

Electronic Supplementary Information

## Identification of the formation of metal-vinylidene interfacial bonds of alkyne-capped platinum nanoparticles by isotopic labeling

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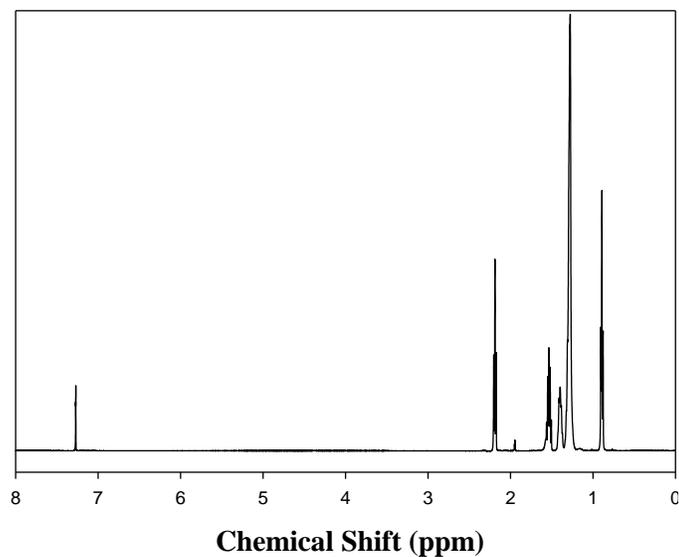
### Experimental Section

**Chemicals.** 1-Dodecyne (HC12, 98%, ACROS), deuterium oxide (D<sub>2</sub>O, 99.9%, Cambridge Isotope Laboratory Inc.), hexane-*d*<sub>14</sub> (99 atom% D, Sigma-Aldrich), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 99.3%, Fisher Chemical), magnesium sulfate (MgSO<sub>4</sub>, anhydrous, ≥ 97%, Sigma Aldrich), chloroform-*d*, (CDCl<sub>3</sub>, 99.6%, ACROS), platinum (IV) chloride (PtCl<sub>4</sub>, 99%, ACROS), and carbon monoxide (CO, 99.5%) were all used as received. All solvents were obtained from typical commercial sources and used without further treatment. Water was supplied by a Barnstead Nanopure water system (18.3 MΩ·cm).

