



Supporting Information

Hydride-containing 2-Electron Pd/Cu Superatoms as Catalysts for Efficient Electrochemical Hydrogen Evolution

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Supplementary Information

Experimental Section

Materials and Measurement

All the reactions were carried out under an N₂ atmosphere using the standard Schlenk technique. The solvents used in this work were distilled before use, following standard protocols. All chemicals were purchased from different commercial sources available and used as received. [Cu₁₁H₂{S₂P(O*i*Pr)₂}₆(C≡CPh)₃]¹ and [Pd(CH₃CN)₂Cl₂]² were prepared by following the procedures reported in the literature. NMR spectra were recorded on a Bruker Advance DPX300 FT-NMR spectrometer that operates at 400 MHz while recording ¹H, 121.5 MHz for ³¹P, and 46.1 MHz for ²H. Used residual solvent proton references: δ, CDCl₃, 7.26 and δ, *d*₆-acetone, 2.10. The ³¹P{¹H} NMR spectra were referenced to external 85% H₃PO₄ at δ = 0.00 ppm. The chemical shift (δ) and coupling constants (J) are reported in ppm and Hz. ESI-mass spectra were recorded on a Fison Quattro Bio-Q (Fisons Instruments, V.G. Biotech, U. K.). UV–Visible absorption spectra were measured on a Perkin Elmer Lambda 750 spectrophotometer using quartz cells with a path length of 1 cm.

Synthesis PdHCu₁₁

The following two methods can prepare the PdHCu₁₁ cluster.

Method A.

In a flame-dried Schlenk tube [Cu₁₁H₂{S₂P(O*i*Pr)₂}₆(C≡CPh)₃] (0.05 g; 0.0219 mmol) were added along with 10 mL acetone; then [Pd(CH₃CN)₂Cl₂] (0.0057 g; 0.0219 mmol) were added under vigorous stirring. The reaction was stirred for 10 minutes under an N₂ atmosphere at room temperature. The solvent was evaporated under a vacuum, and the residue was washed with hexane/water. The hexane layer was separated and evaporated to dryness under vacuum to get a pure black-brown powder of [PdHCu₁₁{S₂P(O*i*Pr)₂}₆(C≡CPh)₄]. Yield: 0.024 g (43% based on Cu). Similarly, a deuterium analog of [PdDCu₁₁{S₂P(O*i*Pr)₂}₆(C≡CPh)₄] was synthesized by starting with [Cu₁₁D₂{S₂P(O*i*Pr)₂}₆(C≡CPh)₃] (0.05 g; 0.0219 mmol) in place of [Cu₁₁H₂{S₂P(O*i*Pr)₂}₆(C≡CPh)₃]. yield: 0.019 g (34% based on the Cu).

Method B

In a flame-dried Schlenk tube $[PdH_2Cu_{14}\{S_2P(O^iPr)_2\}_6(C≡CPh)_6]$ (0.1 g; 0.035 mmol) were added along with 5 mL THF, two equiv. of CF_3COOH (10.0 μL ; 0.07 mmol) with vigorous stirring. The reaction was stirred for 1 hour under an N_2 atmosphere at room temperature. The solvent was evaporated under a vacuum, and the residue was washed with ethyl acetate/water. The ethyl acetate layer was separated and evaporated to dryness under a vacuum to get a pure black-brown powder. The residue was dissolved in ether and passed through a column of Al_2O_3 . The residue in the Al_2O_3 column was dissolved with MeOH to get a brown solution. The pure $[PdHCu_{11}\{S_2P(O^iPr)_2\}_6(C≡CPh)_4]$ were obtained (0.02 g, 9% yield based on Cu).

PdHCu₁₁: ESI-MS = m/z 2554.22 $[PdHCu_{11}+Cu^+]^+$ (Calcd. 2554.32). 1H NMR (400 MHz, d_6 -acetone): 7.39-7.56 (m, 20 H, - C_6H_5), 4.88-4.92 (m, 12 H, - CH), 3.69 (s, 1H, μ_4 -H), 1.42 - 1.44 (dd, 72 H, - CH_3) ppm. ^{31}P NMR (121.49 MHz, d_6 -acetone): 93.3, 95.9, 98.8, 100.2, 101.8, and 103.9 ppm. ^{13}C NMR (100.6 Hz, d_6 -acetone): 132.35, 131.78, 129.68, 128.77, 75.56, 74.35, 77.21 and 23.16 ppm.

PdDCu₁₁: ESI-MS = m/z 2391.37 $[PdDCu_{11}-C_2Ph]^+$ (Calcd. 2389.36). 1H NMR (400 MHz, d_6 -acetone): 7.46-7.752 (m, 20 H, - C_6H_5), 4.89-4.90 (m, 12 H, - CH), 1.11-1.44 (dd, 72 H, - CH_3) ppm. ^{31}P NMR (121.49 MHz, d_6 -acetone): 93.4, 95.9, 98.9, 100.2, 101.8, and 103.9 ppm. 2H NMR (46.1 MHz, acetone): 3.49 (s, 1D, μ_4 -D) ppm.

Synthesis PdHCu₁₂

In a flame-dried Schlenk tube $[PdH_2Cu_{14}\{S_2P(O^iPr)_2\}_6(C≡CPh)_6]$ (0.1 g; 0.035 mmol) were added along with 5 mL THF, then two equiv. of CF_3COOH (10.0 μL ; 0.07 mmol) was added with vigorous stirring. The reaction was stirred for 1 hour under an N_2 atmosphere at room temperature. The solvent was evaporated under a vacuum, and the residue was washed with ethyl acetate/water. The ethyl acetate layer was separated and evaporated to dryness under a vacuum to get a pure black-brown powder. The residue was dissolved in CH_2Cl_2 and passed through a column of Al_2O_3 . The residue in the Al_2O_3 column was dissolved with Ether to get an orange-red solution. $[PdHCu_{12}\{S_2P(O^iPr)_2\}_5\{S_2PO(O^iPr)\}(C≡CPh)_4]$ were obtained (0.03 g, 13% yield based on Cu). Similarly, a deuterium analog of $[PdDCu_{12}\{S_2P(O^iPr)_2\}_5\{S_2PO(O^iPr)\}(C≡CPh)_4]$ was synthesized

by starting with $[PdD_2Cu_{14}\{S_2P(O^iPr)_2\}_6(C\equiv CPh)_6]$ (0.1 g; 0.035 mmol) in place of $[PdH_2Cu_{14}\{S_2P(O^iPr)_2\}_6(C\equiv CPh)_6]$. Yield: 0.026 g (12% based on the Cu).

PdHCu₁₂: ESI-MS = *m/z* 2512.10 [**PdHCu₁₂**] (Calcd. 2512.27). ¹H NMR (400 MHz, *d*₆-acetone): 7.32-7.69 (d, 20 H, -C₆H₅), 4.90 (m, 10 H, -CH of -{S₂P(OⁱPr)₂}), 1.17 (t, 70 H, -CH₃ of -{S₂P(OⁱPr)₂}), 4.53 (m, 1 H, -CH of -{S₂PO(OⁱPr)}), 0.63 (t, 6H, -CH₃ of -{S₂PO(OⁱPr)}), -5.19 (s, 1H, μ₄-H). ³¹P NMR (121.49 MHz, *d*₆-acetone): 101.4, 100.4, 97.0, 96.9, 92.1 (-{S₂P(OⁱPr)₂}) and 66.7 (-{S₂PO(OⁱPr)}) ppm. ¹³C NMR (100.6 Hz, CDCl₃): 132.99, 132.59, 127.91, 127.76, 47.20, 73.89, 53.45, and 23.38 ppm.

PdDCu₁₂: ESI-MS = *m/z* 2413.99 Da, [**PdDCu₁₂**-(C≡CPh)]⁺ (calc. 2411.23 Da). ¹H NMR (400 MHz, CDCl₃): 7.60-7.81 (d, 20 H, -C₆H₅), 4.80 (m, 10 H, -CH of -{S₂P(OⁱPr)₂}), 1.04 (t, 70 H, -CH₃ of -{S₂P(OⁱPr)₂}), 4.45 (m, 1H, -CH of -{S₂PO(OⁱPr)}), 0.56 (t, 6H, -CH₃ of -{S₂PO(OⁱPr)}). ³¹P NMR (121.49 MHz, *d*₆-acetone): 101.4, 100.4, 97.0, 96.9, 92.1 (-{S₂P(OⁱPr)₂}) and 66.7 (-{S₂PO(OⁱPr)}) ppm. ²H NMR (46.1 MHz, CHCl₃): -4.98 (s, 1D, μ₄-D) ppm.

Single-Crystal X-ray Crystallography

Single crystals suitable for X-ray diffraction of **PdHCu₁₁** and **PdHCu₁₂** were obtained by slow diffusion of *n*-hexane into acetone and dichloromethane solution at 4°C, respectively. The single crystal was mounted on the tip of a glass fibre coated with paratone oil and then cooled in the cryo N₂ stream. Data were collected on a Bruker APEX II CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K. Absorption corrections for the area detector was performed with SADABS,³ and the integration of the raw data frame was performed with SAINT.⁴ The structure was solved by direct methods and refined by least-squares against F^2 using the SHELXL-2018/3 package,⁵ incorporated in SHELXTL/PC V6.14.⁶ All non-hydrogen atoms were refined anisotropically. The hydride atom was located from the residual electron densities and refined without constraints in **PdHCu₁₁** and **PdHCu₁₂**. CCDC no. 2215591 (**PdHCu₁₁**) and 2215592 (**PdHCu₁₂**) contain the crystallographic data in this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical measurements

Linear sweep voltammetry (LSV) was performed on an electrochemical workstation (ZIVE BP2, WonATech) in a three-electrode electrochemical cell consisting of a nanocluster-immobilized carbon paper, a Pt foil anode (3 cm^2), and an Ag/AgCl (1.0 M KCl) reference electrode. The electrodes were fabricated by dropcasting a catalyst solution (1:1 CH_2Cl_2 -acetone) onto carbon paper (1 cm^2 , Avcarb - MGL190) with a typical loading of 2.7 nmol cm^{-2} . For comparison, a benchmark Pt/C (20 wt% Pt on VC-72, Premetek) electrode was prepared by dropcasting 200 μL of a catalyst ink, made by dispersing 10 mg of Pt/C with 200 μL of Nafion solution (5 wt%, Sigma-Aldrich) in 800 μL of isopropyl alcohol, onto the carbon paper (2 mg cm^{-2}). The electrolyte solution of 0.5 M H_2SO_4 was degassed with high-purity Ar for 30 min. Before electrochemical measurements. Electrode potentials measured on the Ag/AgCl scale ($E_{\text{Ag/AgCl}}$) were converted to the RHE scale (E_{RHE}) using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.235 + 0.059 \text{ pH} \quad (1)$$

Constant potential electrolysis (CPE) was conducted in an H-cell constructed by compressing two glass compartments under vigorous stirring. One region of the H-cell was used for the cathodic reaction, in which the prepared working electrode (**PdHCu₁₁/C**, **PdHCu₁₂/C** or **PdH₂Cu₁₄/C**) and reference electrode (Ag/AgCl) were immersed in 60 mL of a degassed electrolyte solution of 0.5 M H_2SO_4 . The other region in the H-cell was used for the anodic reaction and contained 60 mL of the same electrolyte solution; a Pt foil anode was dipped into the solution. The two compartments were separated by a Nafion 117 membrane (Dupont). The gaseous products were analyzed using gas chromatography (Agilent, GC 7820A) equipped with a thermal conductivity detector (TCD). The turnover frequency (TOF) and faradaic efficiency (FE) for HER were determined as follows:

$$\text{TOF (s}^{-1}\text{)} = \frac{\text{produced H2 (mol)}}{\text{amount of catalyst (mol)} \times \text{time (s)}} \quad (2)$$

$$\text{FE(%) = } \frac{\text{produced H2 (mol)} \times 2 \times \text{Faraday constant (96485 C/mol)}}{\text{total charge consumed (C)}} \times 100 \quad (3)$$

Computational Details

Density Functional Theory (DFT) calculations were carried out using the Gaussian (R) 16 program.⁷ The valence triple-zeta polarization functions (def2-TZVP) basis set was used, together with the Perdew-Burke-Ernzerhof (PBE0)^{8,9} functional. All the optimized structures were confirmed as true minima on their potential energy surface by analytical vibration frequency calculations. Natural atomic orbital (NAO) populations and Wiberg bond indices were computed with the natural bond orbital NBO 6.0 program¹⁰⁻¹² implemented in the Gaussian (R) 16 package.

References

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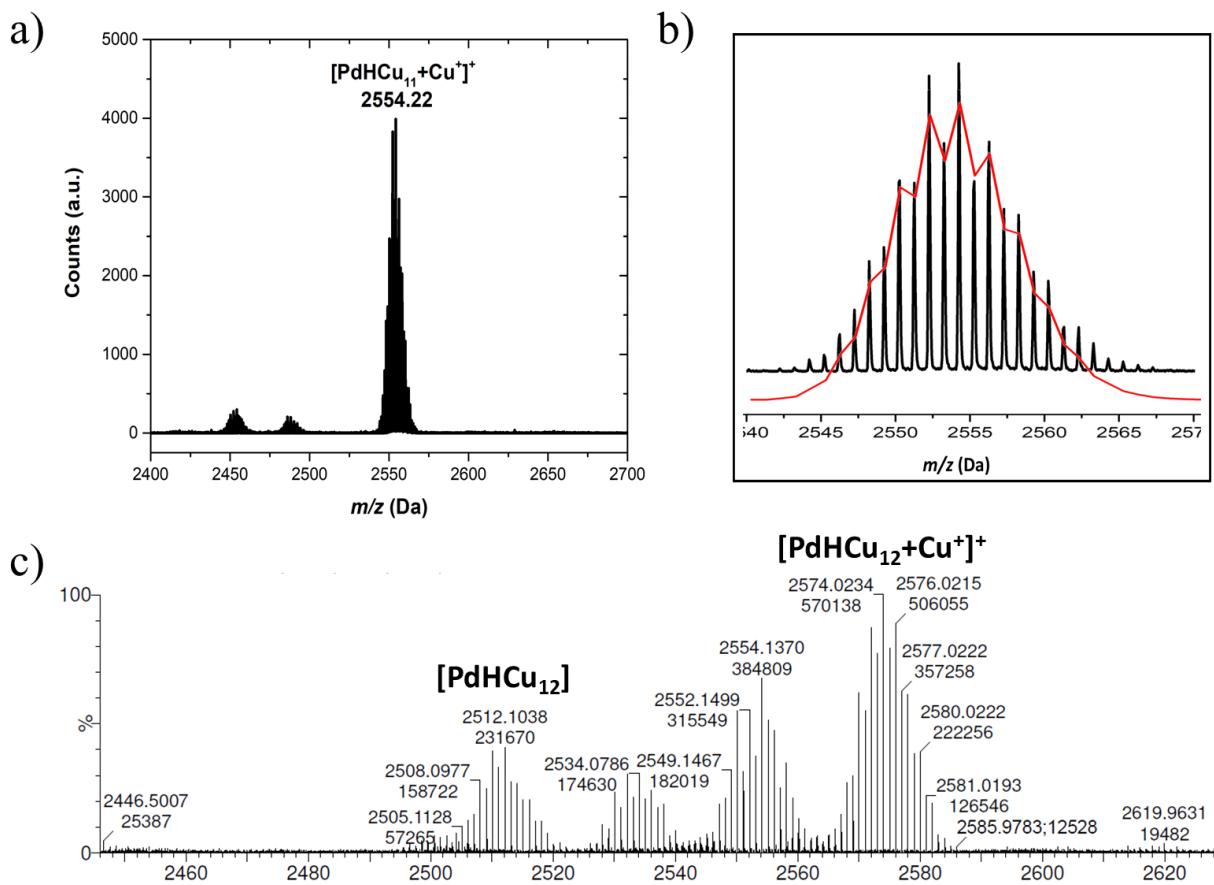


Figure S1. a) Positive-mode ESI-MS of $[\text{PdHCu}_{11}]$ and b) Isotopic patterns of experimental (black) and simulated (red) spectra corresponding to $[\text{PdHCu}_{11} + \text{Cu}^+]^+$. c) Positive-mode ESI-MS of $[\text{PdHCu}_{12}]$.

