Communication

Unexpected Reactivities of Cu(diphosphine) Complexes in Alcohol: Isolation, X-ray Crystal Structure, and Photoluminescent Properties of a Remarkably Stable [Cu(diphosphine)(□-H)] Hydride Complex

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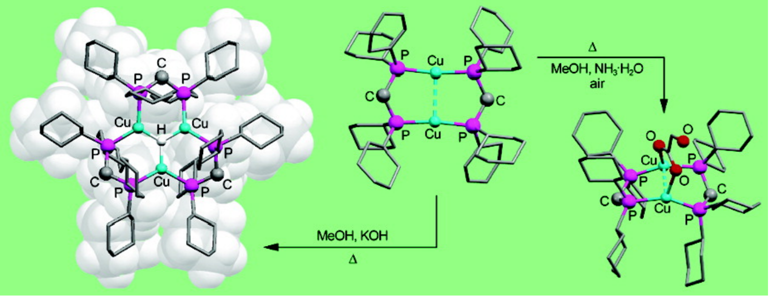
J. Am. Chem. Soc., **2005**, 127 (13), 4562-4563• DOI: 10.1021/ja042335c • Publication Date (Web): 10 March 2005



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COMMUNICATIONS

Unexpected Reactivities of Cu_2(diphosphine)$_2$ Complexes in Alcohol: Isolation, X-ray Crystal Structure, and Photoluminescent Properties of a Remarkably Stable $[Cu_3(\text{diphosphine})_3(\mu_3\text{-H})]^{2+}$ Hydride Complex

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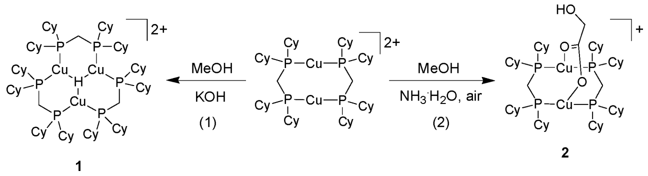
Transition metal complexes containing sterically bulky electron-rich phosphine ligands usually adopt low coordination numbers[1c,f−h] and sometimes display unprecedented properties and reactivities.[1a,b,d,e] In the course of our spectroscopic studies on two-coordinate polynuclear d^{10} complexes with the bridging bis(dicyclohexylphosphino)methane (dcpm) ligand, we observed that treatment of $[Cu_2(\text{dcpm})_2]^{2+}$ with MeOH in the presence of KOH afforded hydride complex $[Cu_3(\text{dcpm})_3(\mu_3\text{-H})]^{2+}$ (**1**) (reaction 1). A similar treatment of $[Cu_2(\text{dcpm})_2]^{2+}$ with MeOH in the presence of $NH_3{\cdot}H_2O$ in air did not afford $[Cu_3(\text{dcpm})_3(\mu_3\text{-H})]^{2+}$ but gave carboxylate complex $[Cu_2(\text{dcpm})_2(O_2CCH_2OH)]^+$ (**2**) (reaction 2). Through these reactions, we isolated analytically pure $[Cu_3(\text{dcpm})_3(\mu_3\text{-H})]Y_2$ (Y = ClO_4^-, **1a**; BF_4^-, **1b**; PF_6^-, **1c**; $CF_3SO_3^-$, **1d**) in ~85% yield and $[Cu_2(\text{dcpm})_2(O_2CCH_2OH)]PF_6$ (**2**) in 40% yield. The formulation of **1** is consistent with the $^{31}P\{^1H\}$ NMR spectrum of **1c** (Figure S1), showing a P(dcpm):P(PF_6^-) molar ratio of 3.06:1, close to the expected ratio of 3:1. Both **1** and **2** are *air-stable*, diamagnetic solids.[2] Their formation from these reactions is completely unexpected.



Complexes **1a**−**d** are, to the best of our knowledge, the first examples of a tricopper hydride complex,[3] exhibiting prominent MS peaks assignable to $[Cu_3(\text{dcpm})_3(\mu_3\text{-H})]^{2+}$ and $[\{Cu_3(\text{dcpm})_3(\mu_3\text{-H})\}Y]^+$ (Y = ClO_4^-, BF_4^-, PF_6^-, or $CF_3SO_3^-$) (Figure S2). In the MS of **2**, an intense cluster peak assignable to $[Cu_2(\text{dcpm})_2(O_2CCH_2OH)]^+$ was observed.

