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Electron Transfer from Hexameric Copper Hydrides

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Supporting Information

ABSTRACT: The octahedral core of 84-electron LCuH hexamers does not dissociate appreciably in solution, although their hydride ligands undergo rapid intramolecular rearrangement. The single-electron transfer proposed as an initial step in the reaction of these hexamers with certain substrates has been observed by stopped-flow techniques when $[(Ph_3P)CuH]_6$ is treated with a pyridinium cation. The same radical cation has been prepared by the oxidation of $[(Ph_3P)CuH]_6$ with $Cp^*{}_2Fe^+$ and its reversible formation observed by cyclic voltammetry; its UV−vis spectrum has been confirmed by spectroelectrochemistry. The 48-electron trimer $[(dppbz)CuH]_3$ has been prepared by use of the chelating ligand 1,2-bis(diphenylphosphino)benzene (dppbz).

Copper hydrides are well-known catalysts for the hydrogenation of α,β-unsaturated carbonyl compounds,[1] of other C═C bonds conjugated to electron-withdrawing groups,[2] and of alkynes.[3] Although electron transfer has been suggested as a possible first step for these reactions,[2b,4] Stryker has shown that electron transfer is not involved in the hydrogenation of α,β-unsaturated carbonyls,[5] noting that "the reaction [affords] major products deriving from hydride delivery to the least hindered face of the substrate".[1] The absence of electrochemical data for copper hydrides, however, has left open the possibility that electron transfer does occur in other reactions.[6] We now demonstrate its occurrence in the transfer of hydride from $[Ph_3PCuH]_6$ (**1a**) to pyridinium cations.

Copper hydrides have been known for many years.[7] Würtz prepared an insoluble CuH in 1844,[8] the first reported transition-metal hydride, while Lutsenko et al. reported soluble LCuH without establishing the extent of aggregation.[9] Several $(\mu\text{-H})_2$ dimers are known,[10] as well as an octamer,[11] a pentamer,[12] a trimer,[13] and a number of clusters with interstitial hydrides.[14] However, hexameric $[LCuH]_6$ clusters form the most widespread and important class of copper hydrides.[7] Osborn, Churchill, and co-workers established the stoichiometry of the Ph_3P derivative **1a** and established its hexameric structure crystallographically in 1971,[15] although they did not locate the hydride ligands. The hydrides in $[P(NMe_2)_3CuH]_6$ were shown by Caulton in 1985 to cap six of the eight faces of an octahedral core of Cu atoms,[11] and the structure was confirmed for $[p\text{-tol}_3PCuH]_6$ (**1b**) by a subsequent neutron diffraction study by Bau and Koetzle.[16] (The structure is similar to that of $[n\text{-BuLi}]_6$.[17])

The solution structure of these complexes has been the subject of debate.[18] The extinction coefficients of **1a** and **1b** have been said to be "concentration dependent".[19] However, Caulton, the first to observe their hydride ligands by ^1H NMR, reported for **1b** a "structured multiplet...five components of a septet" that collapsed with ^{31}P decoupling,[20] suggesting that the hexamer remains intact in solution.

The reactivity of these LCuH complexes varies with the nature of their phosphine ligand. For example, the Ph_3P hexamer (**1a**) is selective for the 1,4 reduction of enones, whereas the Me_2PhP complex (whose extent of aggregation has not been established) gives only 1,2 reduction.[21] We have therefore prepared a number of LCuH complexes and examined their structures, spectra, and reactivity—particularly their ability to transfer an electron.

Clusters $[(p\text{-anisyl})_3PCuH]_6$ (**1c**) and $[(^iPrPh_2P)CuH]_6$ (**1d**) were prepared by established methods,[22] from CuCl, 1 equiv of KO^tBu, and 2 equiv of the phosphine ligand under an H_2 atmosphere in benzene or toluene. The $^iPrPh_2P$ complex **1d** and the $(p\text{-anisyl})_3P$ complex **1c** (structures in Figure 1) have proven isostructural with the previously reported **1a** and **1b**, with the six smaller octahedral faces capped by hydrides. (The Cu−Cu distances around these faces are slightly shorter than the distances in metallic copper, 2.5562 Å.) $[BnPh_2PCuH]_6$ (**1e**) was also prepared, but its crystals were twinned.[23]

