD using either hydrogen or oxygen as carrier gas.[10,11] Since these are particularly effective precursors and since liquid precursors have distinct advantages in applications as a result of their reproducible and constant evaporation rates,[12] it was thought desirable to modify these precursors by introducing larger organic substituents in either the allyl or the β-diketonate groups in order to obtain the first liquid precursors for palladium thin films. This article reports the results of this study; a preliminary account has been published,[13] and the complexes have recently been shown to be useful as catalysts in CVD of metal oxides.[14]

(1) Gurney, P. D.; Seymour, R. J. In *Chemistry of the Platinum Group Metals*; Hartley, F. R., Ed.; Elsevier: Oxford, U.K., 1991.
(2) Sordelli, L.; Martra, G.; Psaro, R.; Dossi, C.; Coluccia, S. *J. Chem. Soc., Dalton Trans.* **1996**, 765.
(3) (a) Saracco, G.; Specchia, V. *Catal. Rev.—Sci. Eng.* **1994**, *36*, 305. (b) Armor, J. N. *Catal. Today* **1995**, *25*, 199.
(4) (a) Spencer, J. T. *Prog. Inorg. Chem.* **1994**, *41*, 145. (b) Puddephatt, R. J. *Polyhedron* **1994**, *13*, 1233. (c) Igumenov, I. K. *J. Phys. IV* **1995**, *C5*, 489. (d) Hampden-Smith, M. J.; Kodas, T. T. *Adv. Mater., Chem. Vap. Deposition* **1995**, *1*, 8.
(5) (a) Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Kruger, C. *J. Organomet. Chem.* **1980**, *191*, 425. (b) Gozum, J. E.; Pollina, D. M.; Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 2688.
(6) Feurer, E.; Suhr, H. *Thin Solid Films* **1988**, *157*, 81. (b) Stauf, G. T.; Dowben, P. A. *Thin Solid Films* **1988**, *156*, L31. Thomas, R. R.; Park, J. M. *J. Electrochem. Soc.* **1989**, *136*, 1661.
(7) Yuan, Z.; Jiang, D.; Naftel, S. J.; Sham, T.-K.; Puddephatt, R. J. *Chem. Mater.* **1994**, *6*, 2151.
(8) (a) Kudo, T.; Yamaguchi, A. *Jpn. Pat.* JP62 207 868, **1987**. (b) Lin, W.; Warren, T. H.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 11644. (c) Bhaskaran, V.; Hampden-Smith, M. J.; Kodas, T. T. *Adv. Mater., Chem. Vap. Deposition* **1997**, *3*, 85. (d) Xu, C. Y.; Hampden-Smith, M. J.; Kodas, T. T. *Chem. Mater.* **1995**, *7*, 1539. (e) Hybertson, B. M.; Hansen, B. N.; Barkley, R. M.; Sievers, R. E. *Mater. Res. Bull.* **1991**, *26*, 1127. (f) Hansen, B. N.; Hybertson, B. M.; Barkley, R. M.; Sievers, R. E. *Chem. Mater.* **1992**, *4*, 749.
(9) Gusev, O. V.; Morozova, L. N.; Peterleitner, M. G.; Peregudova, S. M.; Petrovskii, P. V.; Ustynyuk, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1996**, *509*, 95.
(10) Yuan, Z.; Puddephatt, R. J. *Adv. Mater.* **1994**, *6*, 51.
(11) Hierso, J.-C.; Satto, C.; Feurer, R.; Kalck, P. *Chem. Mater.* **1996**, *8*, 2481.
(12) Maury, F. *J. Phys. IV* **1995**, *C5*, 449.
(13) Zhang, Y.; Puddephatt, R. J. *Adv. Mater., Chem. Vap. Deposition* **1997**, *3*, 81.

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Experimental Section

^1H,^{13}C, and^{19}F NMR spectra in $CDCl_3$ solution were recorded by using a Varian Gemini 300 MHz spectrometer, and chemical shifts are referenced to tetramethylsilane (TMS; ^1H or ^{13}C) or $CFCl_3$ (^{19}F). IR spectra were measured as NaCl disks using a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectra were recorded using a Finnigan MAT 8200 spectrometer with MSS Data System. The thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer thermogravimetric analyzer TGA7. Elemental analyses were performed by Guelph Chemical Laboratories Ltd.

XPS spectra of films were recorded using the SSL SSX-100 small-spot XPS surface-analysis instrument with a monochromatized Mg Kα X-ray source (1253.6 eV). The surface composition in atom percent from XPS spectra were collected after 1−2 min sputtering with argon at 4 keV until a constant composition was obtained. The AES spectra for surface scanning and depth profile were recorded on the Perkin-Elmer PHI 600 scanning Auger multiprobe after sputtering with argon at 3 keV. XPS is most useful for detection of carbon (detection limit, ca. 0.5%), while Auger is useful for detection of O and F in the presence of palladium. In all cases, analyses are corrected for the relative sensitivities of each element. SEM micrographs of the palladium films, as either top or cross-section views, were obtained using an ISL DS-130 scanning electron microscope. Resistivities of the films were measured using a Veeco FPP 5000 four-point probe apparatus.

The organic products from the CVD reactions were collected in a liquid nitrogen cooled trap and were analyzed by FTIR, GC (Varian 3400 gas chromatography with a packed column and a flame ionization detector), and GC-MS.

Typical synthetic procedures, modified from literature methods,[15−20] are given below, and abbreviations used for the β-diketonate ligands are as follows: fod = *t*-BuCOCHCOC$_3$F$_7$; tfac = $CH_3COCHCOCF_3$; hfac = $CF_3COCHCOCF_3$; dpm = *t*-BuCOCHCO-*t*-Bu; acac = $CH_3COCHCOCH_3$.

[{Pd(η^3-CH_2CMeCH_2)(μ-Cl)}$_2$], 2a. A mixture of KCl (0.10 g, 2.36 mmol) and $PdCl_2$ (0.10 g, 0.56 mmol) in distilled water (10 mL) was stirred at room temperature for 1 h to form a clear brown solution, then CH_2═$CMeCH_2Cl$ (0.154 g, 1.70 mmol) was added, and the solution was stirred at 70 °C for 8 h. The mixture was cooled to room temperature and extracted with $CHCl_3$ (3 × 5 mL). The organic layer was collected, and the volatiles were removed in vacuo to give a yellow solid (0.11 g, 98% yield). Similarly were prepared [Pd(η^3-CH_2CHCH_2)(μ-Cl)}$_2$] (**1a**; yield, 95%) and [Pd(η^3-$CH_2CHCHMe$)(μ-Cl)}$_2$] (**3a**; yield: 98%).

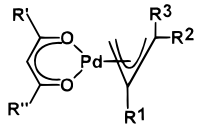
[{Pd(η^3-$CH_2CMeCMe_2$)(μ-Cl)}$_2$], 4a. A mixture of $PdCl_2$ (0.10 g, 0.56 mmol), $NaOAc·3H_2O$ (1.03 g, 7.5 mmol), NaCl (0.42 g, 7.2 mmol), and $Cu(OAc)_2·H_2O$ (0.485 g, 3.4 mmol) in a solvent mixture of glacial acetic acid (10 mL) and acetic anhydride (1 mL) was stirred at 90 °C for 2 h and then cooled to 60 °C. A solution of Me_2C═CMe_2 in THF (1.3 mL of 1 M solution) was added, and the mixture was allowed to react at 60 °C for 3 h, then cooled to room temperature, and poured into distilled water (250 mL). The product was extracted with benzene (3 × 5 mL). The benzene layer was collected, washed with distilled water (3 × 20 mL), saturated aqueous $NaHCO_3$ (10 mL), and saturated aqueous NaCl solution (10 mL), and dried over anhydrous sodium sulfate, and the solvent was removed under vacuum to give a yellow solid (yield, 0.11 g, 88%. Similarly was prepared, from cyclohexene, the cyclohexenyl complex [Pd(η^3-CHCHCHCH$_2$CH$_2$CH$_2$)(μ-Cl)}$_2$] (**5a**; yield 84%).

