Copper Hydrides

DOI: 10.1002/ange.201306736

Bonding and Reactivity of a μ-Hydrido Dicopper Cation**

Chelsea M. Wyss, Brandon K. Tate, John Bacsa, Thomas G. Gray, and Joseph P. Sadighi**

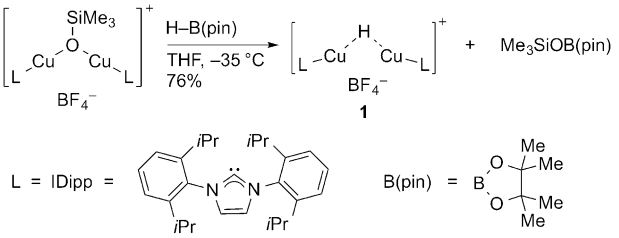
Copper hydride complexes are versatile reagents, with new applications appearing rapidly.[1] Copper hydride was first prepared in the mid-19th century,[2] but its structure remained unknown for more than 80 years.[3] The characterization[4] of $[\{(Ph_3P)CuH\}_6]$ sparked interest in the structure and bonding of well-defined copper hydride clusters,[5] and the use of copper in the industrial reduction of CO to methanol inspired the synthesis of copper hydride clusters through hydrogenolysis.[6] Following the development of mild and selective reductions using $[\{(Ph_3P)CuH\}_6]$,[7,8] numerous methods were developed for the copper-catalyzed hydrosilylation[8,9] and hydrogenation[10] of organic substrates. Recently, Liu et al. reported a Cu_{20} cluster containing the $[Cu_2H_5]^{3-}$ moiety, which releases dihydrogen upon irradiation with sunlight.[11]

Copper hydrides with fewer than six metal centers are rare.[5a,6a,12,13] N-Heterocyclic carbene (NHC)[14,15] and especially cyclic alkylaminocarbene (CAAC)[16] ligands stabilize a $\{Cu_2(\mu\text{-}H)_2\}$ core. The NHC ligand also supports the hydride-bridged dinuclear species $[(LAu)_2(\mu\text{-}H)]^+$[17] and $[(LAg)_2(\mu\text{-}H)]^+$.[18] These cations adopt bent structures with very short intermetallic distances, and there are indications of direct metal–metal bonding. Interactions between d^{10} centers, however, are generally weaker for copper than for silver and gold.[19] We sought to explore the structure and reactivity of a hydrido-bridged dicopper cation.

For a number of oligocopper(I) complexes, short copper–copper contacts have been ascribed to net attractive interaction between d^{10} metal centers,[20,21] to three-center, two-electron bonding,[22] or to geometric constraints imposed by a bridging ligand.[23] In the desired species $[(LCu)_2(\mu\text{-}H)]^+$, the presence of a single, spherical bridging ligand minimizes such constraints, permitting but not requiring a direct metal–metal interaction.[24–26] Theoretical studies of $[Cu_2H]^+$ have variously predicted a linear geometry[27] or a bent geometry[28] with a short copper–copper distance.[29]

We now report the isolation of a hydride-bridged dicopper cation, $[\{(IDipp)Cu\}_2(\mu\text{-}H)]^+$, as its BF_4^- salt. The cation adopts a bent arrangement about the hydride with a short intermetallic distance. Density functional theory (DFT) calculations suggest that the copper–copper interaction is mediated primarily by the bridging hydride. Despite its overall positive charge, this complex displays hydridic reactivity. It undergoes facile methanolysis, and undergoes carboxylation to afford a (κ^2-formate)-bridged dicopper species. Insertion of phenylacetylene affords a *gem*-dicopper vinyl cation.

We prepared the desired hydride complex $[\{(IDipp)Cu\}_2(\mu\text{-}H)]^+$ BF_4^- (**1**) by reaction of a siloxide-bridged dicopper cation with pinacolborane 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HB(pin); Scheme 1). The ^{1}H NMR spectrum of **1** in



Scheme 1. Synthesis of hydride-bridged dicopper complex **1**.

