

Synthesis, Characterization, Reactivity, and Electrochemistry of Palladium Monolayer Protected Clusters

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This paper describes the synthesis, characterization, reactivity, and electrochemistry of monolayer-protected clusters (MPCs) of palladium that are passivated by monolayers of hexanethiolate or dodecanethiolate ligands. The synthetic product is sensitive to the thiol:Pd ratio used in the reaction mixture: a 1:1 ratio or smaller ratio produces metallic Pd(0) clusters that are similar to analogously prepared Au MPCs, but much more ligand-rich, whereas $\geq 2:1$ ratios yield a very different material that is either extremely small Pd(0) clusters or a form of Pd(II) alkanethiolate complex. The monolayers of the metallic Pd(0) MPCs that are synthesized using small thiol:Pd ratios can be modified by ligand place-exchange and coupling reactions. The electrochemistry of the Pd core and of electroactive labels attached to the alkanethiolate ligands was studied. Quantized double-layer core charging is seen but less clearly than with Au MPCs. The Pd nanoparticles were examined using NMR, FTIR, UV-vis, TEM, TGA, and elemental analysis.

Introduction

The fabrication of materials with nanometer-sized dimensions is an important area of research. Nanomaterials composed of, for example, carbon,¹ polymers,² semiconductors,³ and metals⁴ have been synthesized and studied intensely. Metal nanoclusters and colloids are currently receiving attention because of their interesting optical⁵ and electronic⁶ properties. The control of shape (rods,⁷ wires,⁸ and cubes⁹) and size has been demonstrated with a wide range of metals and synthetic procedures.

The metal particles are often stable only as suspensions and tend to irreversibly aggregate over time or when removed from solvent, which limits both their manipulation and the range of analytical tools that can be applied to them.

Stabilization of metal clusters by ligand coatings can, however, enable further manipulation, control solubility characterization, and facilitate their analysis. Brust et al.,¹⁰ combining techniques used in traditional colloid science with those of self-assembly, synthesized 1–3 nm diameter ligand-stabilized Au clusters by protecting the Au with a self-assembled monolayer of dodecanethiolate ligands. These monolayer protected clusters (MPCs) are easy to prepare and handle and can be characterized by the same analytical tools that are used for the analysis of small molecules. A chief enabling attribute of the monolayer protection is the ability to isolate the MPCs as solid, solvent-free powders, without fusion or aggregation of the Au core. The solids can typically be redissolved, unchanged, in nonpolar solvents like toluene and dichloromethane. Research on MPCs since the Brust report¹¹ has been reviewed.¹¹

Alkanethiolate-protected Au MPCs are prepared in toluene by reacting AuCl_4^- with alkanethiols $(\text{HS}(\text{CH}_2)_n\text{CH}_3, n = 3-23)$ and then with BH_4^- . The resulting Au core size decreases with increasing thiol:Au reaction mole ratio.¹² The alkanethiolate MPCs have been studied using a variety of analytical techniques. The nature of the alkanethiolate ligands has been studied with FTIR,¹³

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NMR,^{6,12a,14} and DSC^{12a,14b,d} and that of the Au–S bond with XPS,^{12a} TGA,^{12a,14d} and thermal desorption mass spectrometry.^{12a} The dimensions of the Au core have been studied with TEM,^{12a} XRD,^{5c,12b} and mass spectrometry,^{5c,15} optical properties with absorption spectroscopy,^{5,12a} and electronic properties with electrochemistry^{16,17} and conductivity measurements.⁶ Au alkanethiolate MPCs can be functionalized using ligand place-exchange^{18,19} and organic coupling reactions;²⁰ the ability to chemically manipulate MPCs to produce chemically modified nanoparticles is an important feature that enhances possibilities for their use in technological applications. The double-layer charging of the Au core^{16,17,19b,e} and electrochemistry of electroactive components of the MPC monolayer¹⁹ has been studied for solution phase^{16,19} and surface-attached Au MPCs.¹⁷ The double-layer charging of Au MPCs with <2 nm diameter, monodisperse cores occurs in discrete one-electron steps.¹⁶ Quantized double-layer charging is one of the more interesting properties of small MPCs and may have usefulness in nanometer-scale circuitry.²¹

It is natural to inquire into the extent, qualitatively and quantitatively, that other metals prepared as MPCs by the Brust reaction¹⁰ exhibit compositions, reactivities, electrochemistry, and other properties that are similar to or differ from those of Au MPCs. There have been a few (some preliminary) synthesis and characterization studies of Ag,^{22a–c} Pd,^{22c–e} Ir,^{22e} Pt,^{22f} and alloy MPCs^{22g} and no detailed synthetic, reactivity, or electrochemical studies. In this paper we present a more complete description of the synthesis, characterization, reactivity, and electrochemistry of Pd MPCs, in comparison to Au MPCs. Pd was chosen because it is a technologically important metal, and we observed some unexpected behavior in early

experiments. Pd clusters and colloids have been prepared previously by chemical,^{22c,d,23} H₂,²⁴ and sonochemical²⁵ reduction in the presence of thiols,^{22c–e} polymers,^{24a,c,25} dendrimers,²³ and other ligands.^{24b}

Experimental Section

Chemicals. Dodecanethiol (C12), hexanethiol (C6), 11-mercapotundecanol (C11OH), tetraoctylammonium bromide (Oct₄NBr), sodium borohydride (NaBH₄), potassium tetrachloropalladate (K₂PdCl₄), palladium acetate (PdAc₂), dimethylaminopyridine (DMAP), and ferroceneacetic acid (FcCH₂COOH) were purchased from Aldrich, benzoic acid (BA) from Fischer, dicyclohexylcarbodiimide (DCC) from Sigma, tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) from Fluka, dichloromethane (CH₂Cl₂) and toluene from Mallinckrodt, and tetrahydrofuran (THF) from J.T. Baker. All were used as received.