[Pd(η^3-CH_2CHCH_2)(fod)], 1f. A mixture of distilled water (5 mL), KOH (0.033 g, 0.59 mmol), and fodH (0.173 g, 0.59 mmol) was stirred at room temperature for 1 h and then added to a suspension of [{Pd(η^3-CH_2CHCH_2)(μ-Cl)}$_2$] (0.10 g, 0.280 mmol) in ether (10 mL) and the mixture stirred for 2 h. The ether layer was separated, washed with distilled water (3 × 10 mL) and dried over sodium sulfate; then the solvent was evaporated to give the product as a yellow liquid (yield, 0.19 g, 81%. ^1H NMR: δ 1.14 (s, 9H, ^{t}Bu), 2.95 and 2.98 (d, 2 × 1H, *J*(HH) = 12 Hz, *anti*-H in CH_2), 3.96 (d, 2H, *J*(HH) = 7 Hz, *syn*-H in CH_2), 5.60 (tt, 1H, *J*(HH) = 12, 7 Hz, CH of allyl), 5.89 (s, 1H, CH of fod). ^{13}C NMR: δ 27.9 (*C*H$_3$), 42.9 (*C*Me$_3$), 56.6 and 57.3 (*C*H$_2$ of allyl), 92.2 (*C*H of fod), 113.1 (*C*H of allyl), 204.1 (O*C*^{t}Bu). ^{19}F NMR: δ −80.8 (s, 3F, CF_3), −119.1 (s, 2F, CF_2), −126.95 (s, 2F, CF_2). IR: ν(CO) 1612(s) cm^{-1}. MS: *m*/*z* 442 (33%, *P*), 385 (34%, P − C_4H_8), 147 (100%, P − fod).

A summary of the reaction conditions for synthesis of the related complexes defined in Charts 1 and 2, together with melting points and analytical data for the compounds, is given in Table 1.

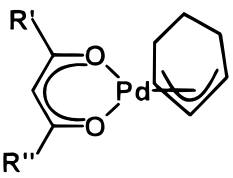
Spectroscopic Data for New Complexes. *Complex **1e***. ^1H NMR: δ 1.12 (s, 18H, ^{t}Bu), 2.82 (d, 2H, *J*(HH) = 12 Hz, *anti*-H in CH_2), 3.75 (d, 2H, *J*(HH) = 7 Hz, *syn*-H in CH_2),

Chart 1. Allylpalladium Complexes Used for CVD



Complex	R^1	R^2	R^3	R'	R''
1b	H	H	H	Me	Me
1c	H	H	H	CF_3	CF_3
1d	H	H	H	Me	CF_3
1e	H	H	H	*t*-Bu	*t*-Bu
1f	H	H	H	*t*-Bu	C_3F_7
2b	Me	H	H	Me	Me
2c	Me	H	H	CF_3	CF_3
2d	Me	H	H	Me	CF_3
2e	Me	H	H	*t*-Bu	*t*-Bu
2f	Me	H	H	*t*-Bu	C_3F_7
3b	H	Me	H	Me	Me
3c	H	Me	H	CF_3	CF_3
3d	H	Me	H	Me	CF_3
3e	H	Me	H	*t*-Bu	*t*-Bu
3f	H	Me	H	*t*-Bu	C_3F_7
4b	Me	Me	Me	Me	Me
4c	Me	Me	Me	CF_3	CF_3
4d	Me	Me	Me	Me	CF_3
4e	Me	Me	Me	*t*-Bu	*t*-Bu
4f	Me	Me	Me	*t*-Bu	C_3F_7

Chart 2



5b, R' = Me, R'' = CF_3

5c, R' = *t*-Bu, R'' = C_3F_7

(14) Zhang, Y.; Choi, S. W.-K.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 9295.
(15) Imamura, S.; Kajimoto, T.; Kitano, Y.; Tsuji, J. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 805.
(16) Jackson, W. R.; Strauss, J. U. *Aust. J. Chem.* **1978**, *31*, 1073.
(17) (a) Davies, J. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Puddephatt, R. J., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 9. (b) Maitlis, P. M. In *Comprehensive Organometallic Chemistry I*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1978; Vol. 6.
(18) Palenik, R. C.; Palenik, G. J. *Synth. React. Inorg. Met.-Org. Chem.* **1992**, *22*, 1395.
(19) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407.
(20) (a) Churchill, M. R. *J. Chem. Soc., Chem. Commun.* **1965**, 625. (b) Malone, J. F.; McDonald, W. S. *J. Chem. Soc. A* **1970**, 3124.

Table 1. Synthesis Conditions, Melting Points, and Analytical Data for η^3-Allyl(β-diketonato)palladium(II) Complexes

	reacn conditions[a]						found		calcd	
complex	*t* (h)	*T* (°C)	S	*R*	*Y* (%)	mp (°C)	C%	H%	C%	H%
1f	2	25	A	1	81	liquid	35.45	3.61	35.27	3.42
1e	6	25	A	1.2	85	88.0−90.5	50.80	7.41	50.84	7.31
2f	12	25	A	1.1	85	66.5−67.0	37.00	3.71	36.82	3.75
2e	2	25	A	1.1	91	88.0−90.0	52.23	7.79	52.26	7.60
3f	4	60	B	1.3	84	44.5−45.5	37.33	3.78	36.82	3.75
3e	4	60	B	1.1	78	101.0−102.0	52.41	7.68	52.26	7.60
3c	4	60	B	1.1	80	61.5−63.0	29.00	2.29	29.33	2.19
3d	4	60	B	1.1	88	65.5−66.5	34.70	3.52	34.36	3.52
3b	4	60	B	1.1	85	82.0−83.0	41.36	5.35	41.48	5.41
4f	2	60	B	1.1	87	liquid	40.00	4.57	39.65	4.37
4e	2	60	B	1.1	84	66.5−67.5	54.85	8.23	54.77	8.11
4c	2	60	B	1.1	85	62.0−63.5	33.72	3.08	33.31	3.05
4d	2	60	B	1.1	89	45.0−46.5	38.97	4.45	38.56	4.41
4b	2	60	B	1.1	86	75.0−77.0[b]	45.84	6.31	45.77	6.28
5c	2	25	B	1.1	65	58.0−60.0				
5b	2	25	B	1.1	70	liquid				

[a] t, time; *T*, temperature; S, solvent; A, diethyl ether and water; B, benzene and water; *R*, molar ratio of β-diketonate/Pd; *Y*, yield. [b] Decomposed.

5.51 (tt, 1H, *J*(HH) = 12 Hz, CH of allyl), 5.66 (s, 1H, CH of dpm). ^{13}C NMR: δ 29.2 (CH_3), 42.4 (CMe_3), 55.7 (CH_2), 90.4 (*C*H of dpm), 112.8 (*C*H of allyl), 197.4 (O*C*^{t}Bu). IR: ν(CO) 1585(w), 1564(s), 1530(w), 1498(w) cm^{-1}. MS: *m*/*z* 330 (37%, *P*), 315 (23%, *P* − CH_3), 275 (100%, *P* − (allyl + CH_2)), 147 (85%, *P* − dpm).

Complex ***2f***. ^{1}H NMR: δ 1.14 (s, 9H, ^{t}Bu), 2.21 (s, 3H, CH_3 of 2-methylallyl), 2.79 and 2.83 (s, 2H, *anti*-H in CH_2), 3.72 (s, 2H, *syn*-H in CH_2), 5.87 (s, 1H, CH of fod). ^{13}C NMR: δ 22.4 (CH_3 of 2-methylallyl), 27.3 (CH_3 of ^{t}Bu), 42.3 (*C*Me$_3$), 54.9 and 55.6 (CH_2), 91.5 (*C*H of fod), 128.7 (*C*CH_3 of 2-methylallyl), 202.2 (O*C*^{t}Bu). ^{19}F NMR: δ −80.8 (s, 3F, CF_3), −119.1 (s, 2F, CF_2), −126.9 (s, 2F, CF_2). IR: ν(CO) 1613(s), 1510(w) cm^{-1}. MS: *m*/*z* 456 (35%, *P*), 399 (42%, *P* − ^{t}Bu), 161 (100%, *P* − fod).

