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Synthesis of Bimetallic Copper-Rich Nanoclusters Encapsulating a Linear Palladium Dihydride Unit

Kiran Kumarvarma Chakrahari, Rhone P. Brocha Silalahi,Tzu-Hao Chiu, Xiaoping Wang, Nadia Azrou,Samia Kahlal, Yu-Chiao Liu, Ming-Hsi Chiang, Jean-Yves Saillard,* and C. W. Liu*

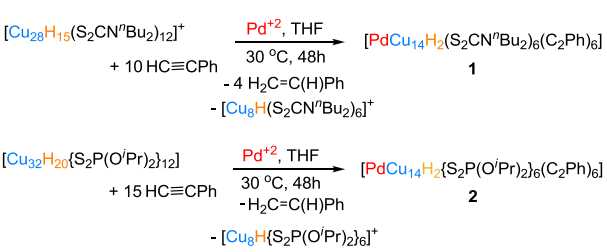
Dedication:

Abstract: The structurally precise Cu-rich hydride nanoclusters $[PdCu_{14}H_2(dtc/dtp)_6(C{\equiv}CPh)_6]$ (dtc: di-butyldithiocarbamate(**1**); dtp: di-isopropyl dithiophosphate(**2**)) were synthesized from the reaction of polyhydrido copper clusters $[Cu_{28}H_{15}(S_2CN^nBu_2)_{12}]^+$ or $[Cu_{20}H_{11}\{S_2P(O^iPr)_2\}_9]$ with phenyl acetylene in the presence of $Pd(PPh_3)_2Cl_2$. Their structures and compositions were determined by single crystal X-ray diffraction and the results were supported by ESI-mass spectrometry. Hydride positions in **1** were confirmed by single crystal neutron diffraction. Each hydride is connected to one Pd(0) and four Cu(I) atoms in slightly distorted trigonalbipyramidal geometry. The anatomies of clusters **1** and **2** are very similar and DFT calculations allow rationalizing the interactions between the encapsulated PdH_2 unit and its Cu_{14} bicapped icosahedral cage. As a result, Pd has the highest coordination number (14) so far recorded.

Atomically precise bimetallic nanoclusters (NCs) have emerged as a new class of nanomaterials.[1] Numerous studies have shown that doping NCs with foreign atoms allows tuning their properties, thus broadening their field of applications.[2] For instance, bimetallic clusters have been found to exhibit an increase in the photoluminescence quantum yield,[3] enhanced catalytic performance and stability compared to their homometallic counterparts.[4] In particular, bimetallic systems made of group 10 metals (Pt, Pd, or Ni) and "host metals" like Cu have been used in many catalytic processes.[5-9] Sub-nanometer Cu-Pd oxide clusters were also used as catalysts.[10] The geometry, electronic properties, and active sites of copper clusters doped with Pd atoms, $PdCu_{n-1}$ (n = 2-6), were alsotheoretically investigated.[11]

Structurally precise alloy NCs were produced from the doping by Pd, Pt, Cu, Ag, Cd and Hg of silver and gold species such as $Ag_{20}[S_2P(OR)_2]_{12}$, $Ag_{21}[Se_2P(OR)_2]_{12}$, $Ag_{25}(SR)_{18}$, $Ag_{44}(SR)_{30}^{4-}$, $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$ and $Au_{144}(SR)_{60}$.[12-16] *Interestingly, there are no reportso far of atomically precise copper clusters doped with group 10 metals*.

Recently, we reported the synthesis of copper-rich bimetallic NCs, $[M@Cu_{12}(dtc)_6(alkynyl)_4]^+$ (M = Ag, Au), from the template galvanic exchange strategy of reacting $[Cu_{13}(dtc)_6(alkynyl)_4]^+$ with corresponding metal salts.[3b] A similar synthetic strategy in inserting group 10 metals into the 2-electron copper superatom was not successful. In this study, we isolated a family of Cu-Pd hydride clusters from a novel synthetic protocol of reacting copper hydrides with alkynes in the presence of Pd(II) salt. Interestingly, our results also provide the first evidence of a linear $[PdH_2]^{2-}$ species embedded within a Cu(I) cage. This is the first "molecular" example consisting of a unique 14-electron anionic complex, originally identified in the solid-state ternary hydride Na_2PdH_2.[18]



Scheme 1. Synthesis of compounds **1** and **2**.