Hexanethiolate Pd MPC Synthesis. For a 1:1 thiol/metal mole ratio reaction, K₂PdCl₄ (0.30 g) dissolved in 50 mL of H₂O was added with stirring to Oct₄NBr (0.75 g) dissolved in 250 mL of toluene in a 500 mL Erlenmeyer flask. The toluene phase turned deep red as the PdCl₄²⁻ phase-transferred into it, presumably as (Oct₄N⁺)₂PdCl₄²⁻. The solution was stirred 15–20 min, the H₂O layer removed, and 130 μL of hexanethiol (C6) added, causing a change to a lighter orange-red color. After cooling the solution in an ice bath for 30 min, NaBH₄ (0.35 g) dissolved in 20 mL of H₂O was added, whereupon the solution quickly (30–60 s) turned black, indicating the formation of clusters. A mole ratio of 1:1.5:10 was used for K₂PdCl₄:Oct₄NBr:NaBH₄; that for thiol:metal was varied. The solution was allowed to stir overnight, remaining black when a 2:1, 1:1, or 0.5:1 C6:Pd ratio was used. These syntheses are referred to as 2x, 1x, and 1/2x 0 °C overnight stir preparations, respectively. Discarding the H₂O layer and removing toluene under vacuum yielded a black solid from the 1x and 1/2x preparations and a black oil from the 2x preparation. The product was collected on a ground glass frit and washed with 400–500 mL of acetonitrile for the 1x and 1/2x preparations. The 2x preparation material was washed with acetonitrile in a round-bottom flask by sonicating and decanting off the solvent. For the 1x and 1/2x preparations, the portion of the product that was soluble in CH₂Cl₂ was obtained by pouring CH₂Cl₂ through the frit, collecting the soluble material, and removing the solvent under vacuum.

In a preparation using a 3:1 C6:Pd mole ratio, the reaction was not cooled in an ice bath and was stirred for only 1 h after NaBH₄ was added. In this synthesis, termed a 3x preparation, the reaction solution again quickly turned black but then gradually reverted to its original orange-red color. The material isolated was a red oil. The product was cleaned as in the 2x preparation.

Dodecanethiolate Pd MPC Synthesis. The synthesis of Pd MPCs with dodecanethiolate (C12) ligands was conducted as above except that the thiol:Pd mixture was not cooled, the NaBH₄ reducing agent was added at room temperature either immediately or after 20–30 min (causing the solution to turn black within 30–60 s), and the reaction mixture was stirred for approximately 1 h. The product solution was black when 0.5:1 or 1:1 C12:Pd ratios were used, but the initially black product solution reverted to a light orange-red color when a 7:1 C12:Pd ratio was employed. These syntheses are referred to as 1/2x, 1x, and 7x room temperature 1 h stir preparations, respectively. The water layer was discarded and the toluene removed under vacuum, producing a black solid product for the 1/2x and 1x preparations and an orange-red solid for the 7x preparation. The products were collected on a ground glass frit and washed with 300 mL of ethanol followed by 150 mL of acetone. The CH₂-

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Cl₂-soluble portion of the product was obtained by pouring CH₂-Cl₂ through the frit, collecting the solution, and removing the solvent under vacuum.

Ligand Place-Exchange and Coupling Reactions. Place exchange^{18,19} of 11-mercaptoundecanol (C11OH) thiolate ligands for C12 ligands on Pd C12-MPCs prepared using low C12:Pd ratios was performed by codissolving the Pd C12-MPC and C11OH thiol in 100 mL of THF and stirring for 4–5 days. The solvent was removed under vacuum, and the solid MPC product was washed with ethanol and acetone as above. The mole ratio C12:C11OH on the resulting MPC product was usually about one-half of the mole ratio of Pd C12-MPC to C11OH thiol ligands (feed ratio) in the initial place-exchange solution.

Esterification of Pd C12/C11OH MPCs with benzoic acid (BA) or Fc-CH₂-COOH was accomplished using a variation of previously described procedures.²⁰ The Pd C12/C11OH MPCs, benzoic acid (or Fc-CH₂-COOH), DCC, and DMAP were codissolved in 100 mL of THF and stirred for 24 h. The mole ratio of MPC:(BA or Fc-CH₂-COOH):DCC:DMAP was 1:20:20:20. The solvent was removed under vacuum and the MPC purified by washing copiously with ethanol and acetone.

Measurements. ¹H nuclear magnetic resonance (NMR) spectroscopy was done at 200 MHz on a Bruker AC200 spectrometer in C₆D₆ or CD₂Cl₂ solutions. FTIR spectra were taken of films dropcast from CH₂Cl₂ solutions onto a KBr salt plate, using a Bio-Rad 6000 spectrometer. UV-vis spectra in hexane solutions were taken with an ATI UNICAM spectrometer. Samples were prepared for transmission electron microscopy (TEM) by dropcasting a dilute (1 mg/mL) hexane solution of Pd MPCs onto standard carbon-coated (200–300 Å) 600 mesh copper grids. The electron microscope was a Phillips CM12 operating at 120 keV. The average cluster diameter was obtained using Scion Image software by averaging at least 500 individual clusters. Thermogravimetric analysis (TGA) was performed with a Seiko RTG 220 robotic TGA.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were done with a Bioanalytical Systems model BAS100B instrument. Measurements were collected with a Pt disk working electrode (0.002 83 cm²), Ag wire quasi-reference electrode, Pt wire counter electrode, in 0.10 to 0.15 M Bu₄NPF₆/CH₂Cl₂ MPC solutions, at a scan rate of 20 or 25 mV/s for DPV and at various scan rates for CV.

Elemental analysis was performed by Galbraith Laboratories.