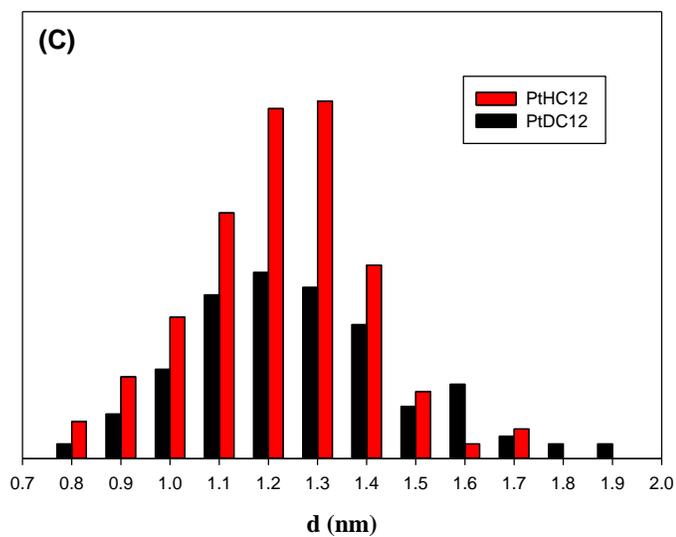
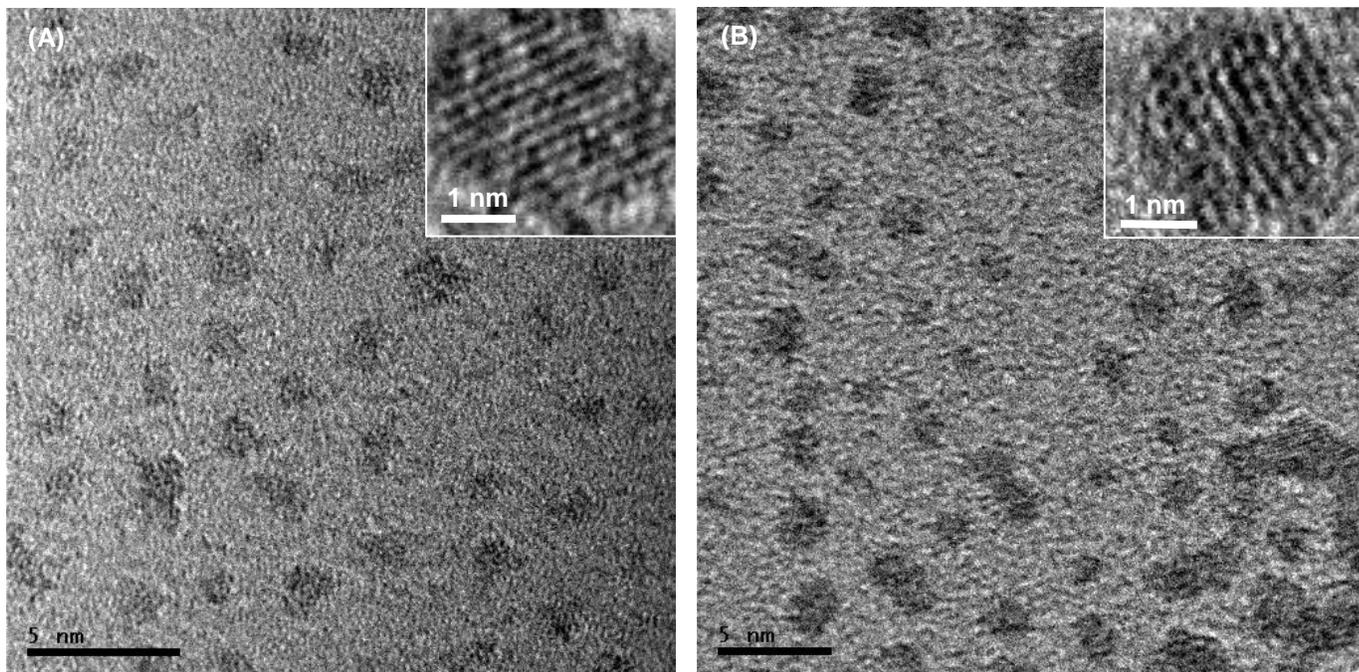
**Synthesis of dodec-1-deuteroyne (DC12).** DC12 was synthesized by following a previously reported procedure.<sup>1</sup> Briefly, a flame dried 20 mL vial was charged with 0.5 mmol (83 mg) of HC12 and 0.75 mmol (103 mg) of K<sub>2</sub>CO<sub>3</sub> in 2 mL of acetonitrile. The mixture was stirred under a N<sub>2</sub> atmosphere for 30 min, followed by the addition of 0.5 mL of D<sub>2</sub>O and then heated up to 50 °C and stirred for 24 h. After the solution was cooled down to room temperature, the organic phase was collected and dried by adding excessive MgSO<sub>4</sub>. The organic solution was then centrifuged to remove solid salts, and the solvent was evaporated by blowing N<sub>2</sub> to obtain the final product of DC12. <sup>1</sup>H NMR measurements showed that about 95% of the original 1-dodecyne was deuterated (Figure S1).

**Synthesis of platinum nanoparticles.** HC12-functionalized platinum nanoparticles (PtHC12) were prepared by adopting the carbon monoxide reduction method described in previous studies.<sup>2,3</sup> In brief, 0.1 mmol of PtCl<sub>4</sub> was first dissolved in 1 mL of H<sub>2</sub>O in a 20 mL glass vial. 40 μL of HC12 was added to the solution, and the mixture was bubbled with CO for 30 min under magnetic stirring. The vial was then sealed and subjected to stirring for overnight. It was found that the bottom aqueous phase became colorless while the thin organic phase turned dark brown. The organic phase was collected and rinsed with copious acetonitrile to remove excessive HC12, affording the PtHC12 nanoparticles. DC12-functionalized platinum (PtDC12) nanoparticles were prepared in a similar fashion except that D<sub>2</sub>O and DC12 were used instead. Both nanoparticles were readily soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF, toluene, alkanes, etc.