$[D_8]$THF solution displays a single set of resonances arising from the two IDipp ligands, and a singlet resonance at $\delta = -4.13$ ppm assigned to the hydride. Reaction of the siloxide-bridged precursor with $PhSiD_3$ likewise affords deuteride-bridged [D]-**1**. The ^{1}H NMR spectrum of [D]-**1** is identical to that of **1** except for the absence of the hydride resonance, and the ^{2}H NMR spectrum shows a singlet resonance at $\delta = -4.13$ ppm.

Slow diffusion of hexanes into a THF solution of **1** afforded colorless crystals suitable for X-ray diffraction (Figure 1).[30] Two crystallographically distinct cations, with similar bond lengths and angles, are present in the asymmetric unit. The BF_4^- anions are located well outside the copper coordination spheres. The C-Cu-Cu angles, ranging from 156.1(3)° to 163.2(3)°, are consistent with the presence of a triangular $[Cu_2H]$ core. The Cu–Cu distances, 2.5331(15) Å and 2.5354(15) Å, are considerably less than twice the van der Waals radius of copper.[31] The positions of the bridging hydrides could be refined; the L-Cu-H angles range from 165(2)° to 175(2)°, and the Cu-H-Cu angles are 121(3)° and 122(3)°.[32]

We applied density functional theory (DFT) calculations to **1′**, a model compound in which the ligand (IMe) bears *N*-methyl rather than *N*-(2,6-diisopropylphenyl) groups, to elucidate the copper–copper and copper–hydrogen interac-

[*] C. M. Wyss, B. K. Tate, Prof. Dr. J. P. Sadighi
School of Chemistry and Biochemistry
Georgia Institute of Technology, Atlanta, GA 30332 (USA)
E-mail: joseph.sadighi@chemistry.gatech.edu
Prof. Dr. T. G. Gray
Department of Chemistry, Case Western Reserve University
Cleveland, OH 44106 (USA)
E-mail: tgray@case.edu
Dr. J. Bacsa
Department of Chemistry, Emory University
Atlanta, GA 30322 (USA)

[**] We thank the U.S. National Science Foundation (CHE-1057659 to T.G.G., CHE-1300659 to J.P.S.) and the Georgia Institute of Technology for support, and Prof. Dr. Seth Marder for the use of an IR spectrometer.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306736.

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

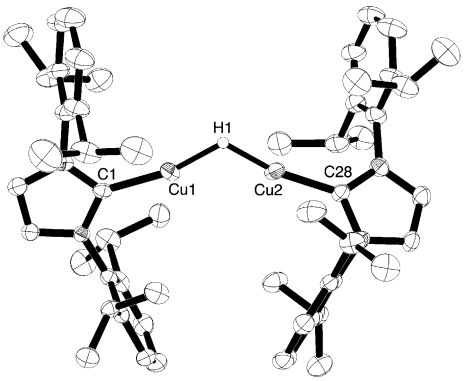


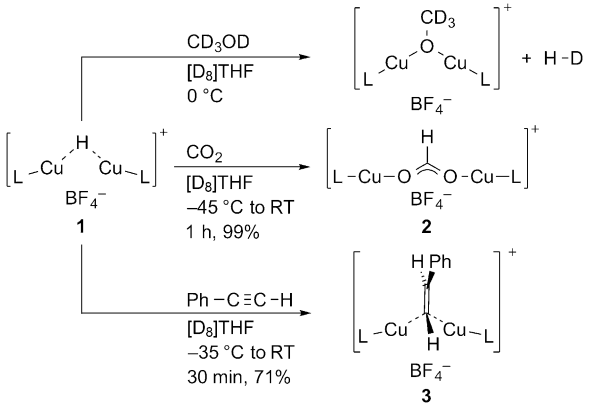
Figure 1. ORTEP view of **1**. Ellipsoids are set at 50% probability; the BF_4^- anion and hydrogen atoms except the μ-hydride are omitted for clarity. Only one cation of two in the asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.5331(15), C1–Cu1 1.873(9), Cu1–H1 1.45(2), H1–Cu2 1.45(2), Cu2–C28, 1.908(8); C1-Cu1-H1 167.4(16), Cu1-H1-Cu2 122(3), H1-Cu2-C28 174.4(16), C1-Cu1-Cu2 163.2(3), Cu1-Cu2-C28 156.1(3).

tions. Geometry optimization of **1′** converged on a potential energy minimum with rough C_2 symmetry. The copper–copper distance was calculated at 2.509 Å, which is close to the experimentally determined values.

