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

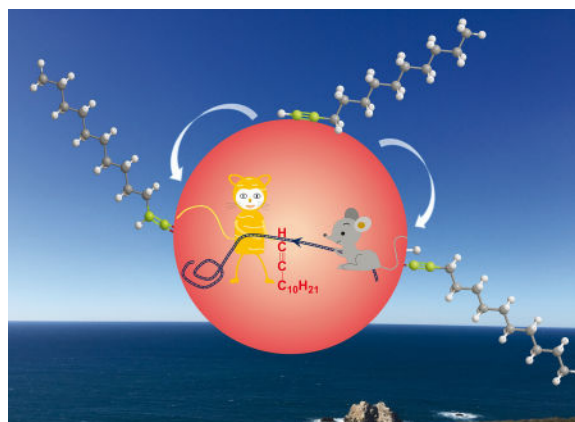
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Abstract

Stable platinum nanoparticles were prepared by the self-assembly of 1-dodecyne and dodec-1-deuteroyne onto bare platinum colloid surfaces. The nanoparticles exhibited consistent core size and optical properties. FTIR and NMR measurements confirmed the formation of Pt–vinylidene (Pt=C=CH–) interfacial linkages rather than Pt–acetylide (Pt–C≡C–) and platinum–hydride (Pt–H) bonds.

Graphical abstract



Showcasing results from a combined NMR and FTIR spectroscopic study with isotopically labelled alkyne ligands carried out by the Chen Group at the University of California, Santa Cruz.

When *n*-alkynes self-assemble onto platinum nanoparticle surface, spectroscopic measurements confirm the formation of Pt–vinylidene (Pt=C=CH–) interfacial linkages rather than Pt–acetylide (Pt–C≡C–) and platinum–hydride (Pt–H) bonds, based on a comparative study with 1-dodecyne and dodec-1-deuteroyne as the capping ligands.

†Electronic supplementary information (ESI) available: NMR, TEM, UV-vis and photoluminescence spectra, and reaction scheme. See DOI: 10.1039/c6cc05626a

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Recently it has been observed that metal–ligand interfacial bonding interactions may be exploited as a new, effective variable in the manipulation of the chemical and physical properties of metal nanoparticles.^{1–3} Of these, acetylene derivatives represent a unique capping ligand, as they may be readily self-assembled onto transition metal surfaces, forming conjugated metal–carbon bonds. This leads to apparent intraparticle charge delocalization between the particle-bound functional moieties and hence new optical and electronic properties. For instance, ruthenium nanoparticles have been functionalized with *n*-octynyl fragments (deprotonated *n*-octyne) through the formation of ruthenium–acetylide (Ru–C≡) bonds.^{4,5} The resulting nanoparticles exhibit an apparent red-shift of the C≡C vibrational energy and photoluminescence emission that is analogous to those of diacetylene derivatives (–C≡C–C≡C–); and with ethynylferrocenyl fragments incorporated into the nanoparticle capping layer, intervalence charge transfer occurs between the ferrocenyl metal centers at mixed valence, a behavior analogous to ferrocene oligomers, which suggests nanoparticle-mediated electronic communication thanks to the conjugated metal–ligand interfacial linkages.^{4,5} More recently, it has been found that metal nanoparticles can also be stabilized by the direct self-assembly of *n*-alkynes onto “bare” metal colloids,^{6–8} which is ascribed to the formation of metal–vinylidene (M=C=CH–) interfacial bonding linkages that are in a dynamic equilibrium with metal–acetylide (M–C≡) and metal hydride (M–H) bonds by a tautomeric rearrangement process (Scheme 1). Such a hypothesis is supported by the specific reactivity of the nanoparticles with imine derivatives. Note that in alkyne-transition metal complexes, the metal–vinylidene (M=C=CH–) structure is thermodynamically favorable.^{9,10} Thus, one immediate question arises. Is metal–vinylidene (M=C=CH–) bond also the dominant interfacial bonding linkages on alkyne-capped metal nanoparticles? This has remained an outstanding question and is the primary motivation of the present study.