In a typical experiment, to a THF suspension of equimolar $[Cu_{28}H_{15}(S_2CN^nBu_2)_{12}]PF_6$[19a] and $[Pd(PPh_3)_2Cl_2]$, a ten-fold excess of phenyl acetylene was added and the reaction mixture was stirred at 30 ºC for 48 hours. The colour of the suspension changed from red to dark brown. Workup of this mixture leads to the isolation of $[PdCu_{14}H_2(S_2CN^nBu_2)_6(C{\equiv}CPh)_6]$ ($\mathbf{1_H}$) as dark red powder in 54% yield. The reaction also yielded styrene and $[Cu_8H(S_2CN^nBu_2)_6]^+$ as byproducts.[19] The hydrogen gas released from the reaction of terminal alkyne's acidic hydrogen with the hydrides of $[Cu_{28}H_{15}(S_2CN^nBu_2)_{12}]^+$ is assumed to be the reductant for the partial conversion of alkyne into alkene (four out of ten equivalents of phenyl-acetylene were reduced to styrene) and Pd(II) to Pd(0). The di-isopropyl dithiophosphate (dtp) analogue of **1** was isolated from the reaction of $[Cu_{20}H_{11}\{S_2P(O^iPr)_2\}_9]$[19b] or $[Cu_{32}H_{20}\{S_2P(O^iPr)_2\}_{12}]$[19d] with excess of phenylacetylene in the presence of $[Pd(PPh_3)_2Cl_2]$ (Scheme 1). The structures were established by both single crystal X-ray and Neutron diffraction. The presence of two hydrides is further confirmed by the isolation of their deuterium

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analogues $[Cu_{14}PdD_2(S_2CN^nBu_2)_6(C_2Ph)_6]$ (**1D**) and $[Cu_{14}PdD_2\{S_2P(O^iPr)_2\}_6(C{\equiv}CPh)_6]$ (**2D**) which were made from $[Cu_{28}D_{15}(S_2CN^nBu_2)_{12}]^+$ and $[Cu_{20}D_{11}\{S_2P(O^iPr)_2\}_9]$, respectively. During the synthesis of **1D** and **2D**, along with monodeuterated styrene $[Cu_8D(S_2CN^nBu_2)_6]^+$ and $[Cu_8D\{S_2P(O^iPr)_2\}_6]^+$ were isolated, respectively, as byproducts. ESI mass spectrum shows the molecular ion $[\mathbf{1_H}]^+$ at m/z 2829.3 (calcd 2828.6), $[\mathbf{1_D}]^+$ at m/z 2831.5 (calcd 2830.7), $[\mathbf{2}]^+$ at m/z 2882.9 (calcd 2881.2), $[\mathbf{2_D}\text{-}\{Cu(C_2Ph)\}_2]^+$ at m/z 2554.4 (calcd 2554.3), and their simulated isotopic patterns match well with experiment (Figure 1, S1-S3). We have also observed fragment ion peaks corresponding to the loss of C_2Ph, $Cu(C_2Ph)$, $Cu(C_2Ph)_2$ and $\{Cu(C_2Ph)\}_2$.

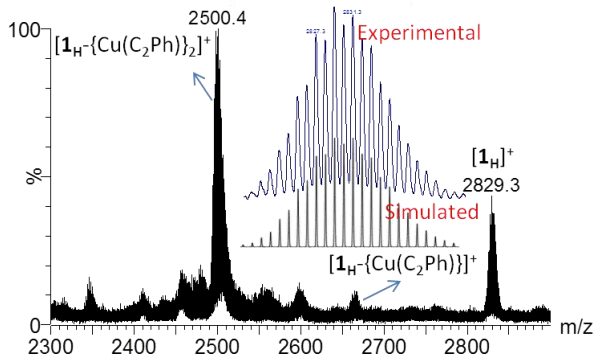

Figure 1. Positive mode ESI-MS of $[\mathbf{1_H}]^+$,. Inset shows experimental and simulated mass spectra.