The highest occupied Kohn–Sham orbital (HOMO) of **1′**, which is largely copper-derived (84% Cu, 16% NHC), is copper–copper antibonding in character (Figure 2). Descriptions of three-center, two-electron bonding in $\{M_2H\}$ complexes depict a similar orbital as the lowest-energy unoccupied level in a three-orbital scheme.[24c–e] This apparent discrepancy is resolved by considering the symmetry-allowed mixing of filled copper 3d orbital combinations with the corresponding 4s/4p orbital combinations. The $\{Cu_2H\}^+$ bonding may thus be viewed as a three-center, six-electron system. Consistent with this interpretation, these calculations find two filled Cu-H-Cu bonding orbitals, which are 1.97 eV and 4.72 eV below the HOMO in potential energy.

According to natural population analysis, the Wiberg bond order[33] between copper centers is 0.386 in the Löwdin basis; the copper–hydrogen bond orders are 0.534 and 0.535. Analysis of the copper–copper interaction using the atoms-in-molecules theory[34] found no bond critical point. These findings suggest that the $[(LCu)_2H]^+$ cation is an example of an open three-center interaction[35] in which the metal–metal interaction occurs mainly through the bridging hydride. For comparison, in a dicopper(I) complex with a σ-bridging acetonitrile ligand, three-center bonding does give rise to a bond critical point between the copper centers.[36]

Addition of CD_3OD to a solution of **1** in $[D_8]$THF results in a rapid reaction to form HD,[37] as judged by ^{1}H NMR spectroscopy, plus a major species assigned as $[\{(IDipp)Cu\}_2(\mu\text{-}OCD_3)]^+ BF_4^-$ (Scheme 2). Complex **1** also reacts readily with CO_2 to form $[\{(IDipp)Cu\}_2(\kappa^2\text{-}O_2CH)]^+ BF_4^-$ (**2**; Supporting Information, Figure S5). Generally, the reactivity of



Scheme 2. Reactions of **1** with selected small molecules.

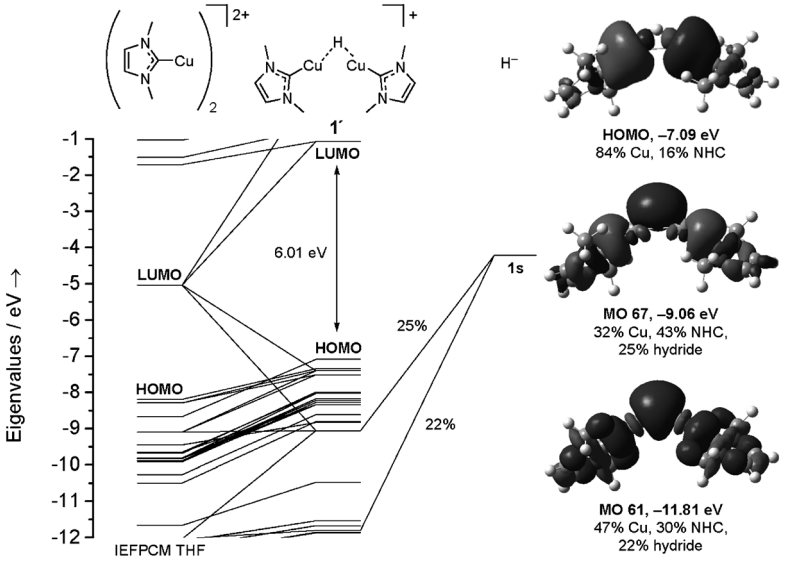


Figure 2. Partial Kohn–Sham orbital energy diagram of **1′**. Plots of selected orbitals, with eigenvalues and percentage compositions in terms of fragments, appear at the right. Implicit THF solvation is included; see the Supporting Information for details.

metal hydrides toward CO_2 depends on the degree of anionic character at hydrogen.[38] In its reactivity toward CD_3OD and CO_2, the $[Cu_2H]^+$ core of **1** displays considerable hydridic character despite its overall positive charge. Consistent with this behavior, natural population analysis of **1′** finds a charge of −0.123 on the bridging hydrogen.