Herein, we compare the spectroscopic characteristics of platinum nanoparticles functionalized with *n*-dodecyne (HC12) and dodec-1-deuteroyne (DC12). FTIR and ¹H and ²H NMR spectroscopic measurements showed clear signatures of platinum–vinylidene (Pt=C=CH–) linkages whereas none for platinum–hydride and platinum–acetylide bonds.

Experimentally, DC12 was synthesized by following a previously reported procedure,¹¹ where HC12 was deuterated by K₂CO₃ in D₂O. ¹H NMR measurements showed that about 95% of the original 1-dodecyne was deuterated (Fig. S1, ESI†). HC12 or DC12-functionalized platinum nanoparticles (PtHC12 or PtDC12) were then prepared by carbon monoxide reduction of PtCl₄ in the presence of HC12 or DC12.^{12,13} The synthetic details were included in the ESI.†

As manifested in TEM measurements (Fig. S2, ESI†), both PtHC12 and PtDC12 nanoparticles were dispersed rather well without apparent agglomeration, suggesting sufficient protection of the nanoparticles by the self-assembly of the alkyne ligands on platinum colloid surfaces, as observed previously.¹⁴ Statistical analysis based on more than 150 nanoparticles showed that the average core sizes of the samples were very close, at 1.26 ± 0.18 nm for PtHC12 and 1.32 ± 0.22 nm for PtDC12, with the majority of the nanoparticles in the range of 1.0 to 1.5 nm in both samples. Moreover, clearly defined lattice fringes can be seen in high-resolution TEM studies where the interplanar distance of 0.232

nm is consistent with that of the Pt(111) crystalline planes (PDF Card 4-802). The optical properties of both nanoparticles were also consistent with prior results.¹⁴ For instance, whereas only featureless UV-vis absorption profiles were observed, both nanoparticles displayed apparent photoluminescence emissions (Fig. S3, ESI[†]), with an excitation maximum around 350 nm and the corresponding emission maximum around 440 nm, that were analogous to those of diacetylene derivatives ($-C\equiv C-C\equiv C-$). This was ascribed to intraparticle charge delocalization between the particle-bound acetylene moieties, as observed previously for noble metal nanoparticles functionalized with acetylene derivatives.^{4,5,15}

As mentioned above, in prior studies, the self-assembly of *n*-alkynes on metal nanoparticles was thought to involve a dynamic equilibrium between metal–vinylidene ($M=C=CH-$) and metal–acetylide ($M-C\equiv$) + metal–hydride ($M-H$) bonds (Scheme 1). These were first examined by FTIR measurements. From Fig. 1, several characteristic bands can be identified for the HC12 free ligands (green curve), 3315 cm^{-1} for the terminal $\equiv C-H$ vibration, 2120 cm^{-1} for the $C\equiv C$ vibrations, and multiple vibration bands at 2956, 2927, and 2853 cm^{-1} that arose from the $-CH_2-$ and $-CH_3$ vibrations of the hydrocarbon chains. DC12 free ligands (blue curve) displayed similar characteristics, except that the terminal $\equiv C-D$ vibration appeared at 2600 cm^{-1} (the fact that the 3315 cm^{-1} band remained visible was because not all alkynyl protons were replaced by the deuterium atoms,¹¹ as shown in Fig. S1, ESI[†]). When the ligands were self-assembled onto Pt nanoparticle surfaces, for both PtHC12 and PtDC12 nanoparticles the $-CH_2-$ and $-CH_3$ vibrations remained virtually unchanged, and the $\equiv C-H$ and $\equiv C-D$ vibrational bands vanished completely. Furthermore, PtHC12 exhibited a vibrational band at 2047 cm^{-1} , a red-shift of 73 cm^{-1} from that of the $C\equiv C$ stretch of HC12 free ligands. Previously this was accounted for by the formation of conjugated $Pt-C\equiv$ interfacial bonds that led to intraparticle charge delocalization and hence a diminishing bonding order of the $C\equiv C$ moiety, with additional contributions from $Pt-H$ bonds on the nanoparticle surface (Scheme 1).¹⁴ These two contributions may be differentiated with the PtDC12 nanoparticles which exhibited a vibrational band at an almost identical position of 2051 cm^{-1} ; yet no vibrational feature was observed around 1450 cm^{-1} that is anticipated for the $Pt-D$ bonds.^{16,17} Instead, a new band emerged at around 2475 cm^{-1} for PtDC12, which is in good agreement with the vinyl carbon deuterium ($=C-D$) stretch.^{18,19} Taken together, these results strongly suggest the formation of the metal–vinylidene interfacial structure, rather than the metal–acetylide + metal–hydride linkages, at the metal–ligand interface (Scheme 1).