Complex ***2e***. ^{1}H NMR: δ 1.12 (s, 18H, ^{t}Bu), 2.17 (s, 3H, CH_3 of 2-methylallyl), 2.69 (s, 2H, *anti*-H in CH_2), 3.51 (s, 2H, *syn*-H in CH_2), 5.65 (s, 1H, CH of dpm). ^{13}C NMR: δ 23.3 (CH_3 of 2-methylallyl), 28.7 (CH_3), 41.9 (*C*Me$_3$), 54.2 (CH_2), 89.8 (*C*H of dpm), 128.0 (*C*CH_3 of 2-methylallyl), 197.4 (O*C*^{t}Bu). IR: ν(CO) 1583(vs), 1529(s), 1498(s) cm^{-1}. MS: *m*/*z* 344 (13%, *P*), 287 (39%, *P* − ^{t}Bu), 161 (100%, *P* − dpm).

Complex ***3f***. ^{1}H NMR: δ 1.14 (s, 9H, ^{t}Bu), 1.26 and 1.32 (d, 3H, *J*(HH) = 6 Hz, CH_3 of 1-methylallyl in cis- and trans-isomers), 2.72 and 2.76 (m, 1H, *anti*-H in CH_2 of 1-methylallyl in cis- and trans-isomers), 3.76 (m, 2 × 1H, *syn*-H in CH_2 and C*H*CH_3 of 1-methylallyl in cis- and trans-isomers), 5.35 (m, 1H, CH of 1-methylallyl), 5.87 (s, 1H, CH of fod). ^{13}C NMR: δ 16.8 (CH_3 of 1-methylallyl), 27.8 and 28.0 (CH_3 of ^{t}Bu in cis- and trans-isomers), 42.3 (*C*Me$_3$), 52.9 and 53.3 (CH_2 in cis- and trans-isomers), 74.2 and 74.7 (*C*HCH_3 in cis- and trans-isomers), 91.9 and 92.3 (*C*H of fod in cis- and trans-isomers), 112.7 and 112.8 (*C*H of 1-methylallyl in cis- and trans-isomers), 204.0 (O*C*^{t}Bu). ^{19}F NMR: δ −80.77 (s, 3F, CF_3), −118.90 and −118.93 (s, 2F, CF_2 in cis and trans-isomers), −126.90 (s, 2F, CF_2). IR: ν(CO) 1612(s), 1508(s) cm^{-1}. MS: *m*/*z* 456 (19%, *P*), 399 (19%, *P* − ^{t}Bu), 161 (100%, *P* − fod).

Complex ***3e***. ^{1}H NMR: δ 1.12 (s, 18H, ^{t}Bu), 1.28 (d, 3H, *J*(HH) = 6 Hz, CH_3 of 1-methylallyl), 2.60 (dd, 1H, J_1(HH) = 12 Hz, J_2(HH) = 1 Hz, anti-H in CH_2), 3.56 (d, 1H, *J*(HH) = 6 Hz, *syn*-H in CH_2), 3.56 (m, 1H, *J*(HH) = 6 Hz, *syn*-H in C*H*CH_3), 5.25 (m, 1H, CH of 1-methylallyl), 5.64 (s, 1H, CH of dpm). ^{13}C NMR: δ 16.57 (CH_3 of 1-methylallyl), 28.61 and 28.79 (CH_3 of *trans*- and *cis*-^{t}Bu), 41.26 and 41.90 (*C*Me$_3$ of *trans*- and *cis*-^{t}Bu), 51.08 (CH_2), 72.34 (*C*HCH_3), 90.02 (*C*H of dpm), 111.93 (*C*HCH_2), 197.18 (O*C*^{t}Bu). IR: ν(CO) 1583(m), 1564(s) 1529(m), 1498(m) cm^{-1}. MS: *m*/*z* 344 (18%, *P*), 287 (53%, *P* − ^{t}Bu), 161 (100%, *P* − dpm).

Complex ***3c***. ^{1}H NMR: δ 1.32 (d, 3H, *J*(HH) = 6 Hz, CH_3 of 1-methylallyl), 2.92 (d, 1H, *J*(HH) = 12 Hz, *anti*-H in CH_2), 3.92 (m, 1H, *J*(HH) = 5 Hz, *syn*-H in C*H*CH_3), 4.00 (dd, 1H, J_1(HH) = 7 Hz, J_2(HH) = 1 Hz, syn-H in CH_2), 5.47 (m, 1H, CH of 1-methylallyl), 6.05 (s, 1H, CH of hfac). ^{13}C NMR: δ 17.08 (CH_3 of 1-methylallyl), 55.40 (CH_2), 89.73 (*C*H of hfac), 113.83 (*C*HCH_2 of 1-methylallyl), 117.99 (q, *J*(CF) = 285.9 Hz, *C*F_3), 175.73 (q, *J*(CF) = 33.8 Hz, O*C*CF_3). ^{19}F NMR: δ −75.65 and −75.73 (s, 3F, *cis*- and *trans*-CF_3). IR: ν(CO) 1635(s), 1552(m) cm^{-1}. MS: *m*/*z* 368 (35%, *P*), 161 (100%, *P* − hfac).

Complex ***3d***. ^{1}H NMR: δ 1.30 (m, 3H, CH_3 of 1-methylallyl), 2.10.(s, 3H, CH_3 of tfac), 2.77 (d, 1H, *J*(HH) = 12 Hz, *anti*-H in CH_2), 3.80 (m, 2 × 1H, syn-H in C*H*CH_3 and *syn*-H in CH_2), 5.36 (m, 1H, CH of 1-methylallyl), 5.70 (s, 1H, CH of tfac).^{13}C NMR: δ 16.90 (CH_3 of 1-methylallyl), 53.24 and 53.55 (CH_2 in cis- and trans-isomers), 74.64 and 74.99 (*C*HCH_3 in cis- and trans-isomers), 95.09 (*C*H of tfac), 112.98 (*C*HCH_2 of 1-methylallyl), 195.50 (O*C*CH_3). ^{19}F NMR: δ −74.70 and −75.28 (s, 3F, CF_3 in cis- and trans-isomers). IR: ν(CO) 1615(s), 1520(s) cm^{-1}. MS: *m*/*z* 314 (22%, *P*), 161 (100%, *P* − tfac).

Complex ***3b***. ^{1}H NMR: δ 1.30 (d, 3H, *J*(HH) = 6 Hz, CH_3 of 1-methylallyl), 1.96 and 1.97 (s, 3H, *cis*- and *trans*-CH_3 of acac), 2.65 (d, 1H, *J*(HH) = 12 Hz, *anti*-H in CH_2), 3.64 (m, 1H, syn-H in C*H*CH_3), 3.66 (d, 1H, *J*(HH) = 5 Hz, *syn*-H in CH_2), 5.30 (m, 1H, CH of 1-methylallyl), 5.33 (s, 1H, CH of acac). ^{13}C NMR: δ 16.95 (CH_3 of 1-methylallyl), 28.10 and 28.30 (*cis*- and *trans*-CH_3 of acac), 51.85 (CH_2), 73.25 (*C*HCH_3 of 1-methylallyl), 100.10 (*C*H of acac), 112.35 (*C*HCH_2 of 1-methylallyl), 187.50 and 188.20 (*cis*- and *trans*-O*C*CH_3 in acac). IR: ν(CO) 1584(s), 1514(m) cm^{-1}. MS: *m*/*z* 260 (22%, *P*), 205 (17%, *P* − 1-methylallyl), 161 (100%, *P* − acac).