We wondered whether **1** would react with an alkyne to form a vinyl-bridged dicopper cation,[39] analogous to the *gem*-diaurated vinyl complexes studied as catalytic intermediates.[40] Vinyl-bridged dicopper(I) complexes are rare,[41] but copper(I) μ-aryl oligomers are well known.[42] Alkyl-bridged cations such as $\{Cu_2(\mu\text{-}CH_3)\}^+$ have been shown to undergo C–C bond-forming reactions with allylic halides in the gas phase.[43] Recently, *gem*-dicopper vinylidene complexes have been identified as intermediates in copper-catalyzed azide–alkyne click cycloadditions.[44]

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Phenylacetylene reacts with **1** in THF solution within 30 min at ambient temperature, forming a product characterized by NMR spectroscopy and by X-ray crystallography as a (*trans*-phenylvinyl)-bridged dicopper(I) complex (**3**, Figure 3). The Cu–Cu distance of 2.6303(4) Å is slightly longer than in hydride-bridged **1**. The C_{NHC}-Cu-C_{vinyl} angles are 154.3(2)° and 151.2(2)°. Key metrics of the *trans*-phenylvinyl moiety are similar to those of *trans*-stilbene:[45] The C=C–(Cu_2 centroid) angle is 119.5°, and the C=C distance is 1.333(8) Å. Bonding in the $\{Cu_2C_{vinyl}\}^+$ core of a model complex, as in the $\{Cu_2H\}^+$ core of **1′**, is calculated to involve an open three-center interaction; results and computational details are provided in the Supporting Information.

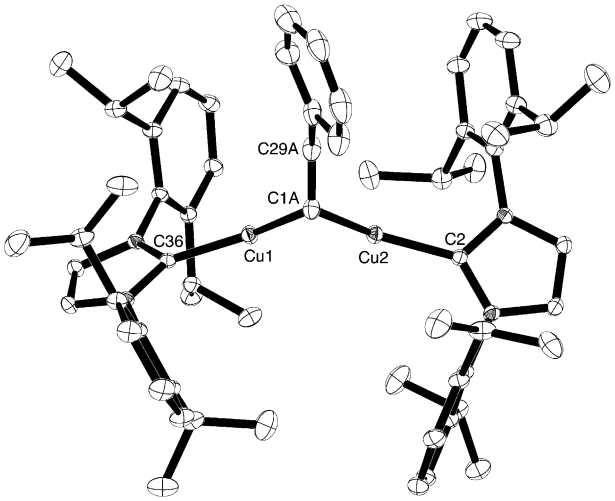


Figure 3. ORTEP view of **3**. Ellipsoids are set at 50% probability; the BF_4^- anion, hydrogen atoms, and THF solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.6303(4), C36–Cu1 1.923(1), Cu1–C1A 2.034(6), C1A–Cu2 2.003(6), Cu2–C2, 1.925(1), C1A–C29A 1.333(8); C36-Cu1-C1A 154.3(2), C1A-Cu2-C2 151.2, C36-Cu1-Cu2 154.21(4), Cu1-Cu2-C2 156.77(4), Cu1-C1A-Cu2 81.3(2), C29A-C1A-Cu1 112.2(4), C29A-C1A-Cu2 111.7(4).

In summary, an N-heterocyclic carbene ligand supports a bent $\{Cu_2H\}^+$ complex with a short intermetallic distance but little direct interaction between the copper centers. The bridging hydride shows significant anionic character, reflected in its reactions with methanol and carbon dioxide. Insertion of a terminal alkyne forms a geminally dicuprated vinyl complex. Future work will explore the potential of cationic dicopper complexes in C–H and C–C bond formation.