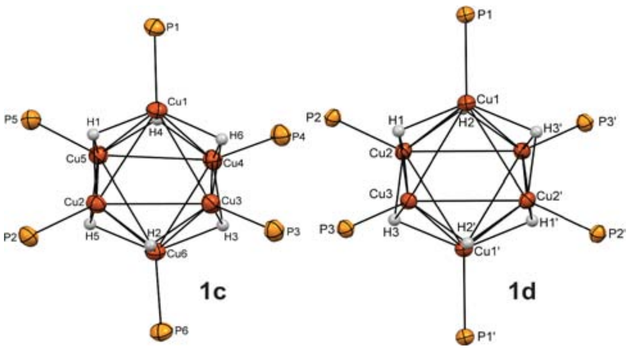

Figure 1. Core ellipsoid plots (50% probability) for **1c** $[(p\text{-anisyl})_3PCuH]_6$ and **1d** $[^iPrPh_2PCuH]_6$. The short Cu−Cu bonds average 2.49 Å (**1c**), 2.47 Å (**1d**); the long Cu−Cu bonds average 2.70 Å (**1c**), 2.76 Å (**1d**).

One equivalent of a chelating ligand, 1,2-bis(diphenylphosphino)benzene (dppbz), gives the related trimer **2** (eq 1), with the ^1H NMR of its hydride ligands at δ 0.60 (C_6D_6). Its X-ray structure (Figure 2) shows that the hydride ligands are μ_2, in the plane of the three Cu atoms; the Cu−Cu

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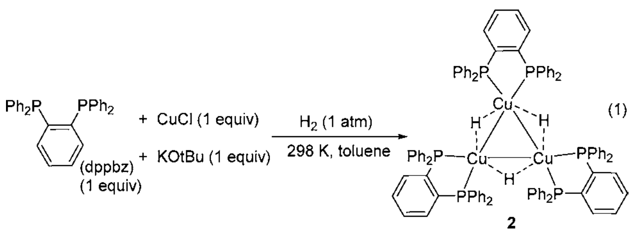


(1)

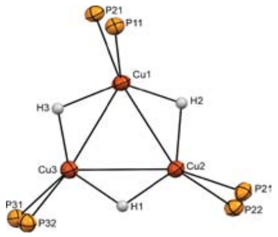


Figure 2. Core ellipsoid plot of **2** [(dppbz)CuH]$_3$. The Cu−Cu bonds average 2.58 Å.

distances average 2.58 Å, about the same as the short Cu−Cu distances (on the capped faces) in the hexamers **1a**−**d**.

The same ligand (dppbz) has been used with excess $Cu(OAc)_2 \cdot H_2O$ and a silane to prepare an apparent (dppbz)-CuH adduct **3** in solution,[24] although the hydride chemical shift reported for **3** (δ 1.49 in C_6D_6) differs substantially from that of **2**.[24a,b,25] We see (by ^{1}H NMR) **3** as an initial product when dppbz is added to a C_6D_6 solution of **1a**, although the final product is **2**.

Molecular Orbital Calculations. The 84 valence electrons in $L_6Cu_6(\mu_3\text{-}H)_6$ are consistent with the 12 Cu−Cu bonds (each a shared electron pair) in its octahedral core, as suggested by the 18-electron rule. DFT calculations in D_{3d} symmetry[26] on a simplified model, with PH_3 in place of the more computationally demanding ligands actually present, confirm that the bonding and nonbonding molecular orbitals are exactly filled, and that the antibonding ones are empty.

The HOMO−LUMO gap is large (3.2 eV). The results of our calculations are consistent with those reported in 2007 for the octahedral cores of the rhodium clusters $[(H_3P)_6Rh_6H_{12}]^{0,1+,2+}$.[27] The Cu−Cu distances predicted by our DFT calculations (2.54 Å on the hydride-capped faces, 2.71 Å on the uncapped ones) correspond well to the crystallographically determined ones.

Similarly, the 48 valence electrons in the trimer **2** are consistent with the three Cu−Cu bonds suggested by the 18-electron rule.