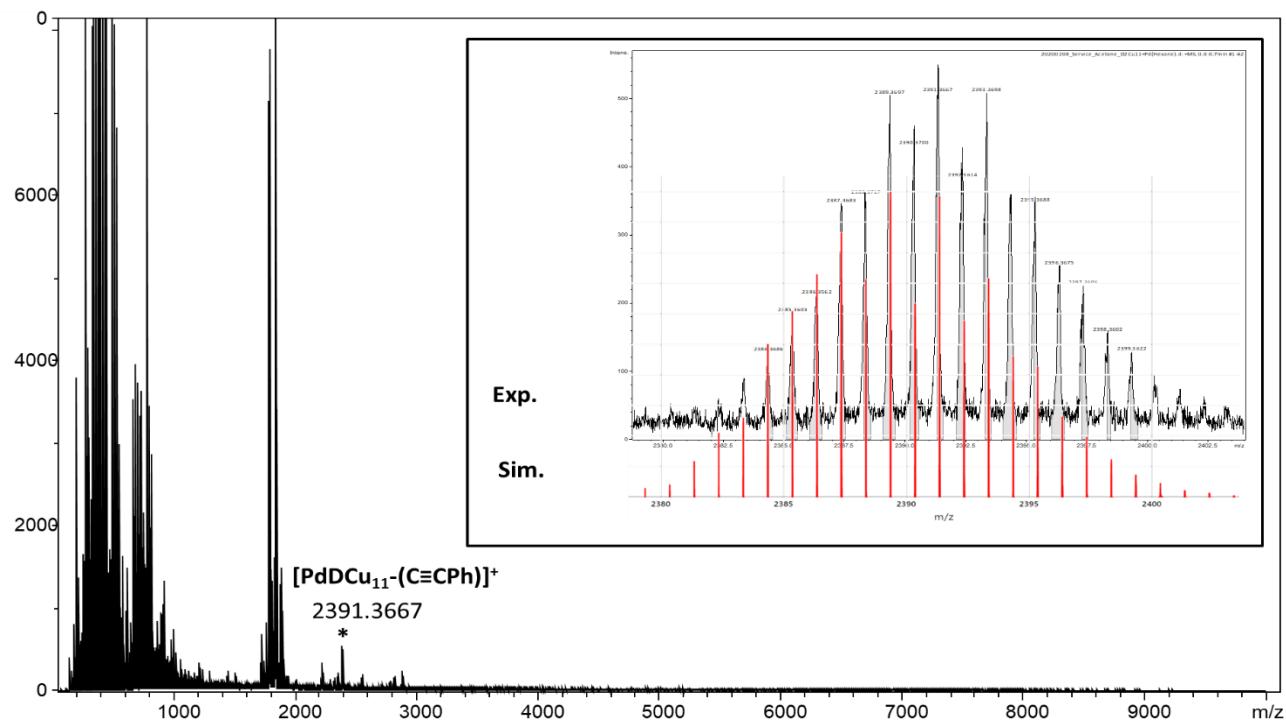


Figure. S2. The positive-ion ESI-MS spectra of $[\text{PdDCu}_{11}-(\text{C}\equiv\text{CPh})]^+$. Inset: experiment (black) and simulation (red) isotope distribution of $[\text{PdDCu}_{11}-(\text{C}\equiv\text{CPh})]^+$.

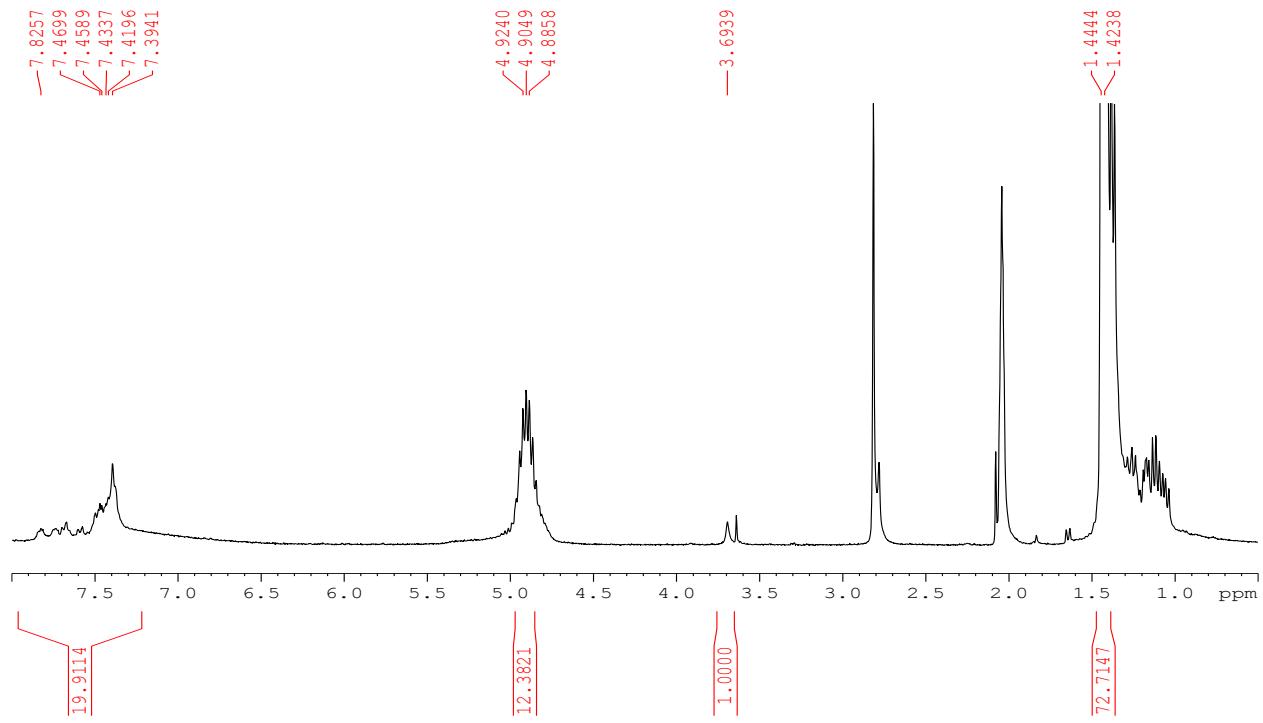


Figure S3. ^1H NMR spectrum of PdHCu_{11} in d_6 -acetone.

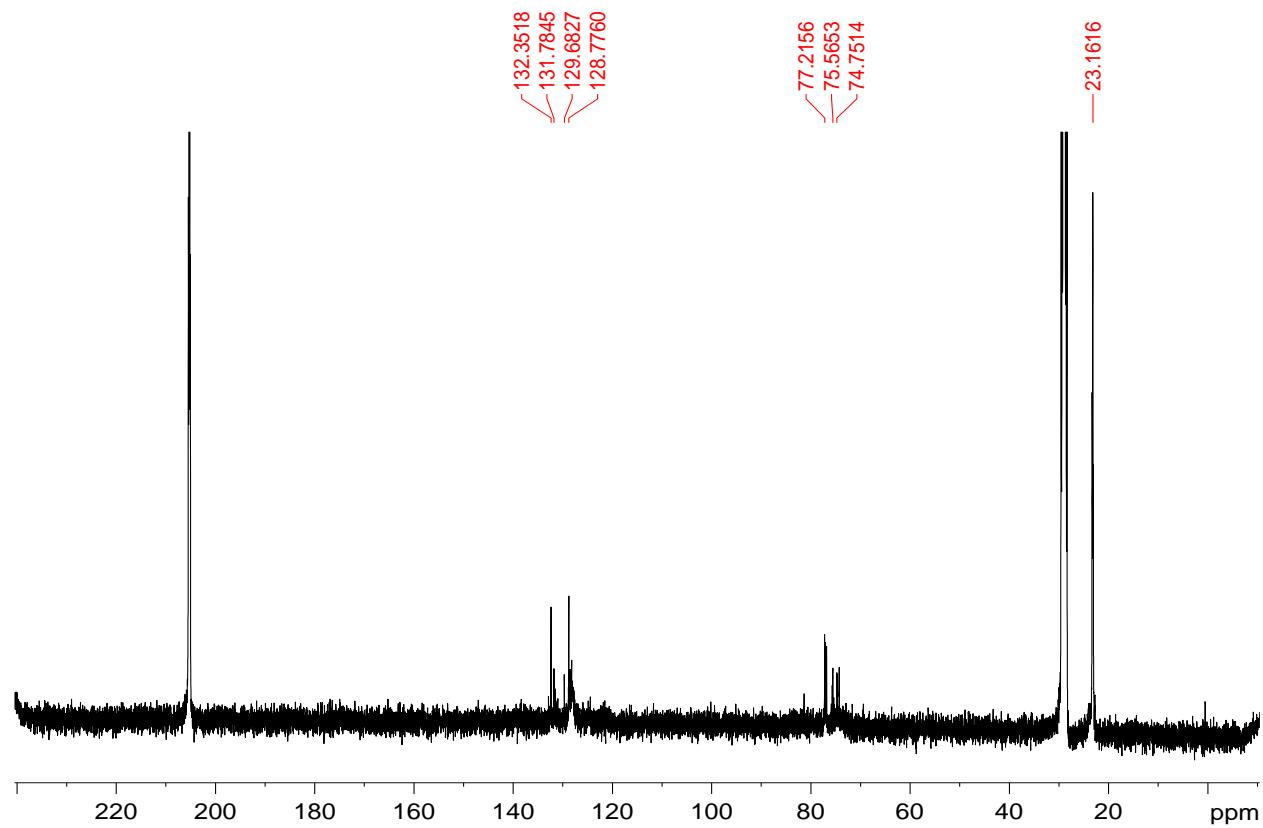


Figure S4. ^{13}C NMR spectrum of PdHCu_{11} in d_6 -acetone.

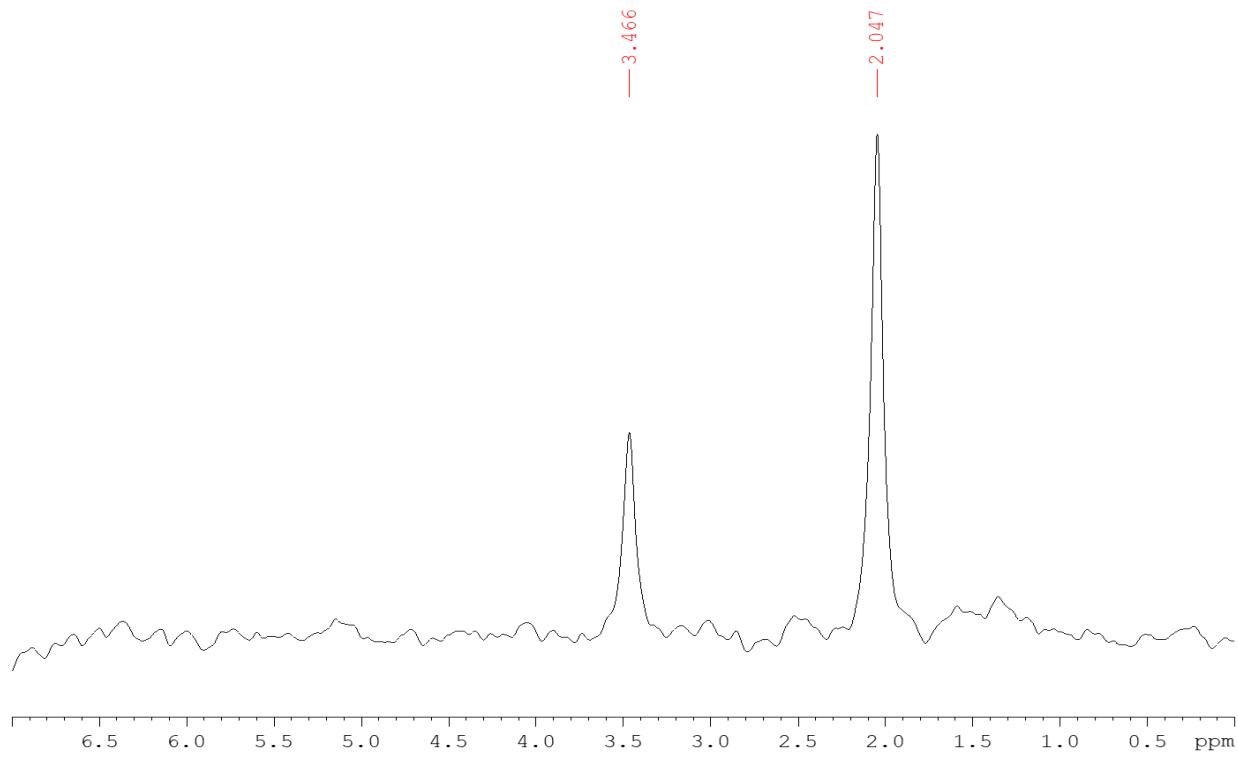


Figure S5. ^2H NMR spectrum of **PdDCu₁₁** in acetone.

