ChemComm
Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. K. Gupta, O. Y. O. Fayet, L. Tian, A. Orthaber, R. Berger and R. Lomoth, *Chem. Commun.*, 2025, DOI: 10.1039/D5CC00783F.




ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

ChemComm

View Article Online
DOI: 10.1039/D5CC00783F

COMMUNICATION

# Base Mediated Alkynyl-Cubane to $Cu_8$-Alkynide Cluster Transformation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Arvind Kumar Gupta,[a] Océane Y. O. Fayet,[a,b] Lei Tian,[a] Raphael J. F. Berger,[c] Reiner Lomoth,[a] Andreas Orthaber[a,*]

We demonstrated that a copper cubane cluster $[Cu_4Cl_4(LH)_4]$ can be converted into an octanuclear cluster $[Cu_8L_8]$ through deprotonation of the triisopropylacetylene ligands. The former displays exclusively side-on coordination of the terminal acetylene, while the latter exhibits both side-on and end-on coordination of the deprotonated acetylide moiety. The octanuclear complex shows solid-state emission around 640 nm, while the cubane displays a thermochromic emission shifting from 563 nm at r.t. to 608 nm upon cooling to 77 K.

Copper alkynyl complexes have attracted great attention due to their structural diversity, and fascinating photophysical properties. Cuprophilic interactions often result in beneficial optical properties and provide novel opportunities in the development of optoelectronic materials.[1, 2] Recent advances concerning the synthesis and characterization of well-defined copper(I) alkynyl complexes has led to new applications in supramolecular chemistry and as materials with interesting emissive properties.[3-6] The isolation and structural elucidation of various organo-copper(I) compounds has led to the development of novel strategies towards interesting organic frameworks.[7, 8] Apart from this, organo-copper(I) complexes are frequently encountered as a key intermediates in copper(I) mediated or copper-catalysed organic transformations.[9] Most importantly copper(I) alkynide species are crucial intermediates in different C-C cross coupling reactions, e.g. Sonogashira, Glaser Hay Chadiot- Chodkiewicz and the Huisgen Copper-catalysed azide–alkyne cycloaddition reactions.[10, 11]

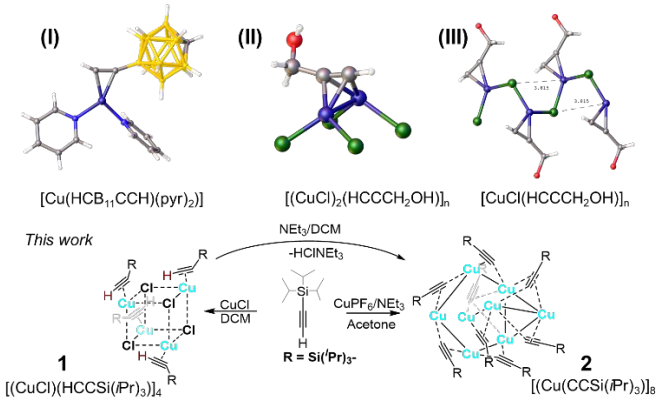


**Figure 1.** Basic structural motif of selected Cu(I)-alkynyl coordination compounds (**I-III**). Synthetic approach to the alkynyl copper cubane **1** and octanucler copper alkynide cluster **2**.

Copper(I) cubane motifs display a large variety of ligand / counter ion combinations. Halide containing cubanes $[Cu_4X_4L_4]$ (where X = Cl, Br, I) are reported for a large variety of ligands,[12-15]

These systems also show fascinating optical properties, such as thermally activated delayed fluorescence and other fascinating excited state dynamics and responsive behavior.[13, 16, 17] Notably, the Cu-cubane is typically highly stable and allows for post-synthetic modifications.[18, 19]Another group of cubanes are the Cu-acetylide family (where X = $^-$C≡CR), where the four copper(I) atoms form a distorted tetrahedral shape and each triangular shaped $Cu_3$-unit is capped with the terminal alkynide.[20-22] However, only very few solid-state structures have been reported to have an alkyne (RC≡C-H)ligand directly coordinating to copper(I) motifs.[23-25] Mononuclear Cu-alkynyl derivatives are only stabile with additional ligands or binding sites within the

[a] Dr. A.K.Gupta, O.Y.O. Fayet, Dr. L. Tian, Dr. R. Lomoth, Dr. A.Orthaber
Department of Chemistry, Ångström Laboratories,
Uppsala University, Box 523, 751 20 Uppsala, Sweden
E-mail: andreas.orthaber@kemi.uu.se
[b] O. Y.O. Fayet,
ENSICAEN
National Graduate School of Engineering and Research Center
Caen. France
[c] . Dr. R.J.F. Berger
Department Chemistry and Physics of Materials
Paris Lodron Universität Salzburg ,
Jakob-Haringerstr. 2A, 5020 Salzburg. Austria
Supplementary Information available: Synthesis details and spectroscopic data of the complexes. Details of quantum chemical calculations. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/D5CC07875



alkynyl ligand (Figure 1).[26-28] In this communication we report the missing puzzle piece in these Cu-cubane structures. The well-established $[Cu_4Cl_4]$-core is stabilized by alkynyls acting as neutral donor ligands. This cluster (**1**) $[Cu_4\{\mu_1\text{-}\eta^2\text{-}HC{\equiv}CSi(^iPr)_3\}_4(\mu_3\text{-}Cl)_4]$, in which four triisopropylsilyl acetylene ligands (**L**-H) stabilize a $[Cu_4Cl_4]$-core can be transformed into an acetylide cluster by addition of triethylamine in a dehydrohalogenation reaction giving rise to an octa-nuclear copper(I) complex, $[Cu(C{\equiv}C\text{-}Si^iPr_3)]_8$ (**2**). The solid state and optical properties of both complexes are studied in detail, and further supported by means of theoretical calculations.

Formation of cubane **1** $[Cu_4(HC{\equiv}CSi(^iPr)_3)_4Cl)_4]$ can be achieved by the reaction of triisopropylsilyl acetylene and CuCl in dry DCM the absence of any base. Expectedly, no deprotonation of the acetylenic hydrogens occurred during the complexion as evidenced by IR analysis of the solid material which was obtained after removal of all volatiles. The identity of this material was further corroborated by single crystal X-ray diffraction studies (SC-XRD, *vide infra*). Further attempts to characterize **1** in solution (NMR and ESI-MS) failed, suggesting deaggregation of the cubane motif. However addition of triethylamine to this solution (DCM) immediately results in a colour change from light yellow to deep orange indicating deprotonation of the acetylenic hydrogens and ultimately formation of **2,** $[Cu(C{\equiv}C^iPr_3Si)]_8$, as evidenced by spectroscopic and crystallographic analysis. Alternatively, complex **2**, can be obtained by the reaction of **L**-H and $[Cu(CH_3CN)_4PF_6]$ in the presence of triethylamine.

IR analysis of complex **1** shows that the typical C≡C stretching vibration of the ligand is shifted by 150 $cm^{-1}$ to lower wavenumbers (1881 $cm^{-1}$, cf **L**-H 2032 $cm^{-1}$) indicative of strong interaction of the triple bond with the metal core, through electron donation from the metal to antibonding orbitals of the ligand. Additionally, we see a band at 3197 $cm^{-1}$ and multiple bands between 550 and 700 $cm^{-1}$ attributable to the terminal C-H stretching (**L**-H: 3294 $cm^{-1}$) and the bending modes (**L**-H: 675 $cm^{-1}$) illustrating the coordination effects on ther terminal acetylene C-H moiety. For complex **2** a shifted C≡C stretching vibration of 1944 $cm^{-1}$ is consistent with a terminal coordination of the acetylide carbon.[23] In order to interpret the IR spectra of **1** and **2** unambiguously we have calculated their respective IR frequencies using DFT (TPSS/def2-TZVPP with a scaling factor of 0.943) supporting these assignments (see figures S3 and S4). The DFT calculation of **1** predicts a C≡C stretching frequency of 1897 $cm^{-1}$ closely matching with the observed band at 1880 $cm^{-1}$. Also, the calculated alkynyl CH stretching frequency of 3225 $cm^{-1}$ (exp. 3197 $cm^{-1}$) in **1** is slightly hypsochromically shifted compared to the free ligand 3277 $cm^{-1}$ (exp. 3420 $cm^{-1}$). For cluster **2** multiple bands for the C≡C stretching modes are calculated (1980, 1950, and 1897 $cm^{-1}$) however experimentally only one distinguishable feature at 1940 $cm^{-1}$ (besides two minor sidebands) was observed, matching the expected range Complex **2** is persistent in solution and ESI-MS of **2** gives a prominent peak of **2** ionized with one additional copper atom $[Cu_8(C{\equiv}C^iPr_3Si)_8]+Cu^+$ at *m/z* = 2022.49156. Proton and carbon NMR data suggest that the structure is dynamic in solution showing only one set of triisopropylsilylacetylide signals. The acetylide signals are detected at 94.8 and 58.9 ppm in the $^{13}C\{^1H\}$-NMR spectra, i.e. strongly shielded resonances compared to the free acetylene, as previously observed for silver acetylide systems (see Figure S2 Supporting Information).[29]

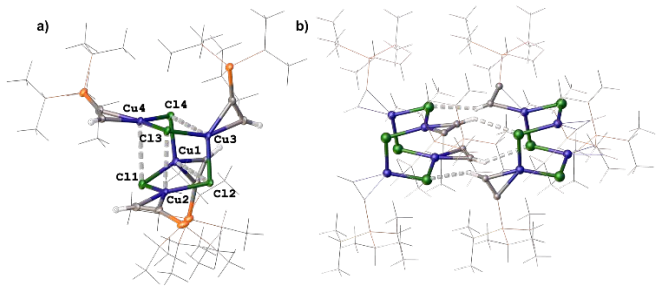


**Figure 2.** Solid-state structure of (**1**) a) $Cu_4Cl_4$-core and SiCCH drawn as thermal ellipsoids (50% probability levels), $^i$Pr-groups are rendered as wire frame for clarity. b) Weak hydrogen bonding (CC-H···Cl) linking clusters of **1** into a 1D-network.

The solid-state structures of **1** and **2** were determined by single crystal X-ray diffraction. The solid-state structure of **1** is solved in the triclinic space group *P-1* with one full molecule in the asymmetric unit. From the crystal structure analysis, it is evident that the $[Cu_4Cl_4]$ core in **1** adopts a highly distorted cubane arrangement (Figure 2a). We speculate that this distortion might be linked to the hydrogen bond of the actylenic proton with a neighbouring cluster chloride atom (Figure 2b). Each of the four copper atoms is tetrahedrally coordinated by three bridging chloride ions ($\mu_3$-Cl) and the acetylene ligand. The latter coordinates symmetrically side-on ($\mu_1$-$\eta^2$) with Cu-$C_{(C\equiv C)}$ distances in the range of 1.976(7)-2.040(1) Å. The Cu-Cl bond lengths vary significantly ranging from 2.255(4) to 3.272(13) Å. The Cu···Cu distances range from 3.383(11) to 3.681(5) Å indicating only weak cuprophilic interactions as these distances are significantly longer than the sum of van der Waals radii for copper (2.8 Å). This type of cubane structure is comparable to those typically observed for phosphine and nitrogen donor ligands.[12, 30-32] To the best of our knowledge this is the first observation of a cubane-like structure supported by neutral acetylene ligand. The acetylene has clearly triple bond character with bond distances ranging from 1.220(10) to 1.241(10) Å while displaying significant distortion from linearity (Si-C≡C angles ranging from 156.7(6) to 158.2(6)°).[33] However, the triple bond length is markedly elongated compared to unsupported silyl acetylenes (ca. 1.181 to 1.197 Å).[34] Such alkyne coordination to Cu(I) centres is rather rare (ca. 30 reports in CSD) and span a variety of mono- to polynuclear complexes (0D to 2D- coordination compounds).[23, 24, 26, 35]A more pronounced elongation of coordinated alkynyls is seen in mononuclear W (ca. 1.27 Å)[35, 36] and Nb (1.28 Å)[37] complexes. The large distortion from linearity and elongation in **1**, qualitatively supports the observed shift of the C≡C stretching frequency ($\Delta\nu_s$



 

= -151 $cm^{-1}$), which is also reproduced in our ab initio calculations (*vide infra*), and in line with acetylene adducts of copper(I) and silver(I).[38] Notably, the sterically demanding TIPS groups shields the individual clusters and allows only for very weak hydrogen bonding of the alkynyl-H to a chloride corner of a neighbouring cluster (Figure 2b). The *i*Pr-groups offer a large degree of rotational freedom evidenced by the disorder and large ADPs.

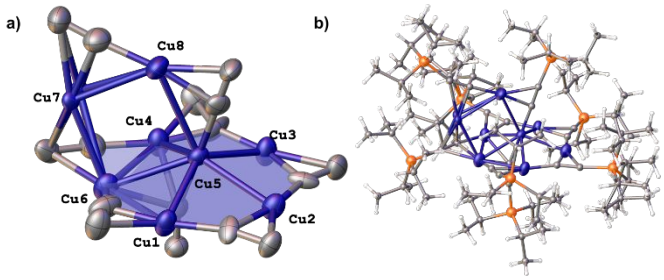


**Figure 3.** Solid-state structure plots of **2**. a) Cu-core and alkynide C-atoms (ADPs at 50% probability level) highlighting the basal plane consisting of $\{Cu_5(CC)_5\}$ The Cu7/Cu7A shows a positional disorder (0.1/0.9). b) View including the TIPS groups (stick model) illustrating the steric shielding. All disordered TIPS groups are shown.

Suitable crystals of **2** for single crystal X-ray measurement were obtained by the slow evaporation of a solution of **2** in acetone and few drops of ethanol. The crystal structure of **2** is solved in the orthorhombic space group $P2_12_12_1$. The structure consists of charge neutral eight copper atom framework coordinated with an equal number of triisopropylsilylacetylide ligands. Four different coordination modes are identified: five $\mu_2$-$\eta^1\eta^2$, and one each of $\mu_3$-$\eta^1\eta^1\eta^1$, $\mu_3$-$\eta^1\eta^1\eta^2$, $\mu_3$-$\eta^1\eta^2\eta^2$. The core of the cluster forms a unique "kite" arrangement (figure 3a) and can be describe by a copper-acetylide pentagon (Cu1-4, 6) holding one additional Cu atom (Cu5) ca. 0.81 Å above the center of that plane combined with two Cu-centres (Cu7/Cu7A[39] and Cu8). The Cu···Cu distances from the central Cu5 to the five membered ring Cu-atoms are in average shorter (ca. 2.65 to 278 Å), whereas "added" Cu7/Cu8 have longer Cu-Cu distances (Cu5-Cu8 2.951(3), Cu6-Cu7 2.814(3), Cu6-Cu7A 2.692(2)). This added copper dimer is held above one face assisted by three bridging acetylide ligands.

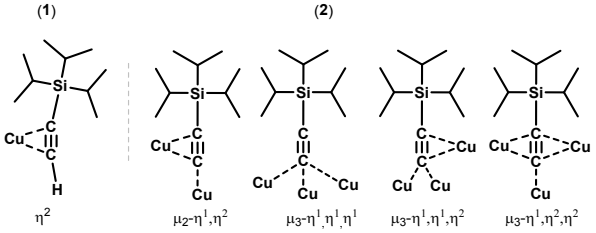


**Figure 4**. Observed coordination modes in complex **1** (left) and **2** (right).

This complex motif reflects the diversity of Cu(I) alkynide coordination modes and the tremendous effect of the steric demand of the alkynide ligands as seen in many other examples.[3, 40-42] Figure 4 summarizes the different coordination modes observed cluster **1** and **2**, respectively. While (**1**) shows exclusive side on-coordination ($\eta^2$), the acetylide complex (**2**) shows a variety of bridging coordination modes. The electronic absorption spectra of solid cluster **1** and **2** display a common UV absorption band at about 370 nm and a lower energy absorption around 420 nm characteristic of **2** (Figure S9-10). Both clusters show solid state photoluminescence (Figure 5) with orange emission for **2** ($\lambda_{em}$ = 640 nm at r.t. and 77 K) and a temperature dependent emission maximum for **1** ($\lambda_{em}$ = 563 nm at r.t., 608 at 77 K). Excitation spectra (Figure S11) are tracing the 370 nm absorption band of both clusters while the visible absorption of **2** matches the excitation spectrum only at low temperature. (Emission lifetime measurements revealed for both complexes a multiphasic decay with the dominating components in the sub-ns regime; Fig. S7 and S8). In depth theoretical studies (of extended solid-state models) and structural investigations will be needed to elucidate the electronic and geometric factors governing these emission profiles. At the moment detailed explanations of the marked different photophysical behaviour of these complexes remains elusive.

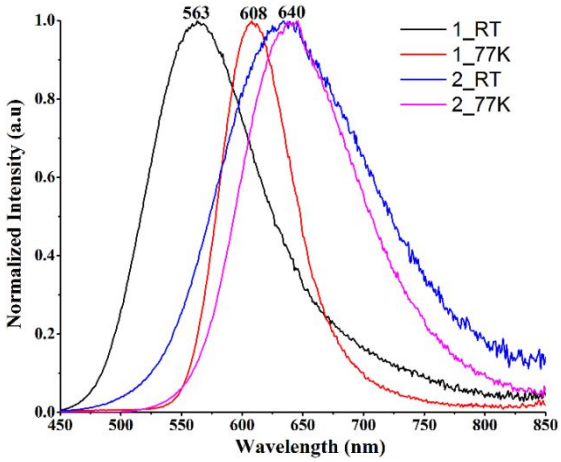


**Figure 5.** Emission spectra in solid state of **1** and **2** at 298 and 77 K (at $\lambda_{exc.}$ = 365 nm)

In summary we have presented a cubane motif consisting of a $[CuCl]_4$ core surrounded by neutral triisopropylsilyl acetylene ligands, which can be transformed into an octanuclear Cu-acetylide cluster upon deprotonation with an organic base. As such these motifs are relevant structures in various organic transformations including C-C coupling and Click reactions. Moreover, interesting luminescent behaviour was investigated revealing a thermochromic behaviour of the cubane **1**, in contrast to the unchanged emission of the acetylide cluster **2**. This facile conversion and variable opto-electronic properties promise interesting applications of these materials as sensors, or in organic electronics.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the Supplementary Information. Crystallographic data for **1** and **2** has been deposited at the CCDC and can be obtained from www.ccdc.cam.ac.uk/structures quoting the accession numbers 2239140 and 2239141, respectively .




1. R. Nast, *Coord. Chem. Rev.*, 1982, **47**, 89-124.
2. V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323-334.
3. X.-Y. Chang, K.-H. Low, J.-Y. Wang, J.-S. Huang and C.-M. Che, *Angew. Chem. Int. Ed.*, 2016, **55**, 10312-10316.
4. H. Lang, A. Jakob and B. Milde, *Organometallics*, 2012, **31**, 7661-7693.
5. S. N. Panda, P. Pradhan, S. Nath, J. Mohapatra, B. K. Patra and B. P. Biswal, *Chem. Commun.*, 2025, **61**, 2536-2539.
6. V. W.-W. Yam, *J. Organomet. Chem.*, 2004, **689**, 1393-1401.
7. M. Ito, D. Hashizume, T. Fukunaga, T. Matsuo and K. Tamao, *J. Am. Chem. Soc.*, 2009, **131**, 18024-18025.
8. W. Geng, J. Wei, W.-X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2014, **136**, 610-613.
9. T. Tsuda, T. Hashimoto and T. Saegusa, *J. Am. Chem. Soc.*, 1972, **94**, 658-659.
10. A. M. Thomas, A. Sujatha and G. Anilkumar, *RSC Adv.*, 2014, **4**, 21688-21698.
11. A. Makarem, R. Berg, F. Rominger and B. F. Straub, *Angew. Chem. Int. Ed.*, 2015, **54**, 7431-7435.
12. T. Agou, N. Wada, K. Fujisawa, T. Hosoya, Y. Mizuhata, N. Tokitoh, H. Fukumoto and T. Kubota, *Inorg. Chem.*, 2018, **57**, 9105-9114.
13. Y. V. Demyanov, Z. Ma, Z. Jia, M. I. Rakhmanova, G. M. Carignan, I. Y. Bagryanskaya, V. S. Sulyaeva, A. A. Globa, V. K. Brel, L. Meng, H. Meng, Q. Lin, J. Li and A. V. Artemev, *Adv. Opt. Mat.*, 2024, **12**, 2302904.
14. M. Białoń, B. Dziuk and V. Olijnyk, *Eur. J. Inorg. Chem.*, 2020, **2020**, 1790-1793.
15. E.-M. Rummel, M. Eckhardt, M. Bodensteiner, E. V. Peresypkina, W. Kremer, C. Gröger and M. Scheer, *Eur. J. Inorg. Chem.*, 2014, **2014**, 1625-1637.
16. A. Kobayashi, Y. Yoshida, M. Yoshida and M. Kato, *Chem. Eur. J.*, 2018, **24**, 14750-14759.
17. R. Utrera-Melero, B. Huitorel, M. Cordier, J.-Y. Mevellec, F. Massuyeau, C. Latouche, C. Martineau-Corcos and S. Perruchas, *Inorg. Chem.*, 2020, **59**, 13607-13620.
18. D. Bissessar, J. Egly, T. Achard, P. Steffanut, M. Mauro and S. Bellemin-Laponnaz, *Eur. J. Inorg. Chem.*, 2022, **2022**, e202200101.
19. R. Utrera-Melero, M. Cordier, F. Massuyeau, J.-Y. Mevellec, A. Rakhmatullin, C. Martineau-Corcos, C. Latouche and S. Perruchas, *Inorg. Chem.*, 2023, **62**, 18157-18171.
20. A. K. Gupta and A. Orthaber, *Chem. Eur. J.*, 2018, **24**, 7536-7559.
21. K. Škoch, I. Císařová and P. Štěpnička, *Inorg. Chem.*, 2014, **53**, 568-577.
22. V. W.-W. Yam, C.-H. Lam and N. Zhu, *Inorg. Chim. Acta*, 2002, **331**, 239-245.
23. K. Brantin, M. Håkansson and S. Jagner, *J. Organomet. Chem.*, 1994, **474**, 229-236.
24. M. Håkansson, K. Brantin and S. Jagner, *J. Organomet. Chem.*, 2000, **602**, 5-14.
25. B. M. Mykhalichko, M. G. Mys'kiv and E. A. Goreshnik, *Russ. J. Coord. Chem.*, 1999, **25**, 65-69.
26. T. Jiang, K. Zhang, Y. Shen, M. Hamdaoui, R. Dontha, J. Liu, B. Spingler and S. Duttwyler, *Dalton Trans.*, 2019, **48**, 17192-17199.
27. C. Martín, M. Sierra, E. Alvarez, T. R. Belderrain and P. J. Pérez, *Dalton Trans.*, 2012, **41**, 5319-5325.
28. N. Nagapradeep, V. Venkatesh, S. K. Tripathi and S. Verma, *Dalton Trans.*, 2014, **43**, 1744-1752.
29. U. Létinois-Halbes, P. Pale and S. Berger, *J. Org. Chem.*, 2005, **70**, 9185-9190.
30. J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, **4**, 831-838.
31. A. Gallego, C. Hermosa, O. Castillo, I. Berlanga, C. J. Gómez-García, E. Mateo-Martí, J. I. Martínez, F. Flores, C. Gómez-Navarro, J. Gómez-Herrero, S. Delgado and F. Zamora, *Adv. Mater.*, 2013, **25**, 2141-2146.
32. S. Lal, J. McNally, A. J. P. White and S. Díez-González, *Organometallics*, 2011, **30**, 6225-6232.
33. The CCH angles are also distorted from linearity (all angles approx. 143°), but due to the uncertainty of the H position these angles are not discussed further.
34. E. Weisheim, C. G. Reuter, P. Heinrichs, Y. V. Vishnevskiy, A. Mix, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Chem. Eur. J.*, 2015, **21**, 12436-12448.
35. J. L. Kiplinger, A. M. Arif and T. G. Richmond, *Organometallics*, 1997, **16**, 246-254.
36. A. F. Hill, N. Tshabang and A. C. Willis, *Eur. J. Inorg. Chem.*, 2007, **2007**, 3781-3785.
37. H. Yasuda, H. Yamamoto, T. Arai, A. Nakamura, J. Chen, Y. Kai and N. Kasai, *Organometallics*, 1991, **10**, 4058-4066.
38. A. Noonikara-Poyil, S. G. Ridlen, I. Fernández and H. V. R. Dias, *Chem. Sci.*, 2022, **13**, 7190-7203.
39. This Cu atom shows a positional disorder Cu7A (0.093) and Cu7 (0.907).
40. L.-M. Zhang and T. C. W. Mak, *J. Am. Chem. Soc.*, 2016, **138**, 2909-2912.
41. L. L.-M. Zhang and T. C. W. Mak, *Angew. Chem. Int. Ed.*, 2017, **56**, 16228-16232.
42. M.-M. Zhang, X.-Y. Dong, Z.-Y. Wang, H.-Y. Li, S.-J. Li, X. Zhao and S.-Q. Zang, *Angew. Chem. Int. Ed.*, 2020, **59**, 10052-10058.


View Article Online DOI: 10.1039/D5CC00783F

View Article Online
DOI: 10.1039/D5CC00783F

## Data availability

The data supporting this article have been included as part of the Supplementary Information. Crystallographic data for 1 and 2 has been deposited at the CCDC and can be obtained from www.ccdc.cam.ac.uk/structures quoting the accession numbers 2239140 and 2239141, respectively .