Solution Structure of [LCuH]$_6$. We have found the absorbance for **1a** at λ_{max} = 524 nm[19] to be *linear* in CH_2Cl_2 (Figure S-1) over a substantial range of [**1a**], implying that ε is 2790(50) L·mol^{-1}·cm^{-1}. This result, and Caulton's early observation by ^{1}H NMR spectroscopy of *intramolecular* hydride exchange within **1b**,[28] suggest that LCuH hexamers remain intact in solution. We have found excellent agreement between the ^{1}H NMR spectrum of **1a** in toluene-d_8 at 263 K and that calculated with J_{H-P} = 5.4 Hz to six equivalent phosphorus atoms (Figure 3). The spectrum broadens as the temperature is raised to 303 K, presumably from residual coupling to ^{63,65}Cu (quadrupolar nuclei that are relaxed more slowly as the viscosity of the solvent decreases). The spectrum also broadens when the temperature is decreased substantially (e.g., to 200 K), presumably because intramolecular exchange becomes slower.

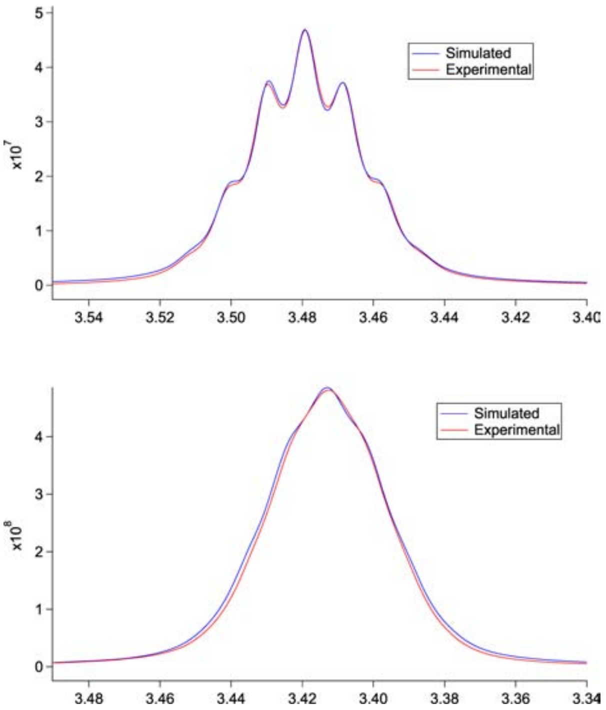


Figure 3. ^{1}H NMR spectra of **1a** hydride at (top) 263 and (bottom) 303 K. J(P−H) = 5.4 Hz.

Intramolecular hydride exchange within $[LCuH]_6$ probably involves the two uncapped faces of the Cu_6 octahedra.

Electrochemistry of [LCuH]$_6$. The hexamers **1a**−**c** have been examined by cyclic voltammetry (CV) in CH_2Cl_2. Reversible waves for $[LCuH]_6^{0/+1}$ ($E_{1/2}$) have been observed at −1.01 (**1a**), −1.20 (**1b**), and −1.15 V (**1c**) vs Fc/Fc$^+$. Reversible cyclic voltammograms for **1a**−**c** (see Figure 4 for CV for **1c**) suggest that an electron is removed from **1a**−**c**, giving a radical cation intermediate without significant structural rearrangement. (The peak separations are 67, 63, and 66 mV, respectively.[29] The fact that little current flows at the beginning of the scan reflects the fact that it starts near the rest potential.[30]) All three hexamers are thus excellent single-electron reductants, with potentials only about 130 mV less reducing than that of $Cp_2Co^{0/+}$ in the same solvent.[31]

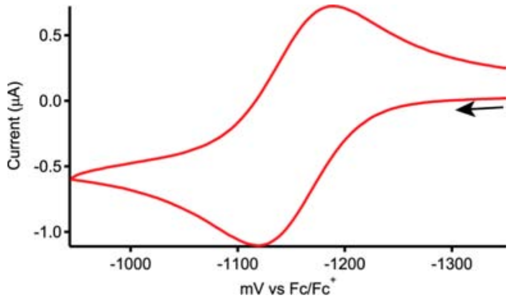


Figure 4. Reversible cyclic voltammogram for **1c** in CH_2Cl_2.