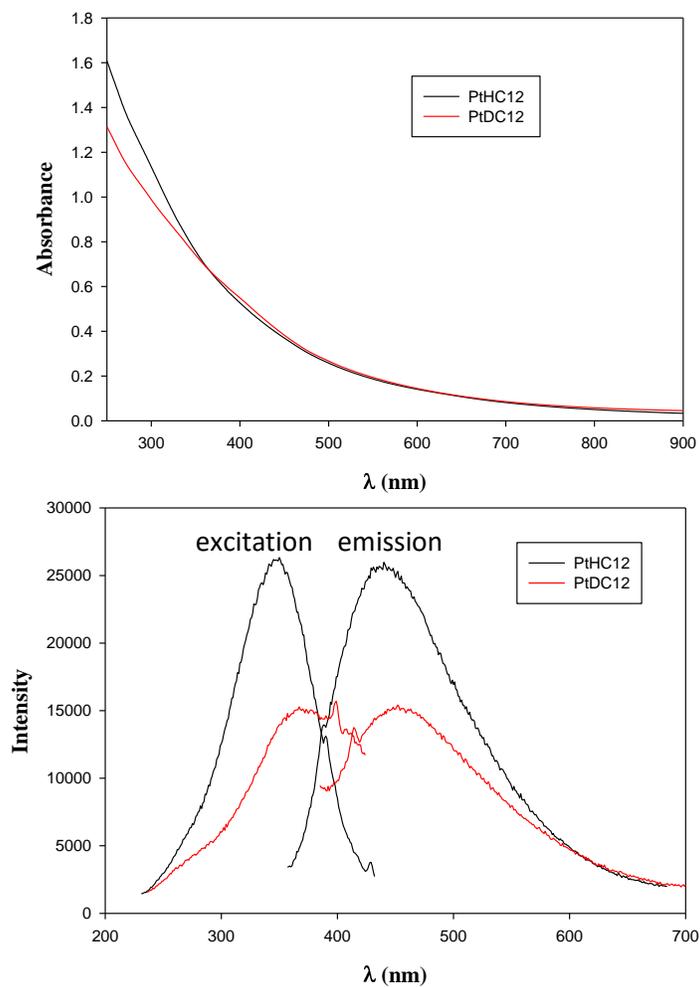
**Characterizations.** Transmission electron microscopic (TEM) measurements were conducted with a Philips CM300/FEG transmission electron microscope operated at 300 kV. UV-vis spectra were obtained with a Perkin-Elmer Lambda 35 UV-vis spectrometer by using a quartz cuvette (1 cm × 1cm) as a sample container, and photoluminescence measurements were performed on a FluoroMax-3 fluorospectrometer with the same samples used for UV-vis absorption measurements. FTIR spectroscopic studies were carried out on a Perkin-Elmer FTIR spectrometer (Spectrum One, spectral resolution 1 cm<sup>-1</sup>), where the samples were prepared by dropcasting on a ZnSe disk. <sup>1</sup>H NMR spectroscopic measurements were carried out with a Varian Unity Inova 500 MHz NMR spectrometer with the samples dissolved in CDCl<sub>3</sub>, while <sup>2</sup>H NMR spectroscopic studies were performed with a Bruker Avance III HD 800 MHz NMR spectrometer with samples dissolved in *n*-hexane-*d*<sub>14</sub>.