Results and Discussion

Spectroscopic Characterization. The Experimental Section noted that the color of the isolated nanoparticle synthesis products differed strongly according to the mole ratio of thiol:Pd used in the synthesis reaction. The 3x and 7x preparations (3:1 hexanethiol/Pd and 7:1 dodecanethiol:Pd, respectively) yield an orange-reddish material whose solutions have the same color, whereas 1x and 1/2x preparations with C6 and C12 thiols gave black powders whose solutions are optically dense (black). The C6 2x preparation gave a black oily material whose solutions are much less optically dense. The colorations of the 1/2x and 1x preparations resemble that of MPCs having Au as the core metal. Spectroscopic NMR and UV-vis evidence confirm that a qualitative difference exists between the synthetic products.

Proton nuclear magnetic resonance (NMR) spectra are shown in Figures 1 and 2 for products obtained at different thiol:Pd mole ratios using C6 and C12 thiols, respectively. In the 1x preparations, the methyl and methylene resonances at 0.9 and 1.3 ppm, respectively, are much broader than those of alkanethiol itself, and the α- and β-CH₂ protons to the S-Pd interface are not observed. The broadening characteristic is just as previously observed for Au MPCs, where it has been attributed to combinations of spin-spin relaxation (T₂) broadening, dipolar broadening,^{12a} and a distribution of chemical shifts.¹⁴ The NMR spectral line widths observed for Au MPCs narrow when larger thiol:Au ratios are used in their

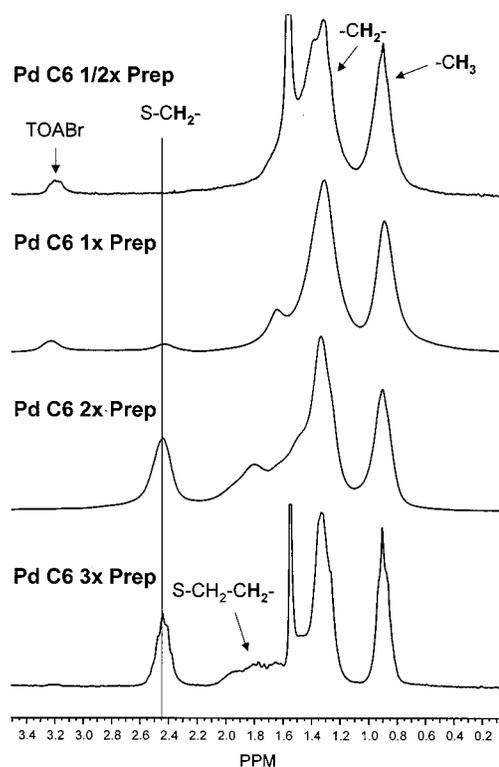


Figure 1. ¹H NMR spectra obtained in CD₂Cl₂ of Pd C6 MPCs synthesized with thiol:Pd ratios from top to bottom of 0.5:1 (1/2x), 1:1 (1x), 2:1 (2x), and 3:1 (3x). The vertical line indicates the position of the α-CH₂ protons to the S-Pd interface. The peak near 3.2 ppm for the 1/2x and 1x preparations corresponds to CH₂ protons adjacent to the nitrogen of tetraoctylammonium bromide (Oct₄NBr) that was incompletely removed from the sample. The sharp peak at 1.5 ppm corresponds to H₂O.

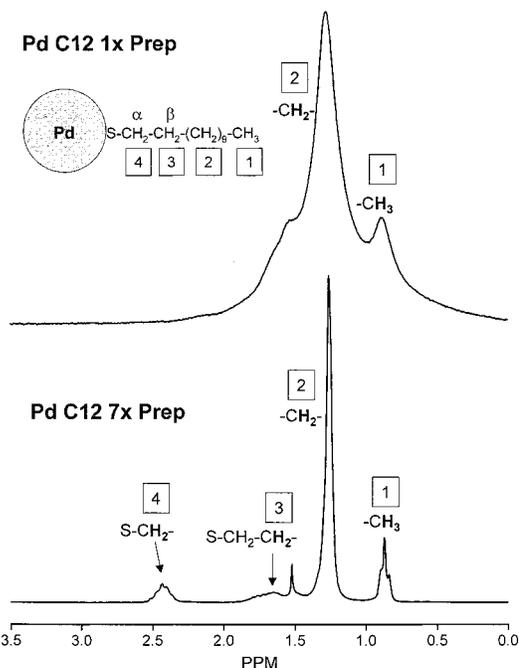


Figure 2. ¹H NMR spectra obtained in CD₂Cl₂ of Pd C12 MPCs synthesized using thiol:Pd ratios from top to bottom of 1:1 (1x), and 7:1 (7x).

synthesis ratios;^{12a} the larger ratios produce MPCs with smaller Au cores. Narrowing is also seen in the spectral line widths of 3x and 7x Pd preparations in Figures 1 and 2, respectively; the narrowing is more pronounced than known^{12a} for Au MPCs. Further, resonances for the α-

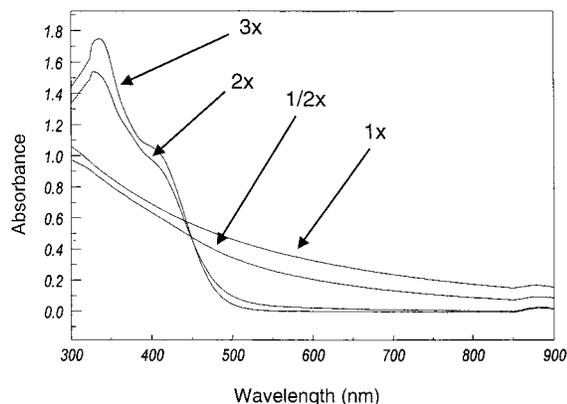


Figure 3. UV-vis spectra in hexane solutions of Pd C6 MPCs synthesized using the indicated thiol: Pd ratios. The spectra of the $1/2x$ and $1x$ preparations are consistent with Pd(0) clusters while those of the $2x$ and $3x$ preparations are consistent with a Pd(II) thiolate species.²⁶

and β -CH₂ protons can be seen at 2.45 and 1.8 ppm, respectively, and display multiplet splitting; the α - and β -CH₂ protons, or their splitting, have not been seen for Au MPCs.^{12a,14}

