

Synthesis and Characterization of Allyl(β -ketoiminato)palladium(II) Complexes: New Precursors for Chemical Vapor Deposition of Palladium Thin Films

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Treatment of β -ketoiminates with $[(allyl)Pd(\mu-Cl)]_2$ affords volatile, air-stable allyl(β -ketoiminato)palladium(II) complexes. The structure of $[(methallyl)Pd(Phacac)]$ (Phacac = MeCOCHCMeNPh) was determined by single-crystal X-ray diffraction. In solution 1H NMR analyses indicate either a direct rotation of a planar allyl ligand about the allyl–palladium axis or a solvent-assisted exchange process involving the transient formation of a mono-dentate ketoiminato ligand. The physical properties of the complexes were modified by altering the β -ketoiminato or the η^3 -allyl ligands. Some derivatives are liquid at room temperature and were known to be suitable for chemical vapor deposition of Pd thin films.

The preparation of thin films of palladium by metal organic chemical vapor deposition (CVD) is becoming increasingly attractive for the fabrication of electronic devices¹ because such films have potentially useful applications in replacing gold as electrical contacts in integrated circuits and in making gas sensors, magneto-optical data storage devices, etc.² The largest obstacle to CVD of Pd films has been the lack of suitable precursors, as most volatile Pd complexes suffer from poor stability in air and moisture.³ Recently, this problem was partially overcome by Puddephatt, who reported the preparation of volatile allyl(β -diketonato)-palladium(II) complexes, which are liquid and stable at room temperature and are excellent CVD precursors for Pd films.⁴ In view of these results, we felt it desirable to investigate analogous complexes having β -ketoimi-

nate ligands, which allow for organic functional group variation on the imine nitrogen as a possible way to fine-tune physical and chemical properties. In this article, we report the synthesis and characterization of such β -ketoiminato complexes and a preliminary investigation of their application in the generation of Pd films.

Experimental Section

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. 1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 or AMX-300 instrument. Mass spectra were obtained on a JEOL SX-102A instrument operating in fast atom bombardment (FAB) mode. Thermogravimetric analyses were made with a Seiko TG/DTA 300 instrument. Melting points were determined using Seiko SSC 5000 differential scanning calorimetry. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

SEM micrographs of palladium films were obtained using a Hitachi S-4000 scanning electron microscope. Resistivities of films were measured using a LR-400 four-wire AC resistance bridge, manufactured by Linear Research Inc. XPS spectra of films were recorded with a Physical Electronics PHI 1600 ESCA instrument with an Al/Mg dual anode X-ray source. The surface compositions in atomic percentage deduced from XPS spectra were determined after 1–2 min sputtering with argon at 4 keV until a constant composition was obtained. AES spectra for surface scanning and depth profile were recorded on a Physical Electronics PHI 670 Xi Auger instrument after sputtering with argon at 3 keV. XPS is most useful for detection of carbon (detection limit, ca. 0.5%), while Auger spectra are useful to detect oxygen and fluorine in the presence

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of palladium. In all cases analyses are corrected for relative sensitivities of each element.

Allylpalladium complexes with the empirical formula $[(\text{allyl})\text{Pd}(\mu\text{-Cl})_2]$ were prepared according to literature procedures.⁵ Ketoimines were prepared from the direct condensation of acetylacetone and amines at room temperature,⁶ or from reaction of hexafluoroacetylacetone and amines using montmorillonite K10 as a catalyst.⁷ Abbreviations used for the β -ketoiminato ligands are as follows: Mehfac = $\text{CF}_3\text{COCHCCF}_3\text{-NMe}$, Buhfac = $\text{CF}_3\text{COCHCCF}_3\text{N}^t\text{Bu}$, Mohfac = $\text{CF}_3\text{COCHCCF}_3\text{NCH}_2\text{CH}_2\text{OMe}$, Alhfac = $\text{CF}_3\text{COCHCCF}_3\text{NCH}_2\text{CH=CH}_2$, Phacac = MeCOCHCMeNPh , Meacac = MeCOCHCMeNMe , Moacac = $\text{MeCOCHCMeNCH}_2\text{CH}_2\text{OMe}$, Alacac = $\text{MeCOCHCMeNCH}_2\text{CH=CH}_2$. Two typical synthetic procedures for the preparation of β -ketoiminato Pd complexes are described below, together with spectral and analytical data for the compounds prepared. Due to thermal instability or physical state, some compounds did not give satisfactory elemental analyses. ^1H NMR spectra for these complexes (**2**, **6**, **8**–**11**, **13**, **14**) have been deposited in the Supporting Information.

[Pd($\eta^3\text{-CH}_2\text{CMeCH}_2$)(Phacac)] (1**).** A mixture of distilled water (40 mL), NaOH (250 mg), and PhacacH (175 mg, 1.00 mmol) was stirred at 45 °C for 30 min to give a homogeneous solution, which was then added to a suspension of $[\text{Pd}(\eta^3\text{-CH}_2\text{-CMeCH}_2)(\mu\text{-Cl})_2]$ (217 mg, 0.55 mmol) in diethyl ether (20 mL). The mixture was stirred for 10 min, and 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 $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{Phacac})]$ as a yellow solid (yield, 289 mg, 86%). Single crystals of **1** suitable for an X-ray diffraction study were obtained from recrystallization in saturated acetone solution at room temperature.

[Pd($\eta^3\text{-CH}_2\text{CMeCH}_2$)(Mehfac)] (15**).** A mixture of diethyl ether (30 mL), NaOMe (200 mg), and MehfacH (450 mg, 2.04 mmol) was stirred at room temperature for 30 min to give a homogeneous solution, which was then added to a mixture of $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\mu\text{-Cl})_2]$ (400 mg, 1.02 mmol) and NaOH (250 mg) in water (50 mL). The mixture was vigorously stirred for 10 min; 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 $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{Mehfac})]$ as a yellow solid (yield, 740 mg, 95%).

