Interfacial and Solvent Effects Govern the Formation of Tris(dibenzylidenediacetone)dipalladium(0) Microstructures

Donovan N. Leonard,³,⁴ Marta Cerruti,³,⁶ Gerd Duscher,⁷ and Stefan Franzen*⁵,⁸

Department of Materials Science & Engineering, Department of Chemistry, and W. M. Keck Center for RNA-Mediated Evolutionary Materials Synthesis, North Carolina State University, Raleigh, North Carolina 27695

Received April 3, 2008

Organometallic palladium adducts have application as catalysts and as precursors for nanoparticle synthesis. Herein, we study the spontaneous formation of molecular crystals of the organometallic reagent tris(dibenzylidenediacetone)dipalladium(0) (Pd₂(DBA)₃) in THF/H₂O binary solvent systems. We report structural and chemical characterization of the resulting diverse structures with shapes including hexagonal platelets, rods, cubes, and stars. Optical microscopy, transmission electron microscopy, scanning electron microscopy, and energy-dispersive spectroscopy were used to determine representative structures and corresponding compositions when formed either in a binary solution or upon evaporation on a surface. The difference in Pd₂(DBA)₃ particle morphology was attributed to differences in the surface tension of growing crystalline faces. The formation of a majority of rods or hexagonal platelets in solution was shown to be determined by the ratio of THF to H₂O in the solvent, whereas supersaturation effects and interfacial surface tension played a major role in creating the shape of particles formed upon evaporation of Pd₂(DBA)₃ droplets on a surface.

Introduction

The formation of nanoparticles of controlled geometry is of interest both for a fundamental understanding of the organization of matter and for applications in optics,¹ electronics,² and catalysis.³–⁵ Shape control has become a focus since many applications of nanoparticles require a nonspherical geometry to maximize the surface to volume ratio, enhance surface plasmon sensing,⁶ or expose specific crystalline planes for catalytic applications. The control of nanoparticle shapes is usually achieved with the use of surfactants such as cetyltrimethylammonium bromide (CTAB),⁷,⁸ sodium dodecyl sulfate (SDS),⁷ and mono-n-dodecyl phosphate (MDP)⁸ or polymers such as poly(vinylpyrrolidone) (PVP),⁷,⁹ sodium polycrylate (NaPA),¹⁰ and poly(ethylene oxide-block-methacrylic acid) (P(EO-b-MAA)) and poly(ethylene oxide-block-styrenesulfonic acid) (P(EO-b-SSH)) diblock copolymers.¹¹ Also the adsorption of ions such as citrate can determine the formation of different morphologies.¹² Recently, chiral molecules such as tartaric acid were also shown to induce the formation of nanoparticles with chiral morphologies.¹³ These strategies have been used to control the morphology of particles made of very different materials, ranging from semiconductors such as PbS or CdSe⁷,¹⁴,¹⁵ to ZnO,¹¹,¹² calcium phosphate,³ calcium carbonate,¹³ or metallic nanoparticles such as Au,⁹ Ag,¹⁶,¹⁷ and Pt.¹⁸ In all these cases it has been observed that the molecules present in the solution adhere to specific faces of the nucleating nanocrystals, thus preventing the growth along particular directions and leading to the formation of particles with geometries that otherwise would not be stable.

In general, during the growth phase, the equilibrium morphology of a particle is achieved when the value of the surface free energy, γ d4, in the mother liquor is at a minimum, where γ is the surface tension and d is the surface area of the crystal faces. Thus, for fcc and bcc metal crystals of sufficient size γ is isotropic, leading to the formation of icosahedral or quasi-spherical crystals as the lowest energy form. The adsorption of surfactants, polymers, or other molecules changes the surface tension of the crystalline faces and leads to the formation of cubes, wires, hexagonal platelets, truncated octahedrons, stars, and many other shapes. Shape control whether by solvent, surfactant, or surface interaction can give rise to novel catalytic or electronic properties.