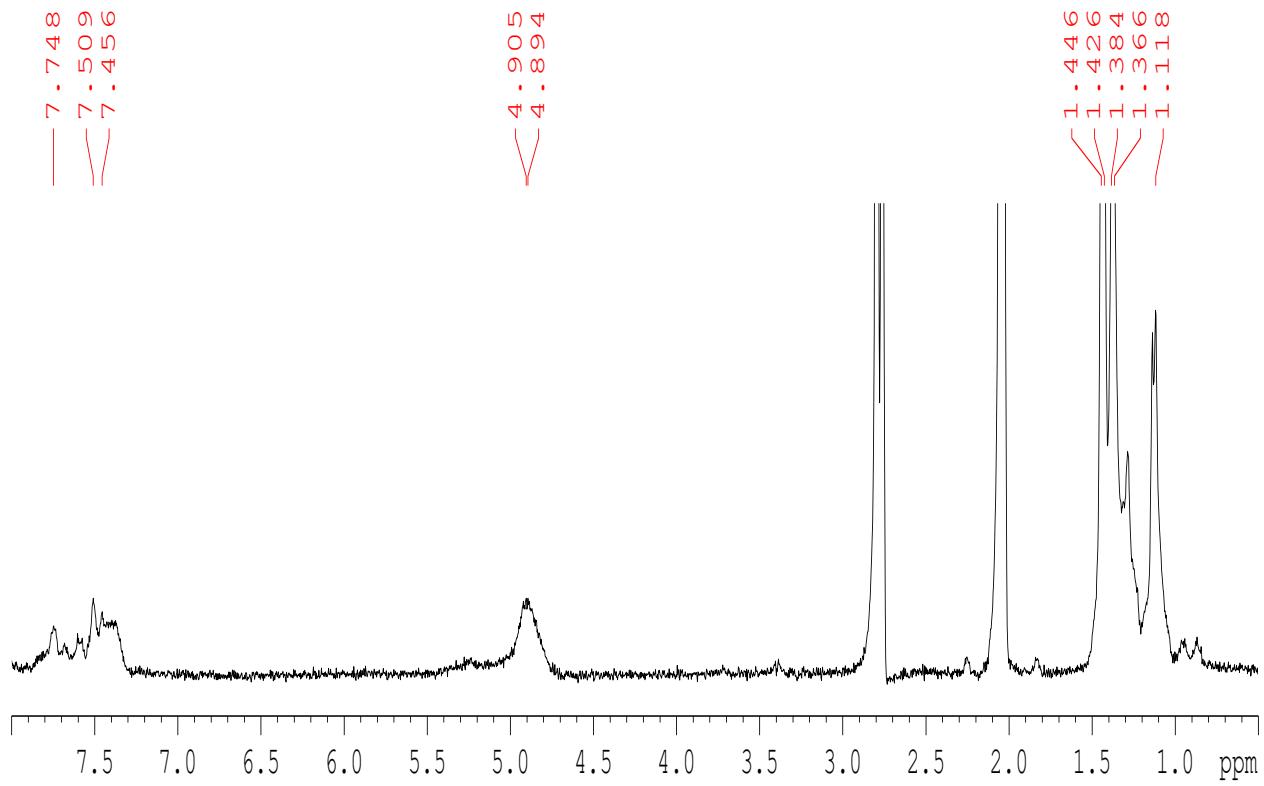


Figure S6. ^1H NMR spectrum of **PdDCu11** in d_6 -acetone.

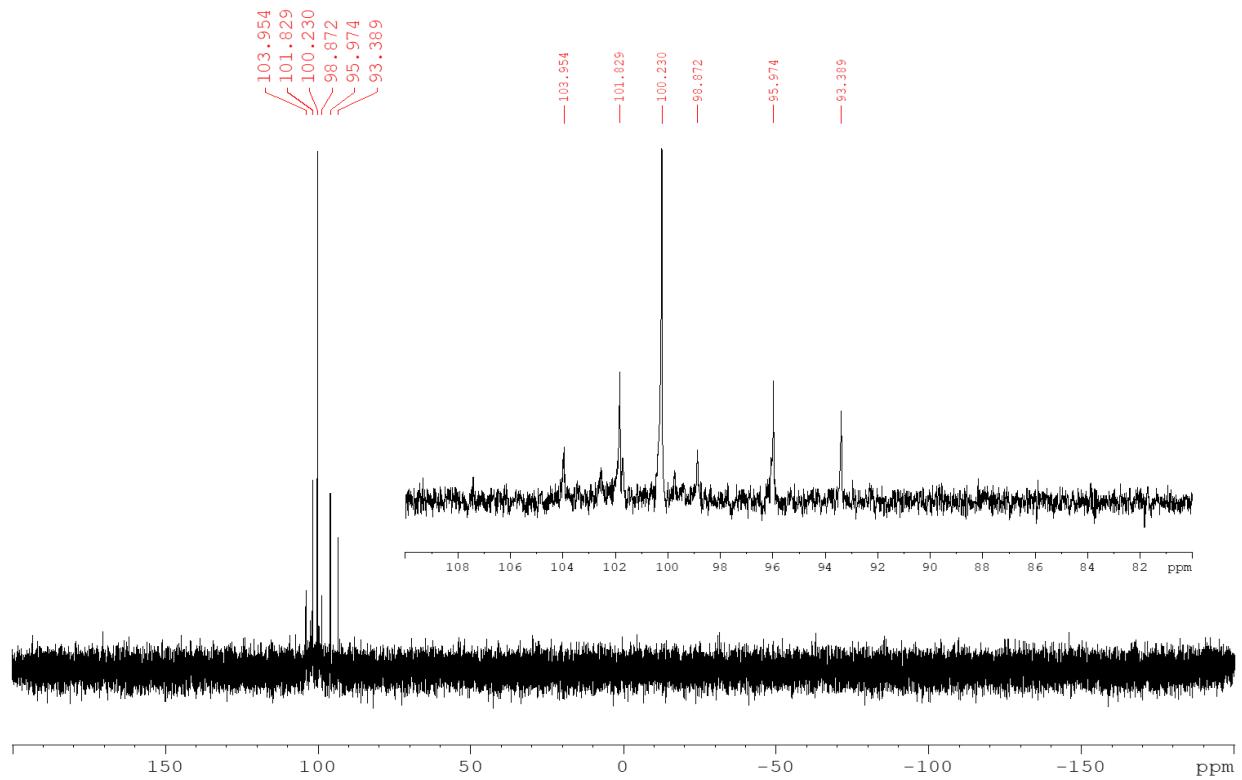


Figure S7. $^{31}\text{P}\{\text{H}\}$ NMR spectrum of PdHCu_{11} in d_6 -acetone.

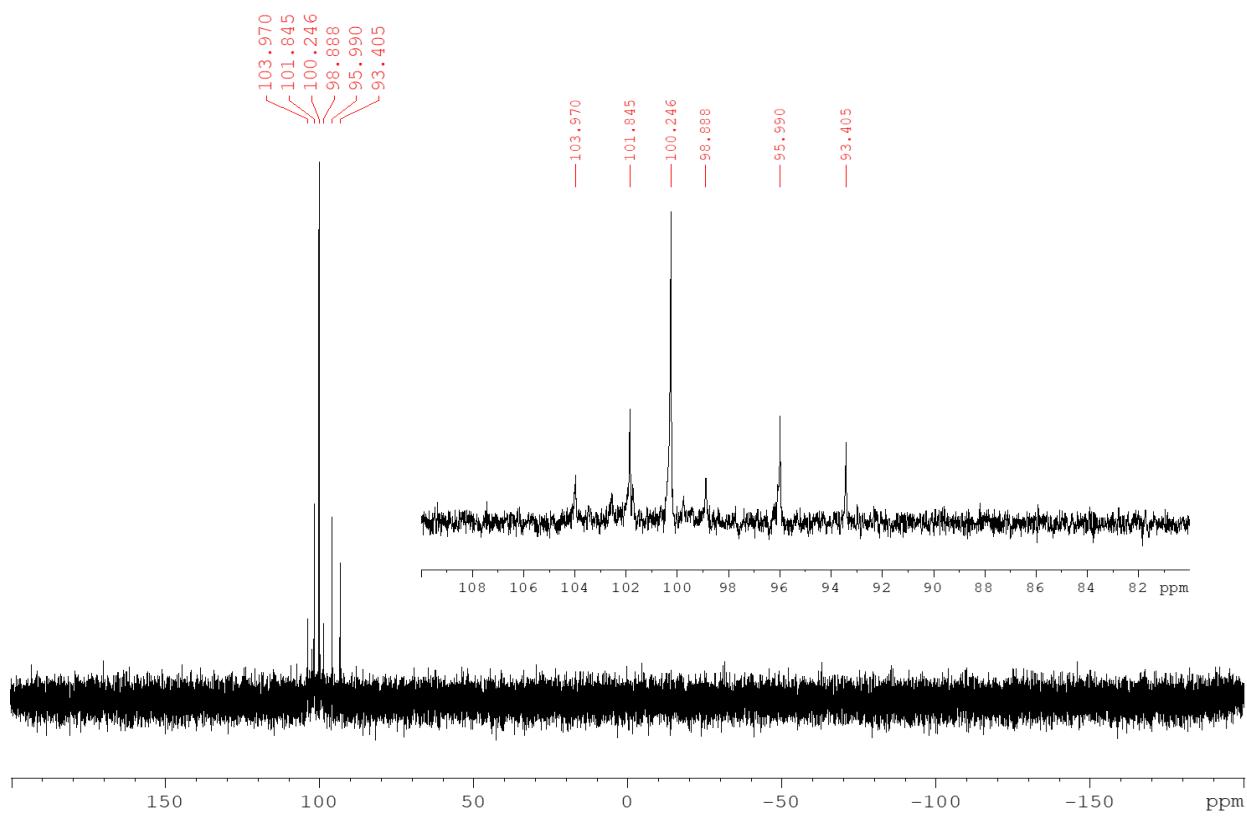


Figure S8. $^{31}\text{P}\{\text{H}\}$ NMR spectrum of PdDCu_{11} in d_6 -acetone.

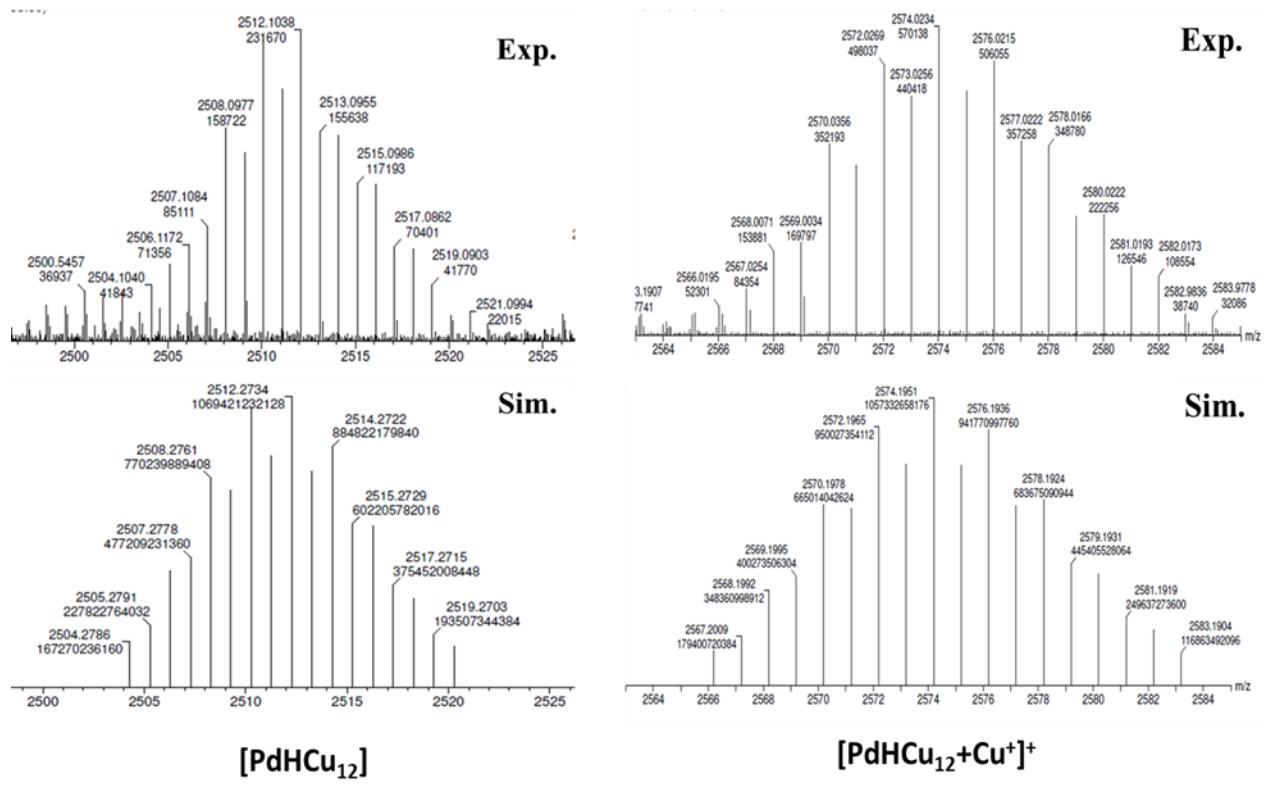


Figure S9. Isotopic patterns of experimental (top) and simulated (bottom) spectra corresponding to PdHCu_{12} and $[\text{PdHCu}_{12} + \text{Cu}^+]^+$.

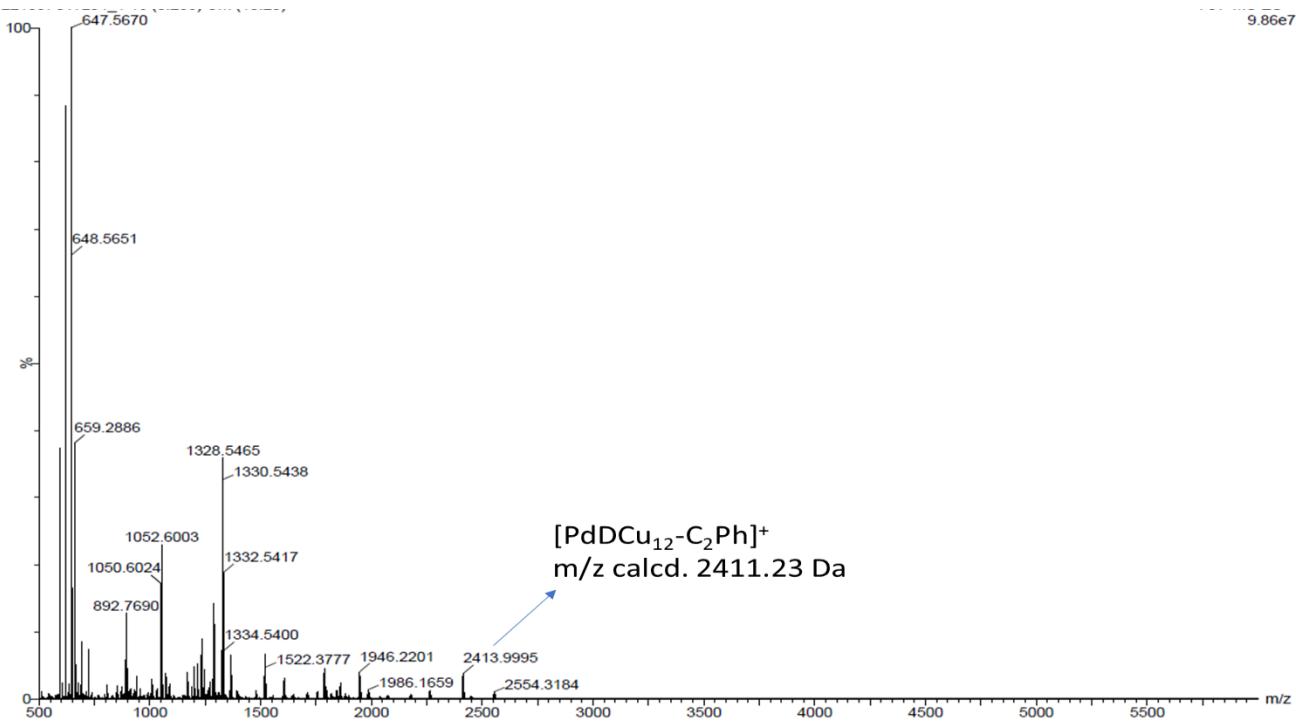


Figure S10. The positive-ion ESI-MS spectra of $[PdDCu_{12}-C_2Ph]^+$.

