Mechanistic Studies of Palladium Thin Film Growth from Palladium(II) β-Diketonates. 1. Spectroscopic Studies of the Reactions of Bis(hexafluoroacetylacetonato)palladium(II) on Copper Surfaces

Wenbin Lin,[†] Benjamin C. Wiegand,[‡] Ralph G. Nuzzo,*[,†,‡] and Gregory S. Girolami*[,†]

Contribution from the School of Chemical Sciences, Department of Materials Science and Engineering, and the Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

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Abstract: The reactions of bis(hexafluoroacetylacetonato)palladium(II), Pd(hfac)$_2$, on copper have been studied. Whereas multilayers of Pd(hfac)$_2$ desorb molecularly from copper surfaces between 200 and 270 K, submonolayer coverages of Pd(hfac)$_2$ react in a multistep sequence. At temperatures below 120 K, Pd(hfac)$_2$ transfers its hfac ligands to the copper surface and the metal center is reduced to Pd^0. The hfac groups adopt a variety of molecular orientations on the surface at 120 K but undergo an apparent ordering transition near 300 K that re-orients the hfac groups to an upright geometry (perpendicular to the surface plane). At low coverages on clean surfaces, further annealing results in the decomposition of the surface-bound hfac ligands to give adsorbed Pd atoms and COCF$_3$, CF$_3$, and fluoride species. These intermediates ultimately yield a partial monolayer of Pd atoms, a carbon (possibly graphitic) deposit, and a variety of organic products that desorb between 500 and 650 K; the desorbing flux after ionization consists of CF$_3$COF, COCF$_3$, CF$_3$, and CO fragments. The activation parameters for the decomposition of hfac groups on copper foils have been determined to be $A = 1.3 \times 10^{13}$ s^{-1} and $E_a = 36.8$ kcal mol^{-1}. When Pd(hfac)$_2$ is dosed onto copper surfaces bearing submonolayer coverages of carbon, a new reaction channel is evident: some of the hfac ligands abstract copper atoms from the surface and generate Cu(hfac)$_2$, which desorbs when the surface is heated. The palladium atoms remain behind and diffuse into the bulk of the Cu crystal. This redox transmetalation reaction (Pd^{II}(hfac)$_2$ + Cu^0 → Pd^0 + Cu^{II}(hfac)$_2$) is the same one that is responsible for the ability of Pd(hfac)$_2$ to effect the chemical vapor deposition of palladium selectively on copper at higher pressures. This redox transmetalation reaction is the first example of the simultaneous etching of copper and deposition of palladium.

Introduction

The fabrication of ultra large scale integrated (ULSI) devices will require significant advances in materials deposition and processing technologies. The metal−organic chemical vapor deposition (MOCVD) of metals is attractive as a process technology for ULSI devices because it offers a number of potential advantages over physical vapor deposition methods such as sputtering; among the attractive features of MOCVD approach are low deposition temperatures, fast growth rates, and the ability to effect the coverage of irregular surfaces conformally and, in some cases, selectively.[1−4] However, the fine scale, complex topologies, and extensive interconnections required for ULSI devices present special challenges in the area of metalization.[5,6] The high current densities of this generation of devices also pose a significant challenge to MOCVD technologies because, at present, the latter are poorly suited to deposit the complex multicomponent alloy phases which are necessary to resist electromigration. As a result, it is essential that methods be found to deposit multicomponent metal films of high quality and purity by MOCVD.

Recently, there has been increasing interest in the chemical vapor deposition of copper with the hope that this metal might eventually replace the tungsten and aluminum−silicon alloy materials currently used as interconnects in microelectronic devices.[7−14] However, in order for copper CVD to be useful in microelectronic devices, the corrosion and electromigration properties of copper thin films must be improved.[15] Selectively alloying these deposited copper films (so as not to require subsequent patterning) with a second metal such as palladium seems to be a logical approach for improving the corrosion and

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[‡] Department of Materials Science and Engineering.

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electromigration properties of MOCVD copper thin films. Palladium and its alloys (especially those with copper) are also attractive as low-cost replacements for gold as contacts in integrated circuits.[16]

We have previously described the discovery of a reaction that makes possible a selective CVD alloying technology for copper.[17,18] We have found that the β-diketonate complex bis(hexafluoroacetylacetonato)palladium(II), $Pd(hfac)_2$, selectively deposits palladium on copper substrates via a novel surface redox transmetalation reaction:

$$Pd(hfac)_2 + Cu \rightarrow Pd + Cu(hfac)_2 \qquad (1)$$

In this process, hfac ligands are brought to the surface in the form of $Pd(hfac)_2$ and eventually are carried away as $Cu(hfac)_2$; at the same time, copper atoms in the surface are replaced by Pd atoms. The redox transmetalation reaction is an example of the simultaneous etching of copper and deposition of palladium and can be used to generate alloy phases of varied composition.

We report here and in the following paper[19] detailed mechanistic studies of the intriguing surface reactions that underlie this unusual process. In this first paper, we describe experiments conducted in the absence of a continuous flux of $Pd(hfac)_2$ to the surface. The insights gained in this way are used in the second paper, along with the data obtained from reactive molecular-beam scattering studies to develop a mechanistically based, quantitatively predictive model of the reaction kinetics.

Experimental Section

The experiments reported here were carried out in three separate UHV chambers with base pressures of $\leq 2.0 \times 10^{-10}$ Torr. The X-ray photoelectron spectroscopy experiments were performed in an ion-pumped (240 L/s) chamber equipped with a single pass cylindrical mirror analyzer (PHI) for Auger electron spectroscopy, an SSL M-probe X-ray photoelectron spectrometer (XPS, Al Kα monochromatic source at 1487 eV), a PRI rear view four-grid low energy electron diffractometer (LEED), and an ion sputtering gun (PHI). The X-ray photoelectron spectra were acquired after an exposed copper surface had been annealed at the desired temperature for several seconds and then cooled to 120 K. The C 1s, O 1s, F 1s, Cu 2p, and Pd 3d spectra were taken consecutively. The temperature programmed reaction (TPR) and integrated desorption mass spectrometric (IDMS) experiments were carried out in a diffusion-pumped (>4000 L/s) chamber equipped with a single pass cylindrical mirror analyzer (PHI) for Auger electron spectroscopy, an ion sputtering gun, and a differentially pumped VG Instruments SXP-300 quadrupole mass spectrometer. Integrated desorption mass spectrometry was performed using the protocol described by Dubois.[20] Infrared studies were carried out on samples mounted in a turbomolecularly pumped (520 L/s) chamber equipped with an effusive molecular beam doser, a single pass cylindrical mirror analyzer for AES (PHI), and a differentially pumped quadrupole mass spectrometer (VG SXP300). The FTIR spectra were collected with a Digilab FTS 60A spectrometer and a wide-band MCT detector in conjunction with external reflection optics. These optics (~f/12), maximized for single grazing angle reflection (~84°), are similar to those described elsewhere.[21] All spectra are reported as $-\log(R/R_0)$ (absorbance). The clean single crystal substrate was used as the reference. The IR spectra were collected after the exposed Cu(111) surface had been annealed to the desired temperature for approximately 1 min and then cooled to 100 K. The IR spectra were collected over 5 min at a resolution of 4 cm^{-1}.

Dosing was accomplished in two ways. For the TPR, IDMS, and AES experiments, hfacH was dosed from the background while the $M(hfac)_2$ species were dosed via an effusive molecular beam doser.[22] The effusive source used was a 3.2-mm-diameter stainless steel tube capped with a Ni disk bearing a 200-μm pinhole. The pressure behind the doser pinhole was monitored with a heated (60 °C) capacitance manometer (MKS, 1 torr full scale). For the FTIR and XPS experiments, dosing was performed from the background. No corrections were made for ion gauge sensitivity and thus the doses cited are only approximate.

The polycrystalline copper foils used were 0.025 mm thick and of >99.999% purity. Each copper foil was mounted on a molybdenum button heater using tantalum wires spot-welded to the side of the button heater. The button heater was mounted in turn on a copper block mounted on an electrically insulated Cu liquid nitrogen reservoir. The foils could be heated above 1000 K and cooled below 90 K. The 12-mm-diameter Cu(111) single crystal used was cut, oriented to within 0.5° by Laue back diffraction, polished mechanically, and electropolished using standard techniques. Three notches cut into the Cu(111) single crystal allowed the crystal to be mounted on a molybdenum button heater with three spot-welded tantalum wires. An additional hole was drilled in the side of the Cu(111) crystal to accommodate a chromel-alumel thermocouple. The Cu(111) crystal could be heated and cooled between 100 and 1000 K. The copper foils and single crystal were cleaned in situ by cycles of sputtering with 1-kV Ar^+ ions at 300 and 950 K, followed by annealing to 950 K. The cleanliness of the copper foils and the Cu(111) single crystal was carefully monitored by AES and XPS. The order of the Cu(111) crystal was checked with LEED. The heating rates used for the TPR experiments were 7 and 4 K/s, while the heating rates for the XPS and RAIR experiments were 2 and 1 K/s, respectively.

The differentially pumped mass spectrometer was isolated from the main analytical chamber using a Ni molecular beam skimmer (2-mm aperture, Beam Dynamics) to minimize interference from material desorbing from the sample support apparatus. In the TPR and IDMS experiments, the samples were held 2−5 mm from the skimmer.