Experimental Section

1: In a glovebox filled with N_2, a solution of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.020 mL, 0.14 mmol) in THF (1 mL) was cooled to −35 °C and added dropwise, with stirring, to a −35 °C solution of $[\{(IDipp)Cu\}_2(\mu\text{-}OSiMe_3)]^+$ BF_4^- (0.125 g, 0.116 mmol) in THF (3 mL). The resulting solution was allowed to stand at −35 °C for 1 h, and then a layer of hexanes (15 mL) was carefully added. The two layers were allowed to mix by diffusion for 18 h, resulting in the formation of colorless crystals. These crystals were collected by vacuum filtration, triturated with hexanes (2 × 2 mL), and dried in vacuo, affording the product as a white powder (0.087 g, 0.088 mmol, 76%). ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 7.56$ (s, 4H, NC*H*), 7.53 (t, $J = 7.8$ Hz, 4H, *para*-C*H*), 7.30 (d, $J = 7.8$ Hz, 8H, *meta*-C*H*), 2.48 (sept, $J = 6.8$ Hz, 8H, C*H*(CH_3)$_2$), 1.17 (d, $J = 6.8$ Hz, 24H, CH(CH_3)$_2$), 1.01 (d, $J = 6.8$ Hz, 24H, CH(CH_3)$_2$), −4.13 ppm (s, 1H, Cu*H*Cu). ^{13}C{^{1}H} NMR (100 MHz, [D_8]THF): $\delta = 178.8$ (NCCu), 146.0 (*ortho*-*C*), 135.1 (*ipso*-*C*), 131.3 (*para*-*C*), 125.6 (NCH), 124.8 (*meta*-*C*), 29.2 (*C*H(CH_3)$_2$), 25.4 (CH(CH_3)$_2$), 23.5 ppm (CH(CH_3)$_2$). IR: $\tilde{\nu} = 3168$ (w), 2964 (s), 1595 (w), 1467 (s), 1059 (s), 806, 757 (s) cm^{-1}. The product was carboxylated (see the Supporting Information) to give a stable sample of formate **2** prior to elemental analysis. Anal. calcd. (%) for $C_{55}H_{73}N_4O_2Cu_2BF_4$: C 63.76, H 7.10, N 5.41; found: C 63.46, H 6.92, N 5.31.

Received: August 1, 2013
Revised: September 25, 2013
Published online: October 16, 2013

Keywords: carbon dioxide · copper · electron-deficient bonds · hydrides · N-heterocyclic carbenes