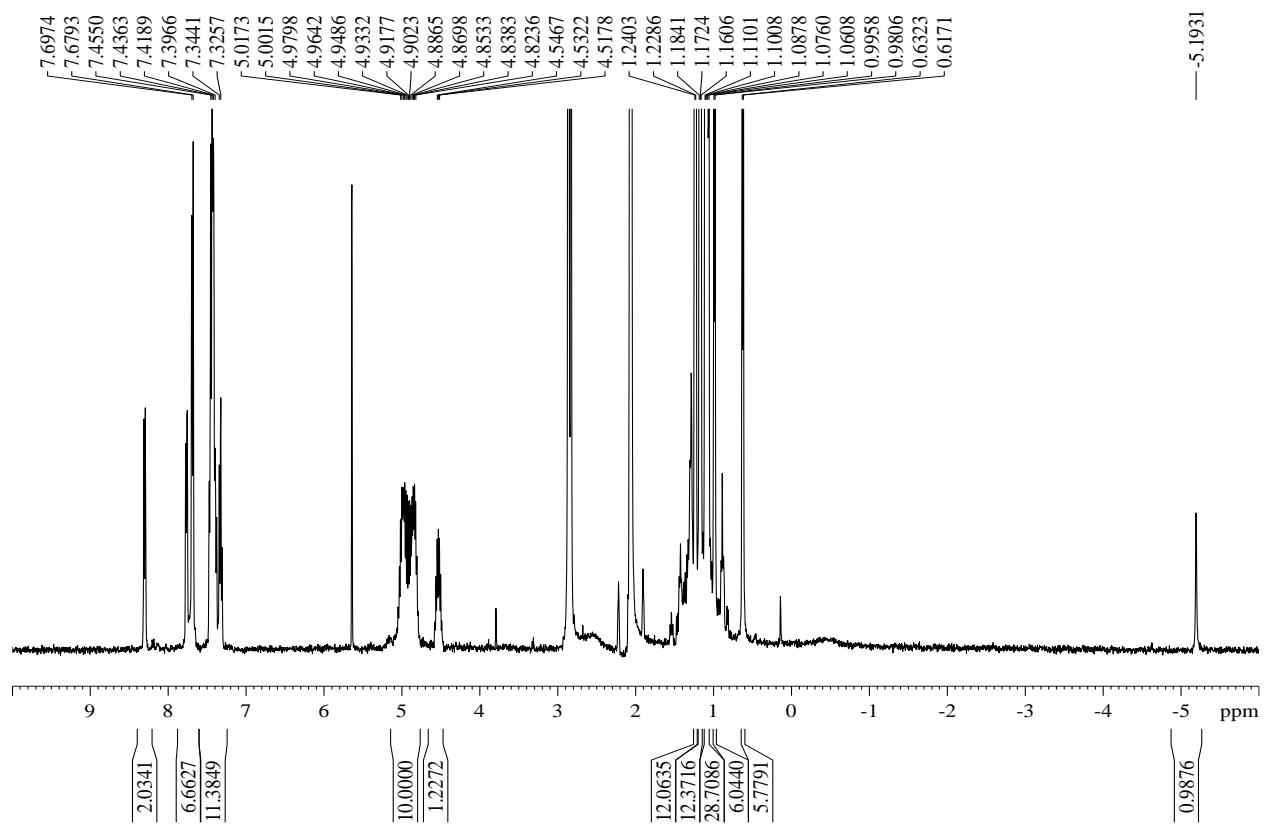


Figure S11. ¹H NMR spectrum of PdHCu₁₂ in *d*₆-acetone.

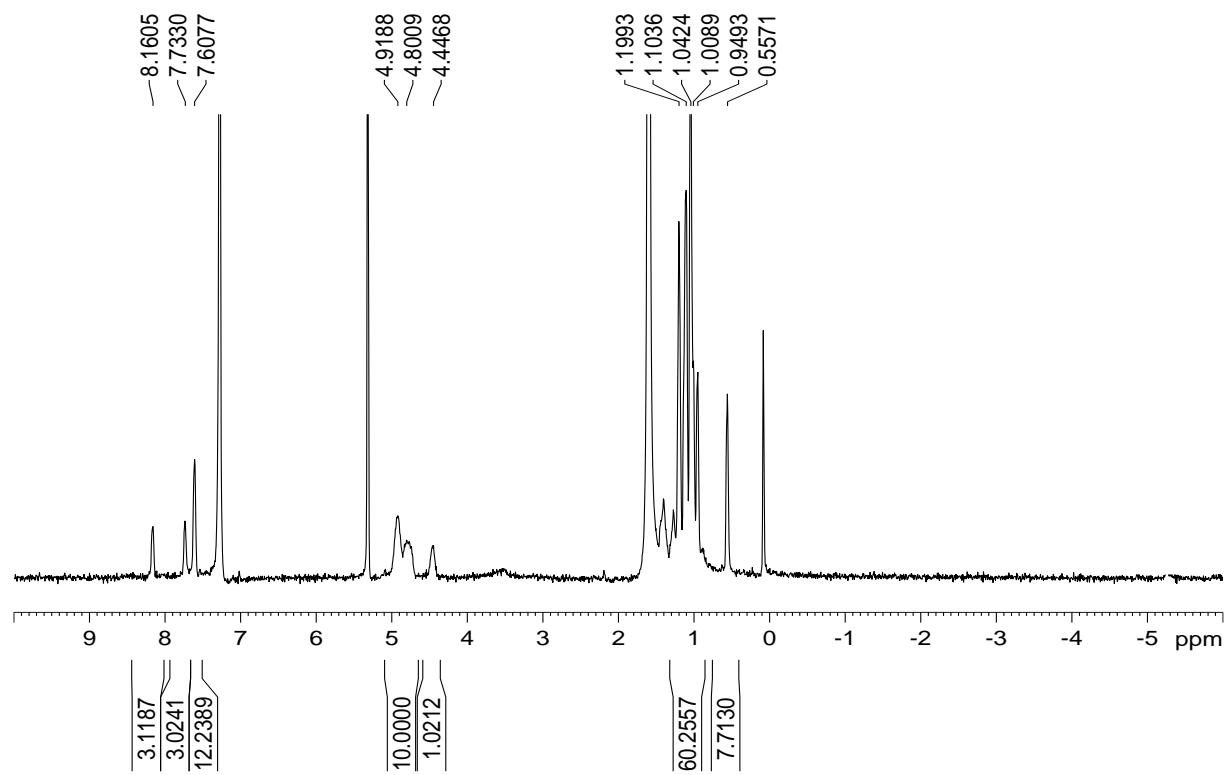


Figure S12. ^1H NMR spectrum of PdDCu_{12} in CDCl_3 .

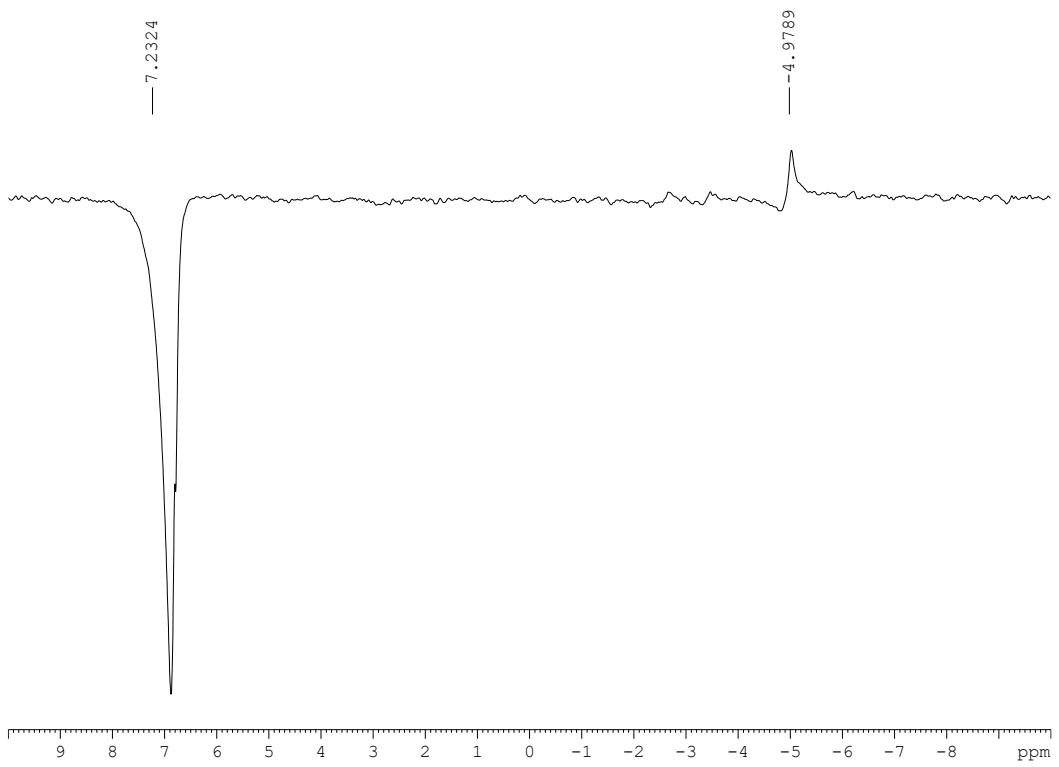


Figure S13. ^2H NMR spectrum of PdDCu_{12} in CHCl_3 .

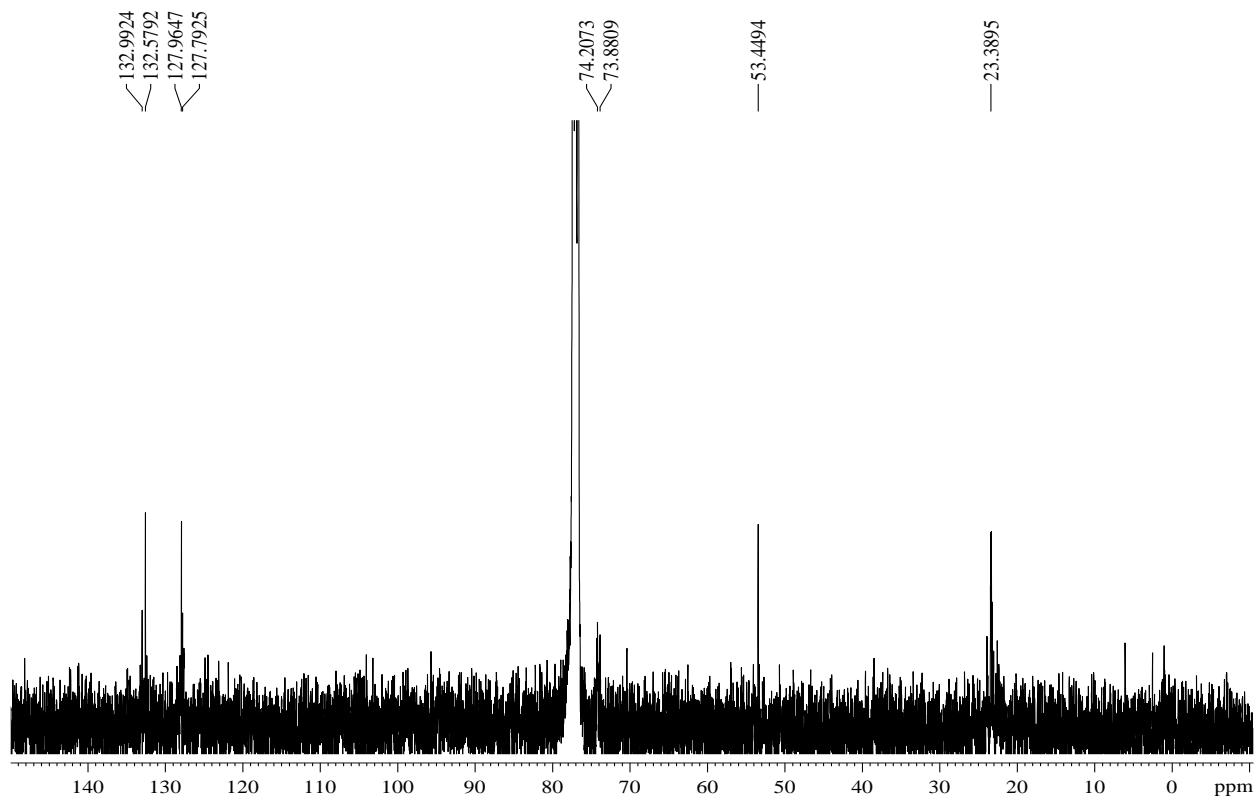


Figure S14. ^{13}C NMR spectrum of PdHCu_{12} in CDCl_3 .