Consistent results were obtained in NMR measurements, as shown in Fig. 2. From the ¹H NMR spectra in panel (A), one can see that both PtHC12 (black curve) and PtDC12 (red curve) nanoparticles exhibited two prominent broad peaks at 0.89 and 1.26 ppm, which can be assigned to the terminal methyl (CH_3) and methylene (CH_2) protons of the HC12 and DC12 ligands, respectively. Notably, the absence of sharp features at these two peaks indicates the successful attachment of the ligands onto the nanoparticle surface, and both Pt nanoparticles were spectroscopically clean and free of excess ligands²⁰ (the sharp peaks at 1.56, 2.01, and 7.26 ppm are due to protons from residual solvents of water, acetonitrile, and chloroform, respectively). In addition, two broad peaks can be identified at 2.10 and 6.01

ppm for both nanoparticles. Of these, whereas the peak at 6.01 ppm (figure inset) is consistent with the vinylidene protons ($\text{Pt}=\text{C}=\text{CH}-$), the peak at 2.10 ppm may be ascribed to the protons of the α -carbon of both Pt-vinylidene ($\text{Pt}=\text{C}=\text{CH}-\text{CH}_2-$) and Pt-acetylide ($\text{Pt}-\text{C}\equiv\text{C}-\text{CH}_2-$). However, for the PtHC12 nanoparticles, the ratio of the integrated peak areas between the vinylidene and α -methylene protons was calculated to be 0.93 : 2 (Fig. S4, ESI[†]), close to the theoretical value of 1 : 2 expected for $\text{Pt}=\text{C}=\text{CH}-\text{CH}_2-$, indicating that indeed the alkyne ligands all formed Pt-vinylidene ($\text{Pt}=\text{C}=\text{CH}-$) rather than Pt-acetylide ($\text{Pt}-\text{C}\equiv\text{C}-$) interfacial bonds on the Pt nanoparticle surface, in agreement with the FTIR results (Fig. 1). Such a ratio was significantly lower for the PtDC12 nanoparticles at only 0.14 : 2 (Fig. S4, ESI[†]), due to the replacement of the vinylidene proton with deuterium (Fig. S1, ESI[†]).

Further structural insights were obtained in ^2H NMR measurements. As shown in panel (B), in sharp contrast to the PtHC12 nanoparticles which only showed two sharp peaks at 0.89 and 1.28 ppm from the methyl and methylene deuteriums of the solvent *n*-hexane- d_{14} , PtDC12 nanoparticles exhibited an additional broad peak within the range of 5 to 8 ppm, which is consistent with vinylidene deuterium ($=\text{C}=\text{CD}-$). This, again, shows good agreement with results from the FTIR measurements (Fig. 1), and further confirmed the formation of Pt-vinylidene ($\text{Pt}=\text{C}=\text{CH}-$) interfacial linkages. One may also notice that there appears another broad peak within the range of 1.5 to 3.5 ppm. While it is plausible that this peak arose from methylene deuterium ($\text{Pt}=\text{C}=\text{CH}-\text{CHD}-$) produced by hydrogen/deuterium migration due to the sigmatropic reaction (Scheme S1, ESI[†]),^{21–24} the exact origin is not clear at this point. Further studies are desired.

Furthermore, in the above ^1H and ^2H NMR measurements, no spectral feature was observed in the negative chemical shift regime, which suggested the absence of metal-hydride linkages in both nanoparticles (Scheme 1).