[1] C. Deutsch, N. Krause, B. H. Lipshutz, *Chem. Rev.* **2008**, *108*, 2916–2927.
[2] A. Wurtz, *C. R. Hebd. Seances Acad. Sci.* **1844**, *18*, 702–704.
[3] H. Müller, A. J. Bradley, *J. Chem. Soc.* **1926**, *129*, 1669–1673.
[4] M. R. Churchill, S. A. Bezman, J. A. Osborn, J. Wormald, *J. Am. Chem. Soc.* **1971**, *93*, 2063–2065.
[5] a) C. F. Albert, P. C. Healy, J. D. Kildea, C. L. Raston, B. W. Skelton, A. H. White, *Inorg. Chem.* **1989**, *28*, 1300–1306; b) D. M. Ho, R. Bau, *Inorg. Chim. Acta* **1984**, *84*, 213–220.
[6] a) G. V. Goeden, J. C. Huffman, K. G. Caulton, *Inorg. Chem.* **1986**, *25*, 2484–2485; b) T. H. Lemmen, K. Folting, J. C. Huffman, K. G. Caulton, *J. Am. Chem. Soc.* **1985**, *107*, 7774–7775; c) G. V. Goeden, K. G. Caulton, *J. Am. Chem. Soc.* **1981**, *103*, 7354–7355.
[7] a) T. M. Koenig, J. F. Daeuble, D. M. Brestensky, J. M. Stryker, *Tetrahedron Lett.* **1990**, *31*, 3237–3240; b) D. M. Brestensky, J. M. Stryker, *Tetrahedron Lett.* **1989**, *30*, 5677–5680; c) W. S. Mahoney, D. M. Brestensky, J. M. Stryker, *J. Am. Chem. Soc.* **1988**, *110*, 291–293; d) H. Brunner, W. Miehling, *J. Organomet. Chem.* **1984**, *275*, C17–C21.
[8] Selected recent examples: a) T. Vergote, F. Nahra, D. Peeters, O. Riant, T. Leyssens, *J. Organomet. Chem.* **2013**, *730*, 95–103; b) T. O. Schrader, B. R. Johnson, L. Lopez, M. Kasem, T. Gharbaoui, D. Sengupta, D. Buzard, C. Basmadjian, R. M. Jones, *Org. Lett.* **2012**, *14*, 6306–6309; c) A. Albright, R. E. Gawley, *J. Am. Chem. Soc.* **2011**, *133*, 19680–19683; d) F. Yu, J.-N. Zhou, X.-C. Zhang, Y.-Z. Sui, F.-F. Wu, L.-J. Xie, A. S. C. Chan, J. Wu, *Chem. Eur. J.* **2011**, *17*, 14234–14240; e) R. Moser, Z. V. Bošković, C. S. Crowe, B. H. Lipshutz, *J. Am. Chem. Soc.* **2010**, *132*, 7852–7853.
[9] For a review, see: S. Rendler, M. Oestreich, *Angew. Chem.* **2007**, *119*, 504–510; *Angew. Chem. Int. Ed.* **2007**, *46*, 498–504.
[10] Selected references: a) S. Werkmeister, K. Junge, M. Beller, *Green Chem.* **2012**, *14*, 2371–2374; b) H. Shimizu, N. Sayo, T. Saito, *Synlett* **2009**, 1295–1298; c) H. Shimizu, D. Igarashi, W. Kuriyama, Y. Yusa, N. Sayo, T. Saito, *Org. Lett.* **2007**, *9*, 1655–1657; d) J.-X. Chen, J. F. Daeuble, J. M. Stryker, *Tetrahedron* **2000**, *56*, 2789–2798; e) J.-X. Chen, J. F. Daeuble, D. M. Brestensky, J. M. Stryker, *Tetrahedron* **2000**, *56*, 2153–2166.
[11] R. S. Dhayal, J.-H. Liao, Y.-R. Lin, P.-K. Liao, S. Kahlal, J.-Y. Saillard, C. W. Liu, *J. Am. Chem. Soc.* **2013**, *135*, 4704–4707.
[12] Z. Mao, J.-S. Huang, C.-M. Che, N. Zhu, S. K.-Y. Leung, Z.-Y. Zhou, *J. Am. Chem. Soc.* **2005**, *127*, 4562–4563.
[13] B. H. Lipshutz, B. A. Frieman, *Angew. Chem.* **2005**, *117*, 6503–6506; *Angew. Chem. Int. Ed.* **2005**, *44*, 6345–6348.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[14] N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 3369 – 3371.

[15] For a related species, see: A. Welle, S. Díez-González, B. Tinant, S. P. Nolan, O. Riant, *Org. Lett.* **2006**, *8*, 6059 – 6062.

[16] G. D. Frey, B. Donnadieu, M. Soleilhavoup, G. Bertrand, *Chem. Asian J.* **2011**, *6*, 402 – 405.

[17] E. Y. Tsui, P. Müller, J. P. Sadighi, *Angew. Chem.* **2008**, *120*, 9069 – 9072; *Angew. Chem. Int. Ed.* **2008**, *47*, 8937 – 8940.

[18] B. K. Tate, C. M. Wyss, J. Bacsa, K. Kluge, L. Gelbaum, J. P. Sadighi, *Chem. Sci.* **2013**, *4*, 3068 – 3074.

[19] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597 – 636.