The ^1H NMR spectra (500 MHz) of **1a**−**d** in CD_2Cl_2 at room temperature (RT) show the hydride signal at $\delta \approx 2.0$ ppm (Figure S3a), with typical $^2J_{PH}$ of 16 Hz. The hydride signal disappears if the MeOH in reaction 1 is replaced by MeOH-d_4. Two-dimensional NMR measurements (Figure S3b) revealed that there is no correlation between the hydride and the dcpm protons. However, owing to significant overlap with intense dcpm signals, the multiplicity of the hydride signal cannot be determined from the RT spectra. We envisioned that increasing temperature may allow a clearer observation of the hydride signal due to signal narrowing that arises from longer relaxation time and more rapid cyclohexyl rotation or conformational change. Indeed, in MeCN-d_3 at 80 °C, the hydride signal was almost fully resolved; six components of a septet centering at $\delta \approx 2.2$ ppm with $^2J_{PH} = 16$ Hz are visible (Figure 1). The septet collapsed to a singlet in ^{31}P-decoupled ^1H NMR spectra, consistent with a coupling of the hydride with six equivalent P atoms. A comparable hydride signal with $\delta = 3.50$ ppm (a multiplet resulting from P−H coupling) was previously reported for diamagnetic $[Cu(P(p\text{-tolyl})_3)(\mu_3\text{-H})]_6$.[3c]

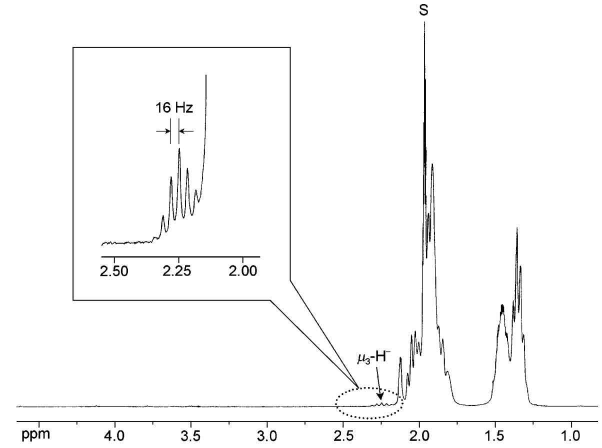


Figure 1. ^1H NMR spectra (500 MHz) of **1d** in MeCN-d_3 at 80 °C.

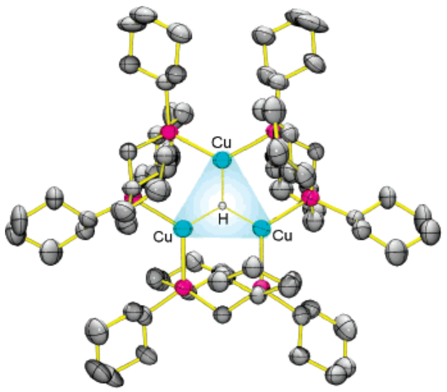


Figure 2. Structure of **1a** with omission of hydrogen atoms (except the hydride) and counteranions.

The crystal structures of **1a**−**d** (Figure 2 and Figures S4−S7) each contain a triangular Cu_3 core and three μ-dcpm ligands, with Cu−P distances of 2.276(2)−2.290(2) Å and mean Cu⋯Cu distances of 2.879(1) (**1a**,**d**) and 2.885(1) Å (**1b**,**c**). These Cu⋯Cu distances are significantly shorter than those in the mono- or dicapped species $[Cu_3(\text{dppm})_3(\mu_3\text{-OH})]^{2+}$ and $[Cu_3(\text{dppm})_3(\mu_3\text{-Cl})_2]^+$ (3.120(2)−3.322(2) Å).[4] The hydride in **1a** was located in the difference Fourier map. However, the quality of the crystals is not sufficiently high to allow determination of the accurate hydride

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10.1021/ja042335c CCC: $30.25 © 2005 American Chemical Society

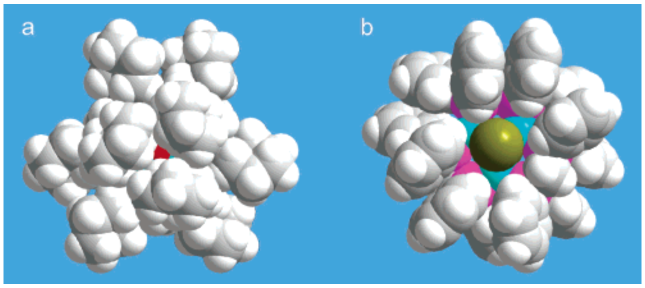

Figure 3. Top-view space-filling representations of the structure of (a) **1a** and (b) $[Cu_3(dppm)_3(\mu_3\text{-}Br)_2]ClO_4$ (ref 7a) with omission of counteranions. For clarity, the hydride in (a) is in red.

position in **1a** and location of the hydride in **1b**−**d**. We found that the conformation of the 12-membered $[Cu_3(diphosphine)_3]^{3+}$ macrocycle in the structures of **1a**−**d** is similar to that in $[Cu_3(dtbpm)_3(\mu_3\text{-}F)](PF_6)_2$, containing a planar $Cu_3(\mu_3\text{-}F)$ moiety (with the μ_3-F^- situated in the center of the Cu_3 core),[5] but is markedly different from that in $[Cu_3(dppm)_3(\mu_3\text{-}OH)](BF_4)_2$,[4b] containing a tetrahedral $Cu_3(\mu_3\text{-}OH)$ moiety (Figure S8). This suggests the location of the hydride of **1a**−**d** in the center of their Cu_3 cores, which gave Cu−H distances of ∼1.67 Å, comparable to those of 1.76(3) Å (average) in tetrahedral $Cu_3(\mu_3\text{-}H)$ moieties of $[Cu(P(p\text{-}tolyl)_3)(\mu_3\text{-}H)]_6$ determined by neutron diffraction analysis.[3e]

Structurally characterized trinuclear metal hydrides containing a planar $M_3(\mu_3\text{-}H)$ moiety, like the $Cu_3(\mu_3\text{-}H)$ moiety in **1**, are not unprecedented but are extremely rare.[6] Moreover, complexes **1a**−**d** are hitherto the only examples of the hydride complexes of a $[Cu_n(diphosphine)_n]^{n+}$ macrocycle, despite previous reports of numerous metal complexes containing $[Cu_n(diphosphine)_n]^{n+}$ macrocycles (Chart S1).

