Angewandte International Edition Chemie

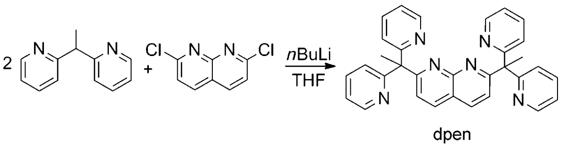
DOI: 10.1002/anie.201106081

Dinucleating Naphthyridine-Based Ligand for Assembly of Bridged Dicopper(I) Centers: Three-Center Two-Electron Bonding Involving an Acetonitrile Donor**

*Timothy C. Davenport and T. Don Tilley**

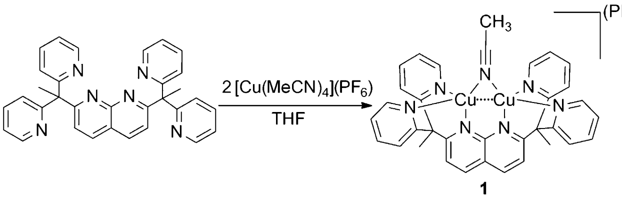
The three-center two-electron (3c-2e) bond is a well-known type of "electron-deficient" interaction that typically involves electron-poor main-group elements, such as aluminum or boron, in combination with strong σ-donor ligands, such as hydride or alkyl ligands.[1] However, 3c-2e bonds have also been observed for transition metals, for example in copper(I) aryl complexes in which the electron-deficient bond is supported by an unusually close Cu^I-Cu^I contact (2.37–2.45 Å) indicative of a cuprophilic interaction.[2] This attractive interaction between copper centers is reminiscent of the M–M interactions observed in 3c-2e bonds of main-group metals.[1] Over the past decade, similar cuprophilic interactions have been observed to result from 3c-2e bonds supported by unconventional L-type (two electron) donor interactions[3] involving, for example, phosphole ligands.[4] The latter complexes represent rare examples of a PR_3 ligand coordinated in the μ-η^1:η^1 bridging mode.[5] Herein we report the formation of a dicopper complex bridged by acetonitrile in this unusual μ-η^1:η^1 mode,[6,7] whereby the bridging ligand formally contributes both electrons to the 3c-2e interaction.

The work discussed herein derives from an interest in dinuclear metal complexes for cooperative substrate activations in catalytic reactions. In particular, the use of dinucleating ligands with rigid frameworks may provide well-defined pockets that promote electronic communication between the metal centers and create selective binding sites for substrates, thereby emulating the role of the protein scaffold in enzymes.[8] For this purpose we developed a ligand system based on 1,8-naphthyridine. The ligand 2,7-bis(1,1-dipyridylethyl)-1,8-naphthyridine (dpen) was synthesized by lithiation of 2,2′-dipyridylethane and subsequent reaction with 2,7-dichloro-1,8-naphthyridine [Eq. (1)]. Ligands based on 1,8-napthyridine have been shown to support a variety of dinuclear metal complexes with metal–metal distances ranging from 2.5 to 4.0 Å.[9] The incorporation of 2,2′-dipyridylethyl groups into the 2,7-positions of 1,8-naphthyridine results in the six-donor dpen ligand that should bind to each metal center in a tripodal manner. This binding mode leaves open coordination sites on both metals that are oriented toward one another, in a manner suitable for cooperative activation of a small molecule.



(1)

Reaction of dpen with two equivalents of $[Cu(NCMe)_4]PF_6$ in THF produced an orange precipitate of $[(dpen)Cu_2(\mu\text{-}NCMe)](PF_6)_2$ [**1**, Eq. (2)]. Compound **1** was crystallized by diffusion of THF into an acetonitrile solution of **1** to give crystals suitable for single-crystal X-ray diffraction.



