Eletter Concerning “RNA-Mediated Metal-Metal Bond Formation in the Synthesis of Hexagonal Palladium Nanoparticles”

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The article entitled “RNA-Mediated Metal-metal Bond Formation in the Synthesis of Palladium Nanoparticles” reports the formation of crystalline Pd hexagonal particles mediated by pyridine-modified RNA cognates in an aqueous solution using Pd2(DBA)3 as the precursor (1). The role of RNA in this process is unclear since Pd2(DBA)3 is completely insoluble in water (3,4). The reported control experiment using poly(vinylpyridine) is not possible since neither poly(2-vinylpyridine) nor poly(4-vinylpyridine) is soluble in water. The authors referred to selected area electron diffraction (SAD) data in (1), which was only recently published in the Ph.D. dissertation of Dr. Gugliotti, released in August, 2007 (2). These SAD data do not support the hypothesis that the hexagons are “crystalline Pd” as claimed in (1). The dissertation states that the ~5nm Pd regions observed by lattice fringes in the “palladium containing” hexagons arose from “radiation damage” in the 200 kV beam. The lattice parameter was reported to be 10.9 Å for the hexagons in an 80 kV beam ((2), p.52). The accepted value for Pd is 3.89 Å (5-12). The reported value is closer to that of the precursor Pd2(DBA)3 (13) The proof for metal-metal bond formation is lacking. The logical explanation is that the authors of (1) were studying insoluble aggregates of Pd2(DBA)3, which form spontaneously under their experimental conditions. (14)

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References
3. MSDS, (52409-22-0).
Response to E-Letter Concerning Study by Gugliotti et al.

The E-Letter by Leonard et al. (1) presents an incomplete view of the chemistry of Pd$_2$(DBA)$_3$ and the role of RNA in nanocrystals grown from aqueous solutions of Pd$_2$(DBA)$_3$. Citing a materials safety data sheet (MSDS), the authors purport that Pd$_2$(DBA)$_3$ is "completely insoluble" in water (2). Concentrations and conditions under which Pd$_2$(DBA)$_3$ may be dissolved in water have been reported by others (3). In that work, Pd$_2$(DBA)$_3$ was made soluble in aqueous solutions at a concentration of approximately 200 M (similar to that used in our work) by adding a small % v/v of the cosolvent triton (0.05 %). We have used a similar strategy in our work (4); our aqueous solutions typically contain 5-10 % organic solvent (THF, DMSO, DMA, ethanol, etc.). As can be observed in Fig. 1, such solutions are free from the gross precipitates reported by Leonard et al.

![Fig 1. Photograph of a 400 μM solution of Pd$_2$DBA$_3$ in a 90% H$_2$O/10 % THF mixture.](image)
Leonard et al. contends that Gugliotti [(5); a Ph.D. dissertation] concluded that lattice fringes observed in her hexagonal particles arose from radiation damage. Actually Gugliotti (5) only provides a statement of caution (not a conclusion) under which any high-resolution electron microscope (HR-TEM) image should be viewed: "Lattice fringes are observed in the HR-TEM image, albeit not uniformly throughout the particle surface, but rather present in localized areas. These areas may be a result of the particle surface being heated by the electron beam and thus forming domains of crystalline material."

Finally, Leonard et al. picks one of several electron diffraction (ED) analyses in (5) and concludes that one reported lattice spacing of 10.9 Å (calculated based upon a fcc unit cell), is "closer" to that for Pd₂(DBA)₃. Our electron diffraction analysis of material formed in the presence of the cycle 8 RNA pool obtained prior to (4) contained reflections that could be indexed to bulk fcc Pd (Fig. 2). Experiments performed in the intervening 4 years have produced patterns that match well with Pd and PdO, and still others that do not to our knowledge correspond well with any known phase of Pd, PdO, or Pd₂DBA₃. These are exciting discoveries indicating that other forms of Pd-containing particles can be produced by these RNA sequences. Our observations have precedent. Scott et al. (6) has examined Pd nanoparticles synthesized within dendrimers and shown that the Pd had oxidized in the presence of O₂. Xiong et al. (7) reported the spontaneous conversion of Pd nanoparticles to PdO@Pd core-shell particles. Many additional reports can be found dating back to the 1930s pertaining to metal nanoparticles and thin films with expanded lattices or lattices that do not conform to the normal bulk fcc structure (e.g., hcp). (8-12) A lattice distortion of as much as 15% has been observed for Pd particles compared to bulk fcc Pd due to dissolved oxygen in the lattice, twinning, or pseudomorphism (13). Similar observations have been made in gold nanoparticles (14-15).

**Fig. 2.** Electron diffraction from hexagonal particles synthesized in the presence of the cycle 8 of the RNA pool of sequences selected as described in (4).

Thus, while the mechanistic details and atomic-level structure of nanocrystals synthesized in the presence of different RNA sequences are still uncertain, studies have shown that solutions may be prepared without spontaneous Pd₂(DBA)₃ precipitation and that RNA
mediates the formation of nanocrystals with morphologies that depend upon RNA primary sequence.

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References and Notes


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