In summary, using isotopically labelled alkyne ligands, FTIR and NMR spectroscopic measurements confirmed that when *n*-alkynes self-assembled on metal nanoparticle surfaces, the dominant interfacial bonding structures entailed metal-vinylidene linkages.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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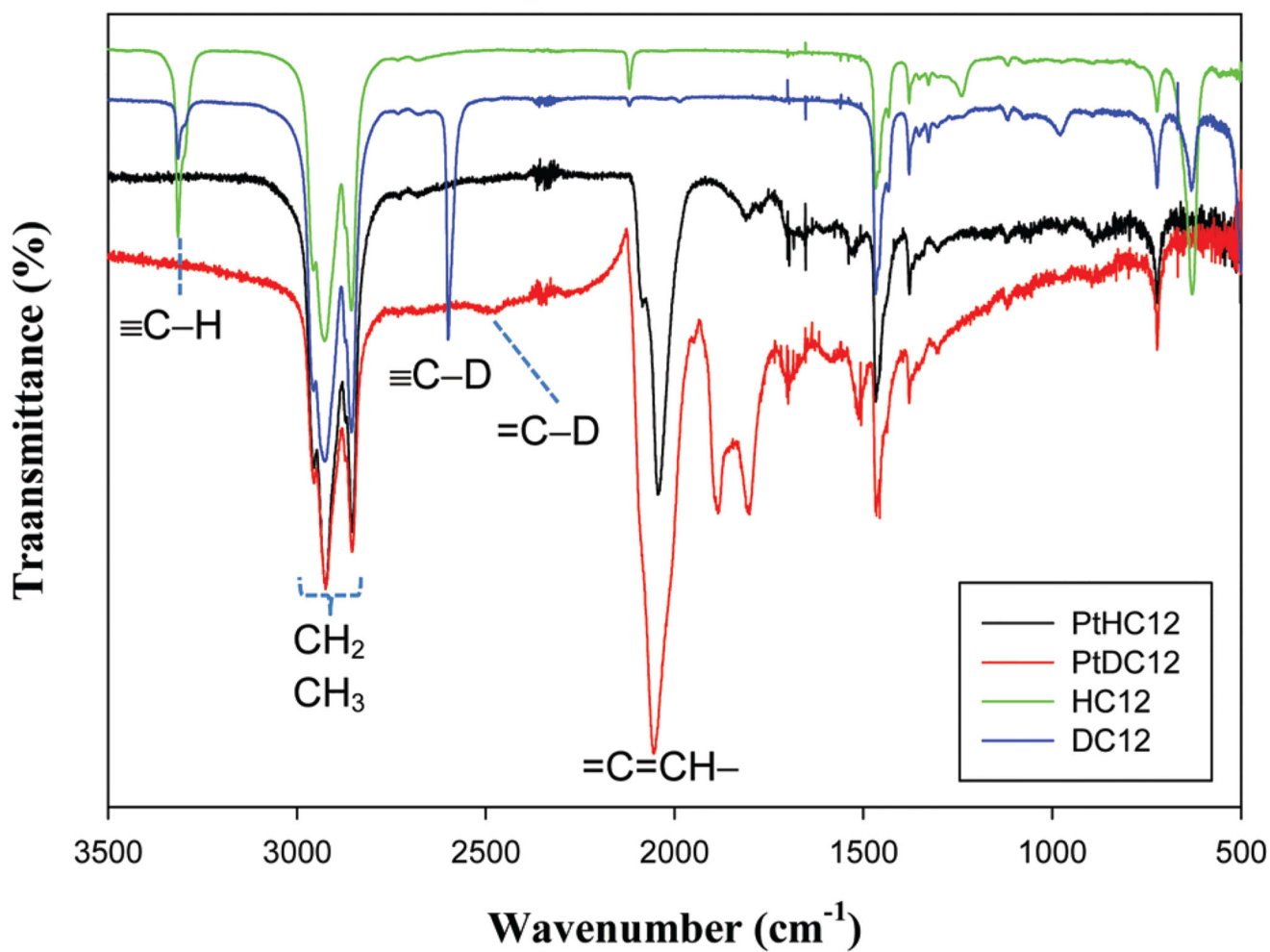


Fig. 1. FTIR spectra of PtHC12 (black) and PtDC12 (red) nanoparticles, along with those of the free ligands of HC12 (green) and DC12 (blue).