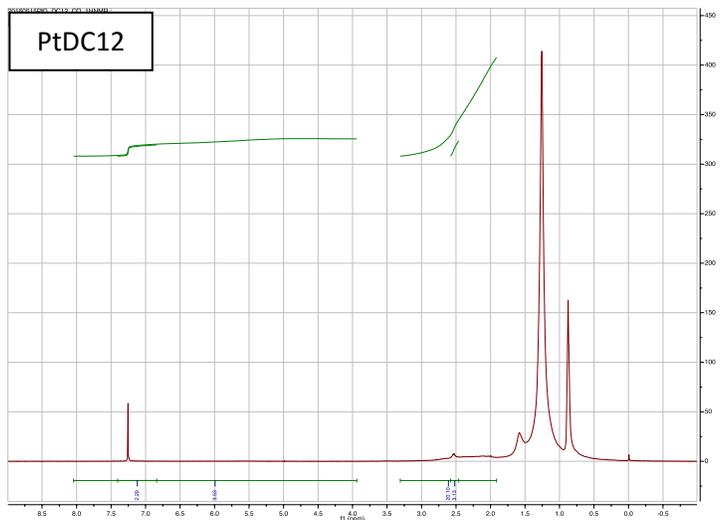
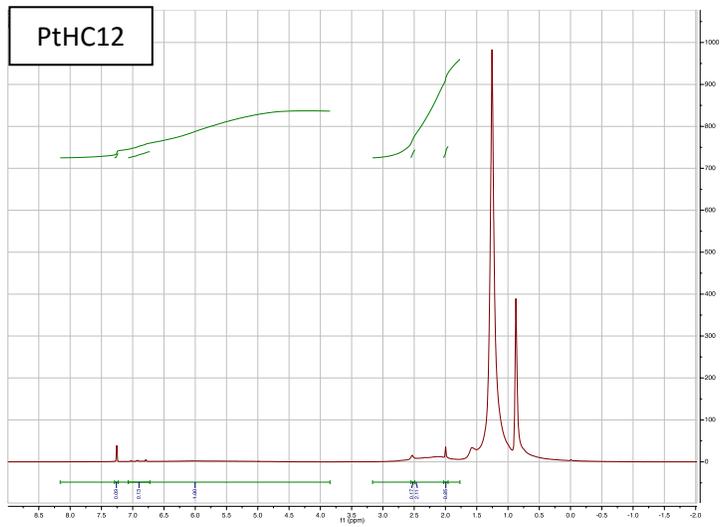
**Figure S1.**  $^1\text{H}$  NMR spectrum of DC12 in  $\text{CDCl}_3$ . Based on the integrated peak areas of the terminal  $\equiv\text{C-H}$  (1.95 ppm) and  $\text{CH}_3$  (0.89 ppm) protons, it is estimated that 95% of the  $\equiv\text{C-H}$  protons are replaced with  $\equiv\text{C-D}$ .



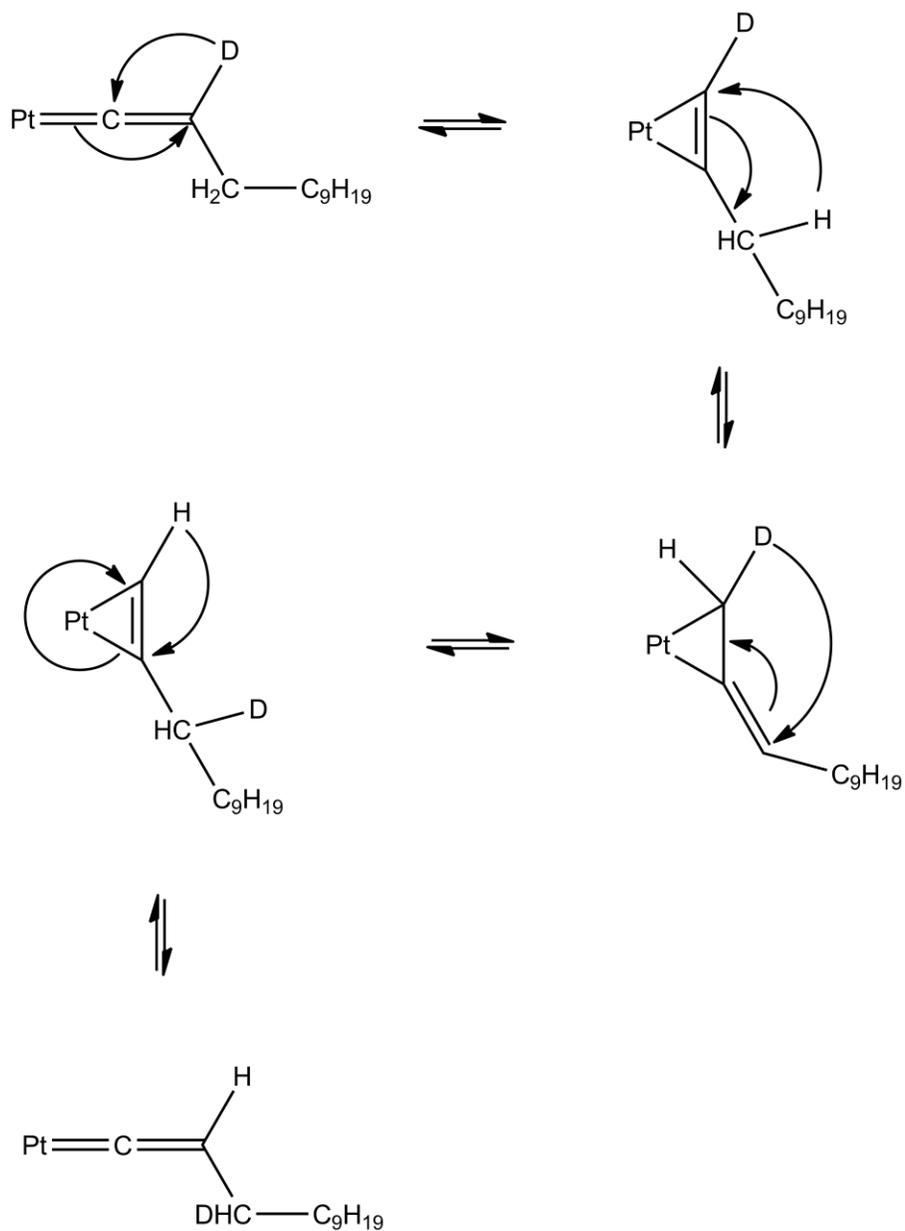
**Figure S2.** Representative TEM micrographs of (A) PtHC12 and (B) PtDC12 nanoparticles. Insets are the corresponding high-resolution images which show the nanoparticle lattice fringes that are consistent with Pt(111). (C) Core size histograms where the average core size is estimated to be  $1.26 \pm 0.18$  and  $1.32 \pm 0.22$  nm for PtHC12 and PtDC12, respectively.



**Figure S3.** (top) UV-Vis absorption and (bottom) photoluminescence spectra of PtHC12 (black) and PtDC12 (red) nanoparticles at the same concentration of 1 mg/mL in  $\text{CH}_2\text{Cl}_2$ .



**Figure S4.**  $^1\text{H}$  NMR spectra of (top) PtHC12 and (bottom) PtDC12 nanoparticles with the corresponding peak integrations. Data are the same as those in Figure 2(A).



**Scheme S1.** Schematic of the sigmatropic reaction of hydrogen/deuterium migration in a Pt-vinylidene linkage.

#### References

1. S. P. Bew, G. D. Hiatt-Gipson, J. A. Lovell and C. Poullain, *Org. Lett.*, 2012, **14**, 456-459.
2. Y. Yu, Z. T. Luo, D. M. Chevrier, D. T. Leong, P. Zhang, D. E. Jiang and J. P. Xie, *J. Am. Chem. Soc.*, 2014, **136**, 1246-1249.
3. P. G. Hu, L. M. Chen, C. P. Deming, X. W. Kang and S. W. Chen, *Angew. Chem. Int. Ed.*, 2016, **55**, 1455-1459.