Complex ***4a***. ^{1}H NMR: δ 1.21 (s, 3H, *anti*-CH_3 in C$(CH_3)_2$), 1.34 (s, 3H, *syn*-CH_3 in C$(CH_3)_2$), 2.04 (s, 3H, CCH_3), 3.15 (s, 1H, *anti*-H in CH_2), 3.69 (s, 1H, *syn*-H in CH_2). ^{13}C NMR: δ 19.72 (*anti*-*C*H_3 in C$(CH_3)_2$), 22.94 (C*C*H_3), 23.54 (*syn*-*C*H_3 in C$(CH_3)_2$), 57.48 (CH_2), 88.38 (*C*$(CH_3)_2$), 118.56 (*C*CH_3). Melting point: 119−120 °C. Anal. Calcd for **4a**: C, 32.03; H, 4.93. Found: C, 32.50; H, 5.07. MS: *m*/*z* 448 (25%, *P*), 413 (34%, *P* − Cl), 296 (51%), 189 (100%), 147(44%).

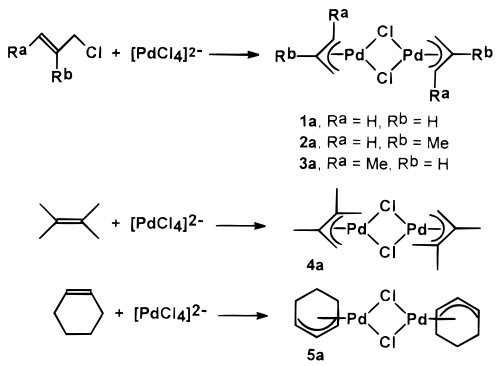
Complex ***4f***. ^{1}H NMR: δ 1.14 (s, 9H, ^{t}Bu), 1.17 (s, 3H, *anti*-CH_3 in C$(CH_3)_2$), 1.37 (s, 3H, *syn*-CH_3 in C$(CH_3)_2$), 2.11 (s, 3H, CCH_3), 3.08 (s, 1H, *anti*-H in CH_2), 3.65 (s, 1H, *syn*-H in CH_2), 5.82 (s, 1H, CH of fod). ^{13}C NMR: δ 19.72 (anti-*C*H_3 in C$(CH_3)_2$), 21.64 (*syn*-*C*H_3 in C$(CH_3)_2$), 23.12 (C*C*H_3), 27.35 (CH_3 of ^{t}Bu), 42.27 and 42.90 (*C*$(CH_3)_3$ in cis- and trans-isomers), 52.3 (CH_2), 81.28 (*C*$(CH_3)_2$), 91.54 (*C*H of fod), 119.86 (*C*CH_3), 203.31 (*C*^{t}Bu). ^{19}F NMR: δ −80.75 (s, 3F, CF_3), −118.83 and 119.26 (s, 2F, CF_2 in cis- and trans-isomers), −126.85 and −126.99 (s, 2F, CF_2 in cis- and trans-isomers). IR: ν(CO) 1613(vs), 1581(s), 1508(s) cm^{-1}. MS: *m*/*z* 484 (16%, *P*), 427 (7%, *P* − ^{t}Bu), 189 (100%, *P* − fod), 161 (7%), 147 (40%).

Complex ***4e***. ^{1}H NMR: δ 1.115 and 1.122 (s, 2 × 9H, *cis*- and *trans*-^{t}Bu), 1.15 (s, 3H, *anti*-CH_3 in C$(CH_3)_2$), 1.34 (s, 3H, *syn*-CH_3 in C$(CH_3)_2$), 2.07 (s, 3H, CCH_3), 2.95 (d, 1H, *J*(HH) = 1 Hz, *anti*-H in CH_2), 3.45 (s, 1H, *syn*-H in CH_2), 5.60 (s, 1H, CH of dpm). ^{13}C NMR: δ 20.57 (anti-*C*H_3 in C$(CH_3)_2$), 21.99 (C*C*H_3), 23.70 (*syn*-*C*H_3 in C$(CH_3)_2$), 28.59 and 28.84 (CH_3 in *cis*- and *trans*-^{t}Bu), 41.17 and 41.96 (*C*$(CH_3)_3$ in *cis*- and *trans*-^{t}Bu), 51.31 (CH_2), 79.11 (*C*$(CH_3)_2$), 89.78 (*C*H of fod), 119.26 (*C*CH_3), 196.99 and 197.19 (*cis*- and *trans*-*C*^{t}Bu). IR: ν(CO) 1582(s), 1565(vs), 1529(s), 1498(s) cm^{-1}. MS: *m*/*z* 372 (31%, *P*), 315 (63%, *P* − ^{t}Bu), 189 (100%, *P* − fod), 161(8%), 147 (34%).

Complex ***4c***. ^{1}H NMR: δ 1.20 (s, 3H, *anti*-CH_3 in C$(CH_3)_2$), 1.37 (s, 3H, *syn*-CH_3 in C$(CH_3)_2$), 2.15 (s, 3H, CCH_3), 3.25 (d, 1H, *J*(HH) = 1 Hz, *anti*-H in CH_2), 3.83 (s, 1H, *syn*-H in CH_2), 6.00 (s, 1H, CH of hfac). ^{13}C NMR: δ 20.26 (anti-*C*H_3 in C$(CH_3)_2$), 22.43 (C*C*H_3), 23.92 (*syn*-*C*H_3 in C$(CH_3)_2$), 54.91 (CH_2), 84.86 (*C*$(CH_3)_2$), 89.61 (*C*H of hfac), 118.04 (*C*F_3), 121.92 (*C*CH_3), 175.63 (q, *J*(CF) = 33.8 Hz, O*C*CF_3). ^{19}F NMR: δ −75.90 (s, 3F, CF_3). IR: ν(CO) 1635(vs), 1551(s) cm^{-1}. MS: *m*/*z* 396 (16%, *P*), 189 (100%, *P* − hfac), 147 (44%).

Complex ***4d***. NMR: ^{1}H NMR: δ 1.07 (s, 3H, *anti*-CH_3 in C$(CH_3)_2$), 1.25 (s, 3H, *syn*-CH_3 in C$(CH_3)_2$), 1.97 (s, 3H, CH_3 of tfac), 2.01 (s, 3H, CCH_3), 2.99 (s, 1H, *anti*-H in CH_2), 3.56 (s,

Scheme 1



1H, J(HH) = 1 Hz, *syn*-H in CH_2), 5.54 (s, 1H, CH of tfac). ^{13}C NMR: δ 21.00 (anti-CH_3 in $C(CH_3)_2$), 22.84 (CCH_3), 24.36 (*syn*-CH_3 in $C(CH_3)_2$), 29.90 and 30.10 (CH_3 of tfac), 53.58 and 53.68 (CH_2), 78.13 ($C(CH_3)_2$), 95.54 (*C*H of tfac), 121.92 (CCH_3). ^{19}F NMR: δ −74.65 and −75.37 (s, 3F, CF_3 in cis- and trans-isomers). IR: ν(CO) 1617(vs), 1519(vs) cm^{-1}. MS: *m*/*z* 342 (21%, *P*), 189 (100%, *P* − tfac), 161 (6%), 147 (57%).

Complex ***4b***. ^1H NMR: δ 1.16 (s, 3H, *anti*-CH_3 in $C(CH_3)_2$), 1.35 (s, 3H, *syn*-CH_3 in $C(CH_3)_2$), 1.93 and 1.94 (s, 3H, *cis*- and *trans*-CH_3 of acac), 2.08 (s, 3H, CCH_3), 2.97 (s, 1H, J(HH) = 1 Hz, *anti*-H in CH_2), 3.52 (s, 1H, *syn*-H in CH_2), 5.27 (s, 1H, CH of acac). ^{13}C NMR: δ 20.52 (*anti*-CH_3 in $C(CH_3)_2$), 22.01 (CCH_3), 23.61 (*syn*-CH_3 in $C(CH_3)_2$), 27.90 and 28.58 (CH_3 of acac), 51.53 (CH_2), 80.45 ($C(CH_3)_2$), 99.82 (*C*H of acac), 119.77 (CCH_3), 187.00 and 188.63 (*cis*- and *trans*-$OCCH_3$). IR: ν(CO) 1586(vs), 1513(s) cm^{-1}. MS: *m*/*z* 288 (39%, *P*), 189 (100%, *P* − acac), 147 (52%).