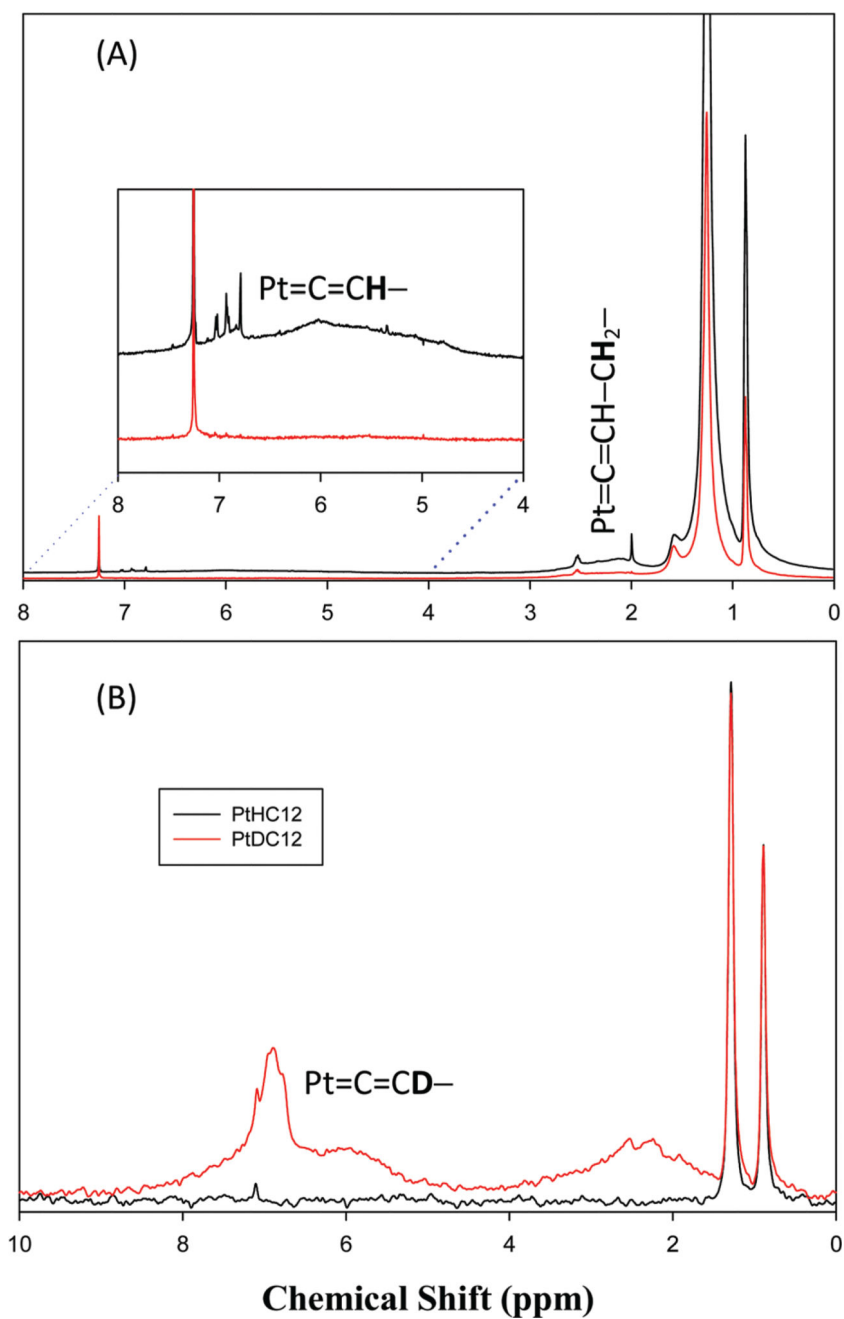
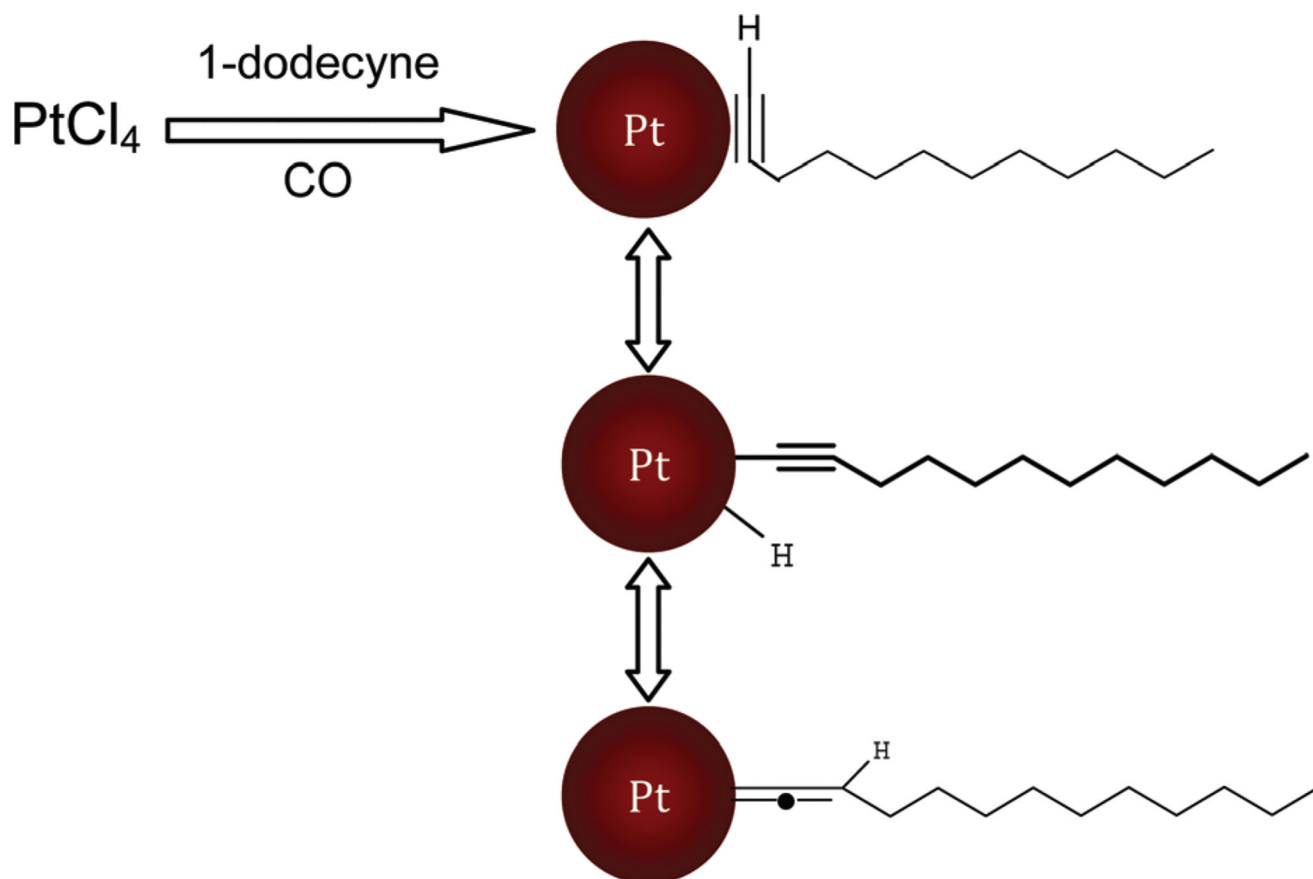


Fig. 2. (A) ^1H and (B) ^2H NMR spectra of PtHC12 (black) and PtDC12 (red) nanoparticles in (A) CDCl_3 and (B) n -hexane- d_{14} . Inset in panel (A) is the zoom-in of the region between 4 and 8 ppm.



Scheme 1.