The formation of intensely green $[Ph_3PCuH]_6^{+\bullet}$ (**1a**$^{+\bullet}$, λ_{max} 655 nm) from red **1a** can be observed by spectroelectrochemistry when a potential of −800 mV vs Fc/Fc$^+$ is applied (Figure 5), although the lifetime of the radical cation is limited (it persists at least 30 min). The radical cation **1a**$^{+\bullet}$ can be reduced cleanly back to **1a** (and the sequence of spectra in Figure 5

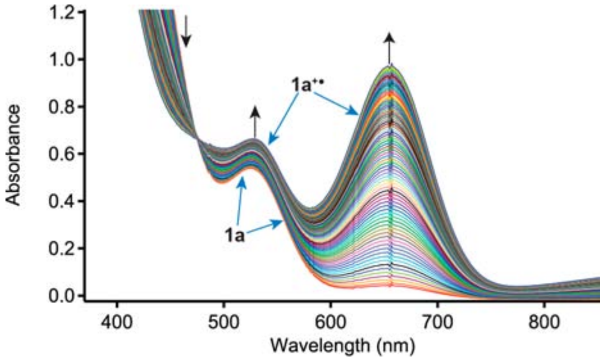
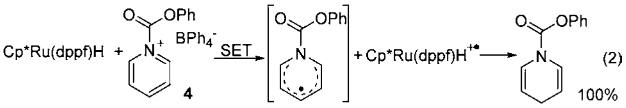


Figure 5. Oxidation of **1a** over 30 s at −0.8 V vs Fc/Fc$^+$.

reversed) if the potential is changed to −1.3 V vs Fc/Fc$^+$ after 100 s of oxidation. The radical cation can also be obtained by chemical oxidation of **1a** with [Cp*$_2$Fe][PF$_6$] (for Cp*$_2$Fe/Cp*$_2$Fe$^+$, $E_{1/2}$ = −590 mV vs Fc/Fc$^+$).[31]

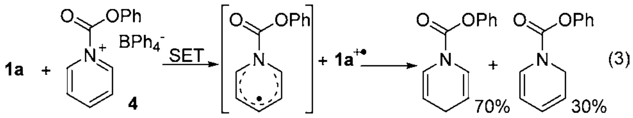
Additional oxidation waves, at less negative potentials, can be observed for some hexamers. For example, a second, irreversible, oxidation is seen with **1a** and **1b**, and four additional oxidations (also irreversible) are seen with **1c** (see Supporting Information).

Electron Transfer during Hydride Transfer from [LCuH]$_6$. These CV data show that the hexamers **1** are better reductants than Cp*Ru(dppf)H, a hydride that is known to undergo electron transfer during its reaction with the pyridinium cation **4** (eq 2).[32]



(2)

We have therefore examined the reaction of **1a** with the cation **4**. The eventual result is hydride transfer (eq 3), but the green color of **1a**$^{+•}$ is seen immediately (<5 ms in a stopped-flow apparatus, Figure 6) when CH$_2$Cl$_2$ solutions of the two compounds are mixed. It appears that hydride transfer to **4** from the hexameric Cu hydride **1a** also begins with the transfer of a single electron.



(3)

We conclude that electron transfer from copper hydride hexamers *can* be mechanistically relevant in reactions resulting in net hydride transfer.

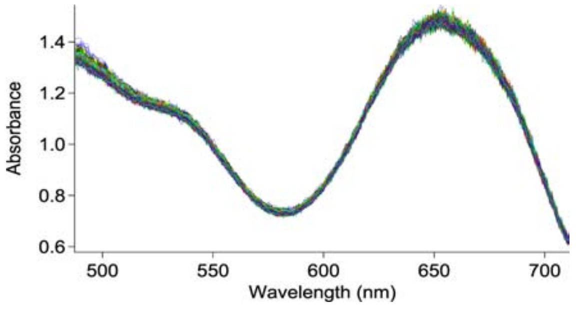


Figure 6. Observation of **1a**$^{+•}$ by stopped-flow reaction of **1a** and **4**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, NMR chemical shifts for ^{1}H, ^{31}P, and ^{13}C, X-ray crystallographic data, and additional CV data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(25) The spectrum shown in the Supporting Information of ref 24b appears to be that of THF.

(26) We actually input the Cu, P, and H coordinates from the reported atomic coordinates in the core of $[(Me_2N)_3PCuH]_6$ (ref 11), which has crystallographic S_6 symmetry. However, the reported structure is close to having D_{3d} symmetry, and its PH_3 derivative surely would, so we assume that our results are valid in D_{3d}.

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(29) The separations increase as the scan rate is increased, as expected if they arise from uncompensated solution resistance.

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