Complex ***5c***. NMR: ^1H NMR: δ 1.00 (m, 1H, anti-H of β-CH_2), 1.13 (s, 9H, ^{t}Bu), 1.65 (m, 2 × 2H, α-CH_2 in $C(CH_3)_2$), 2.03 (m, 1H, *syn*-H of β-CH_2), 5.06 (m, 2 × 1H, 1- and 3-CH of cyclohexenyl), 5.60 (t, 1H, J(HH) = 6 Hz, 2-CH of cyclohexenyl), 5.82 (s, 1H, CH of fod).

Complex ***5b***. ^1H NMR: δ 0.99 (m, 1H, *anti*-H of β-CH_2), 1.70 (m, 2 × 2H, α-CH_2 in $C(CH_3)_2$), 2.02 (m, 1H, *syn*-H of β-CH_2), 2.07 (s, 3H CH_3 of tfac), 5.10 (m, 2 × 1H, 1- and 3-CH of cyclohexenyl), 5.61 (t, 1H, J(HH) = 6 Hz, 2-CH of cyclohexenyl), 5.65 (s, 1H, CH of tfac). ^{13}C NMR: δ 19.20 (β-CH_2), 29.08 (α-CH_2), 29.29 (CH_3), 73.01 (1- and 3-*C*H of cyclohexenyl), 94.82 (CH_3 of tfac), 103.40 (2-*C*H of cyclohexenyl), 119.13 (q, J(CF) = 285 Hz, CF_3), 168.80 (q, J(CF) = 32 Hz, $OCCF_3$), 195.3 ($OCCH_3$).

CVD Procedures. The thermal CVD reactions were carried out using a vertical cold-wall Pyrex reactor either under reduced pressure with dynamic pumping or at atmospheric pressure. A sidearm was present to allow the introduction of the carrier gas. The substrate (glass, Si or SiO_2) was heated by a temperature-controlled heating rod. The deposition time was typically 1 h.

Results and Discussion

Synthesis and Characterization of the Precursors. For a CVD process to be useful, it is necessary that the precursors be easily and economically prepared in good yield, as well as having the needed properties in the CVD process itself, so efforts have been made to improve the literature procedures, where possible, as described below. The complexes [Pd(η^3-allyl)(β-diketonate)] (Charts 1 and 2) are easily prepared in high yield from the reaction of the appropriate β-diketone with the chloro derivative [{Pd(η^3-allyl)(μ-Cl)}$_2$] in the presence of base,[15,16] and the procedures have been optimized for the new complexes reported (see Experimental Section, Table 1, Scheme 1). There are several methods available for synthesis of complexes of the type [{Pd(η^3-allyl)(μ-Cl)}$_2$],[17] and literature methods were modified to give optimum yields. The method of Palenik, in which $[PdCl_4]^{2-}$ is reacted with allyl chloride in aqueous solution, was used to prepare [{Pd(η^3-CH_2CHCH_2)(μ-Cl)}$_2$], **1a**, in high yield.[18] The literature procedure does not give a high yield for many substituted allyl derivatives,[18] but the modified procedure given in the Experimental Section and Table 1 allows easy syntheses of the 2-methylallyl and 1-methylallyl complexes [{Pd(η^3-CH_2CMeCH_2)(μ-Cl)}$_2$], **2a**, and [{Pd(η^3-$CH_2CHCHMe$)(μ-Cl)}$_2$], **3a**, in almost quantitative yields and without the need for sophisticated equipment. The synthetic procedure is summarized in Scheme 1. The more highly substituted complex [{Pd(η^3-$CH_2CMeCMe_2$)(μ-Cl)}$_2$], **4a**, and the cyclohexenyl derivative [{Pd(η^3-$CHCHCHCH_2CH_2CH_2$)(μ-Cl)}$_2$], **5a**, were prepared from the corresponding alkene $Me_2C{=}CMe_2$ or cyclohexene, respectively, by a modification of the literature procedure (see Experimental Section).[19]

The melting points and analytical data for the complexes [Pd(η^3-allyl)(β-diketonate)] (Charts 1 and 2) are listed in Table 1. All these complexes are yellow in color, and they may exist as solids or as viscous liquids (**1f**, **4f**, and **5b**) at room temperature. There is no simple correlation between melting point and the nature of the substituents on the allyl ligands. For example, of the complexes with the β-diketonate fod, **1f** and **4f** are liquids, whereas **2f**, **3f**, and **5c** are solids. However, some consistent trends in melting points as a function of the β-diketonate ligand can be identified from the data in Table 1. Thus, complexes of the bulky, asymmetrical β-diketonate fod always have lower melting points than those with the bulky, symmetrical β-diketonate dpm, and complexes with the fluorinated β-diketonates (tfac and hfac) have lower melting points than those with the nonfluorinated ligand acac. The liquid complex **1f** is of particular value as a precursor for CVD since it contains the simple allyl ligand, it can be stored for long periods at room temperature without thermal decomposition, and it has high volatility.

All new complexes have been characterized by ^1H, ^{13}C, and ^{19}F NMR, IR, and MS, and data are given in the Experimental Section. Assignments are made by reference to literature data on related complexes[17,19,20] and are not discussed in detail. For the complexes of the asymmetric diketonate ligand fod, such as **1f**, there are two resonances in the ^1H NMR for the anti protons of the CH_2 groups of the allyl group and two resonances for the CH_2 carbon atoms of the allyl group, indicating that the allyl group is not fluxional in these compounds, so the two CH_2 groups of the allyl ligand are nonequivalent. Moreover, if both the allyl and diketonate groups are asymmetric, as for example in **3f**, the NMR data indicate the presence of two isomers in solution in approximately equal abundance, again indicating slow rotation of the allyl group.[17]

The IR spectra of the β-diketonate complexes contain characteristic bands in the region 1500−1650 cm^{-1}, which are assigned to ν(C=O) and ν(C=C),[21] that are useful for characterization since the frequency of the strongest band increases in the more highly fluorinated complexes. For example, the relevant frequencies for the complexes [Pd($CH_2CHCHMe$)(β-diketonate)] are

(21) Okeya, S.; Ooi, S.; Matsumoto, K.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1085.

Table 2. TGA Results

complex	wt loss (%)	*T* range[a] (°C)	*T*(30%)[b] (°C)	% decomp[c]
1b	90	100−190	165	23
1c	99	30−150	125	3
1d	96	50−170	135	11
1e	82	85−160	143	55
1f	99	60−165	110	4
2b	88	100−200	165	29
2c	98	30−160	125	7
2d	95	80−180	140	15
2e	90	90−200	180	32
2f	98	70−140	110	8
3b	59	70−120	105	100
3c	89	65−120	102	38
3d	94	80−140	123	18
3e	87	85−140	125	42
3f	95	100−180	130	26
4b	71	85−140	120	79
4c	93	90−150	110	26
4d	84	90−140	120	42
4e	77	90−150	130	81
4f	94	90−150	130	25

[a] Temperature range for observed weight loss. [b] Temperature at which 30% weight loss is observed. [c] Calculated assuming that the residue is pure palladium metal.

1635, 1615, 1612, 1584, and 1564 cm^{-1} for β-diketonate = hfac, tfac, fod, acac, and dpm, respectively. The mass spectra of the β-diketonate complexes exhibit parent ions and so are also useful for characterization. The mass spectra of some complexes contain low-intensity peaks corresponding to ions which contain two palladium atoms, but since the complexes have such high volatility, these are not considered indicative of association of the complexes in the solid or liquid state.