Bis(hexafluoroacetylacetonato)palladium(II) was prepared according to a reported literature method[23] and purified by sublimation before use. $Pd(hfac)_2$-d_2 was prepared by adding $PdCl_2$ (0.92 g, 5.2 mmol) to a mixture of sodium hydroxide (0.45 g, 11.3 mmol) and hexafluoroacetylacetone (1.5 mL, 10.6 mmol) in D_2O (18 mL) and stirring the resulting mixture for 24 h; mass spectroscopy showed that the sample used contained $Pd(hfac)_2$-d_0, $Pd(hfac)_2$-d_1, and $Pd(hfac)_2$-d_2 in a 7:21:72 ratio. Anhydrous $Cu(hfac)_2$ was purchased from Strem and sublimed before use. Hexafluoroacetylacetone (Aldrich, 99%) was used as received for synthetic purposes but was placed over activity 1 alumina for the dosing experiments.

Results

The studies described below employed both single crystal and polycrystalline copper substrates. The latter were examined to model more closely the crystalline habits that would be present in CVD copper films. The reactions we characterize here are sensitive to this structural feature (i.e., the decomposition and reaction kinetics of hfac ligands are different on these surfaces). For ease of presentation, we present the results obtained in an integrated fashion, noting, where relevant, any important differences.

Studies of $Pd(hfac)_2$ Multilayers on Polycrystalline Copper Surfaces. X-ray photoelectron spectroscopy has provided

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Table 1. XPS Core-Level Binding Energies of Pd(hfac)$_2$ Dosed onto a Cu Surface and Annealed to Various Temperatures

			C (1s)				
	Pd (3d$_{5/2}$)	O (1s)	CF$_3$	C=O	CH	other	F (1s)
multilayer at 120 K	339.1	532.8	292.6	287.7	285.1		688.2
submonolayer at 120 K	335.7	533.3, 531.8	292.3	287.1	284.4		688.0
annealed to 270 K	335.7	531.9	292.3	287.2	284.5		688.0
annealed to 373 K	335.8	531.8	292.1	286.9	284.3		687.9
annealed to 473 K	335.8	533.6, 531.0	291.3	288.0	283.8	285.7	687.3, 682.9
annealed to 573 K	335.8	533.6, 530.8	291.6	287.5	284.0	285.8	687.6, 682.9
annealed to 673 K	335.9	533.8				284.0	688.1, 682.9
annealed to 773 K		533.8				284.0	688.0, 682.9

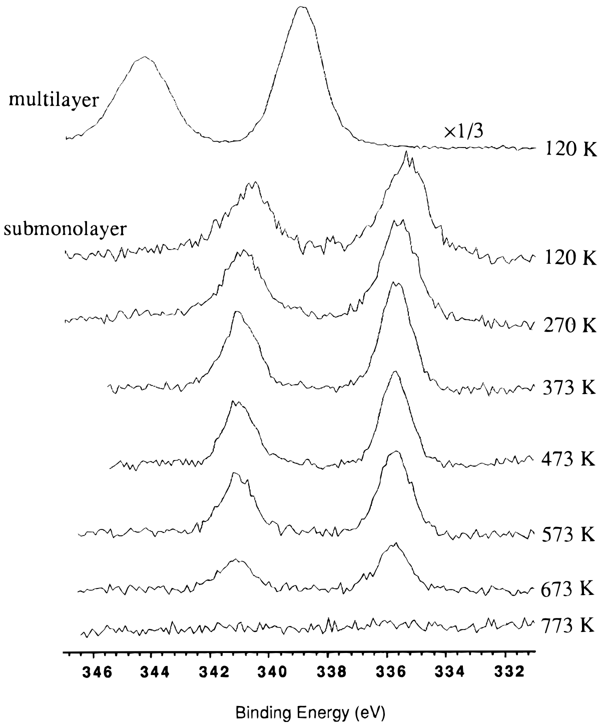

Figure 1. Pd 3d XPS spectra of a clean copper surface exposed to Pd(hfac)$_2$ and annealed to different temperatures. The heating rates were 2 K/s and all the spectra were taken at 120 K.

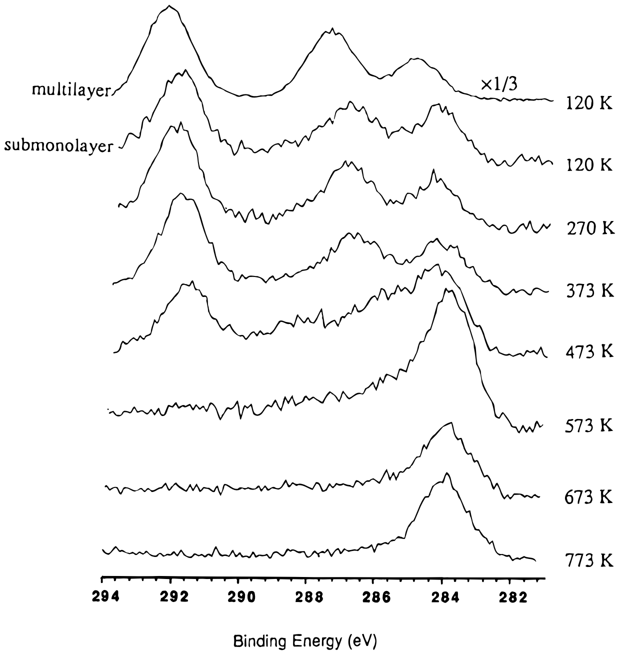

Figure 2. C 1s XPS spectra of a clean copper surface exposed to Pd(hfac)$_2$ and annealed to different temperatures. The heating rates were 2 K/s and all the spectra were taken at 120 K.

important insights into the reactions of Pd(hfac)$_2$ on clean copper surfaces. Spectra were taken after copper foils dosed with varying quantities of Pd(hfac)$_2$ at 120 K were annealed to various temperatures. The measured binding energies of the Pd, C, O, and F core levels are tabulated in Table 1. The upper spectrum shown in Figure 1 is that of a *multilayer* of Pd(hfac)$_2$ adsorbed on copper at 120 K. In this multilayer, the Pd 3d$_{5/2}$ peak appears at 339.1 eV, a value which is indicative of a Pd^{II} oxidation state.[24] For comparison, the Pd 3d$_{5/2}$ binding energy of the related Pd^{II} complex [Pd(hfac)(bpy)][hfac] appears at 338.3 eV.[25] The three peaks seen in the C 1s spectrum at 120 K (Figure 2) are precisely those expected for a hfac group: the C 1s peaks at 292.6, 287.7, and 285.1 eV are assigned to the CF$_3$, C=O, and CH carbon atoms, respectively. The relative intensities of these peaks (2.2:1.7:1.0 rather than the simple 2:2:1 ratio expected on the basis of stoichiometry) are affected by a shake-up transition for the C=O carbon which overlaps with the CF$_3$ peak (Figure 2).[26] The single peaks in the O 1s (532.7 eV) and F 1s (688.2 eV) spectra taken at 120 K (Figures 3 and 4) are consistent with the presence of intact hfac groups on the surface.

Reflection−absorption infrared spectroscopy has provided additional information about the reactivity of Pd(hfac)$_2$ on copper surfaces. Figure 5a shows the IR spectrum of a *multilayer* of Pd(hfac)$_2$ on a Cu(111) surface at 100 K. The spectrum of the Pd(hfac)$_2$ multilayer is essentially identical to that of polycrystalline Pd(hfac)$_2$; the assignments of these peaks are summarized in Table 2. Our assignments of the RAIR bands generally agree with those made in previous studies,[27−29] but several significant misassignments have been corrected by making comparisons with the spectrum of the deuterated molecule Pd(hfac)$_2$-d_2.

The strong peak at 1606 cm^{-1} is assigned to the C=O stretch while the shoulder at 1629 cm^{-1} is assigned to a C=C stretch. Deuterium-labeling experiments show that the weak features at 1562 and 1536 cm^{-1} are predominantly C−C stretches but have some C−H stretching or bending character; they shift to 1526 and 1506 cm^{-1}, respectively, in the spectrum of Pd(hfac)$_2$-d_2. The peaks at 1450, 1442, and 1350 cm^{-1} are assigned to C−CF$_3$ stretching motions because they remain essentially unchanged upon deuteration.

If we base our assignments on those made in a previous study of Cu(hfac)$_2$ on Cu(111), the strong peak at about 1197 cm^{-1}

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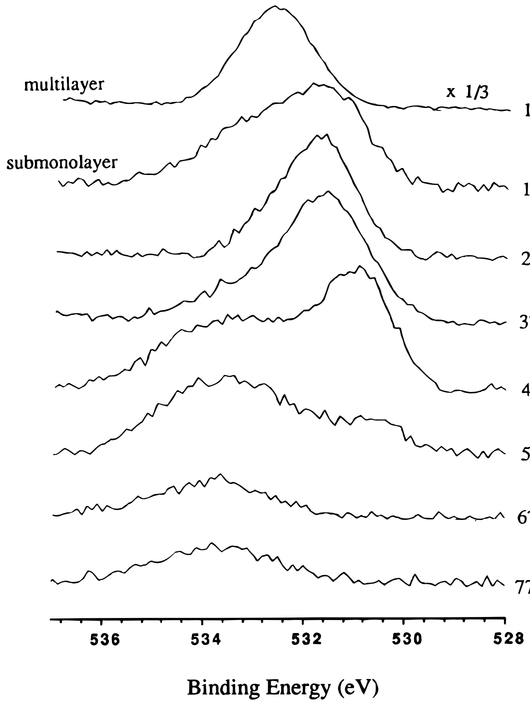

Figure 3. O 1s XPS spectra of a clean copper surface exposed to Pd$(hfac)_2$ and annealed to different temperatures. The heating rates were 2 K/s and all the spectra were taken at 120 K.

