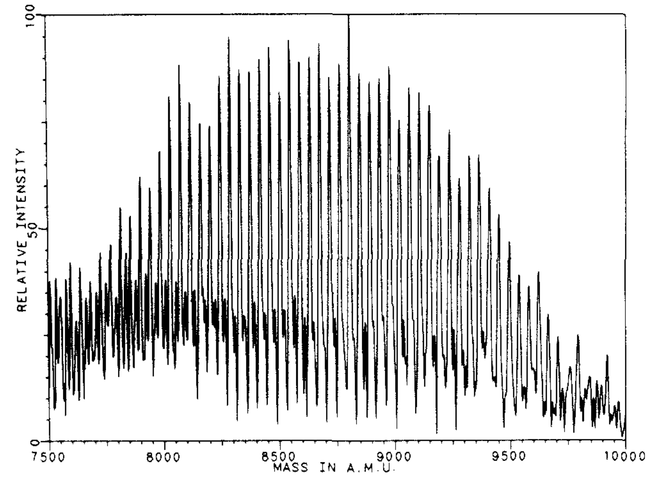

Figure 1. High mass region of laser desorption Fourier transform mass spectrum of poly(ethylene glycol)-8000. Lower mass cutoff m/z 2186.

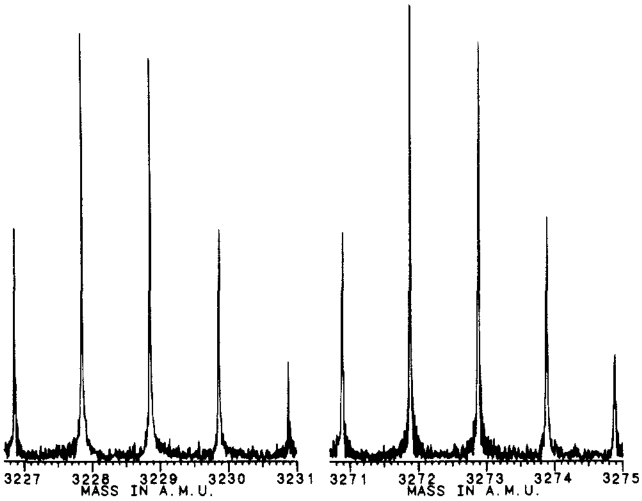

Figure 2. A portion of the high resolution laser desorption Fourier transform mass spectrum of poly(ethylene glycol)-3350 between m/z 2706 and m/z 4012.

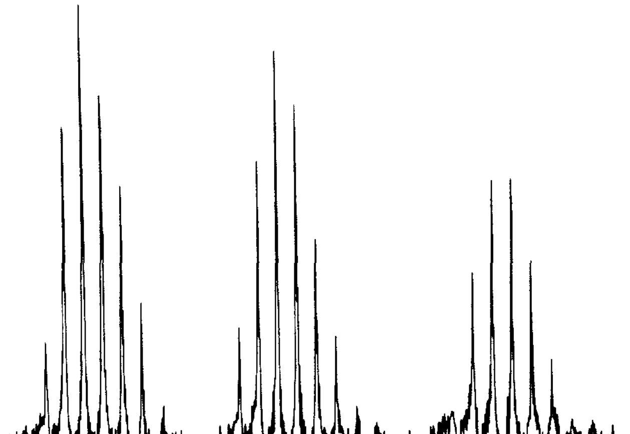

Figure 3. A portion of the high resolution laser desorption Fourier transform mass spectrum of poly(propylene glycol)-4000 between m/z 5500 and m/z 6000. Ions outside that range were ejected.

identifiable potassium-attached oligomer ions up to m/z 9700 is the highest mass range LD-FTMS spectrum yet obtained. Figures 2 and 3 are selected high mass regions of spectra of poly(ethylene glycol)-3350 and poly(propylene glycol)-4000, respectively, demonstrating both unprecedented organic high mass resolution (Figure 2—160 000 at m/z 3200, unapodized, for PEG-3350) (Figure 3—resolution 60 000 at m/z 5922, unapodized, for PPG-4000) and accuracy, with mass measurement accuracy of 8.59 ppm ($\sigma = 6.3$ ppm) for the 48 ions with m/z between 5500 and 6000.