(2)

In the solid-state structure of **1** (Figure 1), each copper center is ligated by four nitrogen donors, one of which is an acetonitrile bridge. The coordination geometry for both Cu centers is strongly distorted from a tetrahedral environment by the rigid nature of the dpen ligand, which enforces approximately 90° N-Cu-N angles involving the N donors of dpen. This arrangement results in a coordination geometry for Cu that resembles a tripodal L_3M fragment of an octahedral complex capped by the bridging acetonitrile ligand.[10] This ligand is bound in a nearly symmetrical bridging position between the copper centers with Cu–N bond lengths of 2.004(3) and 1.979(3) Å. These bond lengths are similar to distances found for terminally bound Cu^I acetonitrile com-

---

[*] T. C. Davenport, Prof. T. D. Tilley
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460 (USA)
E-mail: tdtilley@berkeley.edu

[**] We acknowledge Dr. Xinzheng Yang for help with computational work and Dr. John Curley for helpful discussions. Support for T.C.D. was provided by a National Science Foundation Graduate Research Fellowship and a University of California Chancellor's Fellowship. We gratefully acknowledge the support of the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under contract DE-AC02-05CH11231. Support for the Molecular Graphics and Computation Facility is provided by the National Science Foundation under grant CHE-0840505.

Supporting information (including experimental details, X-ray crystallography data, and computational details) for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201106081.

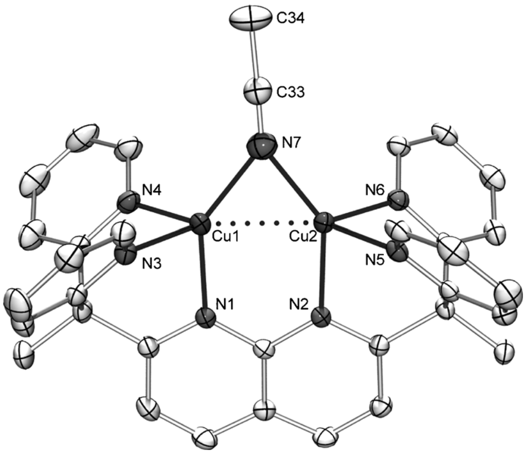


Figure 1. X-ray crystal structure of **1**. Hydrogen atoms and the PF$_6^-$ counterions have been omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.4457(4), Cu1–N7 2.004(3), Cu2–N7 1.979(3), Cu1–N1 2.012(2), Cu1–N3 2.043(2), Cu1–N4 2.035(2), Cu2–N2 2.019(2), Cu2–N5 2.040(2), Cu2–N6 2.043(2), N7–C33 1.111(4); N7-C33-C34 178.8(3), Cu1-N7-C33 138.2(2), Cu2-N7-C33 146.0(2), Cu1-N7-Cu2 75.77(9), N1-Cu1-Cu2 88.28(6), N1-Cu1-N3 90.43(8), N1-Cu1-N4 91.37(8), N4-Cu1-N3 89.76(9).

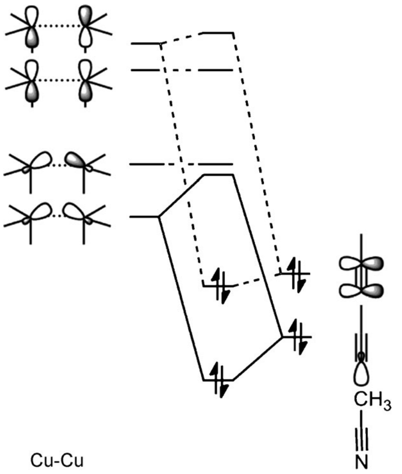
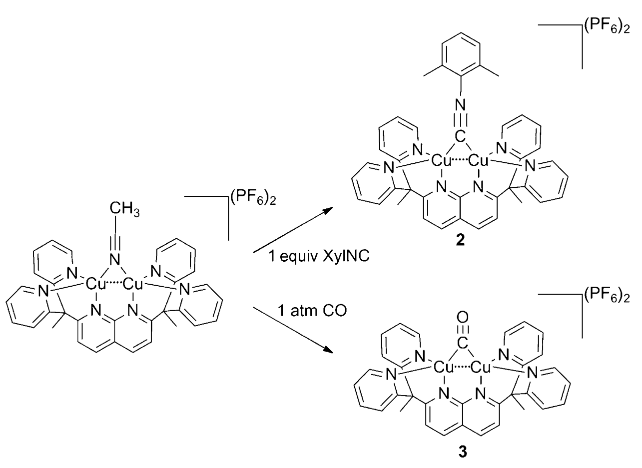


Figure 2. Qualitative molecular orbital diagram for the acetonitrile ligand of complex **1**. The Cu–Cu orbitals are constructed from the lowest energy combination of the empty Cu 4s and 4p orbitals. The N orbital on acetonitrile is from the nitrogen lone pair.

plexes.[11] The ligand leans slightly toward the Cu center associated with the longer Cu–NCMe bond, resulting in somewhat inequivalent Cu-N-C angles of 138.2(2) and 146.0(2)°. This geometry suggests the possibility of a weak interaction with the nitrile π system.[12] The IR spectrum of complex **1** exhibits an acetonitrile stretch at ν(CN) = 2280 cm^{-1}. This value is higher than that for free acetonitrile (ν(CN) = 2255 cm^{-1}) and similar to values for terminally bound complexes of acetonitrile (ν(CN) = 2270-2300 cm^{-1}).[13] This finding is consistent with the presence of a short C–N bond in **1** (1.111(4) Å, compared to 1.157(9) Å in free acetonitrile[14]). On the basis of these observations we suggest that the acetonitrile ligand is best described as a two-electron donor that participates in a three-center two-electron bond (Figure 2). This formal description is supported by the acute Cu-N-Cu angle (75.77(9)°) and a short Cu–Cu contact (2.4457(4) Å) that is characteristic of 3c-2e interactions.[1]

A number of investigations have addressed the nature of short Cu^{I}–Cu^{I} contacts (closer than 2.5 Å) of the type exhibited by **1**, and considerable discussion has been devoted to whether such Cu^{I}–Cu^{I} contacts reflect the presence of a formal bond between the two metal centers[15] or simply result from steric constraints of the bridging ligands.[16] Density functional theory (DFT) calculations on **1** indicate that no formal bond exists between the two copper centers, as the d-type bonding and antibonding Cu–Cu orbitals are all filled. Further analysis of the Cu–Cu interaction by using the quantum theory of atoms in molecules[17] determined the presence of a bond critical point between the two copper atoms. The characteristics of this critical point ($\rho = 0.038$, $\nabla^2\rho = +0.091$) are consistent with a closed-shell interaction.[17] This finding is expected for a cuprophilic interaction but would not be considered a formal single bond. Moreover, DFT calculations performed on the dicopper complex in the absence of a bridging ligand resulted in an increase in the Cu–Cu distance by 0.197 Å. This result indicates that the presence of the acetonitrile ligand is essential for maintaining the close Cu–Cu contact. Due to these findings, the small Cu–Cu separation is attributed to a cuprophilic interaction and is represented in bonding diagrams by a dotted line between the two copper atoms.

Because acetonitrile is commonly employed as a leaving group in ligand-exchange reactions, it was of interest to determine the potential for complex **1** to serve as a precursor for other bridged dicopper complexes (Scheme 1). The yellow xylyl isocyanide-bridged complex [(dpen)Cu$_2$(μ-CNXyl)](PF$_6$)$_2$ (**2**) results from reaction of **1** with one equivalent xylyl isocyanide in acetonitrile. X-ray quality crystals were grown by vapor diffusion of diethyl ether into a nitromethane solution of **2** (Figure 3). Also, the green carbonyl-bridged complex [(dpen)Cu$_2$(μ-CO)](PF$_6$)$_2$ (**3**) was formed when a solution of **1** was stirred in nitromethane in an atmosphere of



Scheme 1. Reaction of **1** with xylyl isocyanide and CO to form **2** and **3**.

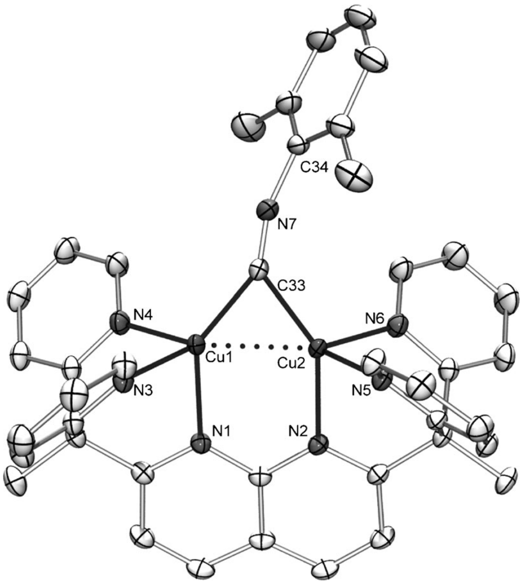


Figure 3. X-ray crystal structure of **2**. Hydrogren atoms and the PF_6^- counterions have been omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.3661(4), Cu1–C33 1.907(2), Cu2–C33 1.910(2), Cu1–N1 2.065(2), Cu1–N3 2.060(2), Cu1–N4 2.012(2), Cu2–N2 2.012(2), Cu2–N5 2.024(2), Cu2–N6 2.028(2), C33–N7 1.179(3); C33-N7-C34 161.8(2), Cu1-C33-N7 147.6(2), Cu2-C33-N7 134.8(2), Cu1-C33-Cu2 76.62(8), N1-Cu1-Cu2 87.24(5), N1-Cu1-N3 86.81(8), N1-Cu1-N4 92.11(9), N4-Cu1-N3 88.78(8).

CO, and crystals were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of **3** (Figure 4).

The solid-state structures of **2** and **3** reveal that the coordination geometry observed for **1** is retained after these simple ligand substitution reactions of acetonitrile. The Cu–C bond lengths in **2** and **3** are significantly shorter (1.907(2) and 1.910(2) Å for **2**; 1.889(3) and 1.898(3) Å for **3**) than the Cu–NCMe distance in **1**. This observation is consistent with the stronger coordinating abilities attributed to xylyl isocyanide and CO than to acetonitrile. The xylyl isocyanide ligand in **2** adopts a somewhat unsymmetrical bridging geometry, as indicated by the bent nature of this ligand (∡(C-N-C) = 161.8(2)°). Involvement of the π system of the isonitrile group of **2** in bonding to the copper centers is suggested by a relatively low ν(CN) stretching frequency of 2045 cm^{-1} (compared to 2119 cm^{-1} for free xylyl isocyanide). A significant π-back-bonding interaction is also reflected in a relatively low CO stretching frequency for **3** (1974 cm^{-1}; $\nu(CO_{gas}) = 2143$ cm^{-1}). This frequency is similar to corresponding values reported for Cu^{I} complexes of bridging carbonyl ligands.[18] These observations for **2** and **3** are consistent with the expected greater π acidity of these ligands relative to acetonitrile. However, it should be noted that Cu^{I} is associated with poor π basicity, as indicated by the significantly high ν(CO) value relative to typical ν(CO) frequencies reported for bridging carbonyl ligands in other transition-metal complexes (1700–1860 cm^{-1}).[19]

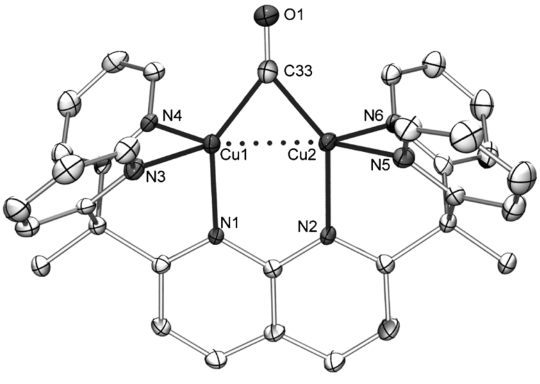


Figure 4. X-ray crystal structure of **3**. Hydrogen atoms and the PF_6^- counterions have been omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.3600(5), Cu1–C33 1.889(3), Cu2–C33 1.898(3), Cu1–N1 2.011(2), Cu1–N3 2.027(3), Cu1–N4 2.027(3), Cu2–N2 2.010(2), Cu2–N5 2.022(3), Cu2–N6 2.039(3), C33–O1 1.135(4); Cu1-C33-Cu2 77.1(1), Cu1-C33-O1 141.5(3), Cu2-C33-O1 141.3(3), N1-Cu1-Cu2 89.24(7), N1-Cu1-N3 89.6(1), N1-Cu1-N4 90.6(1), N4-Cu1-N3 90.9(1).

In conclusion, an unusual μ-η^1:η^1 acetonitrile-bridged dicopper complex was discovered that exhibits a three-center two-electron bonding interaction involving acetonitrile supported by a cuprophilic interaction between the metal centers. Furthermore, this complex serves as a starting material for the synthesis of other bridging complexes by substitution of the acetonitrile ligand, thereby providing a versatile platform for studying the interaction of small molecules with dinuclear copper centers.

Received: August 27, 2011

Keywords: bond theory · bridging ligands · copper · electron-deficient compounds · ligand design

---

[1] J. P. Oliver in *Advances in Organometallic Chemistry*, *Vol. 15* (Eds.: F. G. A. Stone, R. West) Academic Press, New York, **1977**, p. 235–271.

[2] G. van Koten, *J. Organomet. Chem.* **1990**, *400*, 283–301.

[3] M. L. H. Green, *Comments Inorg. Chem.* **2010**, *31*, 90–94.

[4] a) M. Sauthier, B. Le Guennic, V. Deborde, L. Toupet, J.-F. Halet, R. Réau, *Angew. Chem.* **2001**, *113*, 234–237; *Angew. Chem. Int. Ed.* **2001**, *40*, 228–231; b) M. Sauthier, F. Leca, L. Toupet, R. Réau, *Organometallics* **2002**, *21*, 1591–1602; c) F. Leca, M. Sauthier, V. Deborde, L. Toupet, R. Réau, *Chem. Eur. J.* **2003**, *9*, 3785–3795; d) F. Leca, C. Lescop, E. Rodriguez, K. Costuas, J.-F. Halet, R. Réau, *Angew. Chem.* **2005**, *117*, 4436–4439; *Angew. Chem. Int. Ed.* **2005**, *44*, 4362–4365; e) B. Nohra, E. Rodriguez-Sanz, C. Lescop, R. Réau, *Chem. Eur. J.* **2008**, *14*, 3391–3403.

[5] a) T. Pechmann, C. D. Brandt, H. Werner, *Angew. Chem.* **2000**, *112*, 4069; *Angew. Chem. Int. Ed.* **2000**, *39*, 3909; b) T. Pechmann, C. D. Brandt, C. Rçger, H. Werner, *Angew. Chem.* **2002**, *114*, 2398–2401; *Angew. Chem. Int. Ed.* **2002**, *41*, 2301–2303; c) T. Pechmann, C. D. Brandt, H. Werner, *Chem. Commun.* **2003**, 1136–1137; d) T. Pechmann, C. D. Brandt, H. Werner, *Chem. Eur. J.* **2004**, *10*, 728–736; e) T. Pechmann, C. D. Brandt, H. Werner, *Dalton Trans.* **2004**, 959–966.

[6] a) W. J. Evans, M. A. Greci, J. W. Ziller, *Chem. Commun.* **1998**, 2367–2368; b) F. A. Cotton, L. M. Daniels, C. A. Murillo, X. Wang, *Polyhedron* **1998**, *17*, 2781–2793; c) J. D. Beckwith, M. Tschinkl, A. Picot, M. Tsunoda, R. Bachman, F. P. Gabbaï, *Organometallics* **2001**, *20*, 3169–3174; d) P. Lin, W. Clegg, R. W.

Harrington, R. A. Henderson, *Dalton Trans.* **2005**, 2349–2351; e) M. R. A. Al-Mandhary, C. M. Fitchett, P. J. Steel, *Aust. J. Chem.* **2006**, *59*, 307–314; f) C. Lorber, R. Choukroun, L. Vendier, *Organometallics* **2008**, *27*, 5017–5024.

[7] X.-L. Li, X.-G. Meng, S.-P. Xu, *Chin. J. Struct. Chem.* **2009**, *28*, 1619–1624. The dicopper(I) μ-η^1:η^1 acetonitrile complex reported in Ref. [7] differs significantly from complex **1**. In particular, the Cu–Cu distance (3.168(9) Å) and Cu–N_{bridge} bond lengths (2.289(5) and 2.323(5) Å) are significantly longer (by 0.72 and 0.3 Å, respectively) than corresponding values for **1**. Thus, the bonding description outlined above for **1** likely does not apply to the complex in Ref. [7].

[8] A. L. Gavrilova, B. Bosnich, *Chem. Rev.* **2004**, *104*, 349–383.

[9] a) C. He, S. J. Lippard, *Inorg. Chem.* **2000**, *39*, 5225–5231; b) C. He, S. J. Lippard, *Tetrahedron* **2000**, *56*, 8245–8252; c) C. He, A. M. Barrios, D. Lee, J. Kuzelka, R. M. Daavydov, S. J. Lippard, *J. Am. Chem. Soc.* **2000**, *122*, 12683–12690; d) C. He, J. L. Dubois, B. Hedman, K. O. Hodgson, S. J. Lippard, *Angew. Chem.* **2001**, *113*, 1532–1535; *Angew. Chem. Int. Ed.* **2001**, *40*, 1484–1487.

[10] T. A. Albright, J. K. Burdett, M.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, **1985**, p. 381.

[11] J. R. Black, W. Levason, M. Webster, *Acta Crystallogr. Sect. C* **1995**, *51*, 623–625.

[12] M. E. Germain, M. Temprado, A. Castonguay, O. P. Kryatova, E. V. Rybak-Akimova, J. J. Curley, A. Mendiratta, Y.-C. Tsai, C. C. Cummins, R. Prabhakar, J. E. McDonough, C. D. Hoff, *J. Am. Chem. Soc.* **2009**, *131*, 15412–15423.

[13] H. Endres in *Comprehensive Coordination Chemistry*, *Vol. 2* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, p. 261.

[14] J. Demaison, A. Dubrulle, D. Boucher, J. Burie, *J. Mol. Spectrosc.* **1979**, *76*, 1–16.

[15] a) K. M. Merz, Jr., R. Hoffmann, *Inorg. Chem.* **1998**, *37*, 2120–2127; b) C. Kölmel, R. Ahlrichs, *J. Phys. Chem.* **1990**, *94*, 5536–5542; c) C. Mealli, S. S. M. C. Godinho, M. J. Calhorda, *Organometallics* **2001**, *20*, 1734–1742.

[16] a) F. A. Cotton, X. Feng, D. J. Timmons, *Inorg. Chem.* **1998**, *37*, 4066; b) R. Clérac, F. A. Cotton, L. M. Daniels, J. Gu, C. A. Murillo, H.-C. Zhou, *Inorg. Chem.* **2000**, *39*, 4488.

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

[18] a) M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, C. Guastini, *J. Am. Chem. Soc.* **1981**, *103*, 185–186; b) M. Pasquali, C. Floriani, G. Venturi, A. Gaetani-Manfredotti, A. C. Villa, *J. Am. Chem. Soc.* **1982**, *104*, 4092–4099; c) G. Doyle, K. A. Eriksen, M. Modrick, G. Ansell, *Organometallics* **1982**, *1*, 1613–1618.

[19] G. L. Miessler, D. A. Tarr, *Inorganic Chemistry*, 3rd ed., Pearson Prentice Hall, Upper Saddle River, NJ, **2004**, p. 470.