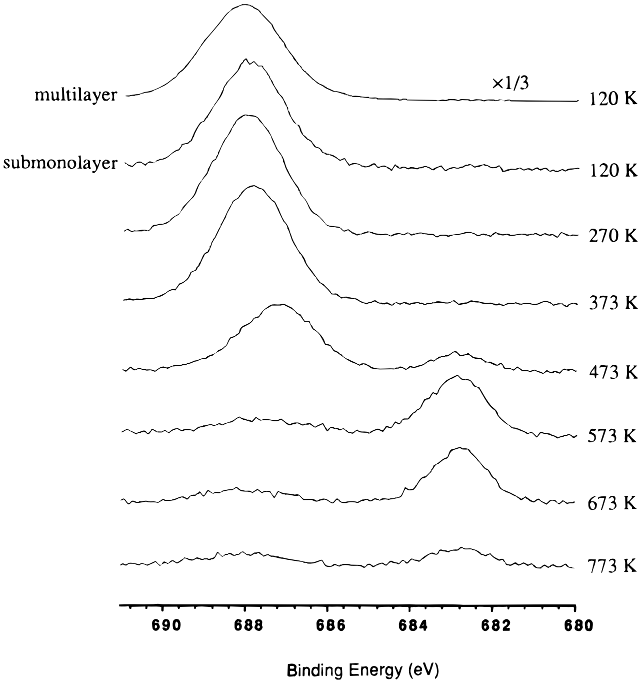

Figure 4. F 1s XPS spectra of a clean copper surface exposed to Pd$(hfac)_2$ and annealed to different temperatures. The heating rates were 2 K/s and all the spectra were taken at 120 K.

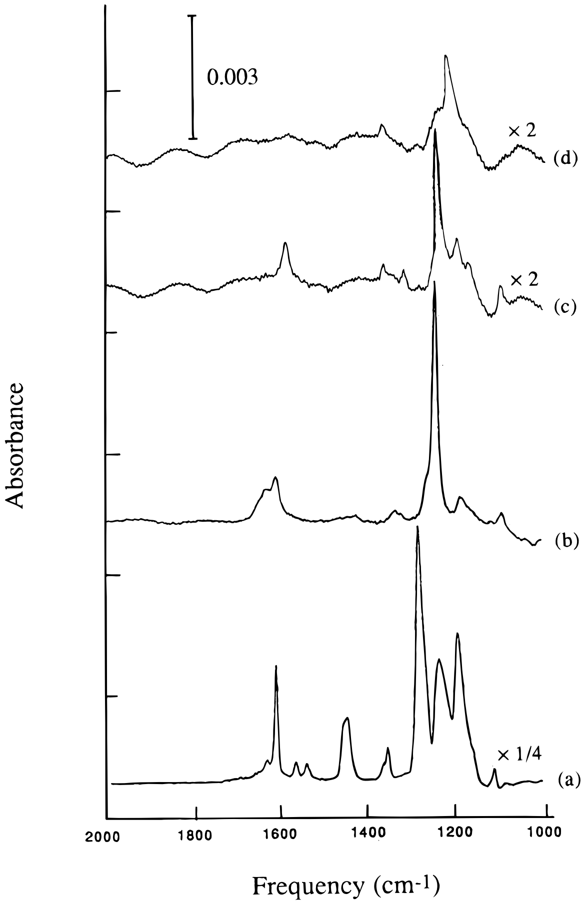

Figure 5. RAIR spectra of 5 L of Pd$(hfac)_2$ on a Cu(111) surface at different temperatures. The spectra were taken (a) at 100 K, (b) after annealing to 300 K, (c) after annealing to 450 K, and (d) after annealing to 500 K. The heating rates were 1 K/s and all the spectra were taken at 100 K.

Table 2. Observed Vibrational Frequencies and Mode Assignments for Pd$(hfac)_2$ On Cu(111) Surfaces[a]

Pd$(hfac)_2$ multilayer at 100 K[b]	Pd$(hfac)_2$-d_2 multilayer at 100 K[c]	Pd$(hfac)_2$ annealed to 300 K[d]	assignment
1629		1629	C=C stretch
1606		1607	C=O stretch
1562	1526		CO stretch + CH bend
1536	1506		CO stretch + CH bend
1450		1422	CC stretch + CCF_3 stretch
1350		1332	CC stretch + CCF_3 stretch
1278			CF_3 stretch
1233		1240	CF_3 stretch
1197		1183	CF_3 stretch
1157	818		CH bend
1109		1090	?

[a] All frequencies in cm^{-1}. [b] Figure 5a. [c] Except for the three bands shown in the table, the frequencies of the other bands are essentially identical to those of Pd$(hfac)_2$. [d] Figure 5b.

would be assigned to a C−H bending mode.[27] We now believe that this earlier assignment is in error. We suggest that all three intense peaks at 1278, 1233, and 1197 cm^{-1} are primarily C−F stretching motions (with possible coupling to the C−C stretching vibrations), since their frequencies are essentially unchanged in the spectrum of a multilayer of Pd$(hfac)_2$-d_2. These assignments will become important in our discussion of the RAIR spectrum of a Pd$(hfac)_2$ monolayer on copper (see below).

Desorption of the Pd$(hfac)_2$ Multilayer from Polycrystalline Copper Surfaces. When a clean copper foil dosed at 90 K with more than 0.5 L of Pd$(hfac)_2$ is heated, temperature programmed reaction (TPR) profiles at *m*/*e* = 244, 106, and 139 each show a single desorption peak between 200 and 270 K (Figure 6). These masses, which can be assigned to Pd(hfac) − CF_3, Pd, and CF_3COCH_2CO species, respectively, are characteristic cracking fragments in the mass spectrum of Pd$(hfac)_2$.[30,31] We therefore conclude that the TPR feature at 200−260 K is due to the desorption of a Pd$(hfac)_2$ multilayer from the surface.[32] This conclusion is further supported by the fact that the intensities of these desorption peaks grow without limit as the exposure is increased.

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(30) Correct isotope patterns were observed for the palladium-containing peaks at *m*/*e* = 244 [Pd(hfac)−CF_3] and 106 (Pd).

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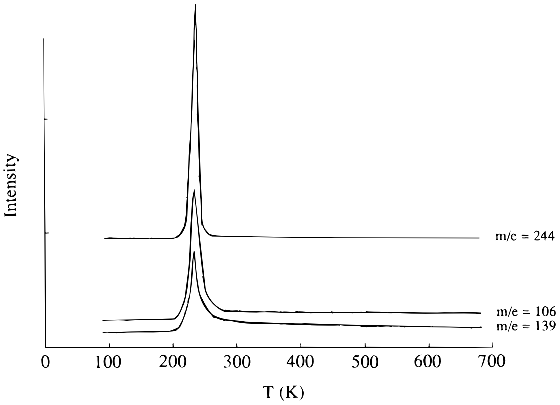

Figure 6. Multilayer desorption of Pd(hfac)$_2$ from a clean copper foil surface; the surface was heated at a rate of 7 K/s.

The $m/e = 69$ amu channel also shows a TPR feature in the 200−260 K temperature range due to the electron-impact-induced fragmentation of the desorbing Pd(hfac)$_2$ molecules; in a previous study of the surface chemistry of Cu(hfac)$_2$, this 69-amu peak was attributed to the CF_3^+ ion. Interestingly, however, TPR profiles taken upon heating a copper surface dosed with the deuterated molecule Pd(hfac)$_2$-d_2 show at least some of the mass 69 species contain a hydrogen atom, since a new peak at $m/e = 70$ appears upon deuteration. We conclude that the $COCHCO^+$ fragment must contribute to the $m/e = 69$ channel in the mass spectrum of the unlabeled molecule. From the relative intensities of the mass 69 and 70 peaks in the mass spectrum of Pd(hfac)$_2$-d_2, we estimate that 43% of the $m/e = 69$ peak in the mass spectrum of Pd(hfac)$_2$-d_0 is due to the CF_3^+ ion and 57% is due to the $COCHCO^+$ fragment (electron impact energy = 70 eV).

Desorption of the Pd(hfac)$_2$ multilayer is also demonstrated by the dramatic changes seen in the RAIR spectrum after the dosed crystal has been heated to 300 K (Figure 5b). The spectrum is now dominated by a single strong C−F stretch at 1240 cm^{-1} and by C═C and C═O stretches at 1629 and 1607 cm^{-1}, respectively. This spectrum, which is very similar to that seen upon transfer of hfac groups from the copper complex Cu(hfac)$_2$ to a Cu(111) surface at 300 K,[27] is due to a monolayer of surface-bound hfac groups. Based on the surface dipole selection rule, Girolami et al. concluded that the surface-bound hfac ligands adopt an essentially upright geometry, as evidenced by the presence in the RAIR spectrum of one strong C−F stretching vibration along with those for the C═O and C═C stretches.[27] Analogously, we conclude that hfac ligands generated from Pd(hfac)$_2$ also adopt a predominantly upright geometry on the copper surface at this temperature, although the small peak at 1183 cm^{-1} may be due to the C−F stretch of hfac ligands oriented parallel to the surface.