An even more dramatic change with the thiol: Pd synthesis ratio can be seen in electronic spectra (Figure 3) of Pd C6 MPCs; the change is consistent with the NMR results. Spectra of the $1/2x$ and $1x$ preparations resemble those of Au MPCs with small, metal-like cores.^{12a} There is no obvious surface plasmon (SP) band (although one has been reported^{22e} at 302 nm for 2.2 nm core diameter Pd C18 MPCs made in a $3x$ preparation, using a different reducing agent than employed here). In contrast, the spectra of the $2x$ and $3x$ Pd C12 MPC preparations show two absorbance peaks, at ca. 350 and 400 nm, and little absorbance above 500 nm. Two peaks near 350 and 400 nm have been observed before for S-containing Pd(II) complexes that correspond to metal-to-ligand and ligand-to-metal charge-transfer bands, respectively.²⁶ This comparison infers that the $2x$ and $3x$ spectra in Figure 3 correspond to some form of Pd(II) thiolate complex (or oligomer; in light of the NMR evidence) rather than Pd(0) complexes.

MPC Composition. We begin with the materials prepared using the highest thiol: Pd reaction ratios. No discernible nanoparticles could be detected in transmission electron microscopy (TEM) of the orange-red $3x$ C6 and $7x$ C12 preparations. Thermogravimetric analysis (TGA) of the $7x$ C12 preparation gives a 73.4% organic composition. Elemental analysis of that preparation gave the empirical formula PdS_{2.2}C_{26.3}H_{56.2}, which corresponds to a 80.6% organic composition. For comparison, elemental analysis of a Pd(II) dodecanethiolate complex (**1**) prepared by mixing PdCl₄²⁻ with a 7-fold excess of dodecanethiol and stirring for 1 h (no NaBH₄ reductant) gave an empirical formula PdS_{2.1}C_{24.6}H_{53.3}, which corresponds to a 78.1% organic composition. The UV-vis, NMR, and FTIR spectra of **1** are very similar to those of the $7x$ C12 preparation.

There exist a number of reports^{26,27} on Pd(II) thiolate complexes; methods for their preparation are similar to that of **1** above. A crystal structure of Pd(II) alkanethiolates shows that they are cyclic, polynuclear complexes;²⁷

complex **1** is presumed to be a similar polynuclear complex, of the form [Pd(SR)₂]_n. It seems reasonable to propose that the $7x$ C12 preparation described above is also some kind of a polynuclear Pd(II) dodecanethiolate complex, with a similar empirical formula. There are, however, some subtle but definite differences between **1** and the $7x$ C12 MPC preparation. (a) The $7x$ C12 material was more soluble in CH₂Cl₂, (b) of a lighter orange-red color, and (c) not reduced by reexposure to a 10-fold excess of NaBH₄, whereas **1** is reduced by exposure to borohydride. This last point is important by implying a structural stability toward reduction which **1** lacks. Therefore, we believe that the $7x$ C12 preparation, while clearly some kind of Pd(II) thiolate complex, has a different, unknown polynuclear structure. In this connection, it must be recalled that the $7x$ C12 material was prepared by a synthetic route involving *initial* formation of nanoscopic metal clusters, which in time reverted to Pd(II) metal complexes.

We turn next to reaction products obtained at lower thiol: Pd reaction ratios. Average formulas for Au MPCs have previously been established^{12a} by transmission electron microscopic (TEM, gives average core diameter) and thermogravimetric (TGA, gives organic fraction) data, combined with an assumption that the average MPC core will have a closed-shell structure and a truncated octahedral^{12a} core shape. A $1x$ synthesis of a Au C12 MPC gives, for example, an average core diameter of 2.0 nm and average formula of Au₃₁₄(C12)₉₁.^{12a}

TEM images of and TGA experiments on $1/2x$ and $1x$ preparations of Pd C12 MPCs (Figure 4) give average core diameters ca. 3.0 and 2.4 nm and 34.7% and 45.0% organic, respectively. Using the previous approach,^{12a} these data give average formulas of Pd₉₇₆C12₂₇₄ and Pd₄₅₉C12₁₉₈, respectively. On the basis of the TEM dimension alone, formulas of Pd₉₇₆C12₁₈₇ and Pd₄₅₉C12₁₁₄, respectively, would be predicted; i.e., a *much smaller number of ligands* is predicted from the TEM data than is observed from TGA data. Three possible conclusions could be drawn from this comparison. First, the possibility exists that a large population of very small MPCs (which would have a larger percent organic) exists but is not resolved above background in the counting of images in Figure 4 TEM. The small-core population would have to be large enough to change the average core diameters to 2.4 and 1.5 nm for the $1/2x$ and $1x$ preps, respectively, for this explanation to be satisfactory. Second, the Pd clusters may exhibit much larger surface coverages than do the Au analogues. The surface coverages for the above average formula would be 70% and 85%, respectively. Such large coverages seem implausible, especially given that the coverage is 48–50% for dodecanethiolate on Au MPCs of similar core sizes to the Pd MPCs studied here.^{12a} A third rationale of the experimental results is that the Pd nanoparticles are covered not with a monolayer of simply thiolate ligands but with structures that include Pd(II) thiolate ring and/or chain structures; i.e., the Pd MPCs are hybrids of metal clusters with protecting surface coatings of Pd(II) thiolate complexes. Such structures would have a larger percent organic composition yet a metal-like Pd(0) core capable of ligand exchange and double-layer charging, properties which will be demonstrated below. Whichever is the case, the TEM/TGA results indicate that the Pd C12 MPC materials obtained at low thiol: Pd ratios, while superficially similar to Au MPCs, possess different, possibly structural, characteristics.