Herein, we report the formation of organometallic crystals of tris(dibenzylidenediacetone)dipalladium(0) (Pd₂(DBA)₃), with different shapes controlled by a binary solvent system consisting of H₂O and THF. The study of the formation of Pd₂(DBA)₃ crystals is important because Pd₂(DBA)₃ is used as a catalyst for...
organic reactions\textsuperscript{18,19} and also as a precursor for Pd nanoparticle synthesis, by mixing with ligands,\textsuperscript{20,21} sonothermal decomposition,\textsuperscript{22} or annealing,\textsuperscript{23} and even with RNA mediation.\textsuperscript{24–26} In our study we will show that Pd\textsubscript{2}(DBA)\textsubscript{3} molecular crystals can be formed in THF/H\textsubscript{2}O binary mixtures using conditions similar to those described previously.\textsuperscript{24–26} We proved elsewhere, using electron diffraction, that these particles are indeed molecular crystals of Pd\textsubscript{2}(DBA)\textsubscript{3},\textsuperscript{27} not metallic Pd crystals.\textsuperscript{24–26} Here we will concentrate our attention on the different morphologies obtained by varying the THF/H\textsubscript{2}O ratio in the nucleating solution, without the addition of surfactants, ions, or any other mediator (e.g., RNA).

Pd\textsubscript{2}(DBA)\textsubscript{3} is not highly soluble in any of the THF/H\textsubscript{2}O binary mixtures,\textsuperscript{27} and it is completely insoluble in H\textsubscript{2}O;\textsuperscript{28} thus, an increase in the H\textsubscript{2}O fraction in the binary mixture induces molecular aggregation and rapid precipitation of Pd\textsubscript{2}(DBA)\textsubscript{3}. According to the phase diagram, THF and water are completely miscible as a binary solution at all mole fractions below the critical temperature of 344 K.\textsuperscript{29–31} However, nucleation and growth of Pd\textsubscript{2}(DBA)\textsubscript{3} crystals may be affected by partitioning of the solvent molecules around the hydrophobic solute. In this study we will show that by simply changing the ratio of THF to water and hence parameters such as the Pd\textsubscript{2}(DBA)\textsubscript{3} solubility, vapor pressure, and surface tension, it is possible to favor the formation of crystals with specific morphologies, ranging from hexagonal platelets to rods, cubes, and stars. The vapor pressures of water and THF are 17.1 and 129 Torr at 20 °C, respectively. This vapor pressure difference implies that solvent evaporation will lead to an increase in the water mole fraction in the binary mixture. The formation of these supramolecular assemblies may also be mediated by the surface tensions of water and THF, which are 72.8 and 26.4 mN/m at 20 °C, respectively. Thus, the solvent surface tension that interacts with a growing nanocrystal also depends on the THF mole fraction in the binary mixture. Taken together, these factors suggest that Pd\textsubscript{2}(DBA)\textsubscript{3} crystals can form in solutions where they are moderately soluble (i.e., 50% THF by volume or greater percentage).\textsuperscript{27} The percentage of THF will decrease as a droplet dries on the surface, leading to a decreased solubility of Pd\textsubscript{2}(DBA)\textsubscript{3} and an increasing tendency for shapes to be dominated by a decrease in the THF molecules available to solvate the crystalline microstructure. We will provide a possible explanation for the observed shape variations on the basis of the interfacial and solvent effects among THF, water, and the Pd\textsubscript{2}(DBA)\textsubscript{3} molecule, and we will compare this system with other systems recently presented in the literature.

**Results**

When the Pd\textsubscript{2}(DBA)\textsubscript{3} solutions of 5 and 30 vol % THF solutions were prepared, a murky red colloidal suspension formed instantaneously. In the 50 and 70 vol % solutions particulates were formed after several minutes and had a tendency to sink to the bottom of the vials.\textsuperscript{27} The presence of precipitates in each of the solutions was confirmed by empirical observations and further morphology data, and the chemical composition of the particulates formed was warranted. Diverse structures with shapes including stars (Figure 1A), rods (Figure 1B), hexagons (Figure 1C), and cubes (Figure 1D) were formed spontaneously by aggregates of Pd\textsubscript{2}(DBA)\textsubscript{3} from 100% THF and the THF/H\textsubscript{2}O binary mixtures.