Pd(hfac)$_2$ Submonolayers on Polycrystalline Copper Surfaces. When a copper foil is dosed at 120 K with a *submonolayer* amount of Pd(hfac)$_2$, the Pd 3d$_{5/2}$ peak (Figure 1) appears at 335.5 eV, a shift of ∼3.6 eV to lower binding energy relative to that for the Pd^{II} oxidation state. This binding energy is indicative of a Pd^0 atom experiencing the electronic screening typically found in a metallic state and suggests that, when Pd(hfac)$_2$ adsorbs on the surface, Pd^{II} is reduced to Pd^0 by the copper. These data are most consistent with the notion that Pd(hfac)$_2$ dissociatively chemisorbs on copper, i.e., the hfac groups are transferred to the copper surface even at 120 K.

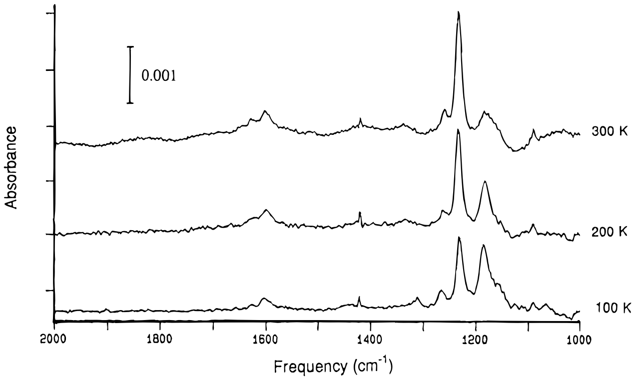

Figure 7. RAIR spectra of submonolayer amounts of Pd(hfac)$_2$ on a Cu(111) surface after being annealed to different temperatures.

The dissociative adsorption of the Pd(hfac)$_2$ molecules and transfer of hfac ligands to the copper surface is further supported by the C 1s, O 1s, and F 1s XPS data (Figures 2−4), which all show significant shifts to lower binding energies relative to those of the multilayer. The change in the O 1s binding energy (Figure 3) is the most pronounced of these: the peak at 531.8 eV corresponds to a shift of ∼1 eV to lower binding energy relative to that of Pd(hfac)$_2$. The shoulder seen at ∼533.3 eV may be due to surface-bound hfac groups which adopt a different orientation;[33] this latter assignment will be discussed in more detail below. The C 1s spectrum (Figure 2) shows three main core level peaks at 292.3, 287.1, and 284.4 eV for the CF$_3$, C═O, and CH carbon atoms, respectively, while the F 1s spectrum (Figure 4) shows a single peak at 688.0 eV. These binding energies, which are shifted 0.2 to 0.7 eV relative to those of a Pd(hfac)$_2$ multilayer, are consistent with the view that the hfac ligands have not fragmented but are no longer bound to the Pd^{2+} center of the starting complex.

It is evident that, at submonolayer coverages, the Pd(hfac)$_2$ molecules strongly (and presumably dissociatively) adsorb on copper surfaces even at temperatures as low as 120 K; transfer of the hfac ligands from the palladium centers to the copper surface results in the reduction of the Pd^{II} centers to metallic Pd^0. This reductive dissociation reaction can be likened to those that occur at electrode surfaces. At 120 K, the half-life of the reductive dissociation reaction must be no longer than several minutes, i.e., fast compared to the time interval between dosing the surface and examining it with the XPS spectrometer. By assuming that the transfer of hfac groups to the surface is unimolecular and taking a typical value of $\sim 1 \times 10^{13}$ s^{-1} for the pre-exponential factor and a half-life for the reaction of 10 min at 120 K, we calculate an upper limit of ∼8.8 kcal/mol for the activation energy of this reductive dissociation.

We have also carried out RAIR studies of a submonolayer coverage of Pd(hfac)$_2$ on Cu at various temperatures (Figure 7) in order to gain more information about the orientations of the hfac groups bound to the surface. On the basis of the XPS studies described above, it was suggested that Pd(hfac)$_2$ dissociatively adsorbs on Cu at 100 K and that the adsorbed hfac groups are bound in two different orientations at this temper-

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(32) The exposures cited are approximate and have been calculated for the experimental geometry of our effusive molecular beam doser. We note that it is difficult to calculate the exact monolayer saturation coverage because a multilayer begins to build up before the monolayer saturates. Parmeter has observed this same phenomenon for the adsorption of Cu(hfac)$_2$ on Pt(111) surfaces.[35] The monolayer saturation coverage was estimated to be ∼0.5 L by dosing the surface with Pd(hfac)$_2$ at 270 K, which is above the multilayer desorption temperature, and then monitoring the intensities of the desorption features when the surface is heated. This monolayer saturation coverage is consistent with that of Cu(hfac)$_2$ on a Cu(111) surface.[27]

(33) We considered whether the 533.3 eV peak could be assigned to the Pd3p$_{3/2}$ XPS feature near 534 eV. The intensity of this peak, however, is too large relative to other palladium XPS features for this to be a Pd 3p$_{3/2}$ signal. Further evidence against such an assignment comes from the XPS spectra after the surface was annealed at 270 K: although the intensity of the Pd 3d$_{5/2}$ peak remains essentially unchanged, the peak at 533.3 eV completely disappears.

ature. Interestingly, the RAIR spectrum of the submonolayer at 100 K also suggests that the hfac groups are *not* all oriented in the same fashion on the surface, while at higher temperatures only a single hfac orientation is present. For example, as the surface is heated from 100 to 200 K, the C−F, C═O, and C═C stretches at 1239, 1607, and 1629 cm^{-1} all increase in intensity, while the C−F stretch at 1183 cm^{-1} disappears. When the surface is heated to 300 K, only the C−F stretch at 1239 cm^{-1} is evident in the spectrum. We assign the C−F stretch at 1183 cm^{-1} to hfac ligands bound parallel to the surface. Additional evidence for this assignment comes from IR and XPS studies of the reactions of the analogous platinum complex, $Pt(hfac)_2$, on copper surfaces.[34]

The data in Figures 5 and 7 establish an interesting and, at first glance, unexpected feature of the vibrational spectra of hfac groups: the antisymmetric stretching modes of the CF_3 groups must be lower in frequency than (at least some of) the symmetric stretching modes. For hfac ligands oriented "parallel" to the surface, only the out-of-plane antisymmetric C−F stretch would be expected to appear in the 1300−1100-cm^{-1} region of the RAIR spectrum; the current experiments and a related study of the closely analogous $Pt(hfac)_2$ complex[34] demonstrate that this mode must be the one seen at ∼1190 cm^{-1}. For comparison, the in-plane symmetric C−F stretch appears at 1239 cm^{-1} in the spectrum of "perpendicular" hfac groups. It has been noted by several authors that the C−F stretching modes in these molecules are likely to be highly coupled to C−C stretching modes.[27,35] There is therefore no reason to presume that the symmetric and antisymmetric C−F stretching frequencies of hfac groups will fall in the same relative locations as those of isolated CF_3 groups.

High-Temperature Reactions of $Pd(hfac)_2$ on Polycrystalline Copper Surfaces. When a copper surface dosed with a monolayer of $Pd(hfac)_2$ is annealed at 373 K, the C 1s, O 1s, and F 1s XPS spectra described above remain essentially unchanged. This result confirms that the hfac ligands bound to the surface have not fragmented at this temperature. No significant changes are seen in the binding energies or intensities of the Pd $3d_{5/2}$ XPS core levels (Figure 1), which suggests that the palladium atoms are still present as Pd^0 centers on the surface.

When the surface is annealed at higher temperatures, however, the C 1s, O 1s, and F 1s XPS binding energies change significantly. At 473 K, the O 1s spectrum (Figure 3) contains two peaks (533.8 and 531.1 eV),[33] and the peak at 533.8 eV suggests that a non-oxygen-bound organic fragment such as an absorbed trifluoroacetyl group ($COCF_3$) has been generated. This conclusion is supported by the C 1s spectrum (Figure 2). The more evident features in the C 1s spectrum can be easily assigned to specific species: the peak at 291.3 eV to a CF_3 group, the peak at 285.7 eV to the carbonyl carbon of a trifluoroacetyl group, and the peak at 283.8 eV either to graphitic carbon or an unsaturated hydrocarbon. The binding energy for the CF_3 group has shifted by 1.0 eV to lower energy relative to that for an intact hfac group, a result consistent with the formation of either surface-bound $COCF_3$ or CF_3 groups or both. The shift of the F 1s peak to lower binding energy (687.3 eV) is also consistent with the presence of surface-bound $COCF_3$ or CF_3 groups. Interestingly, the F 1s region (Figure 4) shows a new peak at 682.9 eV in addition to the peak at 687.3 eV. This new peak can be attributed to fluoride on the copper surface, which suggests that some of the CF_3 groups have been defluorinated.

When the surface is heated to higher temperatures, the intensity of the Pd $3d_{5/2}$ peak diminishes and ultimately can no longer be detected at ∼773 K (Figure 1); the sampling depth for palladium is dictated by the mean free path (λ) of its photoelectrons, which is about 15 Å for photoelectrons with this kinetic energy.[36] Since no palladium-containing species have desorbed from the surface, this result suggests that the palladium atoms have diffused into the bulk. Attenuation of Pd $3d_{5/2}$ core level emission to background levels is expected to occur at a diffusion length of the order of ∼3λ. This implies that, in several minutes, Pd surface atoms diffuse ∼45 Å (and more) into the bulk at this temperature.