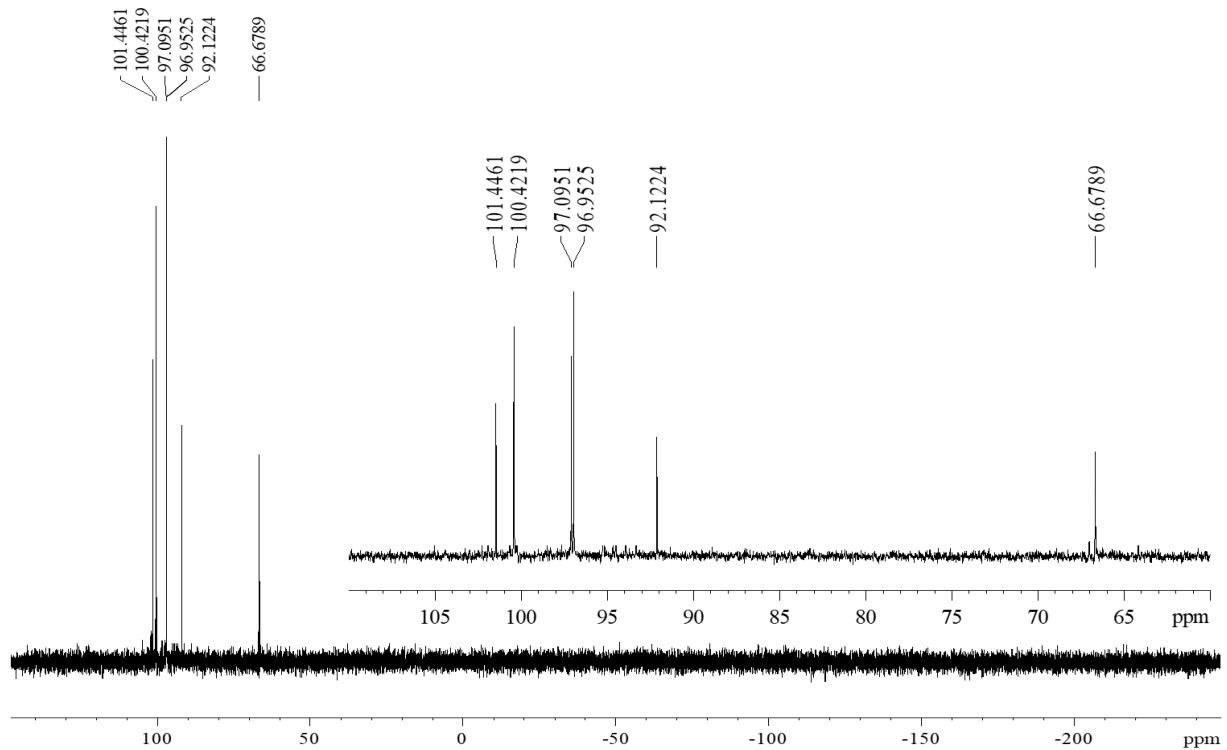


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of PdHCu_{12} in d_6 -acteone.

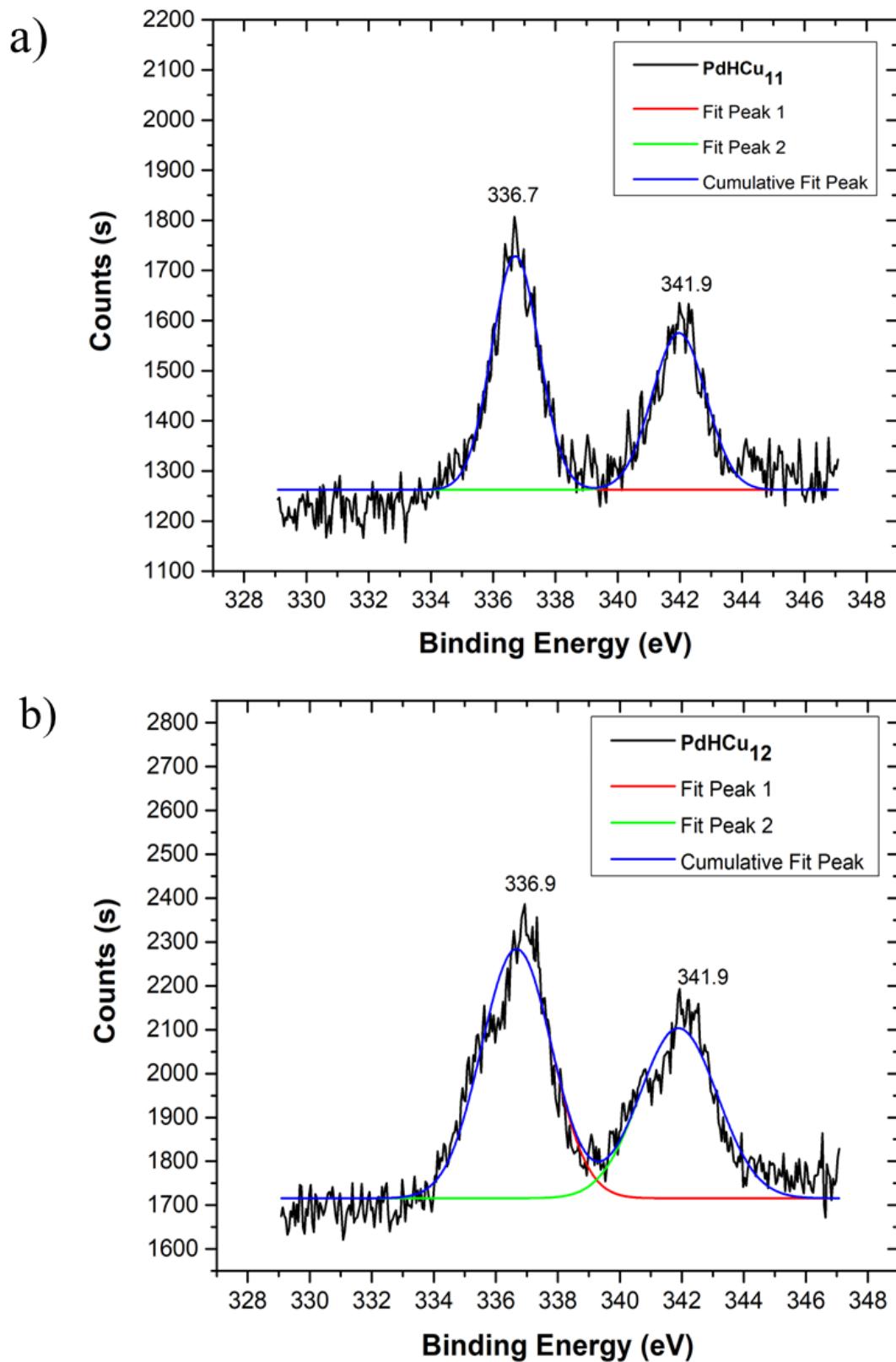


Figure S16. Pd 3d XPS spectra of Pd(0) in a) PdHCu₁₁ and b) PdHCu₁₂.

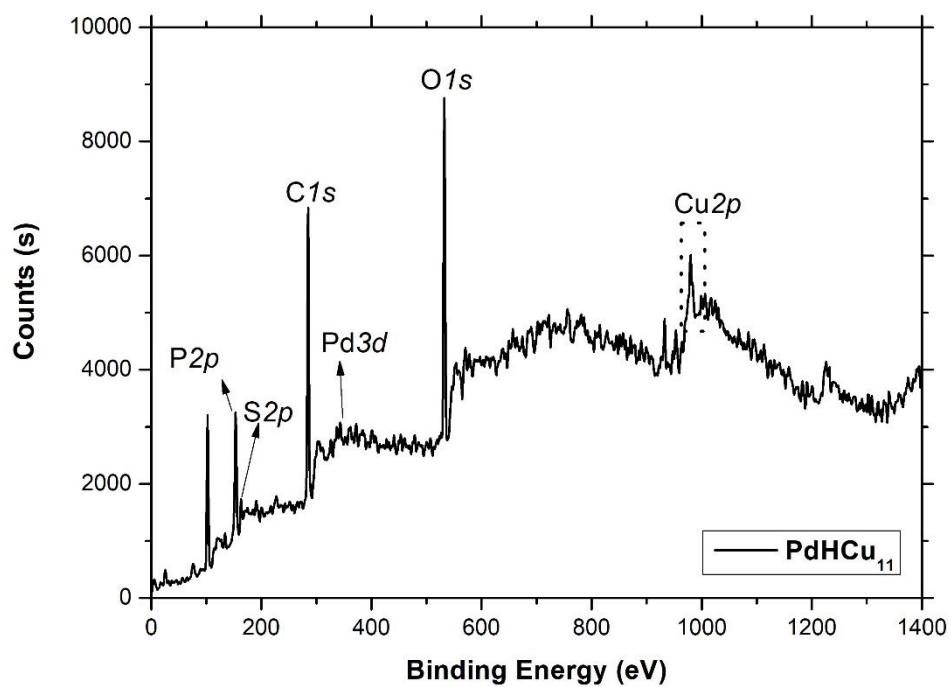


Figure S17. XPS survey spectrum **PdHCu₁₁**, confirming C, Cu, P, Pd, and S.

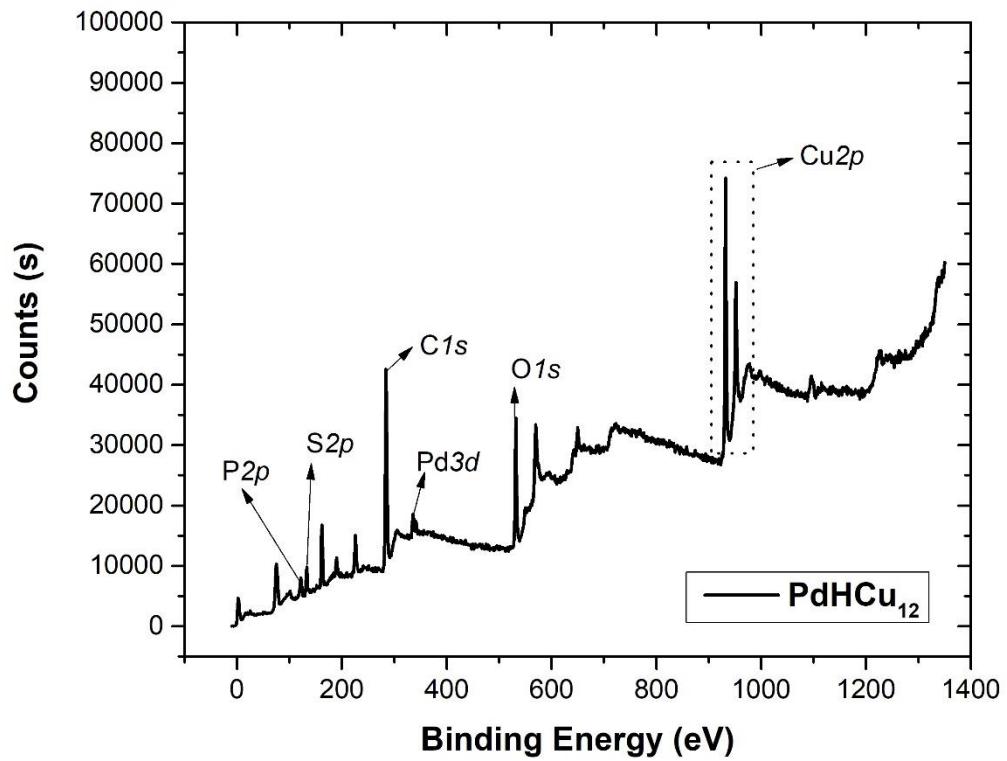


Figure S18. XPS survey spectrum **PdHCu₁₂**, confirming C, Cu, P, Pd, and S.

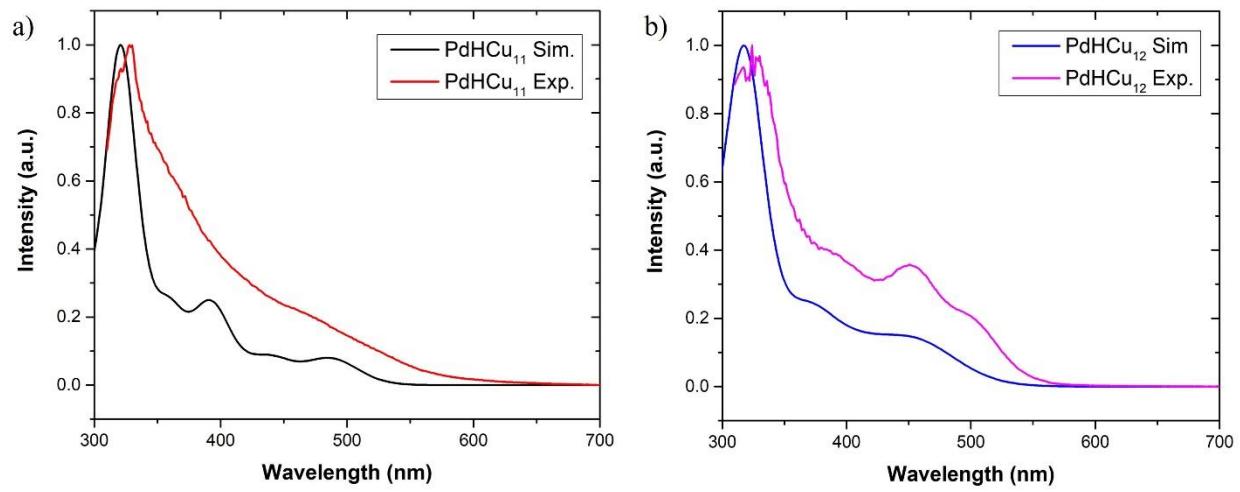


Figure 19. Experimental and TD-DFT-simulated UV-vis spectra of a) **PdHCu₁₁** and b) **PdHCu₁₂**.

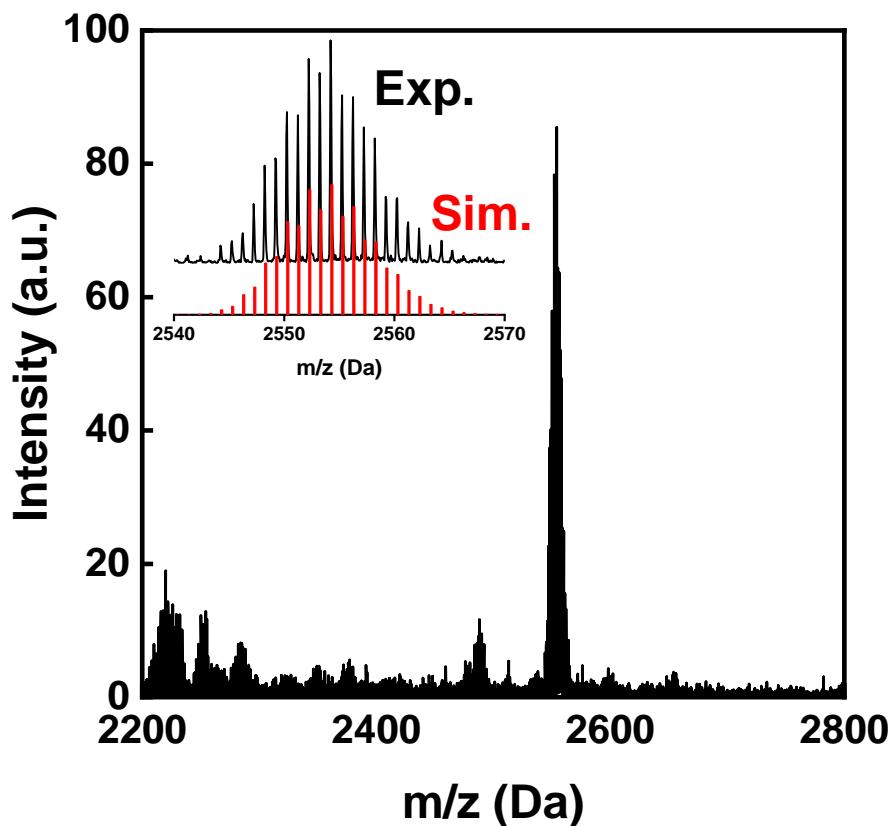


Figure S20. ESI-MS spectrum of the retrieved PdHCu₁₁ catalyst after voltammetric sweeping to the current density of 500 mA/cm² at 50 mV s⁻¹ for 200 cycles in 0.5 M H₂SO₄. Inset compares the experimental data ($m/z \sim 2554$ Da) and simulated isotopic pattern corresponding to $[\text{PdHCu}_{11}+\text{Cu}^+]^+$.