Representative features found in the 5 vol % THF/H\textsubscript{2}O binary mixtures were micrometer-sized structures, lacking any characteristic shape. The representative morphology of particulates formed in the 30 vol % THF/H\textsubscript{2}O mixture consisted of hexagonal structures with micrometer-sized basal planes and nanometer thickness. A cubic morphology was observed as a minority structure. Figure 2 shows micrographs of minority features formed in the 30 vol % solution, which included cube-shaped molecular crystals (Figure 2A,B), an intermediate shape of a faceted cube (Figure 2C), and hexagon/cube clusters (Figure 2D,E). Low-voltage scanning transmission electron microscopy (LV-STEM) of the structures formed in the 50 vol % THF/H\textsubscript{2}O mixture showed that hexagon-shaped crystals were present both as individual platelets (Figure 1C) and in clusters measuring several micrometers across as shown in Figure 3. To investigate the composition of the precipitates and investigate any composition dependence of them when formed in different binary solutions, chemical analysis of the nanostructures with LV-STEM, scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS) was used. We used these high spatial resolution techniques were
able to sample individual particulates and determined the starlike features, rods, hexagons, and cubes all contained carbon as the major element with only minor amounts of Pd present. To minimize electron beam damage,²⁵ low-voltage (20–30 kV) quantitative EDS was used to study the most common precipitate morphology, which was the hexagonal platelet. Several hexagonal platelets were analyzed, and the resulting average chemical compositions determined by EDS were >90 atom % C and <10 atom % Pd, which matches the composition Pd₂(DBA)₃, in agreement with previous measurements.²⁷

Figure 2. BF TEM micrographs of cube-shaped particles formed in a 30 vol % THF mixture. (A) and (B) show cubes formed by kinetic trapping in the 30 vol % binary solution. (C) This feature, a faceted cube, shows defects in molecular packing and can create intermediate structures. (D, E) Both hexagons and cubes could form as agglomerates in this solution as evidenced from the micrographs.

Figure 3. (A) LV-STEM bright-field micrograph showing a micrometer-sized cluster of hexagonal structures formed from Pd₂(DBA)₃ in the 50 vol % THF/H₂O binary solution. The random orientation of platelets in the cluster makes some hexagons appear as rectangular features when viewed edge on. (B) The EDS spectrum of a hexagon in the cluster showed its composition to be a majority of carbon with minor amounts of Pd.
To test the dependence of changes in the particulate morphology on the growth conditions, droplet evaporation on surfaces in an ambient atmosphere was studied in addition to the precipitation in binary solutions reported above. A typical 10 µL as-cast 8 mM Pd₂(DBA)₃ droplet on an ITO surface contained concentric rings of varying contrast bound by a dark outermost ring. When this dark ring was observed at higher magnifications with reflected light optical microscopy (OM), as shown in Figure 4, it was found to be composed of red-colored crystallites (branched structures with morphology similar to snow crystals) having diameters measuring ∼5 µm (Figure 1A). Region [1] of Figure 4A is the bare ITO substrate surface. Region [2] is the perimeter of the droplet containing 3-dimensional Pd₂(DBA)₃ structures shown at higher magnification in Figure 5B,C. Most features created in the bulk of the droplet region had edge lengths measuring hundreds of nanometers and could not be resolved further by OM. With the aid of SEM distinct shapes observed more frequently in the center region of the droplet, region [3] of Figure 4A, were faceted hexagon platelets with large-scale basal planes orders of magnitude larger than the facet thickness.

The SEM micrographs of Figure 5 provide a multilength scale perspective of the representative molecular crystal shapes contained in the droplet region. Figure 5A shows a field of view similar to that of Figure 4A, and for comparison the bare ITO substrate (region [1]) is in the bottom right of the SEM micrograph. Arrows denote the presence of the high aspect ratio rods (Figure 1B) in the droplet region shown in Figure 5A. Higher resolution micrographs of the red organometallic crystallite morphologies in region [2] (Figure 4A) are shown in Figure 5B,C. Parts A and B of Figure 6 show the majority of structures in region [3] of Figure 4A formed during evaporation were nanometer-sized hexagons. Cubelike features are also observed in Figure 6B. Figure 6B is representative of the relative frequency of cubes formed in the Pd₂(DBA)₃ samples studied. Chemical analysis by EDS was also used to determine the chemical composition of the various features found in the evaporated droplet. X-ray signals from the hexagonal and star-shaped structures indicated the features were mostly carbon and contained minor amounts of Pd.

As a control experiment the as-received reagent powder was analyzed to prove the polymorphic shapes of Pd₂(DBA)₃ observed were formed by precipitation and were not present in the unpurified reagent. The presence of only randomly shaped particles, observed by OM and SEM, in the organometallic powder proved molecular crystal shapes were created only after reagent precipitation. The unpurified reagent powder also contained Pd metal nanoparticle agglomerates with a distinct morphology as shown in Figure 6C and reported elsewhere.²⁷

**Discussion**

The structure of Pd₂(DBA)₃ crystallized in CH₂Cl₂, determined by X-ray crystallography,⁳³ reveals a triclinic unit cell with parameters that are close to those of a trigonal unit cell. We reported²⁷ evidence that Pd₂(DBA)₃ molecular crystals formed

---


in THF have a trigonal molecular packing. This subset of hexagonal symmetry was observed in the 6-fold symmetric morphology of stars (Figures 1A and 5C) and the $116^\circ$--$120^\circ$ interior angles of facets found in hexagonal platelets (Figures 1C and 6A,B) and in the faceted ends of rods (Figure 1B).

Pd$_2$(DBA)$_3$ is an organometallic adduct with two central Pd atoms that are encapsulated by three symmetry-related dibenzylideneacetone ligands in the molecular model of Pd$_2$(DBA)$_3$ seen in the top and side views of Figure 7. From this figure it is noted that the side view of Pd$_2$(DBA)$_3$ is mostly made of the hydrophobic DBA moieties, whereas the Pd atoms are accessible mostly from the region observed in the top view.

The formation of hexagonal platelets and rods can be explained by considering the effect of the anisotropic surface tension of growing crystals shaped as hexagonal prisms of height $h$ and side $r$. The favored shape is determined by the relative magnitude of the surface tension $\gamma$ of the top ($\gamma_{\text{top}}$) and the side ($\gamma_{\text{side}}$) of the hexagonal prism. For example, if $\gamma_{\text{side}} < \gamma_{\text{top}}$, the rod morphology will be favored as is observed for precipitation of Pd$_2$(DBA)$_3$ from solution in greater than 70 vol % THF. This result is likely caused by the fact that the exposed hydrophobic side of Pd$_2$(DBA)$_3$ has a lower surface tension in THF than in water.

While hexagonal and rodlike particle formation can be explained on the basis of differences in the surface tension in equilibrated systems, the formation of a minority of cubic particles may be due to kinetic trapping. Evidence for limited kinetic trapping can be found in Figure 2, which shows that some of the features are actually hybrids of cubic and hexagonal shapes. When Pd$_2$(DBA)$_3$ crystals are formed on a surface, interfacial effects may also play a role as shown in Figure 6. The ring form of the drying sessile drop shown in Figure 5 of ref 26 and Figure 4 of this study is consistent with a drying process dominated by convective flow. The darker red color of the droplet rim observed by OM of Figure 4 clearly indicated that a higher concentration of Pd$_2$(DBA)$_3$ was present near the periphery of the drop than in the center. The starlike features, which most closely resemble snow crystals, were formed near the rim. Evaporation started from the center of the droplet and resulted in a higher degree of reagent saturation in the rim of the drop.

Recently, PbS nanocrystals with a cubic rock salt crystal structure have been synthesized in a variety of shapes that closely resemble those reported here for Pd$_2$(DBA)$_3$ crystals. Shape control was achieved for PbS crystals using twin-tail cationic surfactants of varying hydrophobicity. Cubes and hexagonal platelets were observed when high concentrations of the most hydrophobic surfactants were used, whereas stars and leaf-shaped particles were obtained mostly with the least hydrophobic concentration of citrate ions in solution. Citrate ions are hypothesized to specifically adsorb on the (100) crystalline surface of ZnO, which inhibits longitudinal growth of rods and promotes the growth of plates.  

While hexagonal and rodlike particle formation can be explained on the basis of differences in the surface tension in equilibrated systems, the formation of a minority of cubic particles may be due to kinetic trapping. Evidence for limited kinetic trapping can be found in Figure 2, which shows that some of the features are actually hybrids of cubic and hexagonal shapes. When Pd$_2$(DBA)$_3$ crystals are formed on a surface, interfacial effects may also play a role as shown in Figure 6. The ring form of the drying sessile drop shown in Figure 5 of ref 26 and Figure 4 of this study is consistent with a drying process dominated by convective flow. The darker red color of the droplet rim observed by OM of Figure 4 clearly indicated that a higher concentration of Pd$_2$(DBA)$_3$ was present near the periphery of the drop than in the center. The starlike features, which most closely resemble snow crystals, were formed near the rim. Evaporation started from the center of the droplet and resulted in a higher degree of reagent saturation in the rim of the drop. This may have led to kinetic trapping of starlike features with hexagonal symmetry analogous to the kinetic trapping of snow crystals in a cloud. The dominant hexagonal platelet form in the center of the drop is consistent with an equilibrium drying process in which the surface tension of the molecular aggregate involved both the interaction with the binary solvent system and that with the surface during its formation: the surface of the platelet has a larger interfacial contact area with the substrate compared to that of a rod of equivalent volume.

The structure of Pd$_2$(DBA)$_3$ molecular crystals is a distorted trigonal structure. The molecular origin of this crystalline structure can be seen in Figure 7. Experimental electron diffraction data on Pd$_2$(DBA)$_3$ hexagons are consistent with a trigonal unit cell that adopts a hexagonal plate crystal habit. In the THF/H$_2$O binary solvent system, the ratio of THF to H$_2$O seems to play a role for the shape control of Pd$_2$(DBA)$_3$ particles similar to that of the surfactants for PbS structures. This conclusion is depicted in Figure 8, which shows the representative Pd$_2$(DBA)$_3$ molecular crystal shapes with the corresponding percentage of THF. Similar hexagonal plates, rods, and dendritic crystals are also formed when water freezes. The shape of ice crystals has fascinated scholars for years and has been determined to be due to interplay of temperature, pressure, and humidity. In THF/H$_2$O binary mixtures, the THF and water vapor pressure and precursor solubility are the physical parameters that determine the shape of Pd$_2$(DBA)$_3$ crystals.

**Conclusion**

We have observed distinct changes in the morphology of Pd$_2$(DBA)$_3$ molecular crystals, which are attributable to differences in the solvent surface tension in binary solutions of THF and water or on a surface. Crystal growth can be related to the Pd$_2$(DBA)$_3$ molecular structure, which presents a long hydrophobic face of dibenzylideneacetone and a cap that has greater interaction with water due to the exposure of the Pd atom. As a result of varying the solvent concentrations of binary THF/H$_2$O solutions, it was found that hexagonal plates and rods were the most frequent morphologies observed to form in binary solutions, and their relative concentrations could be tuned depending on the THF/H$_2$O ratio. Cubes were also observed, but represented a minority structure. When a droplet of Pd$_2$(DBA)$_3$ solution was cast on a surface, hexagonal platelets dominated the morphology of Pd$_2$(DBA)$_3$ aggregates and crystals can be used to control the shape on the length scale from nanometers to micrometers.

**Materials and Methods**

**Sample Preparation.** The Pd$_2$(DBA)$_3$ reagent powder (STREM, lot no. A4805106) was used as received and unpurified. A 14.65 mg sample was dissolved in 2 mL of tetrahydrofuran (THF; from Fischer, distilled prior to use) to produce 8 mM solutions of Pd$_2$(DBA)$_3$. This solution was added to variable amounts of water and THF to create 400 µM Pd$_2$(DBA)$_3$ solutions and resulted in suspensions of Pd$_2$(DBA)$_3$ in binary solutions with 30 vol % THF/H$_2$O, 50 vol % THF/H$_2$O, 70 vol % THF/H$_2$O, and 100 vol % THF. These solutions were then cast and allowed to dry in ambient atmosphere onto indium tin oxide (ITO; Delta Technologies), lacey carbon TEM grids (Ted Pella part no. 01883), Formvar-coated TEM grids (Ted Pella part no. 01820) or bare Au. More in-depth sample preparation and observations of the solution turbidity and precipitates formed after addition of Pd$_2$(DBA)$_3$ were reported previously.

**Optical Microscopy.** A Nikon SMZ-10 stereo microscope equipped with a Sony DCR-PC101 miniDV camera was employed for capturing low magnification (2–40×) images of the solvent cast droplets. For magnifications between 50× and 500× a Nikon Eclipse upright microscope was used, and the micrographs were captured digitally with the Nikon DXM1200 camera. The OM microscope was calibrated with a standard calibration grating with 0.1 mm spacing per division.
**Scanning Electron Microscopy.** A JEOL 6400F field emission SEM instrument, capable of 1–2 nm spatial resolution at 30 kV and 3–5 nm at 5 kV was used for imaging at magnifications between 250× and 100000×. It was equipped with an Everhart-Thornley secondary electron (SE) detector and Link energy-dispersive spectrometer operated by a 4π controller. Imaging was done in SE mode at a working distance of 12 mm and beam energy of 2.5 kV. The samples were uncoated, and low-voltage imaging was chosen to minimize sample charging. The SEM instrument was equipped with a digital camera and Digital Micrograph 1.6 to capture SE micrographs with a pixel resolution of 1024 × 768. Another SEM instrument, a Hitachi S-3200N, equipped with a Robinson back-scattered electron (BSE) detector (for atomic number contrast imaging) and an Oxford Link ISIS EDS instrument (for quantitative chemical analysis and X-ray dot maps) was also employed in this study. The operating voltage for imaging and chemical analysis was 20 kV, and to eliminate sample charging, the variable pressure of the sample chamber was set to 60 mbar. Digital image acquisition of BSE micrographs was accomplished by using the Oxford Link ISIS software. The ITO was used as a substrate for solvent evaporation of 100% THF solutions because of its conductivity, which makes it possible to analyze samples with SEM without having to add a conductive coating on the sample. Formvar and bare Au surfaces were also used for observations of shapes and structures resulting from solvent evaporation because both are common TEM and OM substrates.

**Energy-Dispersive Spectroscopy.** Collection of X-ray photons was accomplished with solid-state crystal detectors created from Li-drifted Si. All X-ray spectra were acquired under the same beam conditions at a real-time duration of 100 s. The X-ray spectra used for qualitative chemical analysis collected on the JEOL 6400F were captured using a beam voltage of 10 kV and processed with Desktop Spectrum Analyzer (DTSA) developed by the National Institute of Standards and Technology (NIST) and installed on an Apple Mac computer. The DTSA freeware can be downloaded at www.ctsl.nist.gov/div837/Division/outputs/DTSA/DTSA.htm and was developed for Apple Macintosh OS9 and earlier. X-ray dot maps were obtained and quantitative chemical analysis was performed with the Oxford Link ISIS EDS instrument attached to the Hitachi S-3200N operated at a working distance of 15 mm (optimal for the detector geometry) and at a beam energy of 20 kV. X-ray energy calibration for k-ratio determination (X-ray peak intensity comparison) was performed according to standard operating procedures using a Cu metal standard and collecting the emitted Kα radiation (8.047 eV). Spectrum processing for quantitative analysis and atom percentage determination were performed using the Link ISIS software, which contained algorithms for atomic number (Z), absorption (A), and fluorescence (F) corrections.

**Low-Voltage Scanning Transmission Electron Microscopy.** A Hitachi S5500 low-voltage STEM instrument (Pleasanton, CA) equipped with a cold cathode field emission electron source was capable of 0.4 nm resolution in secondary electron mode when operated at 30 kV. This in-lens field emission STEM instrument was equipped with secondary and backscatter electron detectors with the ability to mix both signals and capture images in a magnification range of 100—2000000×. The microscope was also equipped with a bright field and an adjustable dark field detector, allowing a range of collection angles to be captured for diffraction or z-contrast imaging. Micrographs were captured digitally at scan speed 3 and at a final resolution of 1280 × 960 with 100 pixels/cm. Chemical analysis in the microscope was performed with an Oxford INCA (Oxfordshire, U.K.) energy-dispersive X-ray spectrometer attached to the LV-STEM sample chamber. This X-ray detector utilized a liquid nitrogen cooled 30 mm² Li-drifted Si detector for light and heavy element detection and had a 22° takeoff angle and 129 eV energy resolution at the Mn Kα edge. The X-ray dot maps and spectrum reports were generated using the INCA software.

**High-Resolution Transmission Electron Microscopy.** Conventional bright field imaging, at magnifications between 2000× and 40000×, was accomplished with a Topcon 002B TEM instrument operated at 200 kV equipped with a 30° tilt pole piece and double tilt holder. All micrographs were captured on Kodak electron image film (SO-163). After developing, the resulting TEM film negatives were digitized by an EPSON 4990 photo scanner and saved as grayscale.tif files with 800 dpi resolution. Digital scale bar determination was accomplished by first acquiring micrographs of a diffraction calibration grating (Ted Pella product no. 603) with the line pitch measuring 463 nm. After digitization of the film negative magnification series acquired from the calibration grating, by determination of the number of pixels between grid lines, the resulting micrographs were used to determine the number of nanometers per pixel at each magnification chosen. For example, for a magnification of 2400× the average line pitch of 10 squares measured 332 pixels. This value was then used as the dividend for 4630 nm, the calibrated value, and the resulting scale bar constant was 13.95 nm/pixel.

Electron beam analysis with fast electrons can cause temporary or permanent changes to occur in the sampled volume due to both elastic and inelastic scattering of incident electrons. Inelastic scattering can cause ionization damage, changes to the internal structure, and surface hydrocarbon contamination. In crystalline materials of atomic numbers greater than ∼40 the energy required to “knock” an atom from its position in the lattice was well above the incident electron energy used in this study. However, for carbon-based materials (except diamond) multiple inelastic scattering events from 200 keV electrons are above the ∼140 keV limit, which could induce irradiation artifacts. Low-voltage STEM minimized imaging artifacts created by electron beam damage by allowing 30 kV observation and chemical analysis of the Pd₂(DBA)₃ structures. The combined utilization of 10 and 20 kV FESEM/EDS, 30 kV LV-STEM/EDS, and 80 and 200 kV TEM/STEM/EELS improved flexibility for applying the correct “tool” for the analysis needed to identify various organic and inorganic structures on the nanoscale.

**Acknowledgment.** We thank Dr. D. Batchelor, C. Mooney, and R. Garcia of North Carolina State University’s (NCSU’s) Analytical Instrumentation Facility and Dr. T. Rawdanowicz and A. Newell of NCSU’s Atomic Resolution Electron Microscopy Center. Dr. P. E. Russell, Department of Physics & Astronomy, Appalachian State University, provided access to the LV-STEM/EDS system, which facilitated high-throughput nanoanalysis of the samples. This work was supported by the W. M. Keck Foundation.

LA801039J