At the higher temperatures ($\gg$473 K) the organic species disappear from the surface, and only small amounts of graphitic carbon, oxide, and fluoride species are evident in the XPS spectra (Figures 2−4). While most of the organic species desorb from the surface (see below), some of them fragment to give these final products.

The fate of the surface-bound species, which at 300 K consists of palladium atoms and perpendicularly-oriented hfac groups, has been independently studied by RAIR spectroscopy. When the surface is annealed at 450 K, the C═O and C═C stretches of the hfac groups disappear from the RAIR spectrum (Figure 5c) and new peaks at 1590 and 1240 cm^{-1} grow in; these peaks are assigned to the C═O and C−F stretches of a surface-bound trifluoroacetyl (CF_3CO) species. This C═O stretching frequency is only slightly lower than the ∼1650 cm^{-1} values seen for molecular trifluoroacetyl complexes of the transition metals.[37−39] The assignment of these bands to a surface-bound trifluoroacetyl group is consistent with the results of the XPS studies described immediately above.

When the surface is heated to 500 K, the IR spectrum of the adsorbate overlayer changes dramatically (Figure 5d). The spectrum now shows only a single peak at 1200 cm^{-1}, which we assign to a C−F stretching mode of a new fluoroorganic species. Based on the arguments presented in an analogous study of the decomposition reaction of $Cu(hfac)_2$ on copper surfaces (in which a similar band at 1205 cm^{-1} was seen),[27] we conclude that the only organic species remaining on the surface at 500 K are trifluoromethyl (CF_3) groups. Such an assignment is consistent with the XPS data discussed above. Evidently, some of the initially-formed trifluoroacetyl groups decarbonylate to trifluoromethyl groups at temperatures between 450 and 500 K.

When a copper foil dosed with $Pd(hfac)_2$ is heated to higher temperatures, single desorption features are seen in the m/e = 116, 97, 69, 44, and 28 channels between 500 and 650 K (Figure 8). The identifications of the ions responsible for these desorption traces have been made by comparing the integrated desorption mass spectra (IDMS) taken during the temperature-

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[34] XPS studies show that, at temperatures below 120 K, submonolayer amounts of the platinum complex $Pt(hfac)_2$ remain intact on copper surfaces and transfer their hfac ligands to the copper surface only at higher temperatures. This process is completed by 300 K and the hfac ligands on the surface again adopt the upright orientation. The low-temperature IR spectrum of submonolayer $Pt(hfac)_2$ on a copper surface only shows one C−F stretch at 1176 cm^{-1}. This compares very well with the C−F stretch at 1183 cm^{-1} in the low-temperature IR spectrum of submonolayer $Pd(hfac)_2$ on a copper surface. Since the intact monolayer $Pt(hfac)_2$ should orient parallel to the surface to maximize the interaction with the surface, we conclude that the C−F stretch at 1183 cm^{-1} in the low-temperature spectrum of submonolayer $Pd(hfac)_2$ is due to the hfac ligands orientated parallel to the surface. Lin, W.; Wiegand, B. C.; Girolami, G. S.; Nuzzo, R. G. Manuscript in preparation.

[35] Parmeter, J. E. Unpublished observations.

[36] Wagner, C. D.; Riggs, W. M.; Davies, L. E.; Moulder, J. F.; Mullenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin Elmer: Eden Prairie, MN, 1978; p 5.

[37] Kaesz, H. D.; King, R. B.; Stone, F. G. A. *Z. Naturforsch.* **1960**, *B15*, 763−764.

[38] Hieber, V. W.; Beck, W.; Lindner, E. *Z. Naturforsch.* **1961**, *B16*, 229−231.

[39] Hieber, W.; Muschi, J.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 3924−2930.

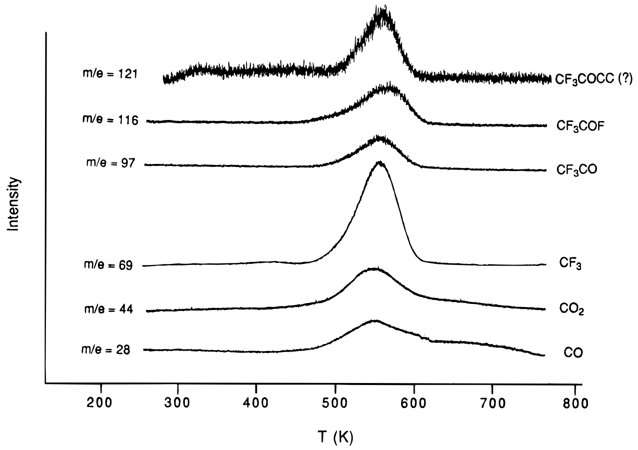

Figure 8. Temperature-programmed reaction profile obtained upon heating a clean copper foil surface exposed at 270 K to one monolayer of Pd(hfac)$_2$; the surface was heated at a rate of 4 K/s.

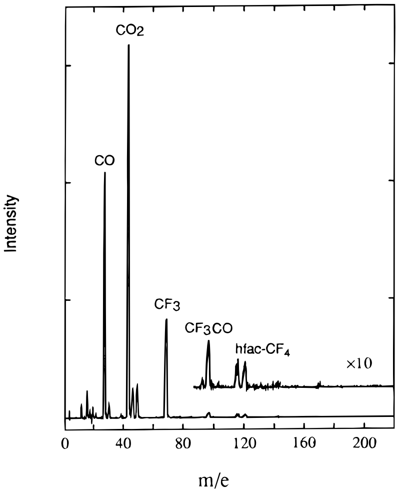

Figure 9. Integrated desorption mass spectrum of the species desorbing from a clean copper foil exposed to one saturation monolayer of Pd(hfac)$_2$ at 270 K. The spectrum was obtained between 500 and 650 K at a heating rate of 7 K/s.

programmed reactions of saturation monolayer coverages of Pd(hfac)$_2$ and the deuterated analogue Pd(hfac)$_2$-d_2 (Figure 9). The m/e = 116, 97, 69, 44, and 28 signals do not disappear upon deuteration of the adsorbate, and thus can be assigned (at least in part) to the hydrogen-free fragments CF$_3$COF, CF$_3$CO, CF$_3$, CO$_2$, and CO, respectively. From the intensities of the m/e = 69 traces for the d_2 and d_0 isotopomers of Pd(hfac)$_2$, we conclude that very little (if any) COCHCO desorbs between 500 and 650 K. Perhaps more significantly, no palladium-containing ions are found to desorb at these temperatures. The intensities of the high-temperature TPR desorption peaks saturate at a Pd(hfac)$_2$ exposure of about 0.5 L,[32] a result which suggests that the features seen in the TPR spectra must arise via fragmentation of molecules bound in a monolayer.

Two lines of evidence show that the high-temperature desorption features noted here are due to the thermolytic decomposition of hfac ligands on the surface, rather than to the direct decomposition of Pd(hfac)$_2$ molecules. First, the XPS and RAIR studies described above clearly show that the hfac ligands dissociate from the palladium centers at temperatures as low as 120 K. Second, the composition of the desorbing flux in the 500−600 K temperature range is essentially identical to that reported for the thermolysis of Cu(hfac)$_2$ on copper,[27] which demonstrates that the hfac decomposition reactions are not sensitive to the identity of the metal atom in the hfac precursor.

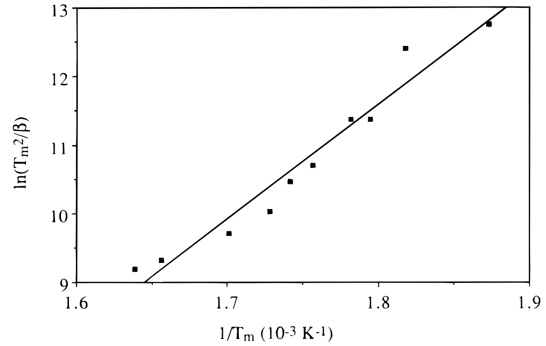

Figure 10. Eyring plot of the rate of decomposition of hfac ligands on clean copper surfaces; T_m is the thermal desorption peak maximum in Kelvin and β is the heating rate in K/s. The surface was dosed with a saturation coverage of Pd(hfac)$_2$ at 300 K and the m/e = 69 channel was used to monitor the desorption.

The mechanism by which the hfac ligands decompose and the identities of the intermediates present in the decomposition pathway have been discussed above; the principal reactions are C−C bond cleavage processes that result in the formation of surface-bound trifluoroacetyl (CF$_3$CO) and trifluoromethyl (CF$_3$) species. The view that C−C bonds are cleaved during the fragmentation of the hfac ligands is consistent with the TPR results, which gave no evidence of a kinetic isotope effect when Pd(hfac)$_2$-d_2 was used in place of Pd(hfac)$_2$. Therefore, we conclude that C−H bond scission is *not* the rate-determining step in the decomposition of the hfac ligands.