In view of these results, obtained under conditions where space-charge effects were limited and by using a 7-T Fourier transform mass spectrometer of significantly lower magnetic field homogeneity (100 ppm over a 6.3 cc vol, drift rate ca. 6.5 ppm/h) than that employed by others, it appears that factors other than the masses involved, space-charge effects, or field inhomogeneity may be limiting in tandem instrument measurements. Not only are the present results fully consistent with expectations based upon the use of a 7-T magnetic field (rather than 3 T, used for our previous LD-FTMS studies) but also demonstrate that high mass laser-desorbed ions can be trapped for nearly 20 s, providing encouraging evidence of the potential of the method for accurate high resolution mass analysis of such species.

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"Tailored" Organometallics as Precursors for the Chemical Vapor Deposition of High-Purity Palladium and Platinum Thin Films

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The fabrication of electronic devices by chemical vapor deposition is a rapidly expanding area of great current interest. Metal-organic chemical vapor deposition (MOCVD) routes to the preparation of semiconductor thin films, such as GaAs from GaMe$_3$ and AsH$_3$, are becoming increasingly attractive, due largely to the high growth rates, high purity, high crystal quality, and ease of process control that are characteristic of the MOCVD method.[1] However, despite the intensive study of the synthesis of main-group materials by MOCVD, relatively few studies of the deposition of thin films that contain transition metals have been reported,[2] largely because suitably volatile and reactive molecular CVD precursors are scarce. For example, palladium films are of interest as a potential replacement for gold as an electrical contact material in integrated circuits.[3] This interest arises from its high electrical conductivity, its resistance to oxidation, and its economic advantages over gold. While palladium films have been made by electroplating,[4] vacuum sputtering,[5] and laser direct-write metallization,[6] no CVD methods have been reported to date, despite the advantages offered by this technique. Here we report the synthesis of high-quality Pd and Pt films by

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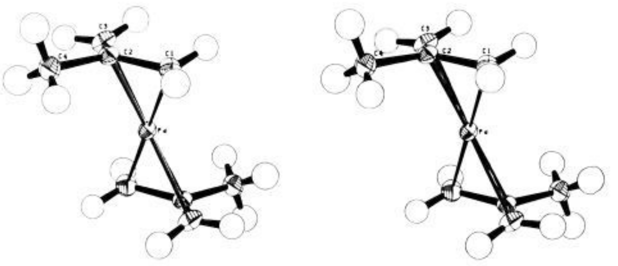

Figure 1. Stereoview of the molecular structure of Pd[$(CH_2)_2CMe]_2$, **2**. Important bond distances (Å) and angles (deg): Pd–C1 = 2.177 (2), Pd–C2 = 2.149 (1), Pd–C3 = 2.172 (2), C1–C2 = 1.407 (2), C2–C3 = 1.410 (2), C2–C4 = 1.502 (2), C(sp^2)–H = 0.96 (3), C(sp^3)–H = 0.93 (3), C1–C2–C3 = 118.7 (1), C1–C2–C4 = 120.2 (1), C3–C2–C4 = 120.3 (1).

MOCVD from "tailored" organometallic precursors under mild conditions.

