

Alkyl Isocyanide-Derivatized Platinum Nanoparticles

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There has been a recent intense interest in the synthesis and characterization of metal nanoparticles stabilized and functionalized with thiol ligands.¹ Self-organization of such clusters and single electron events (Coulomb staircase) have been observed in these nanoscale systems.^{2–5} Many complex structures are now available,⁶ some of which have implications in the construction of nanoscale devices.⁷ The simplicity and versatility of Au–thiol chemistry allows the construction of nanostructures by self-assembly, and therefore most of the research in this field has been limited to the coinage metals, although the preparations of alkanethiol-protected platinum⁸ and Au/Pt alloy⁹ nanoparticles have been described. The aim of the present work was to extend this type of chemistry to transition metals using isocyanides as capping ligands.

Isocyanides are isoelectronic with carbon monoxide and are considered to bind to metals in a similar manner, with σ -donation from the carbon atom to the metal and in some cases, π -back-bonding from the metal to the π^* -orbital.¹⁰ The σ -donor properties of the NC group and the wide variety of organic groups that can be employed¹¹ make isocyanides versatile ligands for transition metal ions. Although the isocyanide group is a stronger σ -donor and a weaker π -acceptor than CO,¹⁰ it strongly binds to metal surfaces, and attachment can be conveniently studied by vibrational spectroscopy.¹² Isocyanides have also been shown to self-assemble on Pt^{13a,b} and Au^{13b–e} surfaces and isocyanides appear

ideal ligands for the functionalization of transition and Pt-group colloidal metals. In addition, they are readily prepared¹¹ and have, in general, low mammalian toxicity.

The preparation of colloidal Pt in water or polar organic solvents is well-known,¹⁴ but relatively few preparations in nonpolar solvents have been reported.¹⁵ The latter is preferred for derivatization with isocyanide for solubility and chemical stability considerations. In the present work, tetra-alkylammonium-stabilized Pt nanoparticles were prepared by a two-phase chemical reduction method.^{1a,4} Stabilization of nanoparticles by tetra-alkylammonium salts¹⁶ leads to stable preparations which are sufficiently reactive to allow further reaction with ligands;⁴ colloidal Pt solutions were reacted with dodecylisocyanide by simple addition of the ligand.¹⁷

All reagents used were of analytical grade or better and were obtained from Fluka unless otherwise stated. MilliQ ultrapure water was used throughout. Toluene solutions of Pt nanoparticles were prepared as follows. A solution containing the phase-transfer reagent tetra-octylammonium bromide (1.1 g, 2×10^{-3} mole) in toluene (40 mL) was added to hexachloroplatinic acid (4.5×10^{-4} mole, Johnson Matthey, U.K.) in water (15 mL). The mixture was stirred until all of the Pt was transferred. The organic phase was separated, and sodium borohydride (0.19 g, 5×10^{-3} mole) in water (15 mL) was added with stirring. A color change from orange to brown was observed almost immediately, and stirring of the two-phase system was continued for a further 30 min. The organic phase was separated, washed once with dilute H₂SO₄ (ca. 0.5 M), twice with dilute K₂CO₃ (ca. 0.5M), and five times with water, and finally dried over anhydrous MgSO₄.

Dodecylisocyanide was prepared by following published procedures.¹¹ The Pt particles in toluene were reacted with dodecylisocyanide by adding 5:1 molar equivalents of the alkyl isocyanide with respect to Pt and left overnight to ensure completion of surface derivatization. The reaction to achieve full coverage is slow, as observed by IR spectroscopy (vide infra). The solvent was evaporated under reduced pressure at ambient temperature, and the residue was dissolved in ethanol (ca. 50 mL, Fluka, puriss) and then cooled at -20 °C for 4 h. A black precipitate formed which was washed with ethanol to remove excess reagents. In the same way as for thiol-derivatized Au nanoparticles preparations,¹ the black solid obtained is readily soluble in nonpolar solvents (e.g., toluene) to give a brown solution. Thus, functionalization protects the particles and allows them to retain their integrity on drying.