[20] a) N. Kuganathan, J. C. Green, *Chem. Commun.* **2008**, 2432 – 2434; b) H. L. Hermann, G. Boche, P. Schwerdtfeger, *Chem. Eur. J.* **2001**, *7*, 5333 – 5342; c) C. Mealli, S. S. M. C. Godinho, M. J. Calhorda, *Organometallics* **2001**, *20*, 1734 – 1742; d) C. Kölmel, R. Ahlrichs, *J. Phys. Chem.* **1990**, *94*, 5536 – 5542; e) K. M. Merz, Jr., R. Hoffmann, *Inorg. Chem.* **1988**, *27*, 2120 – 2127.

[21] a) S.-L. Zheng, M. Messerschmidt, P. Coppens, *Angew. Chem.* **2005**, *117*, 4690 – 4693; *Angew. Chem. Int. Ed.* **2005**, *44*, 4614 – 4617; b) A. Sundararaman, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *Chem. Commun.* **2005**, 1708 – 1710; c) J.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Lin, X.-M. Chen, *Chem. Eur. J.* **2005**, *11*, 552 – 561; d) R. D. Köhn, G. Seifert, Z. Pan, M. F. Mahon, G. Kociok-Köhn, *Angew. Chem.* **2003**, *115*, 818 – 820; *Angew. Chem. Int. Ed.* **2003**, *42*, 793 – 796; e) J.-M. Poblet, M. Bénard, *Chem. Commun.* **1998**, 1179 – 1180; f) K. Singh, J. R. Long, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 2942 – 2943; g) M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, J. Trotter, *Can. J. Chem.* **1990**, *68*, 1444 – 1449.

[22] J. C. Green, M. L. H. Green, G. Parkin, *Chem. Commun.* **2012**, *48*, 11481 – 11503.

[23] a) R. Clérac, F. A. Cotton, L. M. Daniels, J. Gu, C. A. Murillo, H.-C. Zhou, *Inorg. Chem.* **2000**, *39*, 4488 – 4493; b) F. A. Cotton, X. Feng, D. J. Timmons, *Inorg. Chem.* **1998**, *37*, 4066 – 4069; c) J. Beck, J. Strähle, *Angew. Chem.* **1985**, *97*, 419 – 420; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 409 – 410.

[24] For studies of bonding in bent $[M_2(\mu\text{-H})]$ complexes, see for example: a) M. Savoca, J. Langer, O. Dopfer, *Angew. Chem.* **2013**, *125*, 1608 – 1611; *Angew. Chem. Int. Ed.* **2013**, *52*, 1568 – 1571; b) Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P. Power, *Angew. Chem.* **2006**, *118*, 5939 – 5942; *Angew. Chem. Int. Ed.* **2006**, *45*, 5807 – 5810; c) M.-H. Baik, R. A. Friesner, G. Parkin, *Polyhedron* **2004**, *23*, 2879 – 2900; d) B. Jeżowska-Trzebiatowska, B. Nissen-Sobocińska, *J. Organomet. Chem.* **1987**, *322*, 331 – 350; e) R. Bau, R. G. Teller, S. W. Kirtley, T. F. Koetzle, *Acc. Chem. Res.* **1979**, *12*, 176 – 183.

[25] Linear [Ni-H-Ni] complexes: D. A. Vicic, T. J. Anderson, J. A. Cowan, A. J. Schultz, *J. Am. Chem. Soc.* **2004**, *126*, 8132 – 8133.

[26] Calculations of linear $\{M_2(\mu\text{-H})\}^+$ structures for alkali metals: S. J. Grabowski, R. Hoffmann, *ChemPhysChem* **2012**, *13*, 2286 – 2288.

[27] R. A. Flurer, K. L. Busch, *J. Am. Chem. Soc.* **1991**, *113*, 3656 – 3663.

[28] R. Gáspár, I. Tamássy-Lentei, *Acta Phys. Acad. Sci. Hung.* **1981**, *50*, 343 – 347.

[29] Calculations of copper – copper bonding in cyclic copper hydrides: A. C. Tsipis, C. A. Tsipis, *J. Am. Chem. Soc.* **2003**, *125*, 1136 – 1137.