Given the air-sensitivity of previously reported copper hydrides, such as $[Cu(PPh_3)(\mu_3\text{-}H)]_6$,[3a,b] the remarkably high air and thermal stability of **1** deserves attention, which may be attributed to the excellent shielding of the $Cu_3(\mu_3\text{-}H)$ moieties in **1a**−**d** by the sterically demanding dcpm ligands (see Figures 3a and S9). Indeed, extension of reaction 1 to dppm, a sterically less demanding ligand, afforded no $[Cu_3(dppm)_3(\mu_3\text{-}H)]^{2+}$, whose dppm ligands would not provide significant shielding for the $Cu_3(\mu_3\text{-}H)$ moiety in view of the “exposed” Cu_3 cores in, for example, $[Cu_3(dppm)_3(\mu_3\text{-}Br)_2]ClO_4$ [7a] (Figure 3b).

The structure of **2** (Figure S10) features a triply bridged Cu_2 core (Cu···Cu distance = 2.712(1) and 2.739(1) Å), like that of $[Cu_2(dppm)_2(O_2CCH_3)]BF_4$ prepared from reaction of $[Cu_3(dcpm)_3(OH)](BF_4)_2$ with CH_3CO_2Na (Cu···Cu distance = 2.7883(11) Å).[7b] However, perhaps because dcpm is bulkier and more electron-rich than dppm, **2** has a markedly less bent $[Cu_2(diphosphine)_2]^{2+}$ moiety (P−Cu−P = 141.10(8)−149.60(7)°) and a more weakly bound carboxylate ligand (Cu−O = 2.072(5)−2.123(5) Å) than $[Cu_2(dppm)_2(O_2CCH_3)]BF_4$ (P−Cu−P = 128.87(6)−130.56(6)°, Cu−O = 1.993(4)−2.029(4) Å).[7b]

Complexes **1a**−**d** exhibit intense photoluminescence at 298 K both in the solid state and in solution (see Figure S11); complex **2** gives no emission in solution but emits in the solid state at 77 and 298 K (Figure S12).[8] Interestingly, the emission of **1a**−**d** is virtually independent of counteranions and solvents (CH_2Cl_2, MeCN, MeOH), in contrast to the strong counteranion and solvent dependence observed for the emissions of $[Cu_2(dcpm)_2]^{2+}$ [9] and to the marked dependence of the emission of $[Cu_3(dppm)_3(OH)]^{2+}$ on solvents.[10] This should be associated with the excellent shielding of the Cu_3 cores in **1a**−**d** by the bulky dcpm ligands, which prevents the Cu_3 cores from significantly interacting with the counteranions or solvent molecules.

In summary, we have observed two unprecedented reactions of a $Cu_2(diphosphine)_2$ complex in MeOH containing inorganic bases by employing dcpm as a diphosphine ligand, which result in the isolation of a highly unusual copper hydride complex. MeOH apparently serves as the hydride source. Preliminary studies revealed that replacing MeOH in reaction 1 with other primary alcohols, such as EtOH and $PhCH_2OH$, also afforded **1**; however, no **1** was formed if secondary or tertiary alcohol ^{i}PrOH and ^{t}BuOH was substituted for MeOH. Although the generation of metal hydrides from reactions with primary alcohol and base has been well documented,[11] it is unclear how **1** was assembled from reaction 1. The carboxylate ligand in **2** probably arises from copper-catalyzed aerobic oxidation of MeOH;[12] no **2** was formed from reaction 2 in the absence of air or by changing MeOH to EtOH. Efforts are underway to investigate the mechanisms of these interesting reactions in more detail.

Acknowledgment. This work was supported by the Large-Item Equipment Funding of The University of Hong Kong, the Hong Kong University Foundation, Croucher Foundation, and the Hong Kong Research Grants Council (HKU 7039/03P).

Supporting Information Available: Experimental details, Figures S1−S12, Chart S1, and CIF files for all of the X-ray crystal structures reported in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) Evans method was used to measure the magnetic susceptibility of **1** and **2**. The splitting of the solvent signal was comparable to that of the diamagnetic $[Cu_2(dcpm)_2]^{2+}$ species. On going from 25 to −40 °C, the $^{31}P\{^1H\}$ NMR chemical shifts of the dcpm ligands of **1** ($\delta \approx 11$ ppm) increased by ≤0.1 ppm.

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JA042335C