TEM shows particles of 1–3 nm in diameter of well-defined crystalline structure (Figure 1). Lattice fringes are clearly visible, and the diffraction pattern is characteristic of an fcc structure, demonstrating the presence of a metallic core of 2.0 ± 0.4 nm

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(17) Literature evidence suggests that isocyanides are susceptible to reduction by sodium borohydride; therefore, it was considered simpler to add isocyanide to the Pt particles rather than before the reduction step in the particle preparation.

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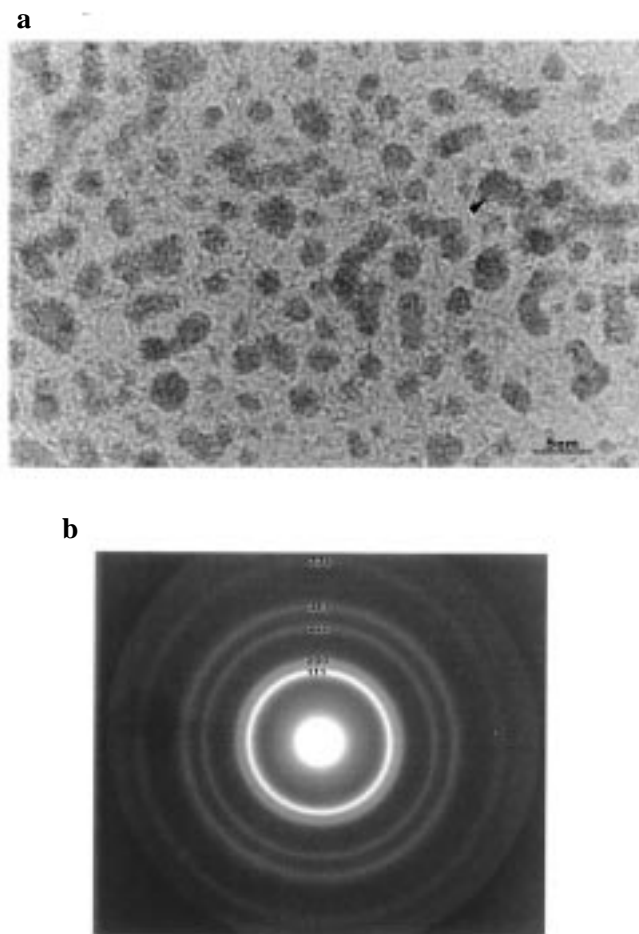


Figure 1. (a) TEM of Pt nanoparticles derivatized with dodecylisocyanide. The highlighted particle shows the lattice image of a fcc crystal viewed along the [110] direction; the 002, 111 and $\bar{1}\bar{1}\bar{1}$ fringes are resolved. (b) Selected area diffraction pattern from a large number of particles. Specimens were examined in a 200 kV JEOL 2000FX transmission electron microscope.

diameter. No evidence of a change in metal core size on reaction with isocyanide was observed. Preliminary time-of-flight mass spectrometry measurements of the Pt–isocyanide particles show a main peak at approximately 28 900 amu corresponding to a cluster containing approximately 150 atoms. Similar mass values for thiol-coated Au particles of approximately the same diameter have been observed.¹⁸ The mass spectrum indicates the presence of particles of ca. 1.8 nm diameter, in agreement with the TEM results.

FTIR spectra (see Supporting Information) of toluene solutions of dodecylisocyanide- and dodecylisocyanide-coated Pt particles evaporated on NaCl plates show that, apart from the bands corresponding to alkyl chain C–H stretch and deformation, the NC-stretching mode can be clearly seen at 2147 cm^{-1} for free isocyanide and at 2218 cm^{-1} for coordinated isocyanide. The increase of approximately 70 cm^{-1} for this vibration is similar to that observed^{12b} for methylisocyanide adsorbed on Pt(111) and for isocyanides self-assembled on Au,^{13c,e} indicating that the NC group is terminally bonded to the metal core. The difference in this vibration frequency between free and bound NC is due to increased electron donation from N to the terminal C, either through a π -bond or a σ -bond,¹⁰ caused by loss of electron density on the terminal carbon as a result of its coordination to the metal. The increase in vibration frequency shows that there is little π -back-donation from the metal core to the ligand which would