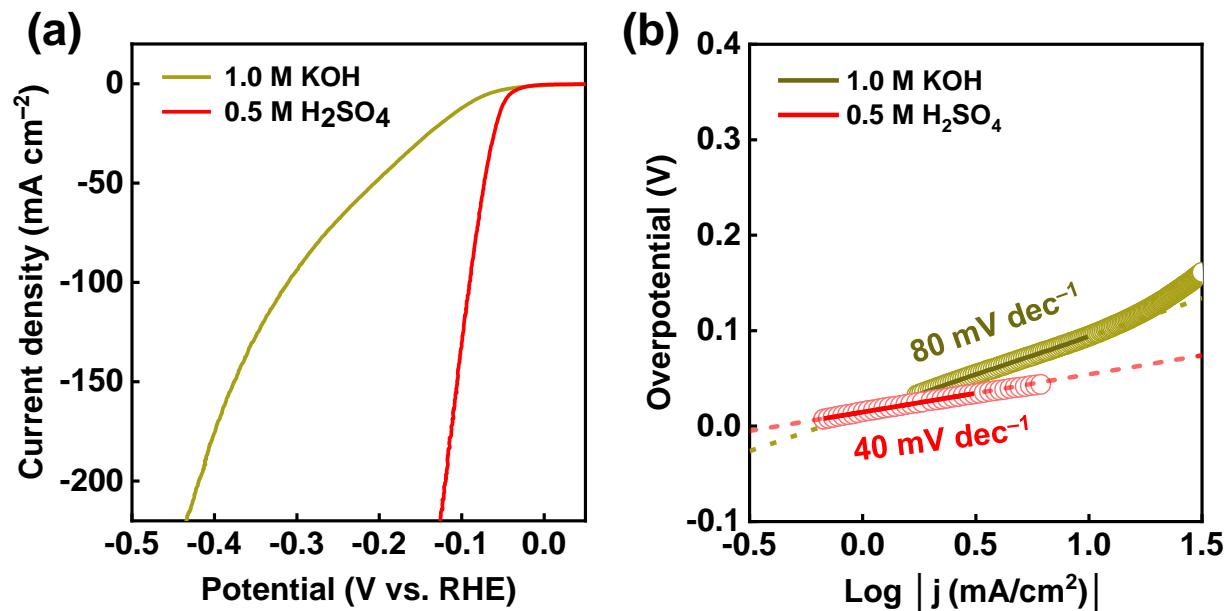


Figure S21. a) LSVs recorded at 1 mV s^{-1} and b) Tafel plots for HER on **PdH_xCu₁₁/C** in 0.5 M H_2SO_4 and 1.0 M KOH.

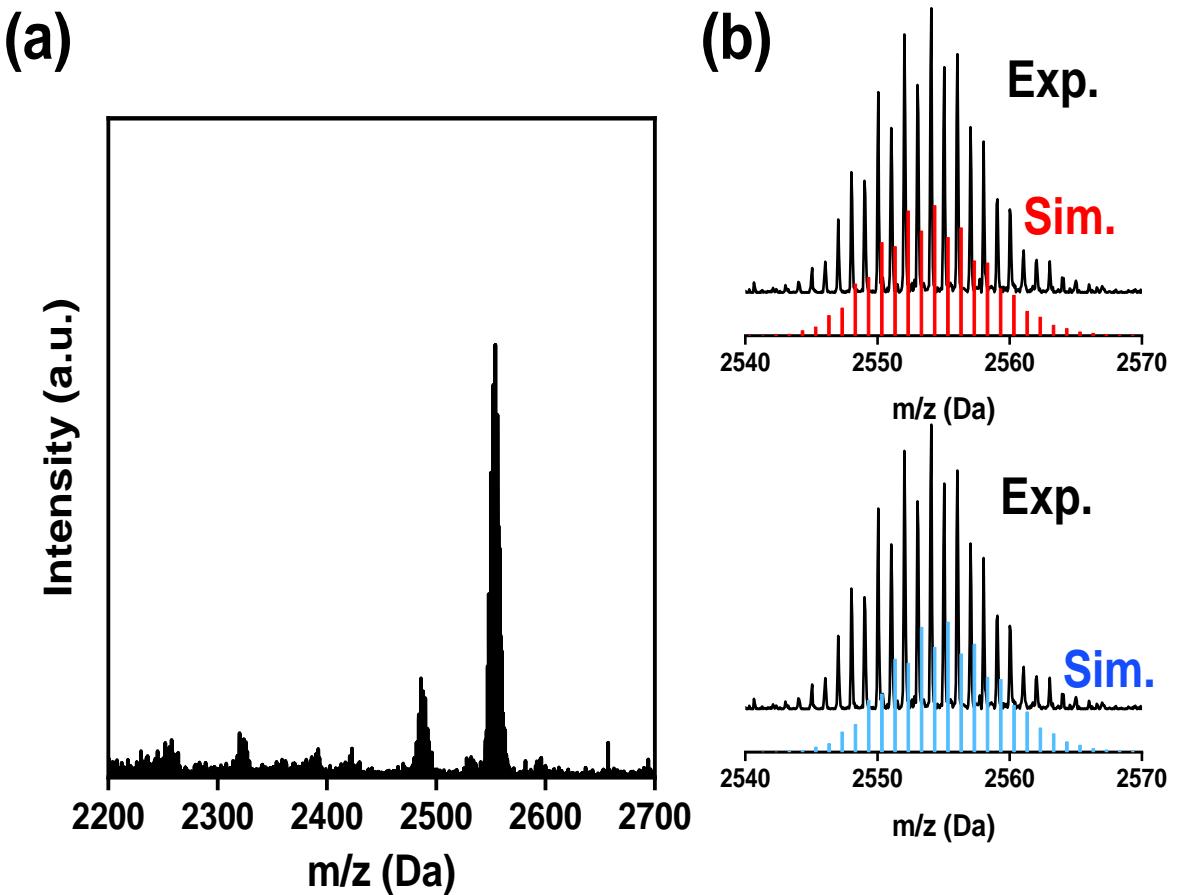


Figure S22. a) Positive-mode ESI-MS of **PdHCu₁₁** retrieved after conducting electrolysis at -0.25 V for 2.5 h in 0.5 M D₂SO₄. b) Comparisons of the experimental data (black) and simulated isotopic patterns (red and blue) corresponding to $[\text{PdHCu}_{11}+\text{Cu}^+]^+$ and $[\text{PdDCu}_{11}+\text{Cu}^+]^+$, respectively.

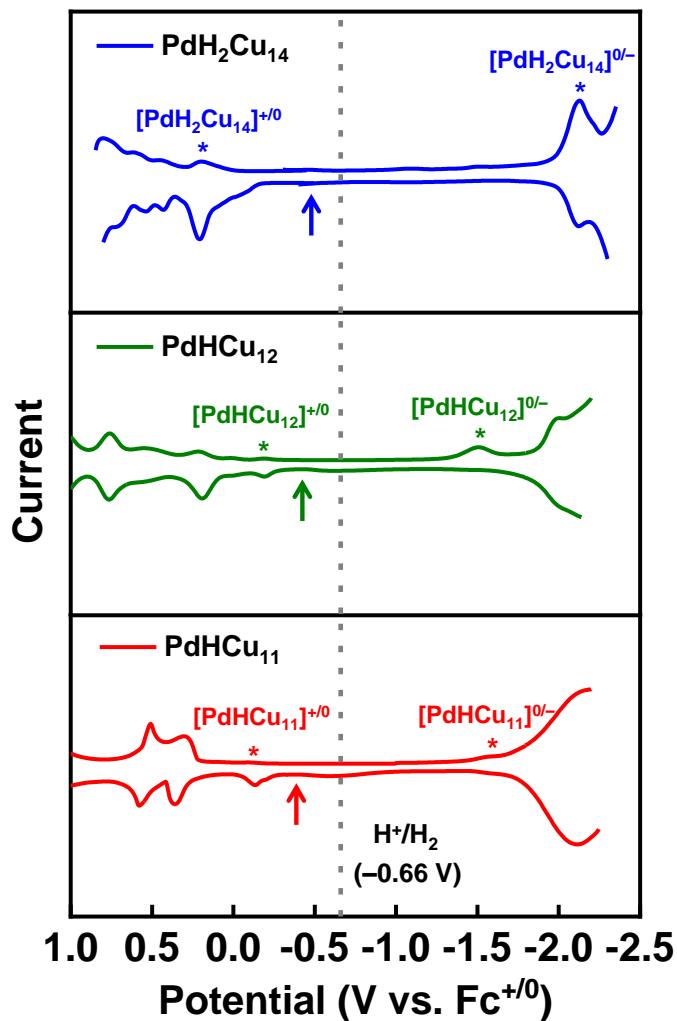


Figure S23. Square wave voltammograms of 1.0 mM Pd-Cu nanoclusters: **PdH₂Cu₁₄** (blue), **PdHCu₁₂** (green), and **PdHCu₁₁** (red) in CH₂Cl₂ containing 0.1 M Bu₄NPF₆. Voltammograms were obtained using a Pt disk working electrode, Pt wire counter electrode and Ag/AgNO₃ reference electrode. The potentials were calibrated using ferrocene (Fc^{+/-}) as an internal standard. The dashed line and arrows denote the thermodynamic reduction potential of the proton in 0.5 M H₂SO₄ and the solution open-circuit potential, respectively. *denotes the first oxidation and reduction potentials.

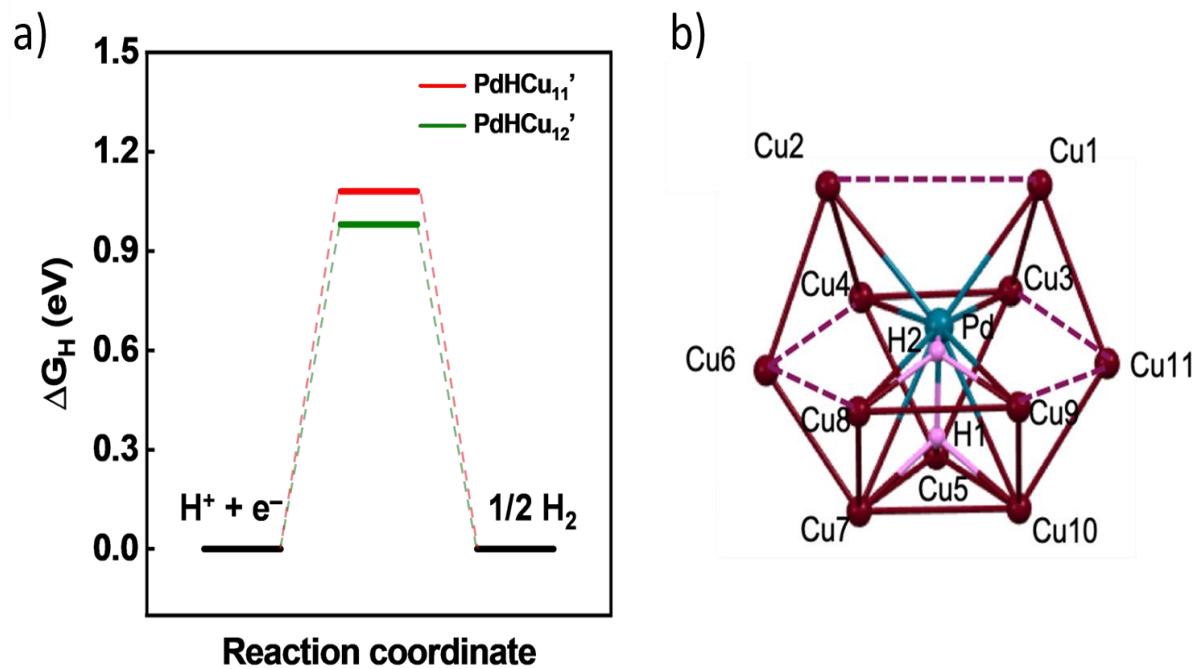
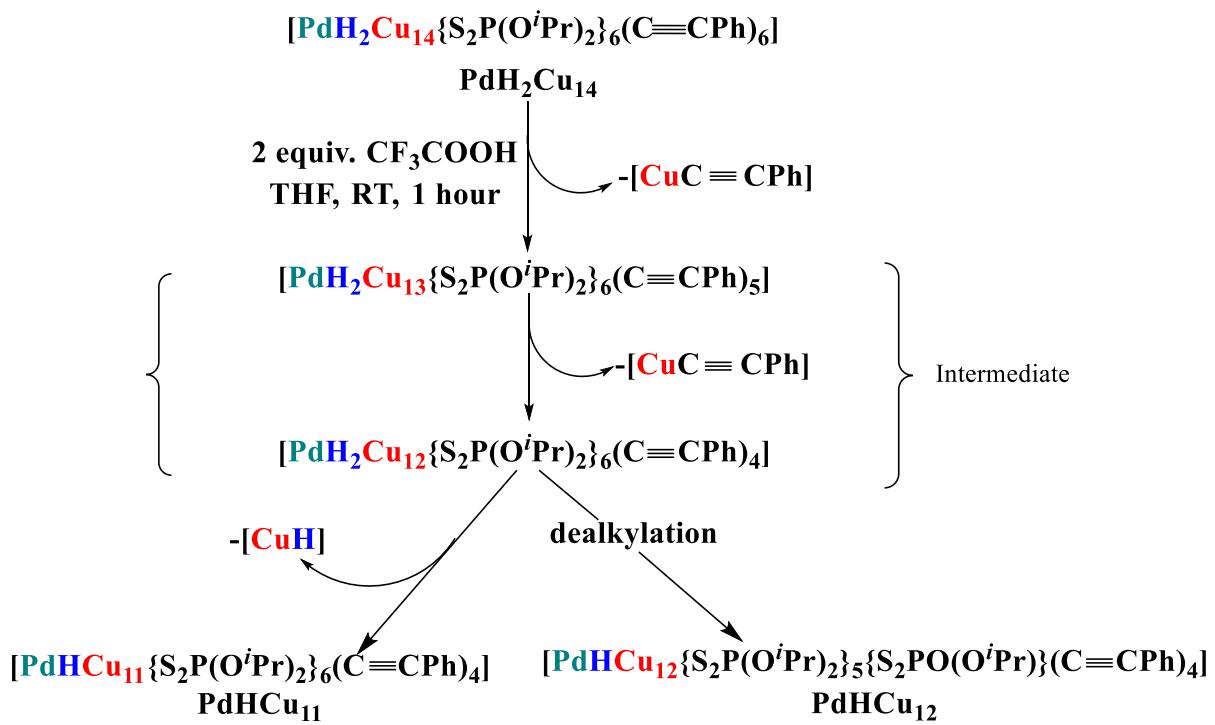
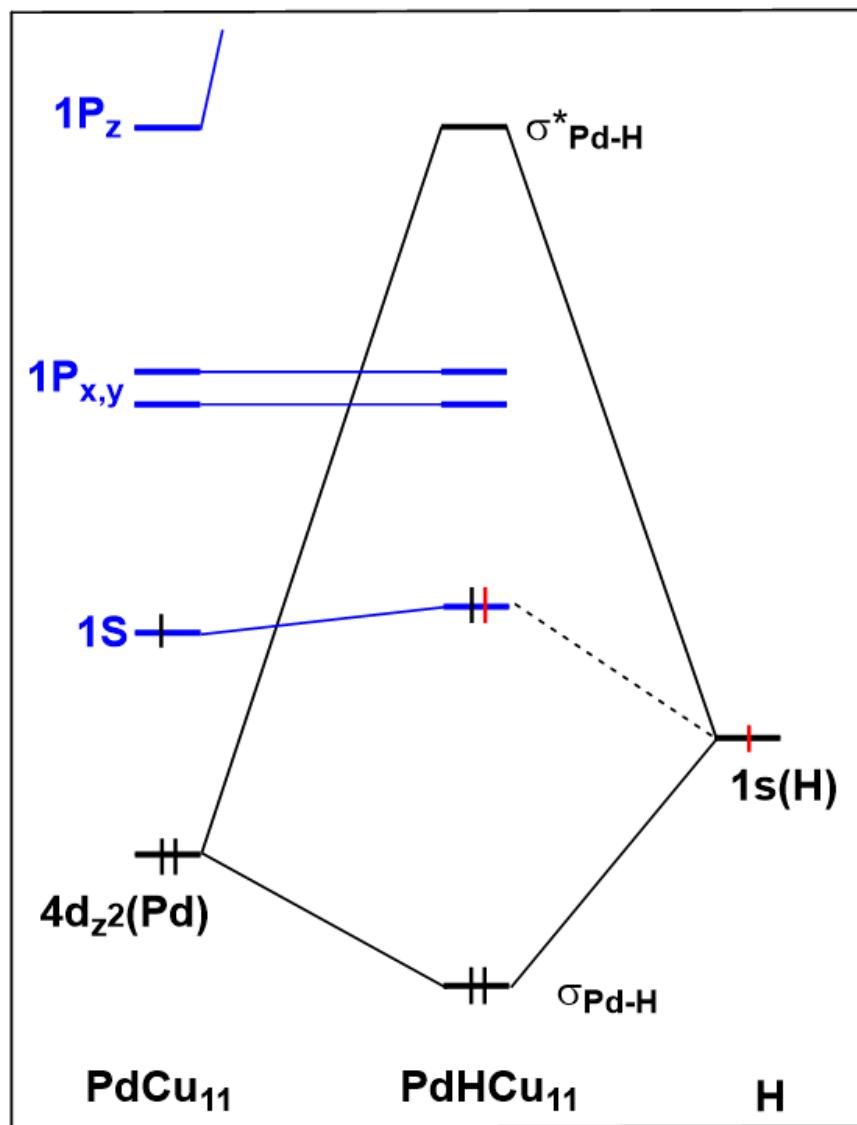


Figure S24. a) Calculated Gibbs free energy diagram describing the H^+ reduction to H_2 on **PdHCu₁₁'** and **PdHCu₁₂'** at zero applied potential. b) The optimized core structure of **[PdHCu₁₁-H']** intermediate. Same colour codes as in Figure 1.



Scheme S1. Proposed mechanism for the degradation of **PdH₂Cu₁₄** into **PdHCu₁₁** and **PdHCu₁₂** upon adding trifluoroacetic acid. Besides **PdHCu₁₁** and **PdHCu₁₂** can not be interconverted in the presence of an oxidizing (H_2O_2) or reducing agent (NaBH_4).



Scheme S2. Simplified MO diagram sketching the interaction between the $[\text{PdCu}_{11}(\text{dtp})_6(\text{CCPh})_4]$ cage and its encapsulated hydrogen atom in PdHCu_{11} , stressing the weak participation of the hydride to the *superatomic* orbitals (in blue), despite the contribution of its electron to the *superatom* 2-electron count.

Table S1. Selected X-ray crystallographic data of **PdHCu₁₁** and **PdHCu₁₂**.

| | PdHCu₁₁ | PdHCu₁₂ |
|--|--|---|
| CCDC no. | 2215591 | 2215592 |
| Empirical formula | C ₇₄ H ₁₁₇ Cu ₁₁ O ₁₄ P ₆ PdS ₁₂ | C ₆₅ H ₉₈ Cu ₁₂ O ₁₂ P ₆ PdS ₁₂ |
| Formula weight | 2606.55 | 2510.85 |
| Temperature, K | 100(2) | 100(2) |
| Wavelength, Å | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic |
| Space group | <i>P</i>  | <i>P</i>  |
| a, Å | 16.5109(4) | 15.9281(17) |
| b, Å | 17.2895(4) | 16.8695(18) |
| c, Å | 216.4847(4) | 21.652(2) |
| α , deg. | 88.9188(6) | 74.483(2) |
| β , deg. | 84.5477(6) | 87.152(2) |
| γ , deg. | 89.5102(6) | 66.151(2) |
| Volume, Å ³ | 4967.7(2) | 5116.0(9) |
| Z | 2 | 2 |
| ρ , Mg m ⁻³ | 1.743 | 1.630 |
| μ , mm ⁻¹ | 2.881 | 2.993 |
| Crystal size, mm ³ | 0.09 x 0.00 x 0.03 | 0.20 x 0.16 x 0.02 |
| θ_{\max} , deg. | 28.586 | 29.255 |
| Reflections collected / unique | 56013 / 24900 ($R_{\text{int}} = 0.0379$) | 61694/27668 [$R_{\text{int}} = 0.0649$] |
| Completeness, % | 99.3 | 99.9 |
| restraints / parameters | 9 / 1106 | 531 / 1010 |
| GOF | 1.027 | 1.045 |
| ^a R1, ^b wR2 [I>2σ(I)] | R1 = 0.0382, wR2 = 0.0879 | R1= 0.0748, wR2 = 0.1830 |
| ^a R1, ^b wR2 (all data) | R1 = 0.0631, wR2 = 0.0983 | R1= 0.1379, wR2 = 0.2130 |
| Largest diff. peak / hole, e Å ⁻³ | 1.561, -0.945 | 2.376, -1.351 |

^a R1 = $\Sigma |F_o| - |F_c| / \Sigma |F_o|$. ^b wR2 = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Table S2. Comparison of HER activities measured on PdHCu₁₁ with Pt and Pd single-atom catalysts in acidic media (0.5 M H₂SO₄).

| Catalyst | Tafel slope (mV dec ⁻¹) | η at 10 mA cm ⁻² (mV) | TOF (s ⁻¹) | Reference |
|-------------------------|--|--|---------------------------|---|
| PdHCu ₁₁ | 40 | 50 | 250@0.1V | This work |
| Pt ₁ /OLC | 36 | 38 | 90@0.2V | <i>Nat. Energy.</i> 2019 , <i>4</i> , 512–518. |
| Pt ₁ /NPC | 28 | 25 | 100@0.1V | <i>ACS Catal.</i> 2018 , <i>8</i> , 8450–8458. |
| Pt SA/WO _{3-x} | 45 | 38 | 35@0.1V | <i>Angew. Chem. Int. Ed.</i> 2019 , <i>58</i> , 16038–16042. |
| Pt-SAs/WS ₂ | 28 | 32 | 273@0.2V | <i>Nat. Commun.</i> 2021 , <i>12</i> , 3021. |
| Pt/hCNC | 24 | 15 | 7.67@0.02V | <i>Nat. Commun.</i> 2019 , <i>10</i> , 1657. |
| Pt PCM | 65.3 | 105 | 12@0.2V | <i>Sci.Adv.</i> 2018 , <i>4</i> , eaao6657. |
| Pd/MOS ₂ | 80 | 89 | 16.54@0.2V | <i>Nat. Commun.</i> 2018 , <i>9</i> , 2120. |
| Pd ⁰ /GDY | 47 | 55 | 16.7@0.1V | <i>iScience.</i> 2019 , <i>11</i> , 31–41. |

Table S3. Comparison of HER activities measured on bimetallic nanocluster catalysts.

| Nanocluster | Onset Potential (V vs. RHE) | TOF (s ⁻¹) | Electrolyte | References |
|---|-----------------------------|------------------------|--------------------------------------|---|
| PdHCu ₁₁ | ~0 | 250@0.1V | 0.5 M H ₂ SO ₄ | This work |
| Au ₂ Pd ₆ S ₄ (PPh ₃) ₄ (SC ₆ H ₄ F ₂) ₆ | -0.15 | 1.15@0.4V | 0.5 M H ₂ SO ₄ | <i>Inorg. Chem. Front.</i> 2018 , 5, 2948-2954. |
| Au ₃₆ Ag ₂ (S-Adm) ₁₈ | -0.10 | - | 0.5 M H ₂ SO ₄ | <i>J. Am. Chem. Soc.</i> 2021 , 143, 11102-11108. |
| Au ₉ Ag ₉ (CCAr ^F) ₁₈ | -0.10 | - | 0.5 M H ₂ SO ₄ | <i>Eur. J. Inorg. Chem.</i> 2022 , e202200176. |
| Au ₂₄ Ag ₂₀ (^t BuC≡C) ₂₄ Cl ₂ | -0.25 | - | 0.5 M H ₂ SO ₄ | <i>Dalton Trans.</i> 2022 , 51, 7845–7850. |
| Au ₂₂ Ag ₂₂ (^t BuC≡C) ₁₆ Br _{3.3} Cl _{2.7} | -0.15 | - | | |
| PtAu ₂₄ (SC ₆ H ₁₃) ₁₈ | -0.07 | 34.0@0.60V | ^a 1.0 M B-R buffer (pH 3) | <i>Nat. Commun.</i> 2017 , 14723. |
| PdAu ₂₄ (SC ₆ H ₁₃) ₁₈ | -0.07 | 13.0@0.60V | ^a 1.0 M B-R buffer (pH 3) | <i>ACS Appl. Mater. Interfaces</i> 2018 , 10, 44645–44653. |
| Pt ₂ Au ₃₆ (SC ₆ H ₁₃) ₂₄ | -0.20 | 28.2@0.60V | | |
| Pd ₂ Au ₃₆ (SC ₆ H ₁₃) ₂₄ | -0.07 | 13.1@0.60V | | |
| NiAg ₂₄ (SPhMe ₂) ₁₈ | -0.05 | 108.5@0.60V | 1.0 M KOH | <i>Bull. Korean Chem. Soc.</i> 2021 , 42, 1672–1677 |

^a B-R buffer: Britton-Robinson buffer

Table S4. Cartesian coordinates of the DFT-optimised structures of **PdHCu₁₁'**, **PdHCu₁₂'**, **PdHCu₁₁-H'**, and **PdHCu₁₂-H'**.

PdHCu₁₁'

Pd -0.008625 -0.010398 -0.429946

Cu 1.283538 1.138917 -2.453515

Cu -0.096646 -2.232377 -2.054857

Cu 2.808362 0.286042 -0.325572

Cu 1.833289 -2.141526 0.032762

Cu 1.707867 -0.422294 1.964802

Cu -1.066781 -2.749406 0.444698

Cu -1.024166 -0.841939 2.180106

Cu -2.757174 -0.654668 0.142921

Cu -1.529139 2.376221 -0.289400

Cu 0.058020 1.794772 1.835688

Cu 1.165274 2.746853 -0.280705

S 3.437686 0.195354 -2.630941

S 2.119524 -3.050837 -2.149158

S -1.571720 -3.903586 -1.563122

S -3.799243 -1.206536 -1.861173

S -2.073520 3.024649 -2.462505

S 1.407860 3.418896 -2.552935
 S 3.448179 2.490847 0.213281
 S 2.023174 1.589323 3.279694
 S 0.816579 -3.996465 1.081043
 S 0.661436 -1.713975 3.730809
 S -3.508655 1.510469 0.598102
 S -1.561364 1.121459 3.507890
 P 2.902259 -1.617380 -3.327710
 P -3.456664 -3.147794 -1.760190
 P -0.480510 4.162963 -2.727409
 P 3.575710 2.256361 2.213587
 P 1.160667 -3.506440 3.006343
 P -3.227211 1.735765 2.582729
 H 0.167618 0.095635 1.234866
 C -0.248607 -0.199076 -2.450498
 C -0.649790 -0.530554 -3.579138
 C -1.230388 -0.731148 -4.862576
 C -1.056231 -1.933299 -5.557600
 H -0.475334 -2.728189 -5.102693
 C -1.632273 -2.110814 -6.803496

H -1.494753 -3.048539 -7.329773
 C -2.382015 -1.093420 -7.377281
 H -2.830213 -1.233572 -8.354279
 C -2.560730 0.102615 -6.693745
 H -3.152289 0.896489 -7.135498
 C -1.996118 0.286961 -5.444868
 H -2.141336 1.210770 -4.897247
 C -2.527592 -2.049474 1.658409
 C -3.585704 -2.542934 2.051710
 C -4.810821 -3.094286 2.505965
 C -4.836375 -4.012466 3.563262
 H -3.904353 -4.298454 4.035428
 C -6.037599 -4.543550 3.997532
 H -6.044341 -5.253496 4.816770
 C -7.229781 -4.170718 3.391084
 H -8.168729 -4.588914 3.734981
 C -7.214907 -3.260262 2.342868
 H -8.142845 -2.965478 1.866125
 C -6.018983 -2.724115 1.899580
 H -6.001148 -2.014207 1.080374

C -0.272937 3.532333 0.898198
C -0.731811 4.665287 1.056787
C -1.269189 5.963622 1.250682
C -2.463275 6.335358 0.617822
H -2.965481 5.618640 -0.022254
C -2.989056 7.600803 0.808987
H -3.913626 7.876332 0.314520
C -2.338757 8.514356 1.627766
H -2.753736 9.504826 1.774501
C -1.154848 8.154825 2.258122
H -0.643894 8.864615 2.898686
C -0.620874 6.891914 2.075197
H 0.301072 6.606278 2.566940
C 3.330850 -1.177520 1.057921
C 4.529424 -1.433804 1.176648
C 5.914359 -1.718702 1.290213
C 6.813871 -1.232148 0.332377
H 6.434698 -0.639763 -0.492032
C 8.165364 -1.506872 0.441168
H 8.851040 -1.124850 -0.306573

C 8.643999 -2.266463 1.500259
H 9.703600 -2.479427 1.581787
C 7.760589 -2.752039 2.454988
H 8.129435 -3.345037 3.284133
C 6.407310 -2.483161 2.355073
H 5.715892 -2.858452 3.099924
H 4.046424 -2.171954 -3.934418
H 2.049770 -1.433222 -4.433957
H -4.000383 -3.777025 -2.899099
H -4.190916 -3.759084 -0.722986
H -0.536061 4.755700 -4.005949
H -0.507309 5.297311 -1.890687
H 4.692587 1.439198 2.473841
H 3.989077 3.495314 2.744023
H 2.527527 -3.733226 3.260654
H 0.553107 -4.503047 3.796891
H -4.330324 1.141951 3.227221
H -3.414275 3.100736 2.875939

PdHCu₁₂'

| | | | |
|----|-----------|-----------|-----------|
| Pd | -0.000032 | -0.211157 | 0.369879 |
| H | 0.000491 | 0.442157 | -1.179430 |
| Cu | -1.747299 | -0.025478 | 2.437901 |
| Cu | -0.001357 | -2.861099 | 0.986004 |
| Cu | 1.746512 | -0.025983 | 2.438415 |
| Cu | 2.847849 | -0.105231 | -0.120668 |
| Cu | -2.847460 | -0.103479 | -0.121369 |
| Cu | -1.520207 | -2.172173 | -1.168239 |
| Cu | 1.518639 | -2.172617 | -1.167271 |
| C | -0.000470 | -1.178671 | 2.227805 |
| Cu | 1.383303 | 0.120125 | -2.316470 |
| Cu | 0.001131 | 2.251231 | -1.236564 |
| Cu | -1.381983 | 0.120612 | -2.316702 |
| Cu | -1.317042 | 2.419882 | 1.047731 |
| S | -3.719807 | -1.087029 | 1.848723 |
| S | -1.748086 | 2.066748 | 3.276544 |
| C | -0.001396 | -1.910101 | 3.240318 |
| S | -2.001287 | -3.866603 | 0.446594 |
| S | 1.998670 | -3.867520 | 0.447683 |
| Cu | 1.318172 | 2.419223 | 1.048571 |

S 1.747938 2.066006 3.277609
S 3.718553 -1.089058 1.850054
S 3.497171 2.128343 0.146812
C 2.994163 -1.026470 -1.968612
C 4.143319 -1.270582 -2.336608
S -3.495917 2.130477 0.145231
C -2.994201 -1.024280 -1.969677
C -4.143651 -1.266681 -2.337890
S -0.000568 -3.423066 -2.468821
S 0.000802 -0.400537 -4.235755
S 1.782309 2.416184 -2.895526
S -1.779444 2.417044 -2.896286
C 0.001107 3.684406 0.166881
P -3.221225 -3.039571 1.830912
P -0.000413 2.081115 4.399481
C -0.002391 -2.699720 4.426891
P 3.217305 -3.040947 1.833370
P 3.412201 2.728022 -1.775029
C 5.471381 -1.549532 -2.748504
P -3.410126 2.728898 -1.776982

C -5.472065 -1.543592 -2.750036
 P 0.001352 -2.397956 -4.205716
 C 0.002210 4.912735 0.238140
 O -0.000966 1.082139 5.494782
 C -0.002745 -2.081874 5.684657
 C -0.003028 -4.099277 4.340235
 C 6.539263 -1.359522 -1.861582
 C 5.738621 -2.015717 -4.041730
 C -5.739612 -2.010943 -4.042779
 C -6.539985 -1.350337 -1.863856
 C 0.003381 6.328914 0.309177
 H -0.002240 -0.996677 5.745333
 C -0.003733 -2.865621 6.825750
 C -0.004022 -4.866293 5.491642
 H -0.002730 -4.572680 3.363394
 H 6.334647 -0.998388 -0.860461
 C 7.835443 -1.630117 -2.262416
 C 7.038183 -2.284227 -4.432196
 H 4.915559 -2.160916 -4.730898
 H -4.916509 -2.158669 -4.731361

C -7.039517 -2.277419 -4.433498
C -7.836507 -1.618916 -2.264946
H -6.335131 -0.988316 -0.863104
C 0.001670 7.097770 -0.861619
C 0.006280 6.979671 1.549184
H -0.004006 -2.383557 7.796596
C -0.004379 -4.251506 6.736923
H -0.004514 -5.947698 5.416486
H 8.653433 -1.478331 -1.567453
C 8.090149 -2.093027 -3.546336
H 7.232581 -2.644525 -5.435938
H -7.234151 -2.638654 -5.436858
C -8.091518 -2.083000 -3.548382
H -8.654522 -1.464634 -1.570563
H -0.000556 6.595271 -1.821598
C 0.002838 8.479384 -0.788835
C 0.007429 8.361571 1.610946
H 0.007606 6.386003 2.455270
H -0.005148 -4.854056 7.638137
H 9.107019 -2.303943 -3.856499

H -9.108655 -2.292334 -3.858741
H 0.001499 9.064338 -1.701603
C 0.005717 9.115822 0.445120
H 0.009676 8.854252 2.576513
H 0.006626 10.198442 0.498289
H -0.000277 3.412322 4.874640
H -4.424760 -3.768998 1.776516
H -2.731233 -3.382581 3.105528
H -4.522007 2.178955 -2.444302
H -3.704531 4.106443 -1.798863
H 4.419932 -3.772074 1.781775
H 2.724671 -3.381959 3.107499
H 4.524700 2.179034 -2.442107
H 3.705992 4.105712 -1.795827
H -1.091138 -2.865030 -4.963027
H 1.096043 -2.864456 -4.960187

PdHCu₁₁-H'

Pd -0.149174 -0.076037 0.414319
Cu -1.282967 1.113938 2.528900
Cu -0.660021 -2.477844 1.719799

| | | | |
|----|-----------|-----------|-----------|
| Cu | -2.797733 | 0.882484 | 0.259680 |
| Cu | -2.388238 | -1.631021 | -0.399670 |
| Cu | -1.784821 | 0.216933 | -2.089506 |
| Cu | 0.389529 | -2.857505 | -0.864491 |
| Cu | 0.829742 | -0.768720 | -2.299616 |
| Cu | 2.562693 | -1.025567 | -0.193742 |
| Cu | 2.168258 | 1.685345 | 0.501505 |
| Cu | 0.357453 | 1.932214 | -1.661679 |
| Cu | -0.571567 | 2.905257 | 0.523478 |
| S | -3.589210 | 0.671268 | 2.514707 |
| S | -3.004308 | -2.717205 | 1.623657 |
| S | 0.581671 | -4.246946 | 1.017407 |
| S | 3.320918 | -2.126359 | 1.756577 |
| S | 2.621396 | 1.967960 | 2.813364 |
| S | -0.665696 | 3.281690 | 2.850438 |
| S | -2.837701 | 3.231789 | 0.005552 |
| S | -1.548221 | 2.388286 | -3.134380 |
| S | -1.716323 | -3.528592 | -1.640246 |
| S | -0.938858 | -1.044700 | -3.978349 |
| S | 4.097908 | 0.803167 | -0.649653 |

S 1.849972 1.139089 -3.367967
 P -3.512469 -1.294761 2.962210
 P 2.571157 -3.910067 1.376768
 P 1.351710 3.439133 3.157657
 P -2.935746 3.283528 -2.010631
 P -1.821678 -2.772096 -3.507465
 P 3.645575 1.426923 -2.503878
 H -0.213747 0.256533 -1.239945
 C -0.174527 -0.576865 2.421873
 C 0.131961 -1.158842 3.475469
 C 0.618237 -1.673190 4.709551
 C 0.116491 -2.863886 5.247606
 H -0.649088 -3.408687 4.706091
 C 0.603307 -3.348342 6.449079
 H 0.211114 -4.274677 6.853119
 C 1.588447 -2.651056 7.134664
 H 1.966299 -3.030638 8.077123
 C 2.092910 -1.469101 6.607141
 H 2.868769 -0.926930 7.135680
 C 1.620170 -0.981606 5.402446

H 2.019573 -0.070369 4.972869
C 2.042068 -2.286950 -1.837258
C 3.154925 -2.752047 -2.095713
C 4.420120 -3.294556 -2.440790
C 4.562630 -4.092528 -3.583463
H 3.694608 -4.288788 -4.201164
C 5.797352 -4.619943 -3.915432
H 5.895898 -5.236733 -4.801486
C 6.906896 -4.360497 -3.121395
H 7.873013 -4.774726 -3.385921
C 6.774906 -3.568969 -1.988503
H 7.638076 -3.363252 -1.365764
C 5.544041 -3.038317 -1.644622
H 5.433048 -2.421845 -0.760027
C 1.127709 3.315830 -0.444690
C 2.089536 4.085512 -0.345916
C 3.142948 5.038051 -0.300033
C 4.335398 4.758627 0.379838
H 4.446528 3.802094 0.877251
C 5.352735 5.696407 0.412714

H 6.271462 5.468809 0.941169
C 5.200958 6.920747 -0.223631
H 6.000456 7.652059 -0.193985
C 4.021092 7.206169 -0.898729
H 3.897814 8.160839 -1.397342
C 2.998482 6.276123 -0.940996
H 2.077057 6.492309 -1.468101
C -3.578725 -0.229587 -1.339643
C -4.807137 -0.145704 -1.377851
C -6.221961 -0.046703 -1.411408
C -6.896067 0.726778 -0.457222
H -6.321774 1.240585 0.304823
C -8.275581 0.826914 -0.488832
H -8.785672 1.428045 0.255236
C -9.004903 0.162330 -1.465524
H -10.085536 0.243226 -1.486783
C -8.345505 -0.607169 -2.414797
H -8.910827 -1.128413 -3.178907
C -6.966552 -0.713758 -2.392093
H -6.448879 -1.312939 -3.131345

| | | | |
|---|-----------|-----------|-----------|
| H | -4.790660 | -1.642487 | 3.440224 |
| H | -2.713819 | -1.458142 | 4.110282 |
| H | 2.899234 | -4.783395 | 2.433471 |
| H | 3.209648 | -4.530229 | 0.283570 |
| H | 1.475524 | 3.851334 | 4.500004 |
| H | 1.711431 | 4.612647 | 2.465018 |
| H | -4.206969 | 2.805275 | -2.382905 |
| H | -3.011412 | 4.641248 | -2.381852 |
| H | -3.185250 | -2.693047 | -3.852801 |
| H | -1.360327 | -3.775929 | -4.382765 |
| H | 4.609780 | 0.894186 | -3.382488 |
| H | 3.920395 | 2.806621 | -2.571423 |
| H | 1.521596 | 0.068906 | 0.666717 |

PdHCu₁₂-H'

| | | | |
|----|-----------|-----------|-----------|
| Pd | -0.044285 | -0.005155 | 0.392294 |
| H | 0.095063 | 0.254102 | -1.270812 |
| Cu | -1.564324 | 1.187089 | 2.327544 |
| Cu | -0.883882 | -2.300049 | 1.673898 |
| Cu | 1.786407 | 0.008169 | 2.428162 |
| Cu | 2.662218 | -1.140133 | -0.082049 |

Cu -2.834873 0.806972 -0.196605
Cu -2.222462 -1.840328 -0.678834
Cu 0.550341 -2.821730 -0.597810
C -0.254597 -0.432813 2.477508
Cu 1.188328 -0.907978 -2.269279
Cu 0.651199 1.849095 -1.782774
Cu -1.435245 0.013343 -2.334414
Cu -0.396535 2.906404 0.358321
S -3.780356 0.648410 1.945705
S -0.806940 3.295612 2.592226
C -0.492614 -1.042225 3.546079
S -3.158025 -2.813664 1.354123
S 0.584733 -4.125939 1.464187
Cu 2.065432 2.007405 0.480236
S 2.487511 2.131611 2.743752
S 3.202919 -1.790450 2.107265
S 3.958591 0.797379 -0.294720
C 2.271178 -2.483528 -1.591451
C 3.264966 -3.123608 -1.938074
S -2.626427 3.123328 -0.472281

C -3.298635 -0.496552 -1.727178
C -4.466540 -0.326098 -2.081791
S -1.341830 -3.854451 -1.707085
S -0.400292 -1.363722 -3.999218
S 2.272001 0.944972 -3.361214
S -1.104047 2.118999 -3.455710
C 1.229759 3.447545 -0.747660
P -3.988500 -1.311263 2.405340
P 0.865869 2.929502 3.771712
C -0.694259 -1.524358 4.874674
P 2.134139 -3.449646 2.556120
P 3.935397 1.177894 -2.273575
C 4.411497 -3.858690 -2.331190
P -2.477006 3.199070 -2.479583
C -5.811736 -0.140078 -2.489616
P -0.997422 -3.236053 -3.583996
C 1.836710 4.518585 -0.758971
O 0.550063 2.205648 5.026202
C -0.441013 -0.677315 5.962947
C -1.141737 -2.832358 5.102631

C 5.566436 -3.842821 -1.538067
 C 4.411561 -4.608162 -3.514338
 C -6.290298 -0.729860 -3.666463
 C -6.683118 0.639880 -1.717832
 C 2.537180 5.751830 -0.756861
 H -0.094410 0.335890 5.778125
 C -0.637289 -1.147135 7.249899
 C -1.332305 -3.285758 6.396093
 H -1.335929 -3.482201 4.255414
 H 5.569243 -3.262122 -0.623094
 C 6.686121 -4.558770 -1.921909
 C 5.535871 -5.321653 -3.888435
 H 3.521759 -4.619431 -4.132035
 H -5.618260 -1.331610 -4.266154
 C -7.604398 -0.543200 -4.055549
 C -7.995259 0.821240 -2.116888
 H -6.314676 1.096988 -0.806812
 C 2.361928 6.677532 -1.792740
 C 3.417502 6.059054 0.288544
 H -0.440600 -0.489181 8.088594

C -1.080733 -2.444658 7.472015
H -1.678592 -4.299028 6.564700
H 7.574066 -4.537912 -1.300467
C 6.675683 -5.300212 -3.095698
H 5.523953 -5.898107 -4.806376
H -7.963754 -1.004881 -4.968113
C -8.460778 0.231560 -3.284461
H -8.659918 1.427258 -1.511882
H 1.682574 6.440646 -2.602713
C 3.049729 7.877759 -1.778854
C 4.100288 7.262162 0.292556
H 3.551875 5.343402 1.091143
H -1.230799 -2.801521 8.484707
H 7.554877 -5.860008 -3.392932
H -9.489575 0.375772 -3.593457
H 2.905975 8.587449 -2.585635
C 3.919919 8.174549 -0.738391
H 4.777714 7.490098 1.107542
H 4.456311 9.116409 -0.730659
H 1.321676 4.247714 3.999260

H -5.376116 -1.551066 2.443034
H -3.628151 -1.470919 3.756874
H -3.745766 2.903191 -3.015137
H -2.315663 4.552764 -2.836635
H 3.070519 -4.498833 2.638157
H 1.711623 -3.330193 3.893755
H 4.963196 0.418773 -2.867387
H 4.402897 2.495353 -2.444732
H -2.155555 -3.492521 -4.344426
H -0.070440 -4.123725 -4.164790