It is particularly striking that the m/e = 121, 116, 96, 69, 44, and 28 TPR line shapes for the peaks appearing between 500 and 650 K are so very similar (Figure 8). Similarly, very little coverage dependence is seen in the TPRS data (not shown). Based on these results, we conclude that these desorption features correspond to a common decomposition process; if we assume that this process is a first-order reaction, then the activation energy and pre-exponential factor can be determined by using Redhead's method.[40] At saturation exposures of Pd(hfac)$_2$, the peak temperature changes by 76 K when the surface heating rate is varied from 0.82 to 38.3 K/s (Figure 10). The activation parameters deduced for the decomposition of hfac ligands are $A = 1.3 \times 10^{13}$ s^{-1} and E_a = 36.4 kcal/mol.

Reactions of Pd(hfac)$_2$ on Single Crystal Cu(111) Surfaces. When a Cu(111) single crystal surface dosed with more than 0.5 L of Pd(hfac)$_2$ is heated, the temperature-programmed desorption profiles show desorption features due to two processes: desorption of the multilayer and decomposition of the monolayer, the latter occuring at high temperatures. Whereas the multilayer desorption behavior of Pd(hfac)$_2$ on a Cu(111) surface is very similar to that seen on copper foils, the thermolytic decomposition processes are quite different. In contrast to the single desorption peaks observed during the thermolytic decomposition of Pd(hfac)$_2$ on a Cu foil, multiple TPRS features between 450 and 750 K are seen for a Cu(111) surface in the m/e = 28, 44, 69, 97, and 116 channels (Figure 11).

The multiple desorption features seen in these data are very similar to those observed previously in TPRS studies of Cu(hfac)$_2$ on a Cu(111) surface.[27] In this previous study, we concluded that the hfac ligands are transferred to the Cu(111) surface at low temperatures, and that the multiple features in the TPRS profiles were the result of a series of sequential hfac

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(40) Redhead, P. A. *Vacuum* **1962**, *12*, 203−211.

(41) The Auger electron spectrum of the pretreated surface did not show any signal for fluorine, probably because of electron-induced desorption of fluorine during the AES experiment. See, for example: Westphal, D.; Goldman, A. *Surf. Sci.* **1983**, *131*, 92−113.

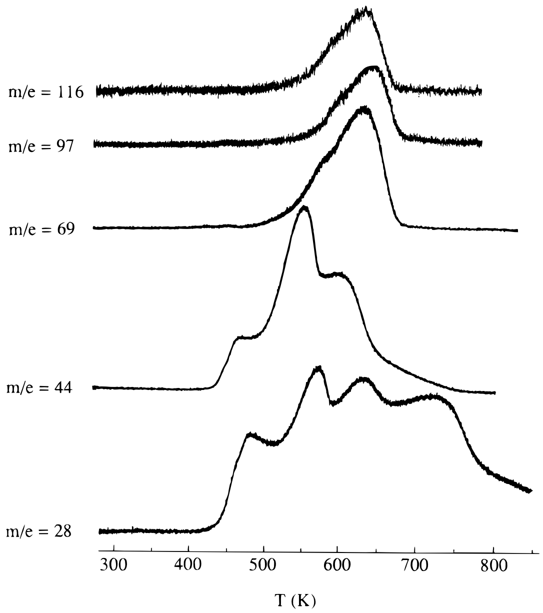


Figure 11. Temperature-programmed reaction profile obtained upon heating a clean Cu(111) surface exposed at 290 K to one monolayer of Pd(hfac)$_2$; the surface was heated at a rate of 4 K/s.

fragmentation reactions. Since the XPS and RAIR studies show that Pd(hfac)$_2$ also transfers its hfac ligands to the Cu(111) surface at low temperatures, it is reasonable to propose that the same series of sequential fragmentation reactions is occurring in the present case as well.

We will discuss below the factors we believe to be responsible for the very different TPR profiles seen on polycrystalline and single crystalline copper surfaces.

Reactions of Pd(hfac)$_2$ on Carbonaceous Copper Surfaces. In order to more closely model the adsorbate-rich surfaces present under MOCVD conditions, we studied the temperature-programmed reaction of Pd(hfac)$_2$ on specially pretreated copper surfaces. In these experiments, the pretreatment was carried out by dosing a clean polycrystalline copper with 1 L of Pd(hfac)$_2$ at 90 K and then heating the crystal to 800 K. The Auger electron spectra taken after this treatment show a peak at ~270 eV; the shape of this peak is characteristic of graphitic carbon. This conclusion is further supported by the presence of an asymmetrically-shaped C 1s peak due to graphitic carbon at 284 eV in the XPS spectrum (Figure 2). As judged by X-ray photoelectron spectroscopy, small amounts of fluoride are also present on the pretreated surface.[41] Both AES and XPS reveal that the submonolayer amount of palladium atoms initially present irreversibly diffuses into the copper bulk when the surface is annealed in this way.

Some of the reactions of Pd(hfac)$_2$ on the pretreated surface are similar to those seen on clean copper surfaces. For example, the Pd(hfac)$_2$ multilayer desorbs between 200 and 260 K and significant hfac ligand decomposition occurs between 500 and 650 K. Even at the limit of low coverages, however, the chemistry of Pd(hfac)$_2$ on this pretreated copper surface differs in one significant respect from that on a clean copper surface. A new desorption feature at 300−530 K is observed in the *m*/*e* = 203 and 201 [Cu(hfac) − CF$_3$] and 65 and 63 (Cu) channels (Figure 12; only the *m*/*e* = 201 and 63 channels are shown). These copper-containing ions are the major cracking fragments of Cu(hfac)$_2$ and we attribute these features to the desorption of Cu(hfac)$_2$ from the surface. This desorption feature is *not* seen when the temperature-programmed reaction experiment is carried out on a clean copper surface, as shown in traces b and d in Figure 12. Integrated desorption mass spectra (IDMS, not shown) taken during the temperature-programmed reactions of Pd(hfac)$_2$ at 300−530 K confirm these assignments.

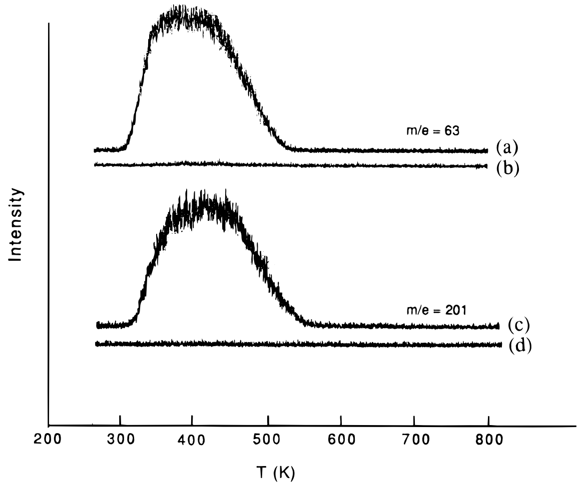


Figure 12. Temperature-programmed reaction profiles obtained upon heating a polycrystalline Cu surface exposed at 250 K to a saturation coverage of Pd(hfac)$_2$. Traces (a) and (c) are the profiles obtained from pretreated copper surfaces. Traces (b) and (d) are the TPR spectra obtained from clean copper surfaces. The pretreated copper surfaces were prepared by heating a clean copper surface dosed with a saturation coverage of Pd(hfac)$_2$ to 800 K at a rate of 7 K/s.

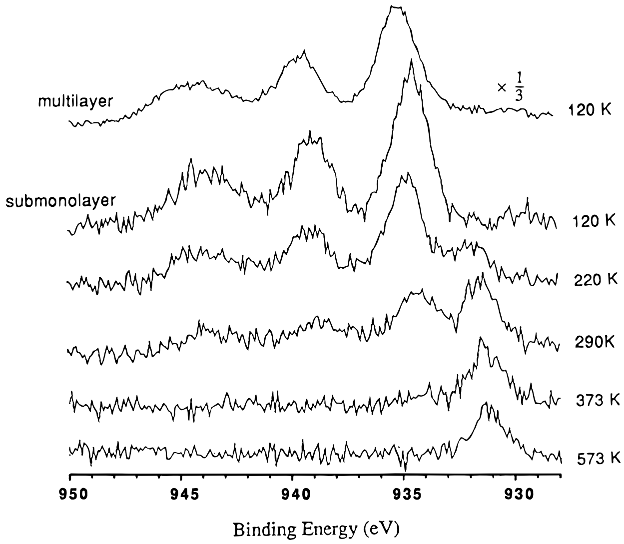
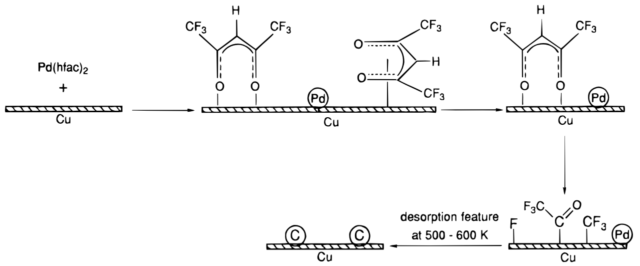


Figure 13. Cu 2p3/2 XPS spectra of a clean Pd surface exposed to Cu(hfac)$_2$ and annealed to different temperatures. The heating rates were 2 K/s and all the spectra were taken at 120 K.