Spectroscopic Data for β -Ketoiminato Complexes.

Complex 1, [Pd($\eta^3\text{-CH}_2\text{CMeCH}_2$)(Phacac)]. MS (FAB, ^{107}Pd): m/z 335 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 7.24 (t, 2H, $J_{\text{HH}} = 7.5$ Hz), 7.00 (t, 1H, $J_{\text{HH}} = 7.5$ Hz), 6.88 (br, 1H), 4.97 (s, 1H), 3.52 (d, 1H, $J_{\text{HH}} = 2.8$ Hz), 2.73 (s, 1H), 2.34 (s, 1H), 2.03 (s, 3H), 1.98 (s, 3H), 1.92 (d, 1H, $J_{\text{HH}} = 2.8$ Hz), 1.64 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 178.7, 163.9, 156.9, 130.5, 128.5 (2C), 123.7 (2C), 122.8, 97.3, 58.8, 57.1, 27.1, 23.3, 22.9. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NOPd}$: C, 53.67; H, 5.70; N, 4.17. Found: C, 53.19; H, 5.65; N, 4.30.

Complex 2, [Pd($\eta^3\text{-CH}_2\text{CHCH}_2$)(Meacac)]. ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.67–5.54 (m, 1H), 4.80 (s, 1H), 3.78 (d, 1H, $J_{\text{HH}} = 6.9$ Hz), 3.49 (s, 3H), 3.22 (d, 1H, $J_{\text{HH}} = 6.6$ Hz), 3.01 (d, 1H, $J_{\text{HH}} = 12.5$ Hz), 2.71 (d, 1H, $J_{\text{HH}} = 11.7$ Hz), 2.00 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 175.8, 165.4, 115.1, 97.8, 60.0, 53.2, 49.1, 26.3, 21.5.

Complex 3, [Pd($\eta^3\text{-CH}_2\text{CHCHMe}$)(Meacac)]. MS (FAB, ^{107}Pd): m/z 273 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 4.78 (s, 1H), 3.54 (d, 1H, $J_{\text{HH}} = 2.6$ Hz), 3.45 (s, 3H), 2.96 (d, 1H, $J_{\text{HH}} = 2.6$ Hz), 2.84 (s, 1H), 2.62 (s, 1H), 2.10 (s, 3H), 1.91 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 176.1, 165.4, 130.7, 97.7, 58.5, 53.5, 49.1, 26.5, 23.4, 21.5. Anal.

Calcd for $\text{C}_{15}\text{H}_{19}\text{NOPd}$: C, 43.89; H, 6.28; N, 5.12. Found: C, 44.27; H, 6.21; N, 5.28.

Complex 4, [Pd($\eta^3\text{-CH}_2\text{CMeCH}_2$)(Meacac)]. MS (FAB, ^{107}Pd): m/z 273 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.31–5.21 (m, 1H), 4.74 (s, 1H), 3.70–3.60 (m, 1H), 3.45 (s, 3H), 3.00 (d, 1H, $J_{\text{HH}} = 6.7$ Hz), 2.46 (d, 1H, $J_{\text{HH}} = 11.5$ Hz), 1.94 (s, 3H), 1.90 (s, 3H), 1.29 (d, 3H, $J_{\text{HH}} = 6.3$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 177.1, 165.4, 114.3, 97.7, 75.6, 49.3, 49.1, 26.9, 21.2, 16.1. Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{NOPd}$: C, 43.89; H, 6.26; N, 5.12. Found: C, 44.20; H, 6.12; N, 5.22.

Complex 5, [Pd($\eta^3\text{-CH}_2\text{CMeCH}_2$)(Moacac)]. MS (FAB, ^{107}Pd): m/z 317 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.31–5.21 (m, 1H), 4.93 (s, 1H), 3.96–3.87 (m, 1H), 3.85–3.76 (m, 1H), 3.71–3.61 (m, 1H), 3.50 (t, 2H, $J_{\text{HH}} = 6.6$ Hz), 3.29 (s, 3H), 2.93 (d, 1H, $J_{\text{HH}} = 6.5$ Hz), 2.44 (d, 1H, $J_{\text{HH}} = 11.6$ Hz), 1.93 (s, 3H), 1.91 (s, 3H), 1.31 (d, 3H, $J_{\text{HH}} = 6.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 177.8, 165.3, 133.7, 98.1, 76.2, 73.5, 59.3, 59.0, 48.8, 27.1, 21.2, 16.0. Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{NO}_2\text{Pd}$: C, 45.37; H, 6.66; N, 4.41. Found: C, 45.80; H, 6.56; N, 4.60.

Complex 6, [Pd($\eta^3\text{-CH}_2\text{CMeCH}_2$)(Alacac)]. MS (FAB, ^{107}Pd): m/z 299 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.91–5.79 (m, 1H), 5.14–5.07 (m, 2H), 4.80 (s, 1H), 4.36–4.33 (m, 2H), 3.56 (d, 1H, $J_{\text{HH}} = 2.8$ Hz), 2.86 (d, 1H, $J_{\text{HH}} = 2.8$ Hz), 2.82 (s, 1H), 2.60 (s, 1H), 2.08 (s, 3H), 1.96 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 176.8, 165.5, 135.6, 130.6, 114.6, 98.0, 62.0, 58.4, 54.5, 26.7, 23.2, 21.0.