^{1}H NMR spectroscopic analyses of **1** and **2** identified one set of acetylide and two sets of alkyl group corresponding to the dtc/dtp ligands. Though, compound **2** shows a single ^{31}P NMR resonance at 103.4 ppm, the alkyl groups corresponding to the dtp ligands exhibit two sets of ^{1}H resonance (Figure S4, S5). This trend of chemical shifts suggests no two-fold symmetry imposed on the dithiolate ligand environment around the cluster core.The presence of two hydrides in cluster **1H** is confirmed by a ^{1}H NMR resonance peak at 1.90 ppm in CD_2Cl_2, which is echoed by the presence of deuteride signal at 1.92 ppm for compound **1D** in dichloromethane at 203 K (Figure 2). Similarly, hydride and deuteride resonance for (**2H**, **2D**) were observed at (0.49, 0.49) ppm in ($CDCl_3$, $CHCl_3$) solvent (Figure S5, S6). Overall compositions of two hydrides, six acetylides and six dtc(**1**)/dtp(**2**) were confirmed by the integration of ^{1}H NMR resonances of the newly synthesized clusters. ^{1}H NMR of **1D** and **2D** shows the presence of hydride peaks with an intensity of 0.52 and 0.32 respectively (Figure S7, S8), indicating that the hydrides in **1D** and **2D** are from both parent cluster and phenylacetylene. Hence the clusters have 74% (**1D**) and 84% (**2D**) deuterium incorporation.

The single crystal X-ray diffraction analyses of clusters **1** (triclinic) and **2** (monoclinic) indicate they have an identical $PdCu_{14}$ metal core. Thermal ellipsoid drawings of **1H** and **2** are depicted in Figure 3 and selected metrical data from single crystal X-ray and neutron diffraction analyses are given in Table 1. Additional structural diffraction data are listed in Table S1 and S2. The copper framework can be viewed as a bicapped icosahedron (green) with a Pd atom at its center (brown). A pseudo-3-fold axis passes through the two capping copper atoms and the central Pd (Figure 3c). Thus, a bicapped-centered icosahedral $PdCu_{14}$ metallic core of D_{3d} symmetry is generated. Two additional interstitial hydrides are located along the C_3 axis on each side of the Pd atom, as authenticated by the neutron structure of **1H**, in which the Pd-H distance is found to be rather short (1.759(14)Å). These two hydrides are located in trigonal-bipyramidal cavities formed by one capping Cu, the corresponding capped Cu_3 face and the Pd atom (Figure 3d). The Cu-H lengths averaged 1.932(18) Å (Figure S9-S11, Table S3). The resulting D_{3d} PdH_2Cu_{14} core is stabilized by six dithiolates and six phenyl acetylides. Half of the alkyl chains corresponding to the dtc(**1**)/dtp(**2**) ligands are oriented towards the acetylide ligands, which are arranged along the waist of the $PdCu_{14}$ core, whereas the remaining half are oriented away from the metal core. This is in full agreement with the above reported NMR spectroscopic results.

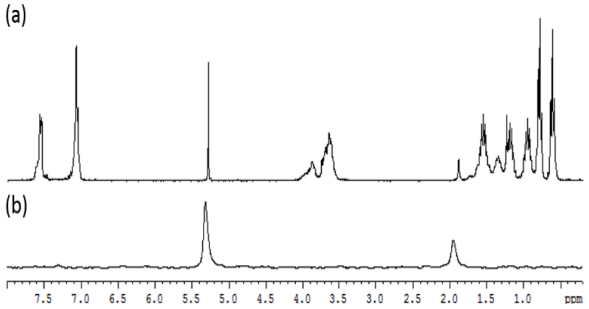

Figure 2. (a) ^{1}H NMR spectrum of compound **1H** in CD_2Cl_2 and (b) ^{2}H NMR spectrum of compound **1D** in CH_2Cl_2 solvent.