TEM images of C6 Pd MPCs are shown in Figure 5. The average core diameters obtained from these images are, for the $1/2x$, $1x$, and $2x$ preparations, 3.0, 2.2, and 1.6 nm, respectively. The core size decreases with increasing thiol:

(26) (a) Perlepes, S. P.; Jacobs, P.; Desseyn, H. O.; Tsangaris, J. M. *Spectrochim. Acta* **1987**, *8*, 1007. (b) Grapperhaus, C. A.; Maguire, M. J.; Tuntulani, T.; Darensbourg, M. Y. *Inorg. Chem.* **1997**, *36*, 1860.

(27) (a) Mann, F. G.; Purdie, D. *J. Chem. Soc.* **1935**, 1549. (b) Hayter, R. G.; Humiec, F. S. *J. Inorg. Nucl. Chem.* **1964**, *26*, 807. (c) Kunchar, N. R. *Acta Crystallogr.* **1968**, *B24*, 1623.

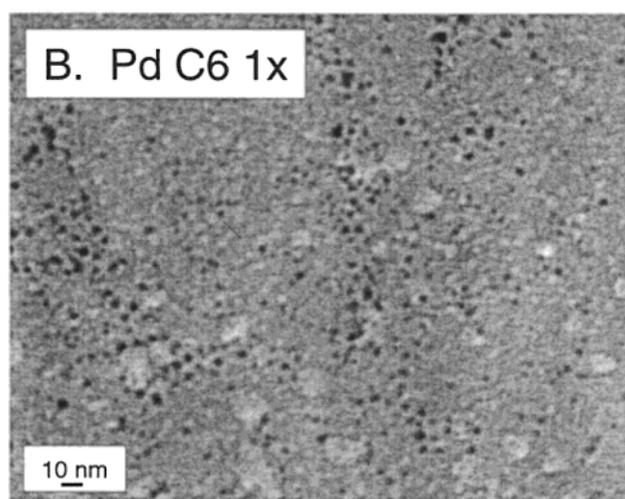
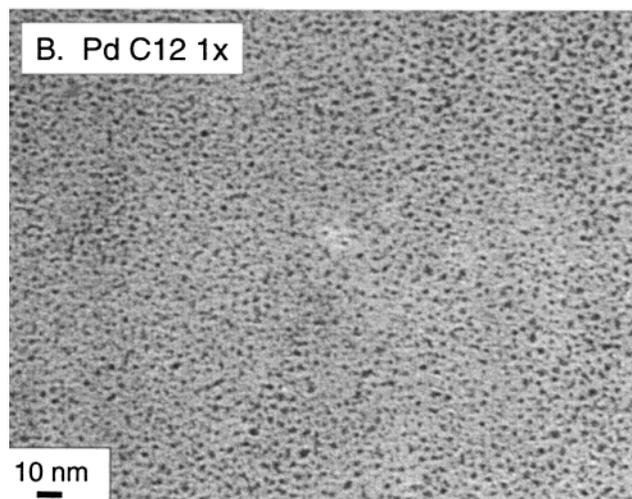
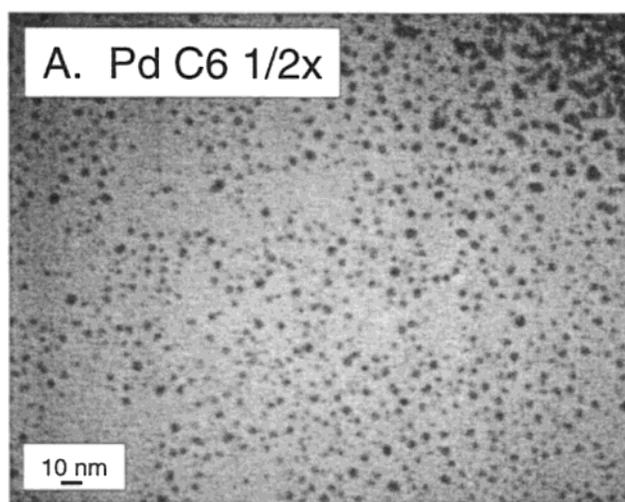
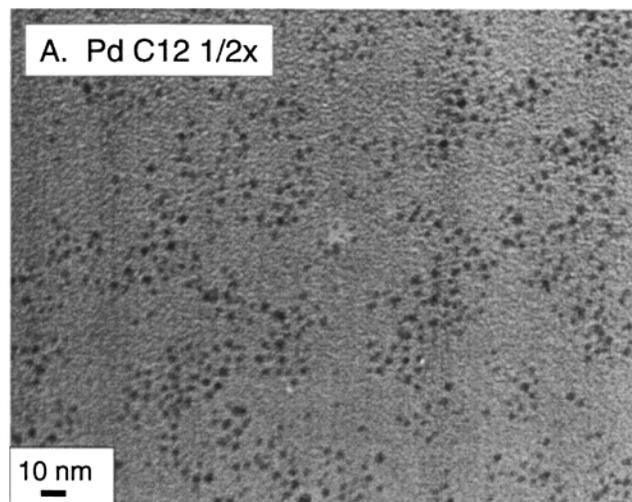


Figure 4. TEM images of dropcast films of (A) Pd C12 $1/2x$ and (B) Pd C12 1x MPC preparations. The average diameters are 3.0 and 2.4 nm, and approximate compositions are Pd₉₇₆C12₂₇₄ and Pd₄₅₉C12₁₉₈, respectively.

Pd ratio and is very similar to Pd C12 MPCs of the same preparation. Considering that the NMR and UV-vis of the 2x and 3x C6 preparations are similar to one another, we were surprised to observe some extremely small clusters in the TEM image of the Pd C6 2x preparation. The C6 2x synthesis appears to produce a mixture of Pd(0) and Pd(II) species. This is important in that the C6 2x reaction may be a crossover point of factors determining stability of MPCs vs Pd(II) alkanethiolate complexes. Its understanding may be key to understanding how to controllably prepare small clusters in high yield without forming the oxidized species.