Complex 7, [Pd($\eta^3\text{-CH}_2\text{CMeCHMe}$)(Meacac)]. MS (FAB, ^{107}Pd): m/z 287 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.06 (dd, 1H, $J_{\text{HH}} = 12.0$, 7.1 Hz), 4.72 (s, 1H), 3.45 (s, 3H), 3.00 (d, 1H, $J_{\text{HH}} = 7.1$ Hz), 2.64 (d, 1H, $J_{\text{HH}} = 12.0$ Hz), 1.89 (s, 3H), 1.84 (s, 3H), 1.40 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 177.8, 165.6, 108.5, 97.5, 88.7, 49.1, 46.7, 27.2, 25.0, 21.0, 20.9. Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{NOPd}$: C, 45.93; H, 6.66; N, 4.87. Found: C, 46.66; H, 6.46; N, 4.95.

Complex 8, [Pd($\eta^3\text{-CH}_2\text{CHCMe}_2$)(Moacac)]. MS (FAB, ^{107}Pd): m/z 331 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.09 (dd, 1H, $J_{\text{HH}} = 12.0$ Hz, 7.2 Hz), 4.74 (s, 1H), 3.97–3.80 (m, 2H), 3.54 (t, 2H, $J_{\text{HH}} = 3$ Hz), 3.33 (s, 3H), 2.96 (dd, 1H, $J_{\text{HH}} = 7.3$ Hz, 1.3 Hz), 2.63 (dd, 1H, $J_{\text{HH}} = 12.0$, 1.3 Hz), 1.93 (s, 3H), 1.92 (s, 3H), 1.44 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 178.6, 165.5, 108.1, 98.1, 86.6, 73.5, 59.3, 59.1, 46.2, 27.4, 25.1, 21.1, 21.0.

Complex 9, [Pd($\eta^3\text{-CH}_2\text{CMeCMeCH}_2\text{OMe}$)(Moacac)]. MS (FAB, ^{107}Pd): m/z 375 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 4.74 (s, 1H), 3.87 (t, 2H, $J_{\text{HH}} = 6.3$ Hz), 3.64 (d, 1H, $J_{\text{HH}} = 10.6$ Hz), 3.51 (t, 2H, $J_{\text{HH}} = 6.3$ Hz), 3.32 (s, 3H), 3.16 (s, 3H), 3.10 (d, 1H, $J_{\text{HH}} = 10.6$ Hz), 2.96 (d, 1H, $J_{\text{HH}} = 1.1$ Hz), 2.86 (d, 1H, $J_{\text{HH}} = 1.1$ Hz), 2.11 (s, 3H), 1.92 (s, 3H), 1.91 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 178.3, 165.4, 123.5, 98.0, 80.7, 73.4, 73.0, 59.1 (2C), 57.3, 51.6, 27.2, 21.2 (2C), 17.1.

Complex 10, [Pd($\eta^3\text{-CH}_2\text{CMeCMeCH}_2\text{OMe}$)(Mehfac)]. MS (FAB, ^{107}Pd): m/z 439 (M^+). ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.60 (s, 1H), 3.74 (d, 3H, $J_{\text{HH}} = 2.0$ Hz), 3.62 (d, 1H, $J_{\text{HH}} = 10.7$ Hz), 3.32 (s, 1H), 3.18 (s, 3H), 3.12 (d, 1H, $J_{\text{HH}} = 10.7$ Hz), 3.11 (s, 1H), 2.17 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 166.1 (q, CO, $J_{\text{CF}} = 32$ Hz), 155.6 (q, CN, $J_{\text{CF}} = 26$ Hz), 126.9, 120.1 (q, CF_3 , $J_{\text{CF}} = 282$ Hz), 120.0 (q, CF_3 , $J_{\text{CF}} = 286$ Hz), 87.5, 84.9, 73.7, 58.3, 55.1, 50.7, 21.6, 18.2.

Complex 11, [Pd($\eta^3\text{-CH}_2\text{CMeCMeCH}_2\text{OMe}$)(Mohfac)]. ^1H NMR (300 MHz, CDCl_3 , 293 K): δ 5.61 (s, 1H), 4.10–4.03 (m, 2H, $J_{\text{HH}} = 6.9$ Hz), 3.65–3.57 (m, 3H), 3.38 (d, 1H, $J_{\text{HH}} = 10.6$ Hz), 3.35 (s, 3H), 3.19 (s, 3H), 3.13 (s, 1H), 3.10 (d, 1H, $J_{\text{HH}} = 10.6$ Hz), 2.19 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 293 K): δ 166.4 (q, CO, $J_{\text{CF}} = 32$ Hz), 156.1 (q, CN, $J_{\text{CF}} = 26$ Hz), 126.6, 120.0 (q, CF_3 , $J_{\text{CF}} = 286$ Hz), 119.9 (q, CF_3 , $J_{\text{CF}} = 279$ Hz), 87.6, 85.2, 74.6, 73.6, 60.8, 59.8, 58.4, 55.6, 21.5, 18.2.

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Complex 12, [Pd(η^3 -CH₂CHCH₂)(Mehfac)]. MS (FAB, ¹⁰⁷Pd): *m/z* 367 (M⁺). ¹H NMR (300 MHz, CDCl₃, 293 K): δ 5.82–5.67 (m, 1H), 5.67 (s, 1H), 4.07 (d, 1H, *J*_{HH} = 6.8 Hz), 3.78 (s, 3H), 3.53 (d, 1H, *J*_{HH} = 6.5 Hz), 3.24 (d, 1H, *J*_{HH} = 12.4 Hz), 2.94 (d, 1H, *J*_{HH} = 11.8 Hz). ¹³C NMR (75 MHz, CDCl₃, 293 K): δ 165.6 (q, CO, *J*_{CF} = 33 Hz), 155.6 (q, CN, *J*_{CF} = 27 Hz), 120.2 (q, CF₃, *J*_{CF} = 282 Hz), 120.0 (q, CF₃, *J*_{CF} = 286 Hz), 117.8, 87.5, 63.3, 57.1, 50.9. Anal. Calcd for C₉H₉-NOF₆Pd: C, 29.41; H, 2.47; N, 3.81. Found: C, 30.30; H, 2.64; N, 4.05.

Complex 13, [Pd(η^3 -CH₂CHCH₂)(Buhfac)]. ¹H NMR (300 MHz, CDCl₃, 293 K): δ 5.81–5.68 (m, 1H), 5.64 (s, 1H), 4.07 (d, 1H, *J*_{HH} = 6.7 Hz), 3.89–3.79 (m, 2H), 3.41 (d, 1H, *J*_{HH} = 6.7 Hz), 3.22 (d, 1H, *J*_{HH} = 12.2 Hz), 2.94 (d, 1H, *J*_{HH} = 12.2 Hz), 1.71 (m, 2H, *J*_{HH} = 7.2 Hz), 1.34 (m, 2H, *J*_{HH} = 7.2 Hz), 0.93 (t, 3H, *J*_{HH} = 7.2 Hz). ¹³C NMR (75 MHz, CDCl₃, 293 K): δ 165.6 (q, CO, *J*_{CF} = 32 Hz), 154.5 (q, CN, *J*_{CF} = 26 Hz), 120.2 (q, CF₃, *J*_{CF} = 277 Hz), 120.1 (q, CF₃, *J*_{CF} = 286 Hz), 117.1, 87.4, 63.4, 62.3, 56.6, 36.5, 20.9, 14.5.

Complex 14, [Pd(η^3 -CH₂CHCH₂)(Mohfac)]. MS (FAB, ¹⁰⁷Pd): *m/z* 411 (M⁺). ¹H NMR (300 MHz, CDCl₃, 293 K): δ 5.82–5.68 (m, 1H), 5.66 (s, 1H), 4.08 (m, 2H, *J*_{HH} = 6.7 Hz), 4.09–4.06 (m, 1H), 3.61 (t, 1H, *J*_{HH} = 6.7 Hz), 3.53 (d, 1H, *J*_{HH} = 6.1 Hz), 3.33 (s, 3H), 3.21 (d, 1H, *J*_{HH} = 12.4 Hz), 2.95 (d, 1H, *J*_{HH} = 11.9 Hz). ¹³C NMR (75 MHz, CDCl₃, 293 K): δ 166.3 (q, CO, *J*_{CF} = 34 Hz), 156.1 (q, CN, *J*_{CF} = 27 Hz), 120.0 (q, 2CF₃, *J*_{CF} = 287 Hz), 117.3, 87.6, 74.4, 63.4, 61.1, 59.8, 57.4. Anal. Calcd for C₁₁H₁₃NO₂F₆Pd: C, 32.09; H, 3.18; N, 3.40. Found: C, 30.89; H, 3.07; N, 3.30.

Complex 15, [Pd(η^3 -CH₂CMeCH₂)(Mehfac)]. MS (FAB, ¹⁰⁷Pd): *m/z* 381 (M⁺). ¹H NMR (300 MHz, CDCl₃, 293 K): δ 5.65 (s, 1H), 3.84 (d, 1H, *J*_{HH} = 2.2 Hz), 3.77 (q, 3H, *J*_{HF} = 2.0 Hz), 3.30 (d, 1H, *J*_{HH} = 2.2 Hz), 3.08 (s, 1H), 2.84 (s, 1H), 2.19 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, 293 K): δ 165.5 (q, CO, *J*_{CF} = 32 Hz), 155.4 (q, CN, *J*_{CF} = 26 Hz), 134.0, 120.2 (q, CF₃, *J*_{CF} = 282 Hz), 120.0 (q, CF₃, *J*_{CF} = 285 Hz), 87.4, 61.7, 57.0, 50.8, 23.9. Anal. Calcd for C₁₀H₁₁NOF₆Pd: C, 31.47; H, 2.91; N, 3.67. Found: C, 32.15; H, 2.90; N, 3.88.

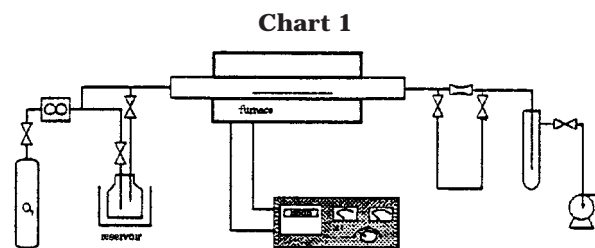
Complex 16, [Pd(η^3 -CH₂CMeCH₂)(Alhfac)]. MS (FAB, ¹⁰⁷Pd): *m/z* 407 (M⁺). ¹H NMR (300 MHz, CDCl₃, 293 K): δ 5.96–5.84 (m, 1H), 5.68 (s, 1H), 5.20 (d, 1H, *J*_{HH} = 10.2 Hz), 5.12 (d, 1H, *J*_{HH} = 18.0 Hz), 4.57 (s, 2H), 3.84 (d, 1H, *J*_{HH} = 2.7 Hz), 3.18 (d, 1H, *J*_{HH} = 2.7 Hz), 3.18 (s, 1H), 2.82 (s, 1H), 2.12 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, 293 K): δ 166.2 (q, CO, *J*_{CF} = 32 Hz), 155.4 (q, CN, *J*_{CF} = 26 Hz), 136.4, 133.6, 120.2 (q, CF₃, *J*_{CF} = 282 Hz), 120.1 (q, CF₃, *J*_{CF} = 286 Hz), 116.6, 87.3, 66.5, 63.4, 58.3, 23.5. Anal. Calcd for C₁₂H₁₃NOF₆-Pd: C, 35.36; H, 3.21; N, 3.44. Found: C, 35.97; H, 3.14; N, 3.61.

X-ray Crystallography. The X-ray diffraction measurement was carried out on a Nonius CAD-4 diffractometer at room temperature. Lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. No significant variation in intensities ($\leq 1\%$) was observed during the course of all data collection. Intensities of diffraction signals were corrected for Lorentz, polarization, and absorption effects (ψ scans). The structure was solved with the NRCC-SDP-VAX package. All non-hydrogen atoms had anisotropic temperature factors, while hydrogen atoms of organic substituents were placed at calculated positions with $U_H = U_C + 0.1$. The crystallographic refinement parameters of complex **1** are summarized in Table 1.

CVD Procedures. Thermal CVD reactions were conducted in a horizontal hot-wall Pyrex reactor, consisting of a Pyrex tube of internal diameter 25 mm, placed within an electric temperature-controlled tube furnace, as described in Chart 1. Precursors were loaded in the glass container. The carrier gas was introduced through a side arm of the container and became saturated with vapors of palladium precursors before entering the hot zone. Si substrates were cleaned using the

Table 1. Crystal Data for the X-ray Diffraction Studies of Complex 1

formula:	C ₁₅ H ₁₉ NOPd
cryst syst:	orthorhombic
mol wt:	335.72
space group:	<i>Pbca</i>
<i>a</i> =	9.0500(20) Å
<i>b</i> =	19.2745(20) Å
<i>c</i> =	16.681(14) Å
<i>V</i> =	2910(3) Å ³
<i>Z</i> =	8
<i>D</i> _c =	1.533 g/cm ³
<i>F</i> (000) =	1351
2 θ (max) =	50°
<i>h, k, l</i> ranges:	0–10, 0–22, 0–19
cryst size:	0.50 × 0.45 × 0.25 mm
μ (Mo K α) =	12.47 cm ⁻¹
transmissn:	0.688 (max), 0.437 (min)
no. of unique data:	2554
no. of data with <i>I</i> > 2 σ (<i>I</i>):	1911
no. of atoms, params:	37, 164
max Δ/σ ratio:	0.0006
<i>R</i> _F , <i>R</i> _w :	0.028; 0.028
GOF:	1.82
<i>D</i> -map, max/min:	0.60/−0.74 e/Å ³



RCA cleaning method; SiO₂ substrates were placed in dilute HF solution for 12 h, and then washed with deionized water and dried at 120 °C for 10 min. The flow rate of carrier gas was adjusted to 20–40 mL/min. The duration of deposition was typically between 30 min and 1 h.

Results and Discussion

Synthesis and Characterization of Precursors.

The synthesis of β -ketoimine ligands involved the simple condensation of acetylacetone and a primary amine (H₂-NR¹; R¹ = Ph, Me, Buⁿ, methoxyethyl, allyl) in an aromatic solvent.⁶ After the mixture was stirred at room temperature for 2 days, the free β -ketoimine was then isolated in 75–89% yields. The preparations involving hexafluoroacetylacetone (hfacH) utilized K-10 montmorillonite as a catalyst⁷ to afford the analogous fluorine-substituted β -ketoimine ligand in 60–85% yield upon heating in CHCl₃ solvent for 2 days (Scheme 1). Formation of the ammonium salt [hfac][NH₃R],⁸ a kinetic product obtained by direct mixing of hexafluoroacetylacetone with amine, was not observed. The latter synthetic procedure is effective for the large-scale generation of the required bis(trifluoromethyl)-substituted β -ketoimine ligands.

Scheme 1

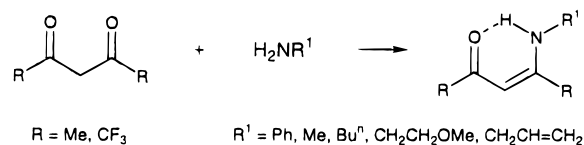
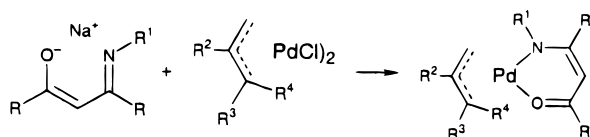


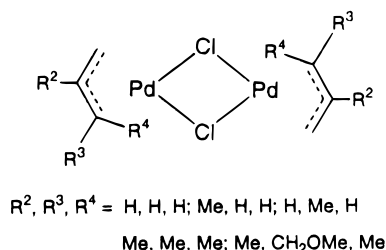
Table 2. Structures and Melting Points of Palladium Precursors 1–16

compd no.	R	R ¹	R ²	R ³	R ⁴	yield (%)	mp (°C)
1	Me	Ph	Me	H	H	86	129–132
2	Me	Me	H	H	H	61	unstable
3	Me	Me	Me	H	H	80	79–81 ^a
4	Me	Me	H	Me	H	86	89–91 ^a
5	Me	CH ₂ CH ₂ OMe	H	Me	H	90	49–51 ^a
6	Me	CH ₂ CH=CH ₂	H	Me	H	80	liquid
7	Me	Me	H	Me	Me	90	70–72 ^a
8^b	Me	CH ₂ CH ₂ OMe	H	Me	Me	87	liquid
9^b	Me	CH ₂ CH ₂ OMe	Me	CH ₂ OMe	Me	73	liquid
10^b	CF ₃	Me	Me	CH ₂ OMe	Me	90	liquid
11^b	CF ₃	CH ₂ CH ₂ OMe	Me	CH ₂ OMe	Me	75	79–81
12	CF ₃	Me	H	H	H	95	118–120
13	CF ₃	Bu ⁿ	H	H	H	87	60–62
14	CF ₃	CH ₂ CH ₂ OMe	H	H	H	88	71–73
15	CF ₃	Me	H	Me	H	95	87–89
16	CF ₃	CH ₂ CH=CH ₂	H	Me	H	80	89–91

^a Sample decomposed upon melting. ^b Selected for CVD experiments.

Scheme 2

The complexes [(allyl)₂Pd(μ -Cl)]₂ were prepared according to literature methods.⁵ Five allyl complexes were synthesized; their molecular structures are



Our synthetic strategy was to select congested, highly substituted allyl ligands while avoiding unnecessarily large organic substituents which could reduce the volatility of the palladium complexes.

In the synthesis of allyl(β -ketoiminato)palladium(II) complexes, the β -ketoimine ligand is first converted to the β -ketoiminato salt on treatment with a slight excess of NaOH in aqueous media or NaOMe in diethyl ether. Mixing this solution with a second solution containing [(allyl)₂Pd(μ -Cl)]₂ in equal proportion generates the allyl β -ketoiminato complexes (allyl = C₃H₅, C₃H₄Me, C₃H₃-Me₂, C₃H₂Me₂(CH₂OMe); Scheme 2). The β -ketoiminato Pd complexes prepared during this study are listed in Table 2, along with their structural properties, reaction yields, and melting points.

The physical properties of the β -ketoiminato complexes differ substantially: **1** possesses the highest melting point and is relatively nonvolatile at room temperature, while **2** is unstable at room temperature and even decomposes to form a Pd film on the wall of the reaction flask during workup. Complexes **1**, **8**–**10**, and **14**–**16** can be stored at room temperature for long periods, whereas other less stable analogues have to be kept below 0 °C to avoid decomposition. The thermal stability of the Pd complexes can be improved by

changing the substituents R on the ketoimine ligand from Me to CF₃, increasing the numbers of methyl substituents on the η^3 -allyl ligand, or attaching a bulky or long-chain hydrocarbon, such as an *n*-butyl, methoxyethyl, or allyl group to the nitrogen of the ketoiminato ligand. Evidently, steric interactions on both the η^3 -allyl and β -ketoiminato ligands is the principal factor that stabilizes these complexes. The presence of a methoxy and a second allyl pendant also seems to improve the thermal stability.

The volatility and thermal stability of the Pd compounds were investigated, since these are important in CVD applications. Using thermogravimetric analysis (TGA) it was found that Pd complexes with ketoimine ligands derived from acetylacetone are less thermally stable. This effect is best seen from the TGA of **8**, which exhibits a sudden weight loss of 68% between 146 and 182 °C and which leaves a black residue nearly equivalent to the theoretical weight of Pd metal. In contrast, complexes derived from hexafluoroacetylacetone are more volatile and robust under conditions of TGA experiments. Thus, most of these fluorine-substituted complexes partially evaporated and partially decomposed, producing a small amount of metallic Pd residue. Of particular interest is the TGA of **10**, which showed a simple one-step loss of nearly 100% within the temperature range 139–175 °C. This observation is consistent with highly effective transportation of Pd metal into the gas phase without decomposition.

The physical properties, such as the melting point, of the Pd complexes can be modified by changing the ligand environment to give liquid CVD precursors having distinct advantages in applications due to their reproducible and steady rates of evaporation.⁹ As indicated in Table 2, complexes **4**–**12** possess fairly low melting points and show potential for CVD application as liquid precursors, while complexes **8**–**10** exist as slightly viscous liquid materials at room temperature.

Structure of Ketoiminato Complexes. Confirmation of the molecular structure was provided by a single-crystal X-ray analysis of the N-substituted phenyl complex **1**. As can be seen from Figure 1, the Pd atom possesses a distorted-square-planar coordination environment consisting of O and N atoms of the β -ketoiminato ligand and C(1) and C(3) of the allyl ligand. The Pd–O distance (2.056(3) Å) is nearly equal to that of

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(9) (a) Maury, F. *J. Phys. IV* **1995**, C5, 449. (b) Maury, F. *Chem. Vap. Deposition* **1996**, 2, 113.

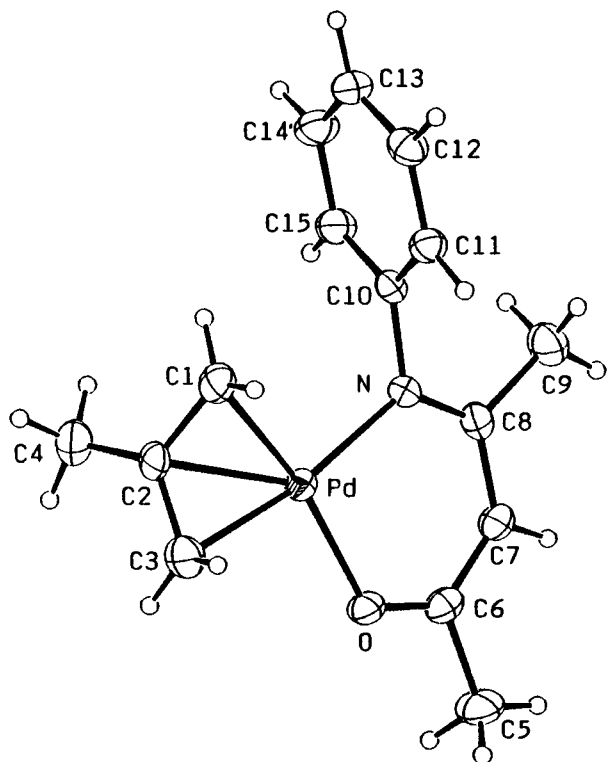


Figure 1. Molecular structure of complex **1**, emphasizing the coordination environment about Pd and showing the atomic numbering scheme. Relevant bond distances (Å): Pd–O = 2.056(3), Pd–N = 2.066(3), N–C(8) = 1.308(5), O–C(6) = 1.275(5), C(6)–C(7) = 1.372(6), C(7)–C(8) = 1.407(6), Pd–C(1) = 2.097(4), Pd–C(2) = 2.116(4), Pd–C(3) = 2.139(4), C(1)–C(2) = 1.410(6), C(2)–C(3) = 1.399(6). Bond angles (deg): O–Pd–N = 91.2(1), N–Pd–C(1) = 101.5(2), O–Pd–C(3) = 99.3(2).

the Pd–N distance (2.066(3) Å), while the N–C(8) distance (1.308(5) Å) and its adjacent C(7)–C(8) distance (1.407(6) Å) are also similar to the O–C(6) distance (1.275(5) Å) and the respective C(6)–C(7) distance (1.372(6) Å), indicating formation of evenly distributed and delocalized π -interactions on the ketoiminato ligand. The Pd–C distances and the N–Pd–C(1) and O–Pd–C(3) angles, respectively, are within the limits of experimental error of the related ketoiminato complex, but the latter contains a nondelocalized ketoiminato ligand.¹⁰

For compounds that contain an asymmetric η^3 -allyl ligand, only one set of ^1H NMR proton signals were observed for all examples at even lower temperature. Thus, only one isomer is present in solution for the asymmetric η^3 -allyl complexes, in which the non-hydrogen substituents are believed to be located at the position *trans* to the nitrogen atom of the β -ketoiminato ligand, because of reduced steric interaction.

Fluxional Behavior in Solution. The allyl(β -ketoiminato)palladium complexes possess novel dynamic behavior in solution, as revealed from the variable-temperature ^1H NMR studies of methallyl complexes **3**, **6**, **15**, and **16** in CDCl_3 , toluene, or DMSO. For instance, olefinic proton signals of the methallyl ligand in complex **6** appear at δ 3.48 ($J_{\text{HH}} = 2.8$ Hz), 2.72, 2.58 ($J_{\text{HH}} = 2.8$ Hz), and 2.33 in d_8 -toluene at room temper-

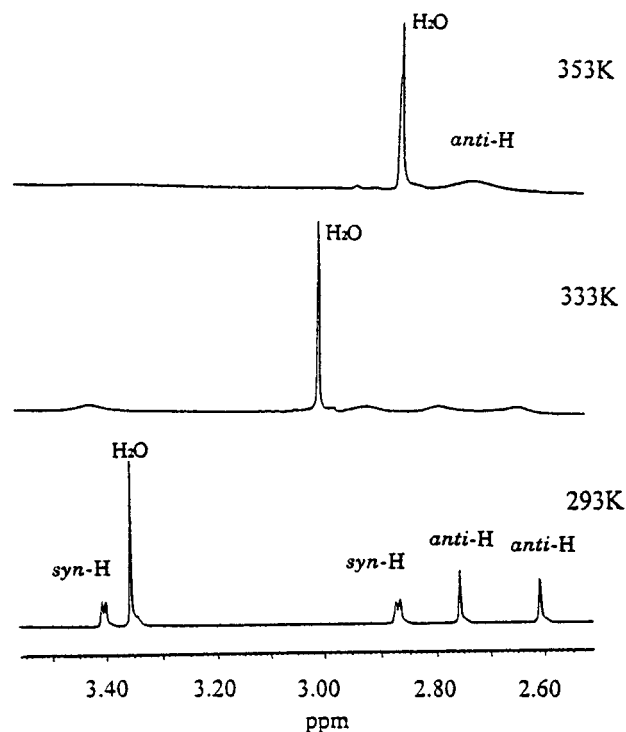


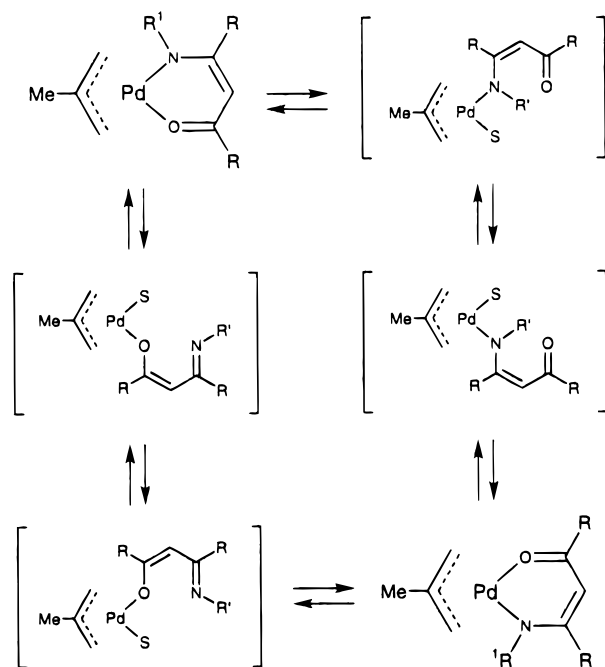
Figure 2. Variable-temperature ^{13}C NMR spectra (d_6 -DMSO) of **6**, showing the olefinic protons of the methallyl ligand.

ature. These four signals are assigned to *syn*, *anti*, *syn*, and *anti* protons on the basis of the pattern of $^4J_{\text{HH}}$ coupling observed. When the temperature is raised to 343 K, all signals broadened substantially, indicating the onset of chemical exchange. This behavior was confirmed by a ^1H NMR spin saturation transfer experiment conducted on complex **3** in CDCl_3 solution at room temperature. In the latter experiment, irradiation of one *anti* proton signal led to the complete suppression of the second *anti* signal but gave no obvious diminution of the *syn* proton signals. The same observation was noted on irradiation of the *syn* proton signals under similar conditions. These ^1H NMR SST experiments clearly indicate the presence of a dynamic process that causes the pairwise exchange between pairs of *anti* protons and *syn* protons but produces no scrambling among the *anti* and *syn* protons.

The fluxional behavior was observed to be more rapid in a polar organic solvent. This is best exemplified by the variable-temperature ^1H NMR studies of complex **6** in d_6 -DMSO. As seen in Figure 2, the *syn* protons at δ 3.41 and 2.87 and the *anti* protons at δ 2.75 and 2.61 observed at room temperature broaden substantially when the temperature is increased. When the temperature is raised to 353 K, the *anti* protons produce a broad signal at δ 2.71, while the *syn* protons completely merge into the baseline; no coalescence of *syn* protons was observed at this temperature because their chemical shifts differ greatly. Moreover, the ^1H NMR spectrum of **16** in d_6 -DMSO at room temperature exhibits only two signals: one is a broad signal at δ 3.62 and the second is a relatively sharp signal at δ 3.07 due to *syn* and *anti* protons, which is in marked contrast to observation of four distinct olefinic signals of η^3 -allyl ligand in CDCl_3 or d_8 -toluene solution, confirming the

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Scheme 3



existence of a similar, but much faster, pairwise exchange of *syn* and *anti* protons.

The lack of interchange between *syn* and *anti* protons in all experiments clearly shows that the fluxional process is not due to a η^3 – η^1 – η^3 interconversion of the allyl ligand.¹¹ Other likely explanations would be 180° rotation of the planar η^3 -allyl ligand about the allyl–palladium axis¹² and the formation of a solvent-coordinated intermediate that contains either an O-bound or a N-bound monodentate ketoiminato ligand, followed by interchange of the solvent molecule and the ketoiminato ligand (Scheme 3), as both latter processes would average the environment of *syn*–*syn* and *anti*–*anti* protons, but not interchange *syn* and *anti* protons. Direct rotation of the allyl ligand seems to be the process occurring in chloroform or toluene, as these nonpolar solvents coordinate poorly to the Pd atom. However, on altering the solvent to DMSO, incorporation of the solvent molecule into the coordination sphere of the palladium atom is more facile; thus, the solvent-assisted pathway becomes the dominant exchange process in solution. Interestingly, this exchange pathway is mechanistically similar to that observed in palladium complexes [(allyl)PdCl], generated by the addition of DMSO, phosphine, or arsine ligand, to allylpalladium chloride complexes [(allyl)Pd(μ -Cl)]₂.¹³

CVD of Palladium. CVD experiments were conducted in a horizontal hot wall reactor with selected ketoiminato precursors **8**–**11** at reduced pressure. Other complexes were not tested in CVD experiments because of low volatility and poor thermal stability. The experiments were carried out at 200–300 °C and precursor samples were kept between 25 and 70 °C, with oxygen as carrier gas (20–40 mL/min) to suppress carbon

Table 3. Deposition Conditions and Thin-Film Properties^a

precursor	sample temp (°C)	deposition temp (°C)	O ₂ flow rate (mL/min)	atom %		
				Pd	C	F
8	70	300	10.0	95	4.2	
8	70	300	40.0	98	1.5	
8	70	200	40.0	98	2.0	
9	70	250	40.0	98	1.2	
10	25	200	34.0	97	1.5	1.4
10	60	200	25.0	97	1.4	1.6
11	60	300	35.0	97	1.2	1.2
11	60	200	25.0	97	1.4	2.1

^a All experiments were carried out under a pressure of (1–3) × 10^{−2} Torr, depending on the O₂ flow rate; substrates were broken Si wafers.

impurities.¹⁴ Although experimental conditions were not optimized, the Pd films obtained were shiny and mirrorlike. They adhered well to silicon substrates but poorly to SiO₂, as tested by scratch or adhesive-tape tests. Preliminary XPS and Auger spectroscopy identify the films prepared from **8** and **9** as ≥98% Pd with ≤2% of carbon and no nitrogen contamination, while films from **10** and **11** differ in that detectable amounts (<2%) of residual fluorine are retained, when the deposition experiments were conducted at 200–300 °C. However, when the deposition temperature is increased to 300 °C and the flow rate of oxygen carrier gas to 40 mL/min, the amount of carbon impurities dropped to ~1%, which represents the best film we obtained in this work. A summary of typical experimental conditions, together with analytical data for palladium films, is given in Table 3. Electrical conductivity measurement of films in one example give a resistivity of 1.6 × 10^{−5} Ω cm, slightly higher than that of bulk Pd metal (1.1 × 10^{−5} Ω cm). Again, this effect is attributed to incorporation of carbon impurities in the Pd films.

Conclusion. Allyl(β -ketoiminato)palladium(II) complexes can serve as precursors for chemical vapor deposition of Pd thin films. Unlike diketonato compounds reported previously,⁴ which require fairly expensive fluorinated diketonato ligands, the compounds discussed herein can be prepared in good yields from easily accessible and inexpensive commercially available materials. Furthermore, the melting points and thermal stabilities of these precursors can be tailored by systematic modification of the η^3 -allyl or β -ketoiminato group. After appropriate adjustment of substituents, some complexes display excellent thermal stability and volatility at or above room temperature. In the case of complexes **8**–**10**, stable liquid phases are obtained: they are among the best CVD precursors for Pd thin films reported to date.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 87-2113-M007-027-COM).

Supporting Information Available: Tables of atomic coordinates and anisotropic thermal parameters for complex **1** and ¹H NMR spectra for complexes **2**, **6**, **8**–**11**, **13**, and **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM980728C

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