The inner icosahedral configuration of twelve copper atoms around the central PdH_2 unit in **1** and **2** is similar to that in $[Pd@M_{12}@\{M_{12}(SR)_{18}\}]^{2-}$ (M = Ag, Au).[12,14] The bicapped icosahedral core centered with a heterometal was also found in $Ag_{26}Pt(2\text{-}EBT)_{18}(PPh_3)_6$ (EBTH = ethylbenzenethiol).[20] *None of these examples has encapsulated hydrides except clusters **1** and **2**.*

The six dtc/dtp ligands are equally distributed on the top and bottom of the cluster along the C_3 axis. Each of the dtc/dtp ligands bridges four metal centres (one capping and three icosahedral copper atoms) in a (μ_2, μ_2) binding mode. The six acetylide ligands are arranged along the waist of the copper icosahedron, alternatively binding the top and bottom triangles in a μ_3-η^1 fashion. As a result, the D_{3d} symmetry identified in metal core is reduced to S_6 symmetry. Being connected to twelve copper and two hydrides, palladium displays a coordination number of 14, the highest value observed so far.

The dtc supported $PdCu_{14}$ cluster (**1**) is reddish, whereas the dtp analogue (**2**) appears to be violet (inset figure S12). The UV-vis spectrum of **1** shows a broad absorption band around 490-560 nm and an intense one at 287 nm. The dtp analogue (**2**) shows similar (495-556 nm) bands, but with lower intensity in the UV region. The stabilities of **1** and **2** in dichloromethane at 25 °C were compared. The absorption spectrum of **2** changed steadily over time and it is completely decomposed within 10 hours, whereas **1** requires seven days (Figures S13, S14).

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Table 1. Selected bond lengths (Å) for $\mathbf{1_H}$, $\mathbf{1_D}$, **2** (single crystal X-ray), $\mathbf{1_H}$* (neutron), **1'** and **2'** (DFT). Values in brackets are the corresponding computed Wiberg indices.

	Pd-Cu_{ico}	Cu_{ico}-Cu_{ico}	Cu_{cap}- Cu_{ico}	Cu-X	Pd-X	Cu-S
$\mathbf{1_H}$	2.684(4)-2.785(3)	2.602(7)- 3.323(4)	2.565(6)-2.606(5)	1.88(3)-1.93(5)[a]	1.84(3)[a]	2.271(1)-2.459(8)
$\mathbf{1_H}$*	2.694(9)-2.795(6)	2.554-3.324	2.555(10)-2.610(10)	1.875(19)-2.020(16)	1.759(14)[a]	2.270(2)-2.500(2)
$\mathbf{1_D}$	2.687(4)-2.784(5)	2.612(1)-3.3178(8)	2.566(1)-2.613(1)	1.77(4)-2.03(6)[b]	1.76(2)[b]	2.266(15)-2.480(15)
1'	2.736-2.780	2.608-3.500	2.599-2.620	1.937-1.989	1.760[a]	2.351-2.514
	[0.052-0.063]	[0.070-0.016]	[0.070-0.068]	[0.066-0.046]	[0.226]	[0.220-0.114]
2	2.690(7)-2.800(7)	2.578(7)- 3.164(6)	2.680(4)-2.768(5)	1.800(3)-1.850(3)[a]	1.80(3)[a]	2.267(7)-2.459(7)
2'	2.735-2.794	2.636-3.264	2.691-2.761	1.865-1.902	1.777[a] [0.214]	2.292-2.463
	[0.050-0.075]	[0.058-0.020]	[0.058-0.066]	[0.077-0.068]		[0.217-0.126]

[a]X=H, [b]X = D

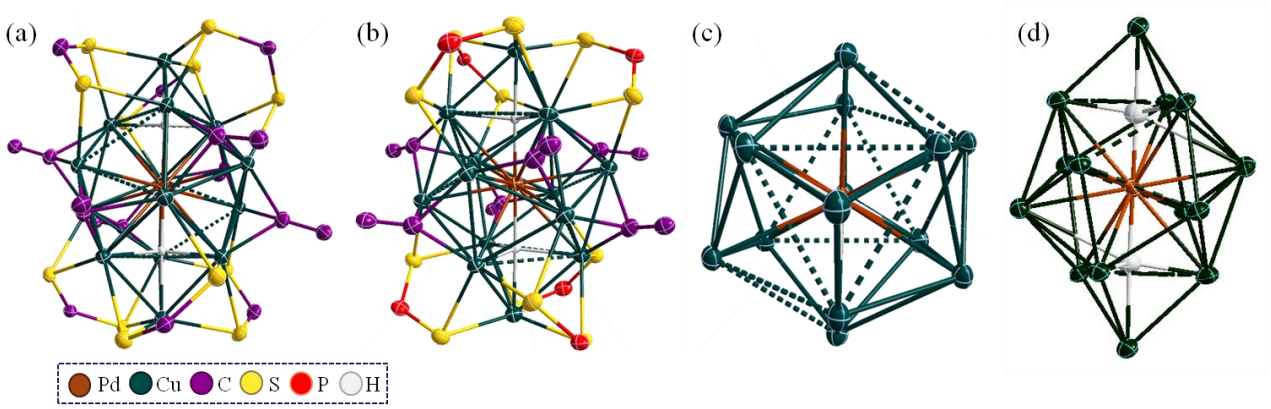

Figure 3. The ORTEP drawing of **1** (a) and **2** (b) with 30% thermal ellipsoid probability. N^nBu_2 (**1**), O^iPr (**2**) and phenyl groups are omitted for clarity. (c) A perspective view along 3-fold axis of PdH_2Cu_{14} core. (d) Side view of a PdH_2Cu_{14} core from neutron diffraction data.

Under the same conditions the stabilities of these clusters were also monitored by ESI-Mass spectra using $[Cu_8H(dtc/dtp)_6]^+$ as reference. The results show that $\mathbf{1_H}$ is extremely stable, whereas $\mathbf{1_D}$ loses its intensity with time (Figure S15, S16). The results indicate that the replacement of dtc with dtp decreases cluster stability. Both **1** and **2** display photoluminescence in solid and solution states at 77 K. The emission maximum in 2-methyl tetrahydrofuran (MeTHF) at 77 K is centred at 623 nm for **1**, which is a blue-shift compared to the emission observed for **2** (680 nm) with almost equal in intensity (Figure S12). Their emission intensity decreases sharply upon raising the temperature to 177K (Figure S17) and the luminescent thermochromism is clearly identified in **2** as the emission maximum shifts from 680 at 77K to 641 nm at 277K.

The photoelectron spectroscopic studies have been used to evaluate the metal oxidation states. X-ray photoelectron spectroscopy (XPS) analysis of $\mathbf{1_H}$ indicates binding energies at 336.0 and 341.0 eV corresponding to Pd(0) $3d_{5/2}$ and $3d_{3/2}$ respectively (Figure S18). The XPS results of **1** fit exactly with the existence of the expected elements.

DFT calculations were performed on simplified models of **1** and **2**, namely $[Cu_{14}PdH_2(S_2CNH_2)_6(C_2Ph)_6]$ (**1'**) and $[Cu_{14}PdH_2(S_2PH_2)_6(C_2Ph)_6]$ (**2'**). Their optimized geometries were found to be of exact C_i and approximate S_6 symmetry. Their metric data are in a satisfying agreement with their single crystal X-ray counterparts in **1** and **2** (Table 1). Their large HOMO-LUMO gaps (3.50 and 3.38 eV for **1'** and **2'**, respectively) are typical for stable Cu(I) hydride NCs.[19] The Kohn-Sham orbital diagram of **1'** is shown in Figure S19. The highest occupied levels have a large 3d (Cu) character with little Pd participation, except for the HOMO which has both significant Cu and Pd character. The LUMO and LUMO+2 are delocalized over the whole cluster, except on the hydrides. A natural atomic orbital (NAO) population analysis led to copper atomic charges indicative of Cu(I) oxidation state (+0.77 and +0.83 for the two types of Cu_{ico} and +0.66 for Cu_{cap}). The small values of Cu-Cu Wiberg indices (avg. = 0.040, see also Table 1) are consistent with this view of weakly interacting Cu(I) centres, as found in other Cu(I) polyhydride clusters.[19] The Pd-Cu Wiberg indices (avg. = 0.059) are also indicative of weak interactions. Contrarily to that of Cu, the Pd NAO charge is fairly negative (-0.68), as well as that of the hydrides (-0.55). As compared to the Cu-H Wiberg indices (avg. = 0.060), their Pd-H counterparts have much large values (0.226), indicating significant covalent bonding. As a whole, these data are consistent with the view of a linear $[PdH_2]^{2-}$ anion encapsulated within a $[Cu_{14}]^{14+}$ cage. For the sake of comparison, calculations at the same level of theory on the free 14-electron $[PdH_2]^{2-}$complex led to Pd-H distances, Wiberg indices and Pd NAO charge of 1.700 Å, 0.535, and -0.92, respectively. These values support the view of anionocovalent interaction between $[PdH_2]^{2-}$ and its cage, with a moderate but non-negligible anion-cation electron transfer of 0.23e (0.18e in

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the case of **2'**). It is noteworthy that the $[PdH_2]^{2-}$ anionic complex is known to exist in the solid state, for example in A_2PdH_2 (A = Li, Na).[18,21] In these ternary phases, the Pd-H distances lie in the range 1.64-1.68 Å.[21]

TD-DFT calculations on **1'** found the simulated low-energy band centered around 460 nm, *i.e.* substantially blue-shifted with respect to experiment (Figure S20). It is associated with two nearly degenerate transitions, both of HOMO→LUMO and HOMO→LUMO+2 character, *i.e.* of dominant MLCT nature. The intense high-energy band is also of MLCT nature.

Herein, we report the synthesis, structure and full characterization of two atomically precise, palladium-alloyed copper hydride clusters, namely $[PdH_2Cu_{14}(dtc/dtp)_6(C{\equiv}CPh)_6]$ (dtc = $S_2CN^nBu_2$, dtp = $S_2P(O^iPr)_2$). The copper atoms display a D_{3d} bicapped icosahedron, the center of which is occupied by Pd. The two hydrides strongly bonded to Pd in a linear fashion are also encapsulated within the $PdCu_{14}$ core, supporting the view of a 14-electron $[PdH_2]^{2-}$ unit encapsulated in a $[Cu_{14}]^{14+}$ cage. As a result, Pd has the highest coordination number (14), hitherto unknown in literatures. UV-Vis study shows that **1** is more stable than **2** in solutions. The emission spectrum of **1** is blue-shifted with respect to that of **2**. Isolation of these novel hydride NCs from pure copper hydrides creates a new frontier in the synthesis of bimetallic species. Such insights are critical for designing novel alloy nanoparticles with enhanced synergistic properties for potential applications in catalysis, energy, and sensing. Future works will direct onto the utilization of new Pd-Cu NCs in energy storage such as electro-catalytic hydrogen evolution reaction (HER).[22]

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Keywords: bicapped icosahedra • nanoclusters • bimetallic• copper • neutron diffraction

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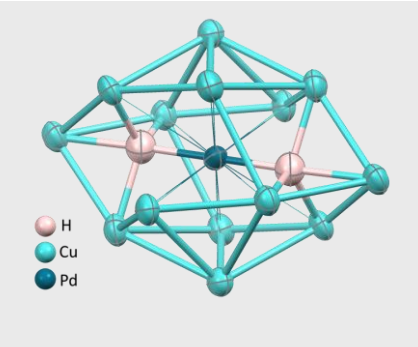
A unique methodology was used to synthesize atomically precise palladium-alloyed copper hydride clusters. X-ray and neutron diffraction revealed that a 14-electron $[PdH_2]^{2-}$ unit is ionocovalently encapsulated within a bicapped icosahedral $[Cu_{14}]^{14+}$ cage and, as a result, the central Pd(0) adopts the coordination number of 14.



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