It was noted in the Experimental Section that, in reactions of PdCl₄²⁻ with large excesses of thiols, the reaction mixture initially turns black upon reduction with NaBH₄ but then reverts back to the initial orange-red color after an hour of stirring. Chen et al.^{22d} have described this effect and proposed that initially formed Pd clusters decompose back into extremely fine particles or oxidized ionic complexes.^{22d} This effect is reminiscent of the report of etching by Whetten et al. of Au clusters formed in the presence of excess dodecanethiol.²⁸ While the exact etching mechanism is still unclear,²⁸ the same phenomenon may well apply to the Pd system.

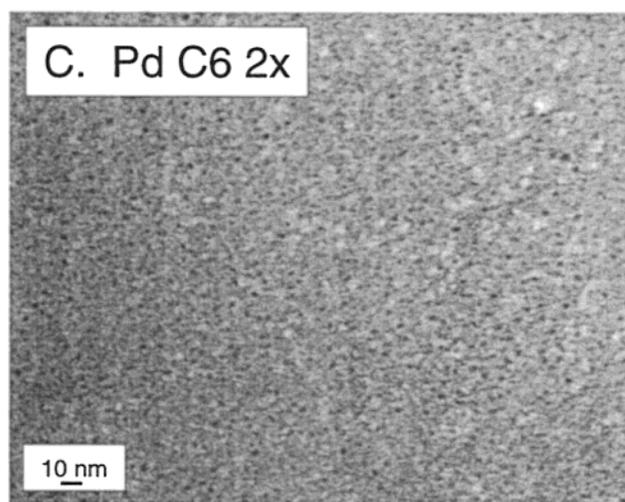


Figure 5. TEM images of dropcast films of (A) Pd C6 $1/2x$ (B) Pd C6 1x and (C) Pd C6 2x MPC preparations. The average diameters are 3.0, 2.2, and 1.6 nm, respectively. No clusters were observed in images of the Pd C6 3x preparation.

The fact that etching occurs with large excesses of thiol shows that thiol is the most important ingredient; however, the large amounts of bromide, chloride, and disulfide present are potentially active components. We ruled out chloride being a major factor by performing a C12 3x reaction using Pd(II) acetate instead of PdCl₄²⁻. The initially black product solution again reverted to an

(28) Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **1999**, *103*, 9394.

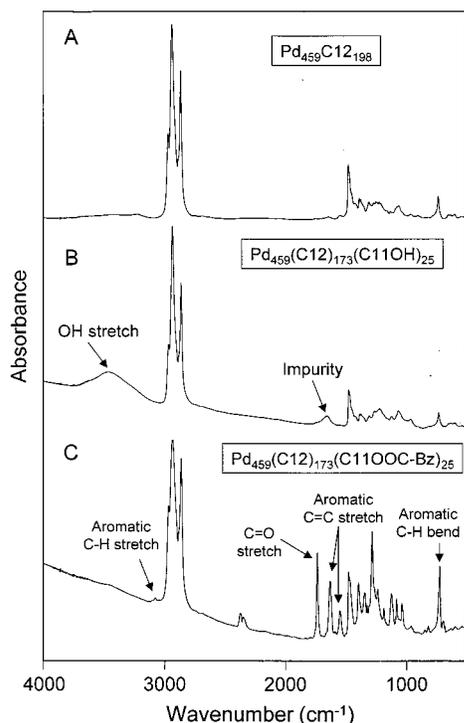


Figure 6. FTIR spectra of films (dropcast on a KBr salt plate) of (A) Pd C12 1x MPCs, (B) Pd C12 MPCs place exchanged with C11OH thiol, and (C) Pd C12/C11OH MPCs esterified with benzoic acid. Approximate compositions are shown in the figure.

orange-red solution within an hour. Bromide from the Oct₄NBr, which is used to phase transfer BH₄⁻ into the toluene phase, was still present, however. Ulman and co-workers²² performed the reaction under halide-free conditions by reducing Pd(acetate) trimer in THF with superhydride in the presence of octadecanethiol (C18).^{22e} They successfully prepared Pd MPCs using a 3x thiol: Pd ratio; there was no mention of an orange-red product material. A further significant point is that Pd MPCs prepared using 1/2x and 1x thiol: Pd ratios, and subsequently isolated and purified, are not etched by dissolving them in solution containing a 7x excess of thiol or when chloride, Oct₄NBr, and NaBH₄ are also added. More evidence needs to be gathered before these interesting Pd materials, which behave quite differently than those obtained using Au, are fully understood. No evidence of oxidized Au complexes in isolate, purified Au MPCs has been described.

Reactivity. Pd C12 MPCs prepared with a 1x thiol: Pd ratio were used for ligand-place exchange and ester coupling reactions. The Pd C12 MPCs were place exchanged with C11OH thiol to introduce hydroxyl functionalities into the MPC monolayer; these groups can be coupled to COOH-containing molecules through esterification. Figures 6 and 7 show results of these reactions as followed by FTIR and NMR, respectively. Figure 6A shows the FTIR spectrum of the 1x prepared Pd C12 MPC; it is similar to the FTIR of Au C12 MPCs.¹³ Figure 6B shows the Pd C12 MPC after it was place exchanged with C11OH thiol, which produced a mixed monolayer Pd C12/C11OH (ca. 173/25) MPC. The spectrum clearly shows the appearance of an O–H stretch at 3453 cm⁻¹. Figure 6C shows the Pd C12/C11OH MPC following esterification with benzoic acid. The O–H stretch disappears and a C=O stretch appears at 1723 cm⁻¹, consistent with the formation of an aromatic ester. Stretches for the benzene ring C=C are between 1530 and 1620 cm⁻¹, and an aromatic C–H stretch is seen at 3064 cm⁻¹. There is also an out-of-plane aromatic C–H bend near 712 cm⁻¹. These

