Preparation of alkanethiol stabilized palladium nanoparticles 2 and 3. Under a nitrogen atmosphere, PdCl$_2$(CH$_3$CN)$_2$ (0.130 g, 0.5 mmol) and [N(n-C$_8$H$_{17}$)$_4$]Br (a surfactant: 1.094 g, 2.0 mmol)) were dissolved in dehydrated THF (80 mL) and stirred until an orange-yellow solution was formed. To the solution, Super-hydride (1.0 M THF solution, 1.5 mL, 1.5 mmol) was subsequently added, and immediately the solution turned dark, which is indicative of the presence of Pd particles. The mixture was vigorously stirred for 30 min. Then alkanethiol (20 mmol) was added, and the mixture was continuously stirred for another 15 min. The solvent was removed by vacuum evaporation until only a small volume (2-3 mL) remained. An excess amount (100 mL) of ethanol was added by pouring, and the mixture was stored in a freezer overnight. The precipitate was collected on a membrane filter (0.45 µm pore size) and washed with ethanol and acetone. The washing continued until the filtrated solution was completely colorless.

Scheme S1. Formation of alkanethiol-protected Pd nanoparticles 2 and 3.

Octanethiol-stabilized palladium nanoparticle 2. 0.240 g. Average particle diameter: 2.3±1.1 nm. Anal. Found: C, 23.02; H, 3.97.
Octadecanethiol-stabilized palladium nanoparticle 3. 0.876 g. Average particle diameter: 2.5±0.9 nm. Anal. Found: C, 49.13; H, 8.55.

Preparation of tertiaryphosphine-protected palladium nanoparticles 4 and 5. Under a nitrogen atmosphere, PdCl$_2$(CH$_3$CN)$_2$ (0.130 g, 0.5 mmol) and [N(n-C$_8$H$_{17}$)$_4$]Br (a surfactant: 1.094 g, 2.0 mmol) were dissolved in dehydrated THF (80 mL) and stirred until an orange-yellow solution was formed. To the solution, Super-hydride (1.0 M THF solution, 1.5 mL, 1.5 mmol) was subsequently added, and immediately the solution turned dark, which is indicative of the presence of Pd particles. The mixture was vigorously stirred for 30 min. Then tertiaryphosphine (20 mmol) was added, and the mixture was continuously stirred for another 15 min. The solvent was removed by vacuum evaporation until only a small volume (2-3 mL) remained. An excess amount (100 mL) of ethanol was added by pouring, and the mixture was stored in a freezer overnight. The precipitate was collected on a membrane filter (0.45 µm pore size) and washed with ethanol and acetone. The washing continued until the filtrated solution was completely colorless.

Scheme S2. Formation of tertiaryphosphine-protected palladium nanoparticles 4 and 5.

![Scheme S2](image)

Trioctylphosphine-protected palladium nanoparticle 4. 0.241 g. Average particle diameter: 2.2±0.9 nm. Anal. Found: C, 15.73; H, 2.69.

Triphenylphosphine-protected palladium nanoparticle 5. 0.381 g. Average particle diameter: 2.1±0.9 nm. Anal. Found: C, 18.57; H, 1.61.
Figure S1. A photograph of special stainless cell for measurement of hydrogen storage.

Figure S2. Bonding isocyanide to palladium.
Figure S3. X-ray photoelectron spectra of palladium nanoparticles 2-5.
Figure S4. Ratios of Pd(0), Pd(II), and Pd(IV) components on the surfaces of palladium nanoparticles 2-5 calculated from XPS.
Figure S5. $^1$H NMR of (a) $n$-octyl isocyanide and (b) Pd nanoparticle 1.
Figure S6. Van’t Hoff plots for (a) Pd nanoparticle 1 and (b) bulk palladium.