The volatility and thermal stability of each β-diketonate complex have been studied since these are important in CVD applications. All complexes can be stored at 0 °C for long periods without decomposition, and **2f** and **4f** can be stored at room temperature. The least stable complexes are the cyclohexenyl derivatives **5b** and **5c**, which decompose in solution over a period of about 1 day with deposition of a palladium mirror, and they are the least suitable of the complexes as CVD precursors. All the β-diketonate complexes can be sublimed or distilled in vacuo at 10^{-2} Torr without decomposition, and complexes **1f** and **2f** can also be evaporated without significant decomposition at atmospheric pressure under an atmosphere of air or nitrogen. All the complexes are decomposed to palladium metal at temperatures below 100 °C under an atmosphere of hydrogen. The volatility at atmospheric pressure was tested more quantitatively by TGA; the results are summarized in Table 2, and typical data are shown in Figure 1. Most complexes partly evaporated and partly decomposed to leave a residue of metallic palladium on heating. The fod complexes of the simpler allyl derivatives gave the least decomposition when tested in this way (Table 2), and complexes **1f** and **2f** evaporate almost quantitatively. Isothermal TGA analysis for **1f** reveals that the evaporation rate is a constant during an isothermal TGA process when the temperature is lower than 120 °C. Using the known relationship between rate of evaporation, *m*, temperature, *T*, and enthalpy of evaporation, ΔH,[22] plots of $\log(mT^{1/2})$ vs $10^3/T$ should

(22) Ashcroft, S. J. *Thermochim. Acta* **1971**, *2*, 512.

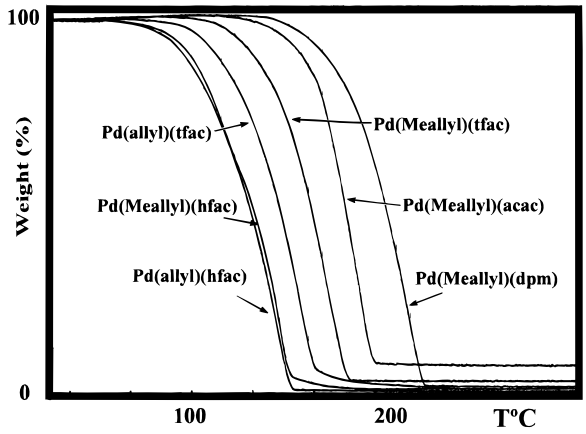


Figure 1. Typical TGA traces for the CVD precursors. The reactions were carried out using a flow rate of nitrogen of 50 mL $min.^{-1}$ and a heating rate of 5 °C $min.^{-1}$.

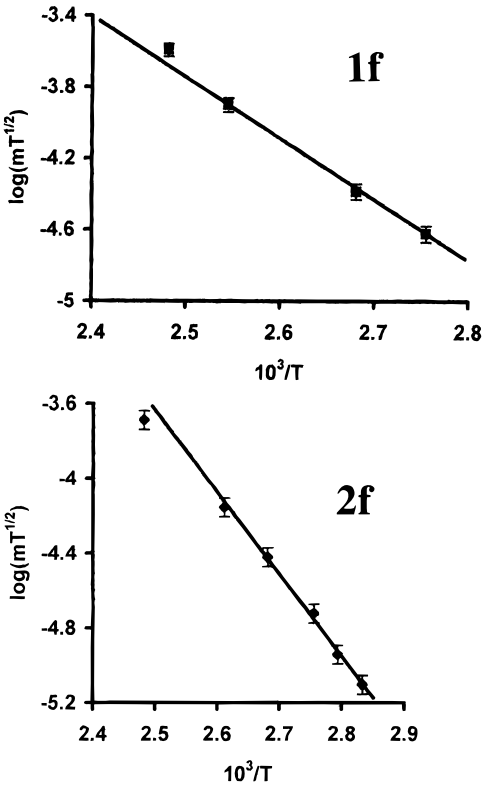


Figure 2. Graph showing the relationship between evaporation rate and temperature for the CVD precursors **1f** (above) and **2f** (below).

have a slope of $-0.0522\Delta H$. These plots (Figure 2) give approximate values for the enthalpy of evaporation of 66 ± 7 and 83 ± 8 kJ mol^{-1} for **1f** and **2f**, respectively. Deviations from linearity are observed at temperatures above 120 °C, and this is attributed primarily to partial decomposition of **1f** under these conditions.

CVD of Palladium. *Formation and Chararacterization of Palladium Thin Films.* CVD of palladium films on various substrates was carried out by using a vertical reactor in which the substrate was heated to the required temperature using a heating rod.

Experiments were carried out using no carrier gas or using nitrogen/hydrogen, air or oxygen as carrier gases either at atmospheric pressure or under partial vacuum. Since hydrogen decomposes many of the precursors at ambient temperature, it was introduced as a reactive

Table 3. Deposition Conditions and Film Properties

precursor	substrate/ t_s[a] (°C)	t_p[b] (°C)	CG/R[c] (mL/min)	P[d] (mmHg)	at. % C %	at. % Pd %
1c	glass/410	30		10^{-4}	22	78
1c	glass/140	30	H_2/50	10^{-1}	15	85
1c	glass/160	30	H_2/H_2O/50	10^{-1}	4	96
1c	glass/330	30	O_2/50	10^{-1}	<1	>99
2c	glass/450	30		10^{-4}	40	60
2c	glass/230	30	H_2/50	10^{-1}	16	84
2c	glass/230	30	H_2/H_2O/50	10^{-1}	<1	>99
2c	glass/370	30	O_2/50	10^{-1}	<1	>99
2b	glass/350	70	O_2/50	10^{-1}	<1	>99
1f	Si/170	70	O_2/50	10^{-1}	5	95
1f	glass/260	70	O_2/50	10^{-1}	<1	>99
1f	glass/285	70	O_2/50	10^{-1}	<1	>99
1f	Si/315	70	O_2/50	10^{-1}	<1	>99
1f	glass/305	70	O_2/50	10^{-1}	<1	>99
1f	glass/305	70	air/50	10^{-1}	<1	>99
1f	Si/260	70	O_2/25	10^{-1}	3	97
1f	glass/240	95	O_2/50	760	<1	>99
1e	Si/290	80	O_2/25	10^{-1}	<1	>99
2f	Si/290	70	O_2/25	10^{-1}	<1	>99
3f	glass/275	100	O_2/25	10^{-1}	8	92
3e	Si/305	90	O_2/25	10^{-1}	<1	>99
3c	Si/300	85	O_2/25	10^{-1}	<1	>99
4f	Si/305	85	O_2/25	10^{-1}	<1	>99
4e	Si/300	85	O_2/25	10^{-1}	2	98
4d	glass/285	85	O_2/25	10^{-1}	3	97
4b	glass/254	65	O_2/25	10^{-1}	5	95

[a] Substrate and its temperature. [b] Temperature for precursor evaporation. [c] Carrier gas and flow rate. [d] Pressure.

gas near the substrate. Substrates used included glass, silicon, and SiO_2 on silicon with only minor differences observed in terms of deposition conditions and film purity or adhesion; typical data for glass or silicon substrates are included in Table 3. In each case, the product film was analyzed by XPS, and several films were also characterized by conductivity measurement and by SEM. A summary of typical experimental conditions used, together with analytical data for the palladium films, is given in Table 3.

Preliminary CVD experiments were carried out using the solid complexes **1b**−**1d** and **2c**−**2d** as precursors as a function of the carrier gas and temperature.[10] When CVD was carried out without a carrier gas or with nitrogen carrier gas, the temperature required for efficient CVD was greater than 400 °C and the palladium films contained considerable amounts, typically 20−40% after surface sputtering, of carbon impurities (Table 3). However, no oxygen impurity was indicated, and no fluorine contamination was observed when using the tfac or hfac derivatives (Table 3); indeed neither oxygen nor fluorine contamination was detected in any of the palladium films prepared in this work.