Three organopalladium compounds have been chosen for study as potential precursors for Pd thin films: bis(allyl)palladium, **1**,[7] bis(2-methylallyl)palladium, **2**,[7] and (cyclopentadienyl)(allyl)-palladium, **3**.[8] While **1** and **2** are conventionally prepared from $PdCl_2$, we find that alkylation of palladium(II) acetate with the corresponding Grignard reagent followed by sublimation at 25 °C gives high product yields. Since no structural studies of any bis(allyl)palladium complex have been reported, the X-ray crystal structure of Pd[$(CH_2)_2CMe]_2$, **2**, has been determined (Figure 1).[10] Molecules of **2** adopt crystallographically imposed inversion symmetry, and thus the two allyl C_3 planes are rigorously parallel to one another. The allyl units are bound to the palladium center in an η^3 fashion, with the terminal Pd–C1 and Pd–C3 bond distances of 2.175 (2) Å being slightly longer than the central Pd–C2 distance of 2.149 (1) Å; the C1–C2 and C2–C3 bonds are equal in length at 1.409 (2) Å. The substituents on all three π-bound carbon atoms are displaced out of the C_3 plane in order to direct the p-orbitals of the π-system more nearly toward the palladium atom. Thus, the methyl group on C2 is displaced downward toward the Pd center, so that the C2–C4 bond makes an angle of 9.4° with respect to the C_3 plane. Most interestingly, the terminal CH_2 groups are rotated in a disrotatory fashion so that the endo hydrogens are some 0.47 Å above the C_3 plane (farther from Pd), while the exo hydrogens are 0.08 Å below this plane. The C1–C2–C3–H and C3–C2–C1–H torsion angles average 34° (endo) and 174° (exo), compared with the idealized angles of 0° and 180°, respectively. The X-ray crystal structure of the nickel analogue[10] Ni[$(CH_2)_2CMe]_2$ is of relatively low accuracy (R = 7.9%), which thus prevents detailed comparisons; overall, however, this molecule possesses a geometry similar to that of **2** but with shorter metal–carbon bond lengths, as expected, of 1.98 (1) – 2.03 (1) Å.[11]

Chemical vapor deposition of the allyl palladium precursors at 250 °C and 10^{-4} Torr was conducted in an externally thermostated Pyrex reaction chamber. Bright silvery metallic films were grown to thicknesses of up to 2 μm on a variety of substrates including glass, steel, copper, and aluminum. X-ray photoelection (XPS) and Auger[12] spectroscopy identify the films from **1** and **2** as >99% Pd, with <1% C, while films prepared from the cyclopentadienyl precursor **3** differ in that detectable amounts (~ 5%) of residual carbon are retained. Depth-profile studies showed that some oxygen was present at the surface of the films, but oxygen contaminants fell to undetectable levels upon sputtering. X-ray powder diffraction experiments revealed that the films were amorphous, while optical and electron microscopy showed the films to be very smooth and featureless. Electrical conductivity measurements of the films give a resistivity of ca. 15 ± 5 $\mu\Omega$-cm, which is comparable to the value of 11 $\mu\Omega$-cm for bulk palladium.[13] Experiments involving the platinum analogue bis(allyl)platinum[7] and the cyclopentadienyl complex $CpPtMe_3$[7] yield high-quality Pt films under similarly mild (250 °C, 10^{-4} Torr) conditions.

Analysis of the gaseous products resulting from the thermolysis of bis(allyl)palladium reveals propene (ca. 59 mol %) and various hexadienes (ca. 30 mol %) as the major organic products, whereas (cyclopentadienyl)(allyl)palladium gives a mixture of cyclopentadiene (ca. 43%), propene (ca. 38%), and only trace amounts of hexadienes (<1%).[14] The product distribution in each case is more consistent with a predominantly radical mechanism than with a reductive elimination sequence, and further studies of the thermolytic pathways are being carried out.

The facile synthesis of more complex thin film structures such as micromodulated quantum well devices is a particular strength of the MOCVD approach.[1] In a similar fashion, we have prepared a double-layer thin film of Pd on titanium carbide by first passing tetra(neopentyl)titanium[2a] and then bis(allyl)palladium in sequence over a glass slide at 250 °C. Depth profiles of these films show a clean transition between the two layers, which is consistent with the low atomic mobilities expected of our low-temperature "tailored" MOCVD approach. The atom-by-atom nature of the MOCVD deposition process may also make it possible to synthesize "alloys" between mutually immiscible materials by simultaneous passage of two tailored precursors over a heated substrate. We are continuing our efforts to explore the generality of the MOCVD approach for the synthesis of thin films from organotransition-metal precursors.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for Pd[$(CH_2)_2CMe]_2$ (2 pages); table of final observed and calculated structure factors for Pd[$(CH_2)_2CMe]_2$ (4 pages). Ordering information is given on any current masthead page.

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