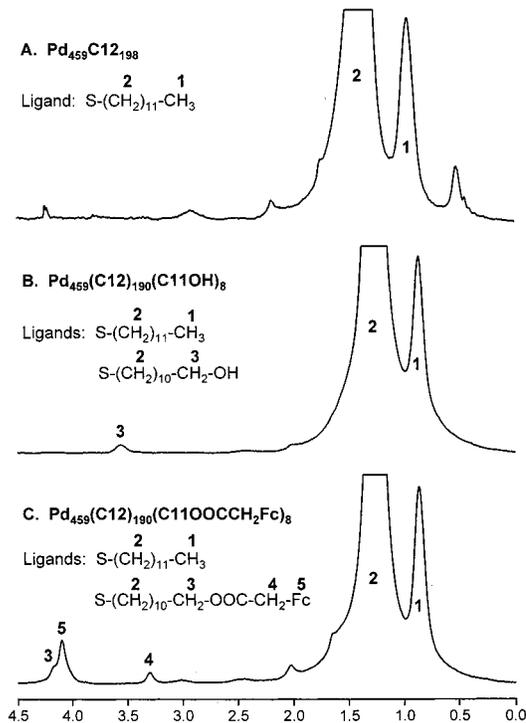


Figure 7. NMR spectra obtained in C₆D₆ or CD₂Cl₂ of (A) Pd C12 1x MPCs, (B) Pd C12 MPCs place exchanged with C11OH thiol, and (C) Pd C12/C11OH MPCs esterified with ferroceneacetic acid. Approximate compositions shown in the figure.

vibrational results are consistent with a successful esterification reaction. The complete loss of the O–H stretch that appeared in Figure 6B and the loss of CH₂–OH protons in the NMR spectrum (not shown) show that the reaction went to completion.

Place exchange and esterification reactions on Pd C12 1x MPCs were also followed by NMR spectroscopy (Figure 7). Figure 7A shows the NMR spectrum of the as-prepared Pd C12 1x MPC and Figure 7B the spectrum after a place-exchange reaction with C11OH thiol. The peak at 3.6 ppm (3) corresponds to the CH₂–OH protons; the ratio of this peak to that of CH₃ (1) protons gives an approximate composition of the mixed monolayer as Pd₄₅₉(C12)₁₉₀–(C11OH)₈. (The preparation studied in Figure 7B is not the same as that in Figure 6B, where more extensive place exchange, as similarly determined by NMR, had occurred.) Figure 7C shows the product of esterification with Fc–CH₂–COOH. The appearance of ferrocene protons at 4.1 ppm (5) and the disappearance of the CH₂–OH protons shows that the esterification reaction again went to completion, giving a new mixed monolayer and a composition of ca. Pd₄₅₉(C12)₁₉₀(C11O–OC–CH₂–Fc)₈.

Figures 6 and 7 are the first demonstrations of chemical reactions on Pd MPCs. Ligand place-exchange and esterification reactions were also performed on Pd C6 MPCs (prepared with low thiol: Pd ratios). In some cases where higher percentages (relative to Figures 6 and 7) of OH-functionalized alkanethiolates (or COOH) groups are place exchanged onto Pd MPCs, the products became insoluble in organic solvents. This is in contrast to Au MPCs, where as many as half of the initial alkanethiolate ligands can be place exchanged with polar-functionalized groups with the MPCs either remaining soluble in THF or becoming soluble in ethanol.

Electrochemistry. Figure 8A shows cyclic voltammetry (CV) of a CH₂Cl₂ solution of the ferrocene (Fc)-labeled Pd MPCs (2 mM total Fc concentration) whose NMR

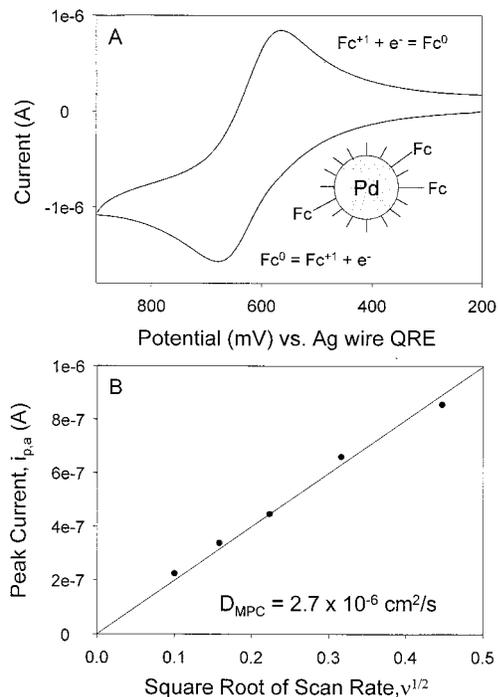


Figure 8. (A) Cyclic voltammetry (CV) of Pd C12/C110OC-CH₂Fc (ca. 190/8) MPCs at 500 mV/s in a 0.15 M Bu₄NPF₆/CH₂Cl₂ solution. The working electrode was a Pt disk (0.00283 cm²), the counter electrode was a Pt wire, and the reference electrode was a Ag wire quasi-reference electrode (QRE). The overall ferrocene concentration was 2 mM. (B) A plot of oxidation peak current (*i_p*) vs square root of scan rate ($\nu^{1/2}$) for the Pd C12/C110OC-CH₂Fc MPCs.

spectrum is shown in Figure 7C. The chemically reversible peak centered at 610 mV corresponds to the Fc^{0/+1} electrochemistry attached to the MPCs. A plot of the equation for peak current (*i_p*),²⁹

$$i_p = (2.69 \times 10^5) n^{3/2} A D_{\text{MPC}}^{1/2} \nu^{1/2} C_{\text{Fc}}^*$$

where $n = 1$, A is the area of the electrode, D_{MPC} is the diffusion coefficient of the ferrocene-labeled Pd MPCs, ν is the potential scan rate, and C_{Fc}^* is the concentration of ferrocene sites in the solution, is given in Figure 8B. The linearity of the plot is consistent with linear diffusion control of transport of the ferrocene-labeled Pd MPCs to the electrode/electrolyte interface. A value of $D_{\text{MPC}} = 2.7 \times 10^{-6}$ cm²/s is obtained from the slope, a value quantitatively consistent with previous electrochemical and Taylor dispersion measurements of diffusion coefficients of various Au MPCs.³⁰

Differential pulse voltammetry (DPV) is shown in parts A and B of Figure 9 for Au C6 MPCs prepared at 3x thiol:Au ratio and acetone-soluble Pd C6 MPCs prepared at 1x thiol:Pd ratio, respectively. The peaks in Figure 9A correspond to single-electron (quantized) double charging (QDL) of individual Au MPCs.^{16,17} The spacing between successive one-electron transfers to/from the MPC metal cores is observable, in short, because of the sub-aF capacitances, C_{CLU} , of individual MPCs and because the Au MPC sample is relatively uniform in core size. The peaks in Figure 9A are on average 288 mV apart, corresponding to an average C_{CLU} of ca. 0.56 aF. Peaks are also observed in Figure 9B, for the Pd 1x MPCs, but

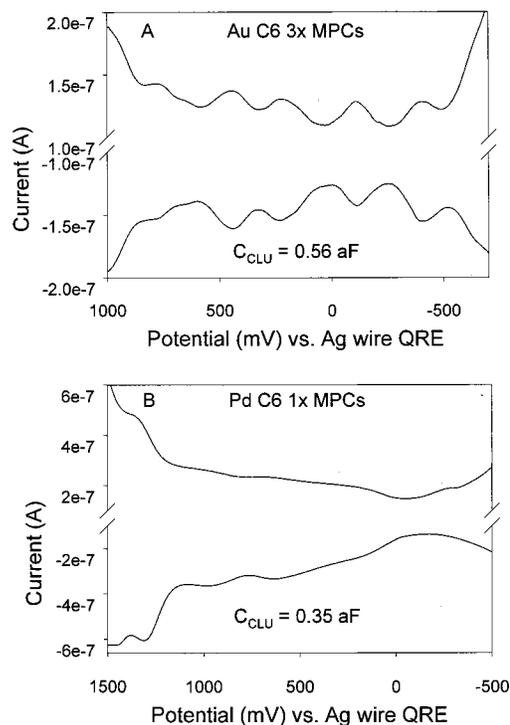


Figure 9. Differential pulse voltammetry (DPV) of (A) Au C6 3x MPCs and (B) acetone-soluble Pd C6 1x MPCs, obtained at potential scan rates of 20 and 25 mV/s, respectively, in a 0.10 M Bu₄NPF₆/CH₂Cl₂ solution. The cluster concentration was ca. 5–6 mg/mL. The working electrode was a Pt disk (0.00283 cm²), the counter electrode was Pt wire, and the reference electrode was a Ag wire QRE.

they are less well-defined (seen also by Chen et al.^{22d}) and on the average more widely spaced (ca. 453 mV). That they arise from a QDL process analogous to the Au MPCs is a reasonable conclusion given that a succession of peaks is seen with more or less regular spacing. The voltage spacing in Figure 9B implies a C_{CLU} of ca. 0.35 aF. That the Pd MPC capacitance is smaller than that of the Au MPCs further implies that the population of Pd MPCs giving rise to the QDL peaks either have core sizes smaller than that of the Au MPCs and of the average of the Pd MPCs in this preparation or have thicker monolayer dielectrics, or both. These two suggestions are consistent respectively with the large population of smaller core images in Figure 5B and with the large ligand content (percent organic) described above.

The narrow waist of the DPV trace in Figure 9B, by analogy to behavior seen often for Au MPCs, corresponds to the potential of zero charge of the Pd C6 MPCs. Thus, the first current peak in the positive potential scan of Figure 9B would correspond to the pseudo-formal potential of the Pd MPC^{0/+} electron-transfer couple, the second peak to the Pd MPC^{+2/+} couple, etc.

We have found, for Au MPCs, that considerable improvement in the definition of QDL charging peaks accompanies a decrease in the dispersity of the MPC core size. Decreasing core size dispersity can be accomplished by selection fractionation or extraction. We have tried to decrease the core size dispersity of Pd MPCs in this paper by extraction, using only acetone-soluble Pd MPCs, but did not find a dramatic improvement in the peak definition. Clearly, it will be interesting to apply further fractionation techniques to the Pd MPCs.

Conclusions

In this paper we describe the synthesis, reactivity, and electrochemistry of Pd monolayer-protected clusters pas-

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(30) Wuelfing, W. P.; Templeton, A. C.; Hicks, J. F.; Murray, R. W. *Anal. Chem.* **1999**, *71*, 4069.

sivated with C6 and C12 alkanethiolates. NMR, UV-vis, TEM, and TGA show that, when synthesized with thiol: Pd reactant ratios of 2:1 or larger, the product does not behave like a metallic, zerovalent cluster but is most likely some type of polynuclear Pd(II) alkanethiolate complex. When synthesized with a 1:1 thiol: Pd ratio or lower, the product in some respects has behavior quite similar to Au MPCs with metal-like cores that have been extensively studied.^{11b} FTIR and NMR show that these Pd MPCs can undergo place-exchange and esterification reactions. On the other hand, there seem to be compositional differences in the ligand content between Pd and Au MPCs. Electrochemical reactions of Pd MPCs could be detected by CV and DPV, both of pendant ferrocene sites attached to the MPC monolayer and quantized double-layer charging

of the Pd core in the Pd MPCs. For the latter, the charging pattern is less well-defined than is the case for Au MPCs. The differences found between Au and Pd MPCs, in synthesis, composition, and behavior, are intriguing and clearly show that further attention should be directed at Pd and other metal (and alloy) MPCs. MPCs based on Pd and other metals may well be more technologically relevant than those based on Au.

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