To reduce carbon impurities, experiments were then carried out using reactive carrier gases. The use of hydrogen as carrier gas led to a dramatic reduction in the CVD temperature, and good palladium films could be prepared from 140 to 230 °C; these films also contained considerably less carbon impurities (Table 3). Purer films could be prepared under similar experimental conditions if the hydrogen was presaturated with water vapor (Table 3). The chief problem in using hydrogen carrier gas was that predecomposition of the precursor often occurred in the precursor reservoir, especially if high partial pressure of hydrogen was used, and so much precursor was wasted. The problem can be overcome by engineering the equipment such that

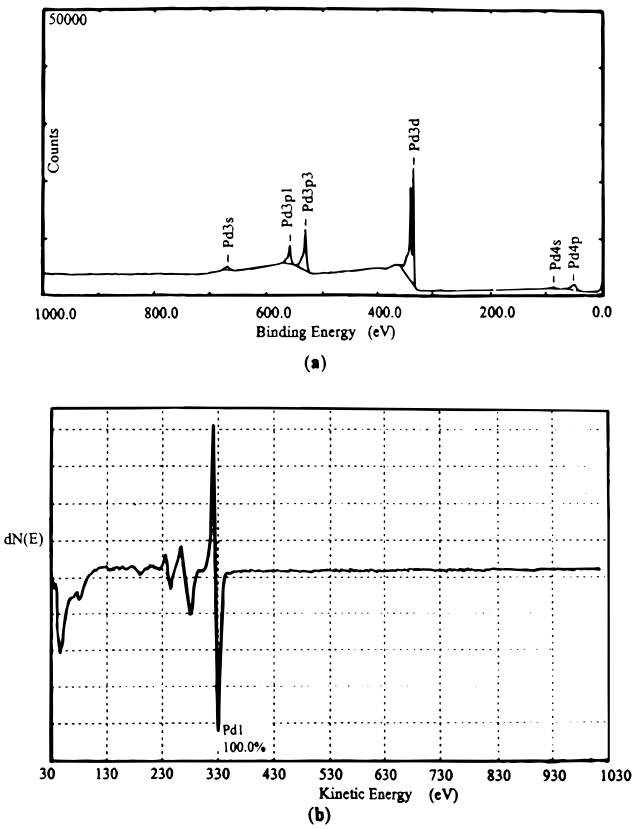


Figure 3. (a) XPS spectrum for Pd thin film obtained from **3c**; (b) AES spectrum for Pd thin film obtained from **1c**.

the precursor is transported in nitrogen carrier gas and mixed with hydrogen close to the substrate and very pure palladium films can then be formed. Kalck and co-workers have obtained similar analytical results and have shown that CVD can be carried out at temperatures as low as 45−60 °C under similar conditions using precursor **1c**.[11]

The highest purity palladium films were prepared from **1b**−**1d** and **2b**−**2d** using oxygen (or air) as carrier gas at CVD temperatures from 330 to 370 °C (Table 3). Under these conditions, no impurities were detected by XPS (carbon detection limit is ca. 0.5%) or AES (oxygen detection limit ca. 0.5%). The temperature required is intermediate between those with no carrier gas or the inactive carrier gas nitrogen and when using the more reactive carrier gas hydrogen.[10] The precursors are not decomposed under the conditions required for transport in oxygen, so the CVD experiment can be carried out with simpler equipment than when hydrogen is used.

Since these complexes clearly are excellent precursors, the development of liquid precursors was considered a priority. Of the liquid derivatives reported above, the fod complexes **1f** and **4f** proved to be good precursors, whereas **5b** was unsatisfactory due to difficulties with premature decomposition on storage and CVD use. The complex **1f** has the best combination of volatility and thermal properties, so it has been studied in greatest detail for CVD of palladium (Table 3). The behavior in CVD is similar to the solid precursors such as **1b**−**1d**. Thus, without a carrier gas or under nitrogen atmosphere, CVD occurs only at temperatures above 400 °C and the films are dark in color and contain much carbon impurity, and, using hydrogen as the carrier gas, there

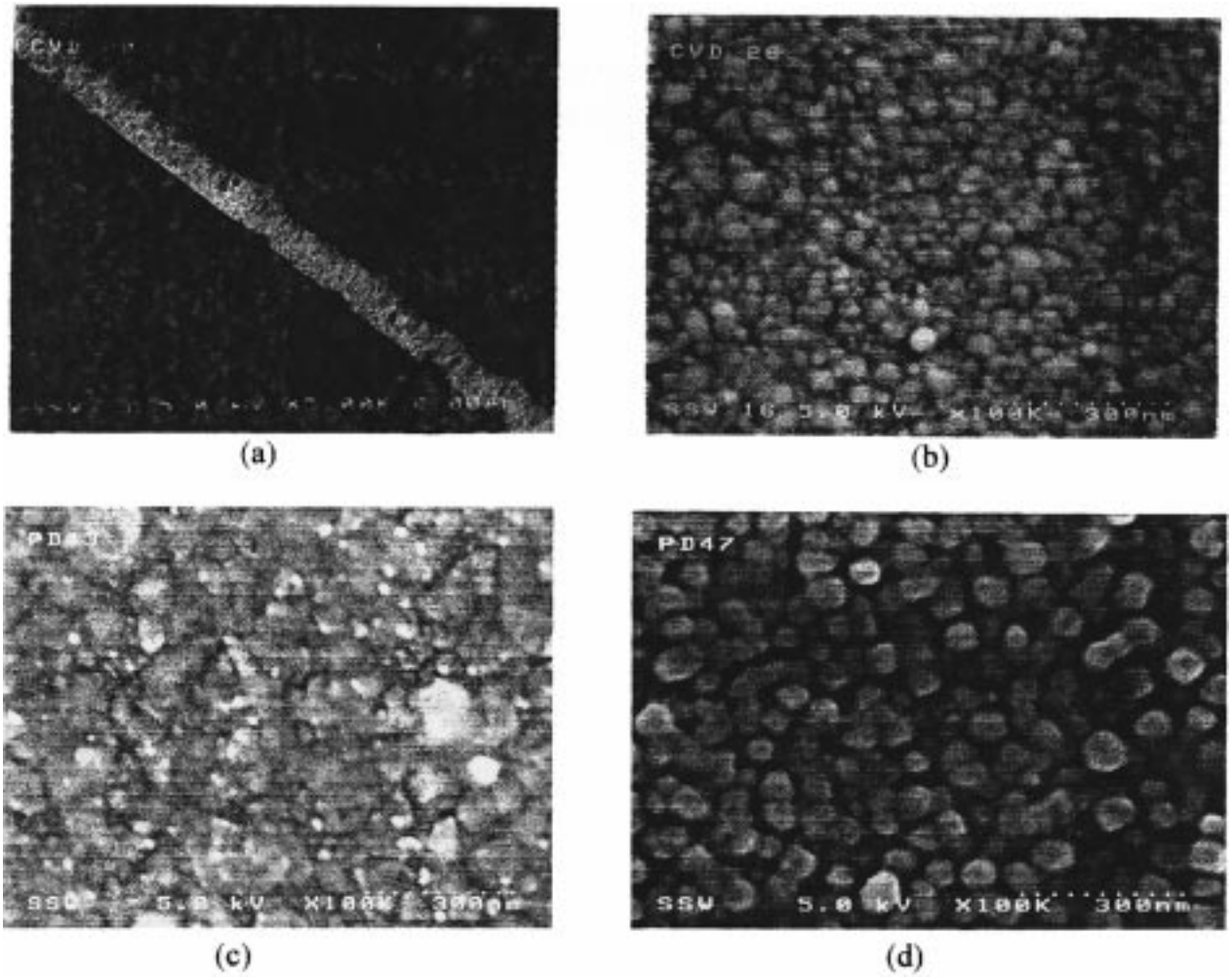


Figure 4. SEM micrographs of palladium thin films grown on silicon at a pressure of 10^{-1} Torr with oxygen as carrier gas, using the following precursors and temperatures: (a) **1f** at 315 °C; (b) **1f** at 170 °C; (c) **1c** at 315 °C; (d) **3d** at 315 °C.