Significantly, desorption of Cu(hfac)$_2$ is also observed when the clean copper surface is pretreated with either Cu(hfac)$_2$ or hfacH before carrying out the temperature-programmed reaction experiments with Pd(hfac)$_2$. These results show that the carbonaceous overlayer itself promotes the transmetalation reaction, probably by inhibiting the fragmentation of the hfac groups. A similar conclusion has been reached from studies of Cu(hfac)$_2$ on copper surfaces.[27]

Studies of the Reverse Reaction: Cu(hfac)$_2$ on Palladium Surfaces. In order to determine whether the redox transmetalation reaction can be driven in the opposite direction, we have carried out studies of the reactions of Cu(hfac)$_2$ on palladium surfaces. These experiments have given us some insight into the driving force for the redox transmetalation reaction of Pd(hfac)$_2$ on copper. Figure 13 shows the Cu 2p$_{3/2}$ XPS spectra of a palladium foil dosed with Cu(hfac)$_2$ and annealed to different temperatures. The Cu 2p$_{3/2}$ spectrum of a multilayer of Cu(hfac)$_2$ at 120 K shows a main peak at 935.8 eV and two

Scheme 1. Schematic Representation of the Reaction of $Pd(hfac)_2$ with a Clean Copper Surface at Submonolayer Coverages[a]



[a] Some oxygen and fluorine also remain on the surface at 600 K.

satellite peaks shifted 4.6 and 9.2 eV, respectively, to higher binding energy. The presence of the satellite peaks is characteristic of the Cu^{II} state which has a $3d^9$ electronic configuration.[42,43] The binding energy of the main peak is slightly higher than that of bulk $Cu(acac)_2$ (935.4 eV), owing to a final state effect involving the higher electron-withdrawing power of the hfac vs the unfluorinated acac ligand.[43−45]

When the Pd surface is dosed with a submonolayer amount of $Cu(hfac)_2$, the Cu $2p_{3/2}$ spectrum shows a main peak at 934.5 eV and two satellite peaks at 939.0 and 943.8 eV. Again the presence of the satellite peaks reveals that little or no charge transfer occurs between $Cu(hfac)_2$ and the palladium surface. These data clearly indicate that submonolayers of $Cu(hfac)_2$ adsorb molecularly on a palladium surface. The small shifts of the peaks to lower energies are probably due to the screening of the surface-bound $Cu(hfac)_2$ molecules by the electron-rich palladium surface.

When the $Cu(hfac)_2$-dosed palladium surface is heated to 220 K, a new Cu $2p_{3/2}$ peak at 932.0 eV appears; this peak can be attributed to metallic Cu^0 resulting from the reduction of $Cu(hfac)_2$ by the Pd surface. Most of the $Cu(hfac)_2$ (∼90%), however, remains unchanged on the surface at this temperature. When the surface is further heated to 290 K, the intensity of the metallic Cu $2p_{3/2}$ peak increases but $Cu(hfac)_2$ is still the dominant species resident on the surface (>75%). When the surface is heated to 373 K, the signals due to $Cu(hfac)_2$ disappear from the XPS spectrum whereas the intensity of the metallic Cu $2p_{3/2}$ peak remains essentially the same as that at 290 K. This behavior presumably reflects the desorption of $Cu(hfac)_2$ from the surface above 290 K.[46] Annealing further to 573 K does not result in any change in the Cu $2p_{3/2}$ spectrum.

These results suggest that the redox transmetalation reaction cannot be efficiently driven in the reverse direction. Further comments on this point will be deferred to the Discussion section.

Discussion

Overview of Reactions of $Pd(hfac)_2$ on Clean Copper Surfaces. The reactions of $Pd(hfac)_2$ on clean copper surfaces at submonolayer coverages are summarized in Scheme 1. The dissociative adsorption of $Pd(hfac)_2$ occurs readily: the transfer of hfac ligands from $Pd(hfac)_2$ to the copper surface takes place at temperatures as low as 120 K. Concomitant with the dissociative adsorption, the Pd^{II} centers are reduced to Pd^0. As shown by the RAIR studies, the surface-bound hfac groups adopt a distribution of orientations at low temperatures, but when the surface is annealed at 300 K the hfac groups reorient and bind predominantly to the surface in an upright geometry through their oxygen atoms. In the absence of an incident $Pd(hfac)_2$ flux, further heating does not result in the formation and subsequent desorption of $Cu(hfac)_2$ from the surface, but instead induces the unimolecular decomposition of the surface-bound hfac ligands. The latter decomposition reactions eventually leave small amounts of graphitic carbon on the surface. The palladium atoms generated by the dissociative chemisorption of $Pd(hfac)_2$ do not remain on the surface but instead diffuse into the bulk; after the surface has been heated to 800 K, no palladium is detectable on the surface either by AES or XPS.

One major question raised by our studies concerns the differing reactivities of hfac ligands on the single crystalline and polycrystalline copper substrates. We ask, why do the TPR profiles show only a single desorption feature when hfac decomposes on a polycrystalline copper surface, but multiple peaks when a single crystal Cu(111) surface is used? There are two alternative explanations of this behavior: the larger number of surface defect sites (adatoms, etc) present on a polycrystalline surface, or the larger number of grain boundaries present on a polycrystalline surface. We will discuss these possibilities in turn.

First, it is well-known that defect sites can accelerate the rates of many types of surface reactions. Such effects are most commonly noted in decomposition processes where the adsorbates undergo dissociative reactions.[47] It is not obvious from the TPRS data in Figures 8 and 11, however, that the hfac decomposition reactions are occurring with lower activation barriers on the polycrystalline vs single crystalline copper surfaces. In fact, the TPRS traces in the $m/e = 28$ and 44 channels have lower temperature features when decomposition occurs on single crystals. We thus conclude that the different hfac decomposition behavior on polycrystalline and single crystal copper surfaces is *not* a consequence of the different numbers of defect sites present.[48]

The second possibility we envision is that the grain boundaries present in the foils could change the relative populations of the various species on the surface by allowing some of the fragments generated by decomposition of $Pd(hfac)_2$ to diffuse into the bulk. It is well-known that diffusion of atoms into the bulk is greatly accelerated by the presence of grain boundaries;[49,50] our XPS studies show that the palladium atoms generated from chemisorption of $Pd(hfac)_2$ do indeed diffuse readily into the poly-

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(42) Frost, D. C.; Ishitani, A.; McDowell, C. A. *Mol. Phys.* **1972**, *24*, 861−877.

(43) The satellite peak with the highest binding energy is due to a simultaneous 3d to 4p transition occurring during the photoionization process; the satellite peak with the smaller energy shift can be explained by a simultaneous 3d to ligand transition. Cotton, F. A.; Harris, C. B.; Wise, J. J. *Inorg. Chem.* **1967**, *6*, 909−915.

(44) Donnelly, V. M.; Gross, M. E. *J. Vac. Sci. Technol.* **1993**, *A11*, 66−77.

(45) Welton, T.; Prasad, J.; Kelber, J. A.; Lujan, R. D.; Fleming, J.; Blewer, R. S. In *Proc. Adv. Metal. ULSI Appl.*; Rana, V. V. S., Joshi, R. V., Ohdomari, I., Eds.; Materials Research Society: Pittsburgh, 1992; pp 383−388.

(46) This is consistent with the temperature range where $Cu(hfac)_2$ desorbs from carbonaceous copper surfaces.

(47) See for example: Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634−1644 and references therein.

(48) There is little doubt that surface structures present on the polycrystal must be more diverse and complex than those found on a high-quality Cu(111) single crystal. It is for this reason that the simple pattern of coincident peaks seen in Figure 8 is so perplexing. Such behavior could be rationalized if other features, such as diffusion to or trapping at strong bonding sites, dominated the adsorbate decomposition kinetics. This type of dynamical effect must be important at some level in the decomposition processes but to what extent it is expressed in the observed kinetics is unclear. We can offer little more here than to point out that "intuitive notions" of rate−structure sensitivities in heterogeneous reaction kinetics can be very misleading. An excellent discussion of the influence of surface heterogeneity in adsorption/desorption kinetics can be found in: Serri, J. A.; Tully, J. C.; Cardillo, M. J. *J. Chem. Phys.* **1983**, *79*, 1530−1536.

(49) For a recent review of the atomic-scale mechanisms that operate in metal-on-metal film structures, see: Chang, S.-L.; Thiel, P. A. *Crit. Rev. Surf. Chem.* **1994**, *3*, 239−296.

(50) Gupta, M.; Kreuzer, H. J.; Weimer, J. J., Eds. *Diffusion and Interfaces: Microscopic Concepts*; Springer-Verlag: New York, 1988.

crystalline copper surfaces. If this happens before the onset of hfac ligand decomposition, then the thermolysis of hfac occurs on a surface that is largely free of palladium atoms. On single crystal copper surfaces, however, the absence of grain boundaries means that the diffusivity will be low and the palladium atoms generated from chemisorption of $Pd(hfac)_2$ would remain on the surface to much higher temperatures. In this case, the decomposition of hfac ligands occurs on a Cu surface "decorated" with palladium adatoms. This scenario might explain why the TPR profiles seen for $Pd(hfac)_2$ on Cu(111) are very similar to those seen for $Cu(hfac)_2$ on Cu(111): in the latter case, the hfac ligands decompose on a Cu surface decorated with copper adatoms. Thus, the hfac decomposition chemistry on single crystals and foils could differ because on one surface (single crystals) there are numerous metal adatoms, whereas on the other (foils) there are fewer due to the rapid removal of metal adatoms by a step-growth and grain boundary diffusion mechanism. We must emphasize, however, that the factors responsible for the reactivity differences seen on foils and single crystals are still incompletely understood; the structural correlations, while intriguing, remain qualitative.

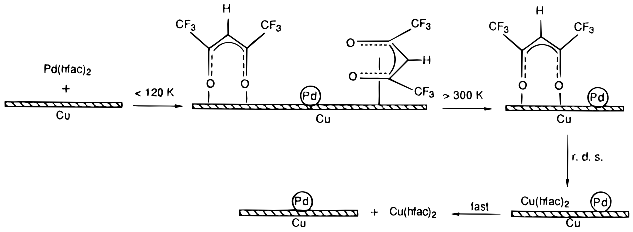
One clear similarity is seen in the reaction of $Pd(hfac)_2$ on Cu(111) and polycrystalline copper substrates, however. On both single crystals and on foils, the major high-temperature process that occurs in UHV is the decomposition of adsorbed hfac ligands. This reactivity pattern is different from that seen under MOCVD conditions, where, in the presence of a continuous adsorbate flux, the hfac ligands do not fragment but instead combine with surface copper atoms and are carried away as $Cu(hfac)_2$. The net result of this MOCVD reaction is the replacement of surface copper atoms by palladium. The difference between this reaction pathway and that seen under macroscopic MOCVD conditions may be attributed to the generally lower surface coverages obtained under ultrahigh-vacuum conditions, which greatly disfavor the bimolecular reactions that are necessary for the assembly of the $Cu(hfac)_2$ product. We will discuss in detail in the following paper the intriguing kinetic and mechanistic features of this latter reaction pathway, defining both the pressure and atomic diffusion dependences which so sensitively influence the product partitioning in this system.

Interestingly, the transmetalation reaction can be observed under UHV conditions under certain circumstances; whether transmetalation or hfac decomposition takes place depends sensitively on the sample history. On clean surfaces, Pd is deposited via the thermolytic decomposition of the hfac groups as discussed above. On surfaces bearing submonolayer quantities of carbon, however, transmetalation (i.e., deposition of Pd and evolution of $Cu(hfac)_2$) competes with the thermolytic decomposition.

It is striking that the reactivity of $Pd(hfac)_2$ on the carbon-bearing copper surface is similar to that seen under MOCVD conditions; in both cases, $Cu(hfac)_2$ is present in the desorbing flux of molecules at 300−500 K. This observation suggests that a submonolayer of carbon may also be present on the copper surface during the chemical vapor deposition of palladium from the $Pd(hfac)_2$ precursor at higher pressures.

We can envision at least two explanations of the different reactivities of $Pd(hfac)_2$ on the clean and pretreated copper surfaces: the presence of carbon (and/or fluorine) contaminants on the pretreated surface could serve either to inhibit hfac ligand decomposition on the copper surface or to facilitate the formation $Cu(hfac)_2$. Since TPR data suggest that the hfac ligands decompose on the pretreated surfaces at about the same temperature as on the native surface, the latter mechanism seems more likely to us. We cannot rule out, however, the possibility that both mechanisms are working jointly. It is important to note that this surface "contamination" does not build up during a CVD deposition, since XPS data show that the Pd/Cu alloy films that result are of high elemental purity.[17,18] We do not know what steady state concentrations of surface contaminants are present during the CVD process, but they must be low enough to avoid poisoning the film growth even at the limit of very thick films (>1 μm).

Scheme 2. The Overall Mechanism for the Transmetalation of $Pd(hfac)_2$ on Copper Surfaces under CVD Conditions



Rate-Limiting Step and Driving Force for the Transmetalation Reaction. Four chemical processes are necessary to sustain the transmetalation reaction and final conversion of $Pd(hfac)_2$ to $Cu(hfac)_2$: (1) dissociation of hfac ligands from the Pd centers; (2) recombination of hfac ligands with a copper surface atom to form $Cu(hfac)_2$; (3) desorption of $Cu(hfac)_2$ molecules once they are formed; and (4) interdiffusion of Pd and Cu, thus bringing fresh Cu atoms to the surface. The *in situ* XPS and RAIR studies at submonolayer coverages demonstrate that even at 120 K, chemisorption of $Pf(hfac)_2$ on copper surfaces results in the reduction of the Pd^{II} center of $Pd(hfac)_2$ to metallic Pd^0, and the transfer of the hfac ligands to surface terrace atoms. The ease with which the hfac ligands migrate to the copper surface shows that this step cannot be rate limiting. The temperature-programmed reaction studies have further shown that submonolayers of $Cu(hfac)_2$ desorb from the pretreated copper surface at a peak temperature of 320 K; this result suggests that desorption of $Cu(hfac)_2$ cannot be the rate-limiting step.[51] The XPS, RAIR, and TPR studies therefore strongly indicate that the process which limits the rate of desorption of $Cu(hfac)_2$ under all circumstances, including those involving an incident flux of the precursor,[19] is its production from surface-bound hfac groups and copper atoms. The overall mechanism for the conversion of $Pd(hfac)_2$ to $Cu(hfac)_2$ as deduced from these *in situ* kinetic and spectroscopic studies is summarized in Scheme 2; the energetics of the rate determining step in this mechanism will be discussed in the following paper.

An important point left unanswered in the discussion above concerns the thermodynamic driving force for the transmetalation reaction of $Pd(hfac)_2$ and Cu. One possibility is that the reaction is driven by mass action: at the beginning of a deposition run, the surface is copper-rich and palladium-poor, and as a result the hfac groups form $Cu(hfac)_2$ preferentially. If mass action controls the identity of the reaction product, then it should be possible to run the reaction in the reverse direction, and use $Cu(hfac)_2$ to deposit copper on palladium. The XPS studies described above clearly show that $Cu(hfac)_2$ remains intact on a Pd surface up to ~300 K; above this temperature, desorption of $Cu(hfac)_2$ ensues. Only about 15% of the $Cu(hfac)_2$ originally dosed on the Pd surface dissociates, as judged from the low coverage of Cu adatoms that results. Thus, the XPS data clearly show that the reduction of Pd^{II} to Pd^0 on a Cu surface is facile, while Cu^{II} appears to be stable on a Pd surface.

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(51) Further evidence that the desorption of $Cu(hfac)_2$ from the surface is reaction limited (rather than desorption limited) is that $Cu(hfac)_2$ molecules are not observable on the surface under these conditions: there are no IR bands due to parallel-oriented hfac groups[27] and there are no Cu^{II} species on the surface as judged by XPS studies.

These results suggest that the primary driving force for eq 1 is not mass action but rather a favorable redox potential. The transmetalation reaction is a redox process and the thermodynamic potentials associated with this must figure centrally in the overall energetics. Formal tabulations of reduction potentials (standard half cell potentials) provide additional support for this contention, although admittedly the conditions under which they pertain are quite different. The standard potential for the cell $Pd/Pd^{2+}//Cu^{2+}/Cu$ is 0.61 V so that the reduction of palladium(II) by copper(0) is thermodynamically favorable.[52] This result suggests that the aqueous-based potentials are indeed descriptive of the surface reactions of oxygen−chelate hfac complexes.

In the transmetalation chemistry, copper metal reduces palladium(II); the direction of this redox reaction is opposite to that of a key step in the Wacker alkene oxidation process, where palladium metal reduces copper(II).[53] We note that the redox reaction in the Wacker process is driven by the presence of O_2, which maintains a high concentration of copper(II) species, and by reductive elimination processes, which spontaneously reduce palladium(II) to palladium(0).[54]

Conclusions

On clean copper surfaces under ultrahigh-vacuum conditions, $Pd(hfac)_2$ readily transfers its hfac ligands to terrace atoms of the metallic substrate. At higher temperatures, decomposition of the hfac groups is favored over the competing reaction: formation of $Cu(hfac)_2$ and deposition of palladium via the redox transmetalation reaction. The decomposition of the hfac ligands on the surface is self-limiting to some extent: the presence of graphitic (and possibly other hfac-derived) impurities on the surface inhibits the decomposition pathway and simultaneously promotes the formation of $Cu(hfac)_2$. Three important features of the redox transmetalation reaction have been elucidated: (1) the reduction of $Pd(hfac)_2$ by the copper surfaces to Pd^0 occurs readily at low temperatures (∼120 K); (2) the rate-limiting step in the transmetalation process is the formation of $Cu(hfac)_2$ from surface copper atoms and surface-bound hfac groups; and (3) the driving force for the redox transmetalation reaction is the favorable redox potential of the $Pd/Pd^{2+}//Cu^{2+}/Cu$ cell.

In the following paper, we will show that the competing thermolytic decomposition pathway can be avoided altogether by imposing a continuous flux of the precursor onto the surface; this adsorbate flux promotes the combination of surface-bound hfac ligands and copper atoms relative to the first-order decomposition of hfac. In addition, the interplay between the surface reactions and the bulk interdiffusion of copper and palladium will be discussed.

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(52) Vanýsek, P. In *Handbook of Chemistry and Physics*, 68th ed.; Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press: Boca Raton, FL, 1988; pp D152−D154.

(53) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 826.

(54) There is at least one other example of a redox reaction in which palladium metal is proposed to reduce a copper(II) salt: the thermolysis of a mixture of palladium and copper acetates to Pd/Cu alloys is proposed to occur via reduction of Cu^{II} acetate by an initially generated palladium particle. However, this is not the only possibility. See: Bradley, J. S.; Hill, E. W.; Klein, C.; Chaudret, B.; Duteil, A. *Chem. Mater*. **1993**, *5*, 254−256.