otherwise lower the vibration frequency by increasing electron density in the NC antibonding orbitals, as is the case for Pt(0)–isocyanide complexes.^{19a} This increase in vibrational frequency is greater for Pt(II) metal ion complexes.^{19b} Thus, the ability of the Pt metal core to participate in π -back-donation to the isocyanide ligand is between that of Pt(II) and Pt(0) complexes and is similar to that previously noted for bulk metal surfaces.^{12b,13c,e}

Immediately after the addition of isocyanide to the Pt particles solution, FTIR spectra of the solution evaporated onto NaCl plates showed, in addition to the free isocyanide NC stretch, a band corresponding to a bound NC with an increase of approximately 100 cm^{-1} compared to that of the free ligand. The intensity of the unbound NC band decreases with time, and the vibrational frequency of the bound NC also decreases with time, reaching 2218 cm^{-1} after several hours. This indicates that, as the coverage of isocyanide on the particles increases, there is an increase in electron density at the metal center available for π -back-donation which leads to a lowered stretching frequency.^{13c,e}

The ¹H NMR data for the derivatized particles²⁰ also indicates the presence of isocyanide. The NMR spectrum is similar to that of the free isocyanide²⁰ except that the fine structure of all the methylene protons of the latter is lost and some line broadening is in evidence. (NMR spectra are provided in the Supporting Information.) Line broadening in the ¹H NMR and ¹³C NMR spectra of thiol-derivatized Au particles has been attributed to the effect of the metal center on the ligand by Murray et al.^{1b} and to the “solidlike” nature of the chains by Lennox et al.^{1c} and has been observed to decrease for nuclei further away from the metal center. The methyl group signal (0.88 ppm) retains its triplet structure, and a smaller degree of broadening than that observed for thiol-coated Au particles can be seen. This may be related to the different NMR properties of the Pt metal center, as compared to Au,²¹ or to a lower surface packing of the ligand on the metal core.²⁰ Further work is required to elucidate these details.

¹³C NMR data in CDCl₃ resembles that for isocyanide²⁰ for the methylene and methyl carbons. As observed in the ¹H spectra, the degree of broadening for the outer methylene carbon nuclei is less than that for the carbon nuclei of thiol-derivatized Au. The signal for the isocyanide carbon, assigned by its absence in DEPT spectra, shows a large change, from 156.31 ppm when unattached to 59.52 ppm when attached to the particle, indicating a substantial shielding by the metal. Similar shielding effects have been observed for isocyanides coordinated to Pt(II).²² The signal for the isocyanide carbon is difficult to obtain, probably due to a combination of quadrupolar relaxation by the N^{10b} and coordination to the metal.¹⁰ The signal corresponding to the α -carbon on the derivatized particles is also of very low intensity. This effect has been previously observed for thiol-derivatized Au nanoparticles.^{1b,c} Thus, the NMR spectra give additional strong evidence that the isocyanide ligand is chemically bonded to the metal core.

The use of isocyanides as ligands for transition metal nanoparticles offers exciting new possibilities for extending the range of metals from which stable nanosized materials can be prepared and manipulated as simple chemical compounds, thus broadening the established use of thiols in nanoparticle synthesis.

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Supporting Information Available: Details of dodecylisocyanide synthesis, TOF mass spectrum, FTIR spectra, ¹H and ¹³C NMR spectra, elemental analysis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) See Supporting Information.

(21) Pt and Au have differing nuclear spin; Pt being 34% NMR active with spin $1/2$ and Au being 100% active with spin $3/2$. Murray et al. have shown that the inclusion of Group 10 metals in Au alloy nanoparticles decreases the degree of broadening.⁹

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