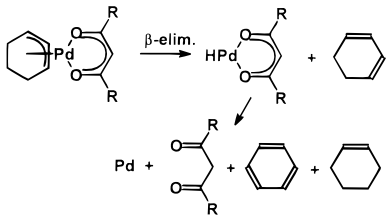
are similar problems with premature decomposition of the precursors by reaction with hydrogen. However, with oxygen or air as carrier gas, highly pure palladium thin films can be grown under relatively mild conditions of CVD. Parts a and b of Figure 3 show typical XPS and AES spectra of palladium films, indicating that the films are free of either carbon, oxygen, or fluorine impurities. The rate of film growth and the quality of the films are dependent on deposition temperature. At 315 °C, carbon-free films grew on silicon at a rate of 1.7 μm h^{-1}, while at the minimum CVD temperature of 170 °C films grown under otherwise similar conditions grew at a rate of only 0.05 μm h^{-1} and contained about 5% carbon impurity (Table 3). A high flow rate of oxygen or air was desirable to give the highest purity films. Thus, for low-pressure deposition on silicon or glass at 260 °C, a flow rate of oxygen of 50 mL min^{-1} gave pure palladium films whereas a flow rate of only 25 mL min^{-1} gave films containing 2−4% carbon impurity (Table 3). Atmospheric pressure CVD using **1f** as the precursor and air or oxygen as carrier gas gave pure palladium films over the temperature range 240−300 °C on either glass or silicon substrates. The rate of film growth at 240 °C was 0.16 μm h^{-1}, and the film had a shiny, metallic appearance.

The morphology of the thin films was studied using SEM. Figure 4 shows typical SEM images of the thin films as either a top or a cross-sectionional view. The film grown from **1f** at 315 °C on silicon (Figure 4a,b) consists of large crystalline particles with sizes ranging from 200 to 700 nm; films of this type have a metallic but somewhat matte appearance. In contrast, the particles of the film deposited from **1f** at 170 °C are globular with sizes of approximately 40 nm without identifiable crystal faces (Figure 4c); such films have a bright metallic appearance. A film grown from **3c** at 300 °C is composed of particles of size ca. 80 nm with only partly defined crystalline faces (Figure 4d). In general, the morphology depends on the precursor and the temperature of deposition, with higher temperatures favoring faster growth but also larger, more crystalline palladium particles.

The resistivity of thin palladium films (ca. 1 μm) on glass varied from 24 to 45 $\mu\Omega$·cm. For example, a resistivity of 24 $\mu\Omega$·cm was obtained for a film grown at 285 °C at low pressure and a value of 45 $\mu\Omega$·cm for a film grown at atmospheric pressure and at 260 °C. A pure thick palladium film (0.16 mm) gave a resistivity value of 11 $\mu\Omega$·cm, in agreement with the literature value for bulk palladium. The lower conductivity of the thin palladium films probably reflects the open crystalline morphology, since the analytical data indicate that the purity is high.

The more complex solid precursors have been studied in less detail, but it is clear that they can also give highly pure palladium thin films under similar experi-

Scheme 2. Decomposition by β-Elimination



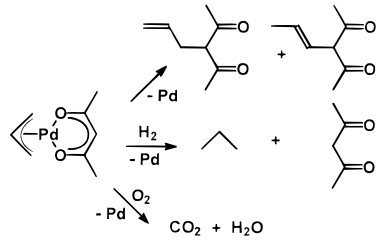
mental conditions (Table 3). The films obtained from **4b**−**4f** all contained some carbon impurity, but the CVD conditions were not optimized for these complexes and there is probably little significance to these observations. Since these complexes have lower volatility than **1**−**3**, they are unlikely to be preferred precursors.

Organic Products of CVD and Mechanistic Hypotheses. The least stable complexes **5b** and **5c** decompose over a period of 1 day at room temperature in $CDCl_3$ solution in an NMR tube with deposition of a palladium mirror. Analysis by ^1H NMR and GC showed that the organic products were benzene (0.5 mol), cyclohexene (0.5 mol), and the corresponding β-diketone (1 mol). It is likely that the primary reaction is a hydride transfer from the cyclohexenyl group to the diketonate ligand (presumably via palladium, by β-elimination/reductive elimination) to give the diketone and 1,3-cyclohexadiene, followed by disproportionation of the 1,3-cyclohexadiene to benzene and cyclohexene catalyzed by the palladium metal formed (Scheme 2). This β-elimination mechanism[17,23] may also be important in thermolysis of the complexes **4** under vacuum or in the presence of oxygen; thus thermolysis of **4f** under CVD conditions with oxygen carrier gas gave 2,3-dimethyl-1,3-butadiene and Hfod as major products as determined by GC/MS analysis.

The situation is more complex in the case of the thermolysis of allylpalladium(II) complexes in which the allyl group does not contain a β-hydrogen atom and the products depend on the carrier gas used. Thermolysis of **1b** under vacuum is known to give coupling of the allyl and β-diketonate groups to give 3-allyl-2,4-pentanedione and 3-propenyl-2,4-pentanedione (Scheme 3).[15] However, decomposition under CVD conditions with either dry or moist hydrogen as carrier gas gave propane and acetylacetone as the only detected products as determined by GC/MS analysis. Clearly, this represents an overall hydrogenation reaction and is consistent with catalysis at the forming palladium surface. Finally, decomposition under CVD conditions with oxygen carrier gas gave mostly CO_2 and H_2O as products (Scheme 3), with only minor amounts of propane, propene, and acetylacetone detected. Again, this clearly indicates that the major part of the reaction must occur at the forming palladium surface, leading to products of combustion of the organic ligands.

(23) (a) Donati, M.; Conti, F. *Tetrahedron Lett.* **1966**, 4953. (b) Howsan, R. W.; McQuillin, F. J. *Tetrahedron Lett.* **1968**, 3667.

Scheme 3. Decomposition of 1b under Vacuum, Hydrogen, or Oxygen



The organic products formed from **1c** under hydrogen were identified as propane and hexafluoroacetylacetone, as expected from the above observation. However, decomposition under oxygen or air gave a more complex mixture of products, including significant amounts of CO_2 and H_2O, but also hexafluoroacetylacetone as a major product and several other unidentified organic molecules. Similar decomposition of **1f** under oxygen gave CO_2 but also traces of propene, propane, and benzene and much Hfod, along with other unidentified organics. It seems that the fluorinated ligands are less susceptible to exhaustive oxidation and that they are able to find the extra hydrogen atom needed to give the free β-diketone, probably from the water produced by oxidation of organic material at the palladium surface.

Conclusions

Complexes of the type η^3-allyl(β-diketonato)palladium(II) are easily synthesized and are excellent precursors for CVD of palladium films. By modifying substituents on the allyl and β-diketonate groups, the first liquid precursors for CVD of palladium have been prepared. The complexes have excellent volatility and are easily stored and handled; they are suited to low-pressure thermal CVD or, in some cases, to atmospheric pressure CVD. High-purity palladium films are grown by using either hydrogen or oxygen as carrier gases. The use of hydrogen allows CVD at lower temperatures but requires special equipment to avoid pre-decomposition of the precursors, while the use of oxygen carrier gas requires higher temperature but is easier to carry out using simple equipment. The organic products formed during CVD incorporate either hydrogen or oxygen from the carrier gas, and it is assumed that the major part of the decomposition occurs at the forming palladium surface. This allows CVD at lower temperature than with an inert or no carrier gas and gives purer palladium films, presumably because adsorbed organics can be removed from the palladium surface by either hydrogenation or oxidation.

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