[30] CCDC 953635 (**1**), 953636 (**2**), and 953634 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[31] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441 – 451.

[32] X-ray diffraction tends to underestimate M–H distances; see for example Ref. [24e]. The Cu-H-Cu bending in **1** may thus be more pronounced than the experimentally determined angle suggests.

[33] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083 – 1096.

[34] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.

[35] a) M. R. Churchill, D. G. DeBoer, F. J. Rotella, *Inorg. Chem.* **1976**, *15*, 1843 – 1853; b) M. R. Churchill, S. W.-Y. Ni, *J. Am. Chem. Soc.* **1973**, *95*, 2150 – 2155.

[36] T. C. Davenport, T. D. Tilley, *Angew. Chem.* **2011**, *123*, 12413 – 12416; *Angew. Chem. Int. Ed.* **2011**, *50*, 12205 – 12208.

[37] B. D. Nageswara Rao, L. R. Anders, *Phys. Rev.* **1965**, *140*, A112 – A117.

[38] a) J. T. Muckerman, P. Achord, C. Creutz, D. E. Polyansky, E. Fujita, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15657 – 15662; b) C. J. Curtis, A. Miedaner, W. W. Ellis, D. L. DuBois, *J. Am. Chem. Soc.* **2002**, *124*, 1918 – 1925; c) D. J. Darensbourg, H. Pickner Wiegreffe, P. W. Wiegreffe, *J. Am. Chem. Soc.* **1990**, *112*, 9252 – 9257; d) S. Sakaki, K. Ohkubo, *Inorg. Chem.* **1989**, *28*, 2583 – 2590.

[39] Reactions of alkynes with neutral copper hydrides: a) K. Semba, T. Fujihara, J. Terao, Y. Tsuji, *Chem. Eur. J.* **2012**, *18*, 4179 – 4184; b) T. Fujihara, T. Xu, K. Semba, J. Terao, Y. Tsuji, *Angew. Chem.* **2011**, *123*, 543 – 547; *Angew. Chem. Int. Ed.* **2011**, *50*, 523 – 527; c) T. Konno, J. Chae, T. Tanaka, T. Ishihara, H. Yamanaka, *J. Fluorine Chem.* **2006**, *127*, 36 – 43; d) J. F. Daeuble, C. McGettigan, J. M. Stryker, *Tetrahedron Lett.* **1990**, *31*, 2397 – 2400; see also Ref. [14].

[40] Selected references: a) A. Zhdanko, M. E. Maier, *Organometallics* **2013**, *32*, 2000 – 2006; b) D. Weber, T. D. Jones, L. L. Adduci, M. R. Gagné, *Angew. Chem.* **2012**, *124*, 2502 – 2506; *Angew. Chem. Int. Ed.* **2012**, *51*, 2452 – 2456; c) A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wieteck, M. Rudolph, F. Rominger, *Angew. Chem.* **2012**, *124*, 4532 – 4536; *Angew. Chem. Int. Ed.* **2012**, *51*, 4456 – 4460; d) T. J. Brown, D. Weber, M. R. Gagné, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2012**, *134*, 9134 – 9137; e) G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem.* **2010**, *122*, 8644 – 8648; *Angew. Chem. Int. Ed.* **2010**, *49*, 8466 – 8470; f) D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem.* **2009**, *121*, 5843 – 5846; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733 – 5736.

[41] P. Schulte, U. Behrens, F. Olbrich, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1692 – 1696.

[42] For a review of mesitylcopper and related complexes, see: M. Stollenz, F. Meyer, *Organometallics* **2012**, *31*, 7708 – 7727.

[43] G. N. Khairallah, T. Waters, R. A. J. O'Hair, *Dalton Trans.* **2009**, 2832 – 2836.

[44] B. T. Worrell, J. A. Malik, V. V. Fokin, *Science* **2013**, *340*, 457 – 460.

[45] J. A. Bouwstra, A. Schouten, J. Kroon, *Acta Crystallogr. Sect. C* **1984**, *40*, 428 – 431.

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim