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Theoretical Analysis of Bonding and Stereochemical Trends in Doubly Bridged Copper(I)−Copper(I) Dimers

Carlo Mealli,*[,†] Sofia S. M. C. Godinho,[‡] and Maria José Calhorda*[,‡,§]

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132 Firenze, Italy, ITQB, Av. da República, Apart 127, EAN, 2781-901 Oeiras, Portugal, and Dep. Química e Bioquímica, FC, Universidade de Lisboa, 1749-016 Lisboa, Portugal

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DFT/B3LYP calculations on known and hypothetical doubly bridged Cu(I)−Cu(I) dimers and other $d^{10}-d^{10}$ analogues have been carried out. The bridging ligands may be only σ donors (hydrides) or have added π-donor (halides) or π-acceptor (carbonyls, as yet unknown) capabilities. In particular, the few reported $L_nCu(\mu\text{-}C{\equiv}CR)_2CuL_m$ frameworks have been investigated. The latter are symmetric (type **c**) or asymmetric (types **a** and **b**), depending on the nature and number of terminal ligands ($n = 1, 2$; $m = 1, 2$). Beside the accurate geometric and energetic computations, the nature of the chemical bonding is explored in terms of perturbation theory arguments (EHMO approach). Thanks to the σ donor power of the bridges, electron density is driven into the bonding combinations (σ and π) of empty metal s and p_π orbitals. In the presence of π-donor ligands, population of the corresponding σ^* and π^* levels occurs and the M−M bond vanishes. In contrast, insufficient back-donation from copper d orbitals prevents the formation of bridged carbonyl dimers and trigonal-planar monomers are favored. A case study is that of the heterobinuclear $d^{10}-d^{10}$ complex $(CO)_2Cu(\mu\text{-}CO)_2Co(CO)_2$, where the lone pairs of the CO bridges are preferentially directed toward cobalt for electronegativity reasons. A similar situation is highlighted for the model $(PH_3)_2Cu(\mu\text{-}C{\equiv}CH)_2Cu(PH_3)$ (type **b**), where both bridges orient toward the unique fragment $(PR_3)Cu$ because of the different hybridization of L_2M and LM σ orbitals. In the species $L_nCu(\mu\text{-}C{\equiv}CH)_2CuL_n$ ($n = 2$ or $n = 1$, type **a** or **c**), the potential energy surface for the symmetric to asymmetric rearrangement of the central Cu_2C_2 ring is quite flat. However, a symmetric $Cu_2(\mu\text{-}C{\equiv}CR)_2$ framework is achieved with η^2-bound alkynes (type **c**). This is attributable to the π^* levels of the latter ligands, which stabilize the metal p_π orbitals involved in bridge bonding. The asymmetric Cu_2C_2 arrangement is preferred again in models where the terminal alkynes are substituted for by single phosphine ligands.

Introduction

M−M $d^{10}-d^{10}$ interactions have been the subject of many experimental and theoretical studies due to their biological relevance (e.g. cytochrome oxidase and hemocyanins contain a Cu(I)−Cu(I) active site[1]). The topic has become of even greater interest after the report[2] that in cuprite a degree of covalent Cu−Cu interaction can be demonstrated by empirical electron density measurements which highlight the hybridization of metal z^2 orbitals. Even though other authors[3] have quickly criticized the viewpoint by recalling the intrinsic difference between electron density and orbital density contour plots, more reports have appeared on the imaging of the MOs under a scanning tunneling microscope (STM).[4]

Among the most significant works on Cu(I)−Cu(I) interactions, Cotton et al.[5] properly reproduced by DFT methods the short Cu(I)−Cu(I) distance of 2.45 Å experimentally observed in $[Cu(hpp)]_2$ (hpp is an anionic chelate with NCN bite). Still, the authors excluded direct Cu−Cu bonding on the basis of the overwhelming d orbital character of the populated MOs and on the small value of the Cu−Cu overlap population. Insignificant Cu−Cu covalent bonding in dimers (with the exception of species with bridging hydrides) has been also pointed out by authors who attributed the short separations to dispersion-like attractions (electron correlation) and to relativistic effects.[6−8] A comparison of HF and MP2 calculations demonstrated the importance of correlation effects in shortening the M(I)−M(I) distance (M = coinage metal).[8] On the other hand, it is

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[‡] ITQB.

[§] Universidade de Lisboa.

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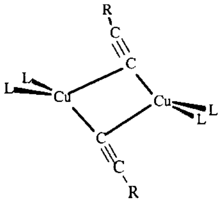
Table 1. Cu(I)−Cu(I) Species Which Contain the Inner Core $Cu_2(\mu\text{-acetylide})_2$ and Appear in the Cambridge Structural Database[a]



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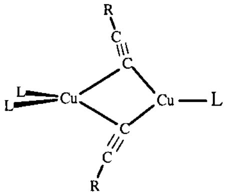
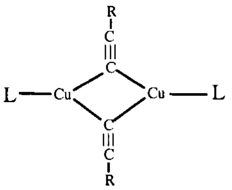


b



c

type	refcode	L	R	Cu_1-Cu_2	Cu_1-C_2	Cu_2-C_1	$Cu_2-C_1-C_2$	ref
a	TISKEL, **1**	4 PPh_2Me	Ph	2.454	2.011	2.209	159.3	15
a	CAHMED, **2**	2 dppf[b]	^{p}tol	2.447	2062	2.136	154.0	16
a	PETPCU, **3**	4 $PPhEt_2$	Ph	na[c]	na	na	na	17
b	YIGSEM, **4**	2 $PPh_3/P(C_6H_{11})_3$	^{t}Bu	2.389	2.143	2.054	150.2	18
c	LEXDOH, **5**	cycloalkyne[d]	Ph	2.385	2.023	2.014	142.1	19

[a] Distances are given in Å and angles in deg. For the Cambridge Structural Database (version 5.19, April 2000), see ref 13. [b] dppf = 1,1′-bis(diphenylphosphino)ferrocene. [c] Structural details not available. [d] cycloalkyne = (4,5-η)-3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (the alkyne group lies coplanar with the $Cu_2(\mu\text{-}C{\equiv}CPh)_2$ framework).

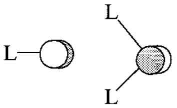
chemically intuitive that repulsion between filled d shells may be overcome by mixing (however small) of the higher s and p metal orbitals into the d levels. The latter viewpoint has been addressed by several authors,[9−12] including some of us, relative to the interactions between other closed-shell metals.[13]

The present study has been prompted by the limited, yet significantly varied, structural situations observed in Cu(I)−Cu(I) dimers with bridging acetylides. Table 1 lists all of the complexes of general formula $L_nCu(\mu\text{-acetylide})_2CuL_m$ (n, m = 1, 2; L = two-electron-donor ligand) which appear in the latest release of the Cambridge Structural Database.[14]

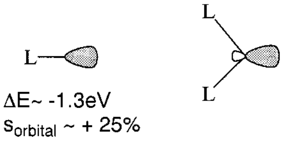
The three major types (**a**−**c**) correspond to different sets of terminal ligands ($n = m = 2$; $n = 1$, $m = 2$; $n = m = 1$, respectively). Although the bridging acetylides are invariably η^1-bonded to both metals, only in compound **5** (type **c**, with L being a terminally bound η^2 alkyne group) are the bridges symmetrically arranged. Otherwise (at least in the solid state), each acetylide ligand orients its σ lone pair toward one of the metals which is also coordinated more strongly. The species **a** ($m = n = 2$) are characterized by a pseudo-2-fold axis, and due to a ca. 20° tilting of the terminal L_2M planes, local trigonal-planar coordination of the metals is approximated. In actuality, each acetylide bridge maintains a sufficient interaction also with the other metal. Finally, in the compounds of type **b**, both acetylide ions are oriented toward the metal carrying the single terminal ligand, but again interaction is maintained with the other metal.

In all of the bridged acetylide complexes the Cu−Cu distance is rather short (ca. 2.40 Å), essentially similar to that (2.37 Å) experimentally found in the dihydride dimer $[(\eta^2\text{-}CH_3C(CH_2PPh_2)_3Cu(\mu\text{-}H)]_2$.[20] Much longer separations (in the range 2.70−3.58 Å) are observed for the plethora of complexes with formula $L_nCu(\mu\text{-}X)_2CuL_m$ (m = 1, 2; n = 1, 2), which contain X bridges having both σ- and π-donor capabilities such as halide, alkoxide, sulfide, etc. In the latter, direct Cu−Cu bonding has to be excluded, as the separation exceeds by at least 0.35 Å two copper covalent radii (1.17 Å). Recall that direct bonding has been questioned even for Cu(I)−Cu(I) distances as short as 2.35 Å.[5]

The electronic distribution in $L_mM(\mu\text{-}X)_2ML_n$ complexes as well as the Cu−Cu interaction depends not only on the nature of the bridge but also on the combination of the terminal fragments such as LM and L_2M or a mixture of the two (M = d^{10}). Both fragments have the same p_π-acceptor orbital (**I**) and a different sp σ hybrid (**II**).



I



II

On the basis of EHMO results,[21,22] the σ hybrid of LM is ca. 1.3 eV lower in energy. Moreover, the percentage of s orbital character is almost double in LM (55% vs 30% in L_2M), and it will be highlighted in the discussion that remarkable differences ensue.

To summarize some common ideas about the electronic structure of these compounds, bridging hydrides induce major M−M bonding, as they contribute to the

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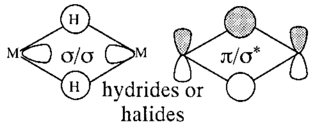
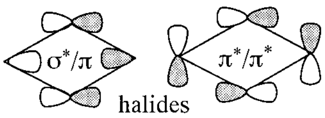
population of the empty σ and π M−M bonding orbitals (see **III**). In common chemical terms, the two hydrides allow the combination of two *three-center/two-electron* interactions.



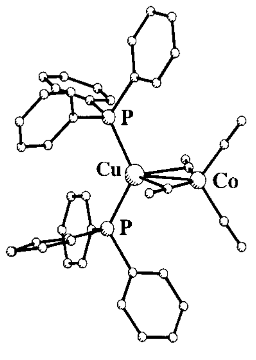
III



IV

In view of the involvement of both σ and π components, an alternative description invokes a M=M double bond supported by the H bridges. The dichotomy parallels that for the diborane B_2H_6.[23] As an extension, in line with the concept of *isolobal analogy*,[24] also the η^2 coordination of the anion BH_4^- to fragments of the type $(PR_3)_2Cu(I)$[25−27] can be described by considering a Cu=B bond supported by the H bridges.

The bonding network changes significantly with halide bridges, which possess σ-donor as well as π-donor capabilities. In addition to the bonding combinations **III**, also the corresponding σ^* and π^* combinations become populated (see **IV**); hence, all of the M−M bonding vanishes. Less addressed is the behavior of π-acceptor bridges, such as carbon monoxide, and, in turn, that of acetylides, whose π-donor and π-acceptor capabilities are in principle competitive. While the latter species are those listed in Table 1, analogues with CO bridges are unknown. However, there are structures of $d^{10}-d^{10}$ heterobinuclear species of the type $L_2Cu(\mu\text{-}CO)_2Co(CO)_2$ (L = CO,[28] nitrogen,[29,30] phosphorus donor[31]). As an example, the diphosphine species, reported in **V**, is strictly related to the complex **4** (type **b**), provided that the set of terminal ligands is $n = m = 2$ and not $n = 2$, $m = 1$. In any case, the bridging ligands direct their σ lone pairs toward one metal atom (either cobalt or the copper bound to the unique terminal ligand).



V

We present in this paper a series of DFT/B3LYP calculations on selected models $L_nCu(\mu\text{-}X)_2CuL_m$. Our primary goal is that of evaluating, from both the energetic and the MO picture viewpoints, the factors which affect the symmetry of the bridges as well as the Cu−Cu bonding in the different cases. The role of the bridging acetylides will be mainly addressed, although we examine also species with naked atom bridges (hydrides, halides), as well as unknown Cu dimers with two bridging carbon monoxides which combine π-acceptor and σ-donor capabilities. The discussion of the numerical results will also exploit perturbation theory and symmetry arguments, which always provide rich and intuitive pieces of chemical information.

Computational Details

The DFT calculations were carried out with GAUSSIAN94[32] and GAUSSIAN98[33] packages. To reduce computational time, phosphine and acetylide ligands were simplified as PH_3 and CCH groupings. All of the computations were performed with the hybrid B3LYP density functional,[34,35] and the basis set was 6-311G with the important addition of the polarization functions (d, p) for all atoms, including hydrogens. The effective core potential (LANL2DZ) has been used for the metal Cu.[36] Occasionally, we adopted the more complete basis set TZVP of Ahlrichs et al.[37,38] in order to verify how significant certain energetic differences may be. Frequency calculations were performed to check whether the optimized geometries were actual stationary points.

The development of qualitative MO analysis was possible with the routine usage of the program CACAO,[39,40] whose utilities permit a quick evaluation of the topology and sym-

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metry properties of the MO's as well as of the trends in the Mulliken population analysis.

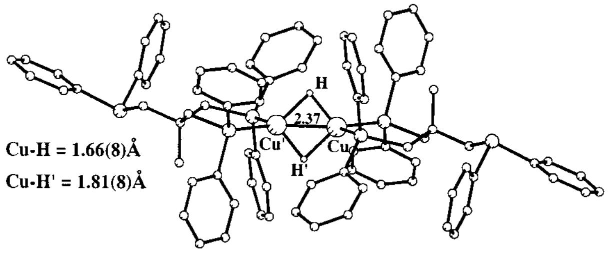
Results and Discussion

$(PH_3)_nCu(\mu\text{-}X)_2Cu(PH_3)_m$ (X = H, Cl; $n = m = 1, 2$). Alemany and Alvarez[11] have related the wide range of observed Cu−Cu separations to the number of electrons available in the bridged framework $Cu(\mu\text{-}X)_2Cu$ (FEC = framework electron counting). Thus, the direct M−M interaction decreases dramatically on going from FEC = 8 to FEC = 4. As we have pointed out in the Introduction, two bridging hydrides provide only four electrons (FEC = 4), which populate in part the M−M σ- and π-bonding combinations (see **III**). Conversely, two bridging halides can donate four lone pairs (FEC = 8) into all of the empty M−M bonding and antibonding combinations (**III** and **IV**); hence, the Cu−Cu bond vanishes.

To start with, we have optimized the D_{2h} model $[(PH_3)_2Cu(\mu\text{-}Cl)_2Cu(PH_3)_2$. The Cu−Cl distances of 2.44 Å are only slightly longer than those (ca. 2.39 Å) found in actual structures which contain terminal PPh_3[41] and diphosphine[42] ligands. Conversely, the calculated Cu−Cu separation of 3.07 Å is shorter than the experimental ones (~3.30 Å). Other authors have already noticed that the potential energy surface (PES) is quite flat for these molecules,[10] and we shall not analyze in depth the reason, beyond the Cu−Cu bonding distance (>2.5 Å), that the intermetallic separation is affected by the type of bridging halide ($I < Br < Cl$) and by the nature of the terminal fragment (ML or ML_2) as well. Rather, we focus on systems (FEC = 4) for which a good Cu−Cu interaction is expected. Alvarez and Alemany[11] analyzed a system with two PR_3 bridges which, owing to their major σ-donor character, are comparable with hydrides.[43,44] Since systems having the core $Cu(\mu\text{-}H)_2Cu$ are the simplest and have been insufficiently studied with ab initio methods, we report them in some detail.

The X-ray structure of the complex $[(\eta^2\text{-}CH_3C(CH_2PPh_2)_3Cu(\mu\text{-}H)]_2$[20] (**6**) shows one of the shortest Cu−Cu separations ever found (2.37 Å), while the Cu−H bridges appear asymmetric (see **VII**). A D_{2h} model with four terminal PH_3 ligands, **7** (shown in **VI**), reproduces well the intermetallic distance (2.36 Å). Since such a highly symmetric geometry was characterized as a true minimum (its consistency was also confirmed by lower symmetry calculations), the proposed asymmetry of the bridges[20] becomes questionable. In other words, the computational result supports the idea that, in view of the large errors affecting the experimental Cu−H distances (ca. 0.08 Å), there are no meaningful differences between the reported values of 1.66 and 1.81 Å, respectively (see **VI**). The calculated Cu−H distance of 1.77 Å is intermediate between the latter values.

Another interesting question about the nature of complex **6** was originally raised by the authors.[20] In fact, the formation of the $Cu_2(\mu\text{-}H)_2$ framework eliminates an arm of the tripodal ligand $CH_3C(CH_2PPh_2)_3$ from the coordination sphere of copper. Implicitly, the energy gained with the formation of the $Cu_2(\mu\text{-}H)_2$ core overcomes that of the extra two Cu−P bonds which would be present in the two monomeric hydrides $(\eta^3\text{-}CH_3C(CH_2PPh_2)_3)CuH$. To find a quantitative answer, we have optimized the C_{3v} model **8** with three terminal PH_3 ligands in place of the tripod, and also the trigonal-planar model **9** as well as the free PH_3 ligand **10**, all shown in **VIII**.



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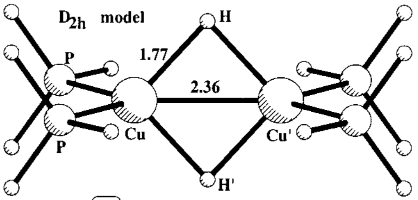
VI



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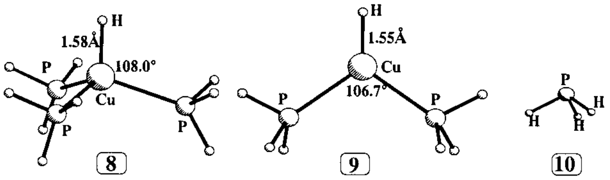
VII



8 9 10

VIII

Since $E[Cu-PH_3] = E_8 - (E_9 + E_{10}) = -6.0$ kcal mol^{-1} and $E[Cu_2(\mu\text{-}H)_2] = E_7 - 2E_9 = -31.5$ kcal mol^{-1}, the energetic balance for the formation of dimer **6** is estimated as $\Delta E = E[Cu_2(\mu\text{-}H)_2] - 2E[Cu-PH_3] = -31.5 - (2 \times 6.0) = -19.5$ kcal mol^{-1}. The overall energy gain is sufficiently large and is consistent with the experimental facts. On the other hand, the result is surprising, as the net energy gain associated with the third $Cu-PH_3$ bond (6 kcal mol^{-1}) is rather small (it includes, however, the deformation energy needed to pyramidalize the trigonal-planar species $(PH_3)_2CuH$). Also, it must be considered that in a d^{10} tetrahedron the ligands destabilize three filled d orbitals (classical e/t_2 splitting) so that the electron repulsion between metal and ligands is large. A qualitative evaluation of the latter feature can be gained, at the EHMO level, by comparing trends for the Cu−P overlap populations in models **8** and **9** (0.51 vs 0.55, respectively) after imposing the same distances (with such a technique at EHMO level it is possible to evaluate the strength of a bond). Perhaps indirect evidence of greater electronic repulsion in the monomeric tetrahedron is the absence of $(PR_3)_3CuH$ compounds in CSD.[14] However, it is found that one

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[41] Balog-Hergovich, E.; Parkanyi, L.; Speier, G. *New Cryst. Struct.* **1998**, *213*, 265.

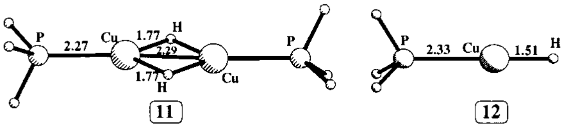
[42] Wang, H.-E.; Liu, S.-T.; Lee, G.-H.; Cheng, M.-C.; Peng, S.-M. *J. Chin. Chem. Soc.* **1991**, *38*, 565.

[43] Olofsson, O. *Acta Chem. Scand.* **1965**, *19*, 229.

[44] Möller, M. H.; Jeitschko, W. *Z. Anorg. Allg. Chem.* **1982**, *491*, 225.

H atom can complete the tetrahedral coordination of copper if it belongs to a BH_4^- anion.[45,46] The hydride, now in a bridging position, has reduced donor capabilities and the repulsion with the filled metal orbitals is diminished.

By analogy with the many dimers having a single terminal ligand and two bridging halides, we have attempted to predict whether species of the type LCu-(μ-H)$_2$CuL, as yet unknown, may be stable. The model **11** with L = PH_3 (left side in **IX**) could be optimized only in the point group C_1 but with the Cu_2H_2 ring still planar and symmetric.



IX

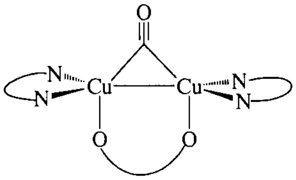
The Cu−Cu separation of 2.29 Å is significantly shorter than in **7** (2.36 Å). In fact, compared to L_2Cu(I), the σ hybrid of LCu(I) has more s character and lies at lower energy (see **II**). As a consequence, the in-phase combination of H_{1s} orbitals interacts better with the Cu−Cu σ bonding combination and drifts more electron density in the diffuse s metal orbital components. Not only is the Cu−Cu bond strengthened but also more mixing of the s (as well as p) orbitals helps to depopulate axial d orbitals, thus reducing electronic repulsion. In addition to the different optimized distances at the DFT level, also the different Cu−Cu overlap populations at the EHMO level (0.16 vs 0.11, for an always fixed Cu−Cu separation of 2.34 Å) confirm that the Cu−Cu bond must be definitely shorter in the LCu(μ-H)$_2$CuL species.

To learn more about the relative stabilities of the mixed phosphino−hydride complexes of copper(I), we have also optimized the most simple linear adduct **12**, shown at the right side in **IX**. Again, the energy gained to form the dimer **11** with a Cu(μ-H)$_2$Cu core (ca. −27 kcal mol^{-1}) is definitely larger than that gained by addition of one phosphine to monomer **12** to form the trigonal-planar species **9** (ca. 2 kcal mol^{-1}). Conversely, it is calculated that adding two phosphine ligands to **12** to obtain the dimer **7** provides a net energy gain of −12 kcal mol^{-1}. It is noteworthy that the metallophilic attractions between two units of the type (PH_3)MX (M = Cu, Ag, Au; X = halide, hydride), constrained to be linear, have been theoretically evaluated at long M−M separations (>3.0 Å).[7] Obviously, the associated energies are definitely lower than those presented here for the system **11**, which combines M−M and M−H bonds.

Finally, other authors[6] have calculated the Cu−Cu separation for the naked Cu(μ-H)$_2$Cu framework, and we have repeated the calculations using our conditions. We have optimized a consistent D_{2h} model with a very short Cu−Cu separation of ca. 2.21 Å. It is confirmed that the absence of terminal ligands strengthens the bond. The very significant difference confirms, in our opinion, the larger involvement of the metal s orbitals in the bonding combinations **III**. Since they are not destabilized by the terminal ligands, these orbitals mix more and adsorb more electron density from the bridging hydrides.

Calculations on $(PH_3)_nCu(\mu\text{-}C{\equiv}X)_2Cu(PH_3)_m$ (X = O, CH; $n = m = 1, 2$). The basic orbitals of the acetylide and carbon monoxide ligands are a σ lone pair and one pair of filled and empty π and π^* levels. On the basis of electronegativity and energy gap arguments,[24] the π^* levels lie at least 3 eV higher for acetylide than for C≡O, which is a much better π-acceptor. Also, since oxygen is more electronegative than carbon, the C≡O π levels are lower than the corresponding C≡C π levels (ca. 2 eV), with acetylides being better π-donors. We pointed out above how bridging π donors (halides) force the elongation of the Cu−Cu bond, as they provide electron density to the empty σ^* and π^* combinations (see **IV**). While there is no experimental evidence that two acetylide bridges cause a significant elongation of the Cu−Cu bond (see Table 1), it cannot be excluded that the observed deformations of the Cu(μ-C≡CH)$_2$Cu framework are attributable to a minor involvement of the π system at the bridges. It is also important to establish the basic differences between π-donor and π-acceptor capabilities of the bridges and eventually how these compete with each other.

First, we consider the prototype of π-acceptor bridges. Significantly, in CSD[14] there is no single example of a Cu(I)−Cu(I) dimer with two such bridges. While the strictly relatable Cu(I)−Co(−I) complexes[28−31] (see an example in **V**) will be given some attention later, it is noteworthy that Cu(I) dimers with a single CO bridge are well-known.[47−49] As sketched in **X**, the latter systems are of the type $L_3Cu(\mu\text{-}CO)CuL_3$, thanks to a 1,3- or 1,4-diolate shared by the metals.



X

The average intermetallic separation of 2.415 Å is rather short also, because the total electron count is 34 and a Cu−Cu single bond is predicted. The qualitative MO scheme in **XI** shows how the back-donation from the copper atoms into the CO π^* level ($d_\pi{}^* \rightarrow \pi^*$) is a fundamental component of bridge bonding. For analogous situations, it was pointed out[50,51] that the M−M bonding ensues because the metal combinations $(d_\pi)^*$ and σ (left side of **XI**) are involved in bridge bonding,

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[45] Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096.

[46] Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Mors, K, W.; Wei, C.-Y.; Bau, R. *J. Am. Chem. Soc.*, **1981**, *103*, 5165.

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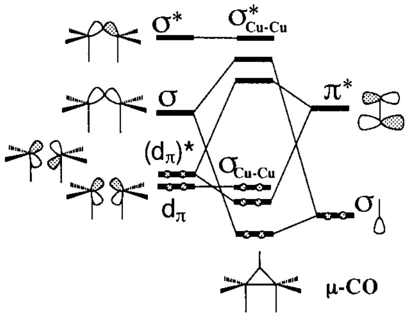
[48] Doyle, G.; Eriksen, K. A.; Modrick, M.; Ansell, G. *Organometallics* **1982**, *1*, 1613.

[49] Pasquali, M.; Floriani, C.; Manfredotti, A.; Guastini, C. *J. Am. Chem. Soc.*, **1981**, *103*, 185.

[50] Mealli, C.; Lopez, J. A.; Yan, S.; Calhorda, M. J. *Inorg. Chim. Acta* **1993**, *213*, 199−212.

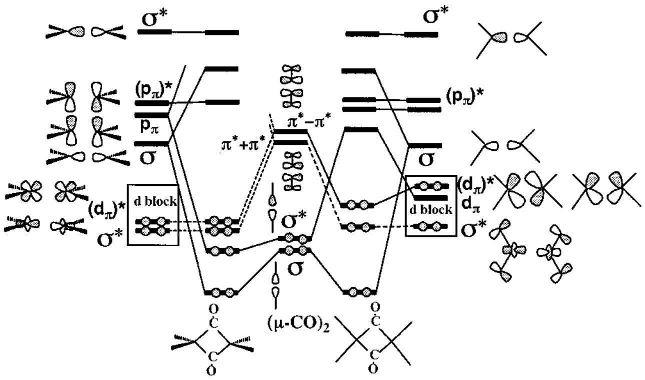
[51] Hunstock, E.; Mealli, C.; Calhorda, M. J.; Reinhold, J. *Inorg. Chem.* **1999**, *38*, 5053−5060.



XI

whereas the unperturbed partners d_π and σ^* (filled and empty, respectively) determine a direct M−M single bond.

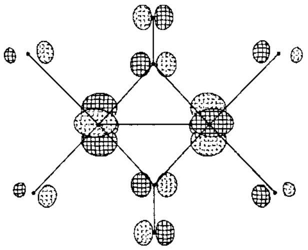
For the unknown dimers $L_2Cu(\mu\text{-}CO)_2CuL_2$, a major problem arises from the insufficient metal π-back-donation. In principle, two D_{2h} conformers, with symmetric bridges and L_2M fragments either perpendicular or coplanar to the central ring, could be possible. Qualitative MO arguments, illustrated in **XII**, help in understanding the electronic features in the two cases. With a stereochemistry comparable to that in **VII** (see the left side of **XII**), the in-phase and out-of-phase filled combinations of the hybridized d_π orbitals (typical of L_2M fragments[24]) are orthogonal to the central ring and are buried in the block of the 10 filled d orbitals. Evidently, the latter frontier orbitals are not involved in the annular σ bonding network. Rather, they cause a direct four-electron repulsion between the metals, partially reduced by some back-donation into $\pi_\perp^*$ CO levels.



XII

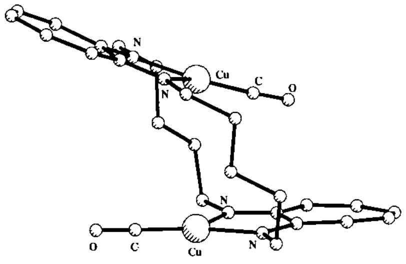
Concerning the overall $Cu(\mu\text{-}CO)_2Cu$ σ bonding, the CO lone pairs drift electron density into the σ and p_π combinations of the metals. This is analogous to the double two-electron/three-center interaction invoked for bridging hydrides (see **III**). Additionally, two combinations in the d block, $(d_\pi)^*$ and σ^*, have the proper symmetry to interact with in-plane CO π* levels ($\pi^* + \pi^*$ and $\pi^* - \pi^*$, respectively). However, pure d orbitals of copper are low in energy and are significantly contracted, so that back-donation is scarce. The requirements for the formation of four Cu−C bridge bonds are not fulfilled.

The overall planar isomer cannot be a viable solution for $d^{10}-d^{10}$ species, although it is well tailored for systems with two fewer electrons, such as the d^9-d^9 dimers $[Cl_2Pd(\mu\text{-}CO)_2PdCl_2]^{-2}$.[52] A rationale for the electronic structure of the latter is given at the right side of **XII**. Now, the classical d_π hybrids of L_2M fragments[24] are deeply involved. The in-phase combination d_π overlaps well with the σ* combination of CO lone pairs and obviously needs to be empty (d^9-d^9 species) to convert an otherwise intolerable four-electron repulsion into a bonding attraction. At the same time, the out-of-phase $(d_\pi)^*$ combination (filled) is suited for back-donation into $\pi^* - \pi^*$ whereas $\pi^* + \pi^*$ can receive some electron from low-lying σ* combination of pure metal d orbitals. The latter interaction is enhanced by the contribution of the in-plane p_π orbitals of terminal chlorides (see **XIII**). Thus, the stability of the system is partially due to the overall electronic delocalization of the planar structure which extends to the terminal ligands.



XIII

In conclusion, π-acceptor bridges seem unable to support the combination of two homonuclear d^{10} centers. Not only are the latter are experimentally unknown but also our DFT calculations, after many cycles of optimization, predict the splitting of the model $[(PH_3)_2Cu(\mu\text{-}CO)_2Cu(PH_3)_2]^{2+}$ into two trigonal-planar $[(PH_3)_2CuCO]^+$ units. This result is also supported by important experimental evidence. Lippard and co-workers[53,54] used a tropocoronand macrocycle in which flexible aliphatic chains hold together two NN chelates. Nonetheless, the system features two separated N_2CuCO units which face each other but avoid direct contacts (see **XIV**).



XIV

As mentioned, one type of $d^{10}-d^{10}$ binuclear system, Cu^+-Co^-,[28−31] is stable, with two bridging carbonyls pointing toward the cobalt atom. DFT/B3LYP calculations for a simplified model of the diphosphine derivative (shown in **V**) reproduce well the latter feature. Experimentally,[31] the compound is close to C_{2v} symmetry with the terminal $(PH_3)_2Cu$ and $(CO)_2Co$ moieties

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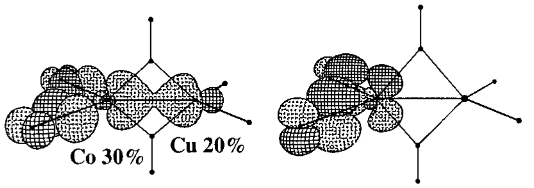
(52) Goggin, P. L.; Goodfellow, R. J.; Herbert, I. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1981**, *1077*.

(53) Villacorta, G. M.; Gibson, D.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6732.

(54) Villacorta, G. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 3672.

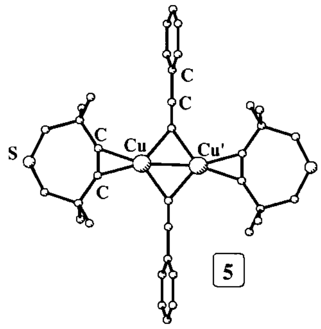
being mutually orthogonal. In comparable cases with nitrogen donors,[28−30] the N_2Cu unit is rotated somewhat from the orthogonal disposition. Computationally, the presence of imaginary frequencies excludes stable C_{2v} symmetry, although the corresponding C_1 model is almost superimposable. Other important details are satisfactorily reproduced. Thus, the Cu−Co distance is 2.48 Å vs the 2.55 Å value of the experiment and the Co−CO bridge bonds of 1.77 Å are definitely shorter (2.36 Å) than the Cu−CO ones (to be compared with the 1.74 and 2.39 Å values of the experimental structure). The latter feature is attributable to the σ-donor power of the carbonyls mainly exerted toward the cobalt atom. For a symmetric disposition of the bridges, the fragment orbitals of $(CO)_2Co\cdots Cu(PH_3)_2$ able to accept electron density from both the in-phase (left) and out-of-phase (right) combinations of the CO lone pairs are largely localized at the cobalt side (**XV**). The feature is imposed by a difference in electronegativity and diffuseness of the metal orbitals, which act as driving forces reorienting and pushing the bridges toward the cobalt atom. Given the large difference between Co−C and Cu−C distances and the quasi-linearity of the Co−C≡O arrangement, the major force which keeps the metals together seems to be a dative $Co^- \rightarrow Cu^+$ bond from a filled d orbital of the former to the s hybrid of the latter (typical of the L_2M d^{10} fragment). To assess more clearly the nature of the Cu−(CO) linkages, a detailed analysis of the electron density distribution is also in progress[55] using Bader's AIM method.[56]



XV

At variance with carbonyls, acetylide bridges are able to hold together $L_2Cu(I)$ and LCu(I) fragments or a mixture of them (see Table 1). In view of the above considerations on carbonyls, the π-acceptor capabilities do not seem to play an important role and also the insignificant Cu−Cu elongation reflects the limited role played by the π-donor capabilities of the acetylides. Also consider that η^2 coordination of the bridging acetylides is avoided in any case. Certainly, the greatest cementing force is attributable to the σ lone pair of the acetylide (analogously to the H_{1s} orbital of a bridging hydride). However, it is also clear that, as soon as the C≡CH axis redirects toward one of the metals, at least the orthogonal p orbital of the bridging carbon atom must be involved.

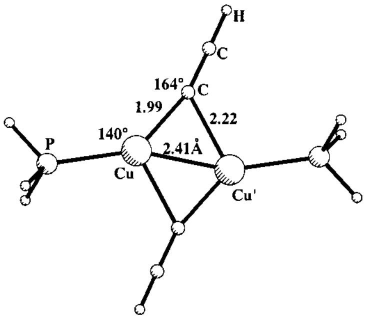
To shed some light on the causes and the effects of the electronic distribution in $Cu(\mu\text{-}CCR)_2Cu$ rings, it is best to start from the only symmetric dimer that is experimentally known, namely the compound **5** (type **c** in Table 1), sketched in **XVI**.



XVI

A D_{2h} model of **5**, with terminal HC≡CH molecules η^2-bound to the metals and H atoms replacing the phenyl rings of the bridges, was optimized by DFT calculations as a stable point, in good agreement with the experimental data. A second D_{2h} conformer with the alkynes perpendicular to the central ring was optimized. If the terminal ligands behaved only as simple π-electron donors, there should be a minimum difference between the conformations. However, free rotation of the η^2-bound alkyne does not seem possible, not only because the upright conformation is ca. 15 kcal mol^{-1} higher in energy but also because it is affected by four imaginary frequencies. A visual analysis of the latter indicates that the alkyne's rotation is not the only vibration mode but also asymmetry of the bridges is suggested. Also the geometric parameters change significantly when the alkynes are upright. The Cu−Cu distance (2.33 Å) is shorter than in the planar structure (2.38 Å in both the experimental and the calculated structures), whereas the terminal Cu−C distances of 2.28 Å are longer (2.02 and 2.08 Å in the experimental and calculated structures, respectively).

Before proposing qualitative explanations, we note that a model of the type $LCu(\mu\text{-}C{\equiv}CH)_2CuL$, where the terminal alkynes are substituted by PH_3 ligands, has been optimized with the asymmetric geometry depicted in **XVII** (stationary point).



XVII

A structure of this type has not been detected experimentally as yet. Also, we could optimize a conformer with symmetric bridges (the distances are Cu−Cu = 2.37 Å and Cu−C = 2.09 Å) which, in view of one imaginary frequency, may be considered the transition state between **XVII** and its mirror plane image. A quite small barrier of ca. 3 kcal mol^{-1} indicates that the potential energy surface for the rearrangement of the bridges is in any case very flat. In **XVII** the bridges are definitely asymmetric (1.99 vs. 2.22 Å) and each acetylide attempts to be collinear with the shortest Cu−C vector (the corresponding angle Cu−C−C is 164°).

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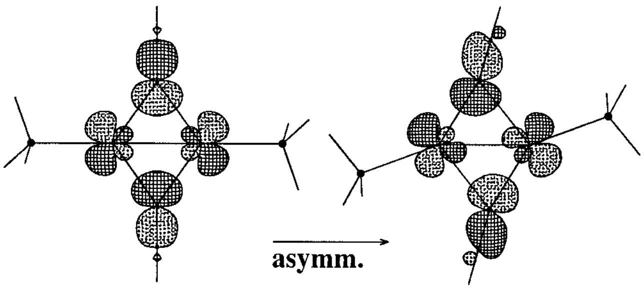
(55) Mealli, C.; Tejerina, B. To be submitted for publication.

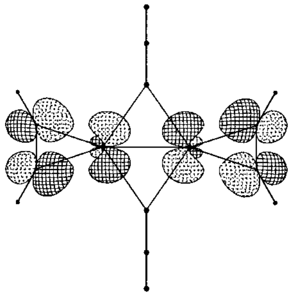
(56) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.

Although the moieties PCu(C≡CH) are far from being linear, the phosphine ligands are tilted (ca. 20°) with respect to the Cu−Cu axis. Despite the very small energies involved, the trend is correctly reproduced also at the EHMO level. The evolution of the HOMO (**XVIII**) is mainly responsible for the total stabilization of ca. 7 kcal mol^{-1}. In fact, the four-electron repulsion between the combined metal d_π orbitals and acetylide lone pairs diminishes.



XVIII

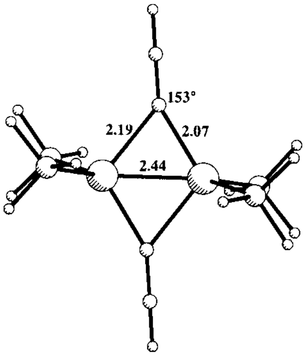
For the systems LCu(μ-C≡CH)$_2$CuL, the important difference between σ-donor phosphines or η^2-bound alkynes is due to the in-plane π^* level of the alkyne. The latter orbital keeps lower the energy of both the out-of-phase (**XIX**) and the in-phase combinations of the metal p_π orbitals (by as much as 2 eV with respect to the case of the terminal phosphines).



XIX

Because of the significantly reduced energy gap, the FMO **XIX** interacts well with the proper symmetry combination of the bridging acetylide π-bonding orbitals. Such a dative interaction is much less effective in the analogue with terminal phosphine ligands and stabilizes significantly the symmetric framework. Analogously, the σ^* combination of the acetylide lone pairs can donate more effectively in the in-phase combination of the metal p_π orbitals, while the four-electron repulsion problem highlighted in **XVIII** persists. The Cu−Cu bond is somewhat longer in the planar structure because more electrons populate the M−M π^* combination **XIX**. Even though the π-donor capabilities of the bridges are invoked, the Cu−Cu elongation does not appear as dramatic as with halides or other π-donor bridges. Moreover, as seen in Table 1, the intermetallic separation is longer in the dimers of type **a** with two terminal ligands on each metal. In this case the upright p metal orbital is totally engaged for σ bonding to the terminal ligands, whereas in **5** it could be considered formally unused or, as has also been pointed out by other authors,[10] could receive additional $\pi_\perp$ donation from bridges having a double set of filled π orbitals (e.g. halides). In the case of acetylides the through-bridge $\pi_\perp$ interaction accounts well for the shorter Cu−Cu separation in type **c** vs type **a** compounds.

The DFT calculations for the models (PH$_3$)$_2$Cu(μ-C≡CH)$_2$Cu(PH$_3$)$_2$ indicated an extremely flat PES in the symmetric−asymmetric rearrangement. This caused technical problems in the identification of the stationary points, and the choice of the basis set proved to be critical. Here, it suffices to mention that in working with the hybrid functional B3LYP, the search for the asymmetric conformer (C_i symmetry), shown in **XX**, was a very long process using the basis set [6-31G+(d,p)].



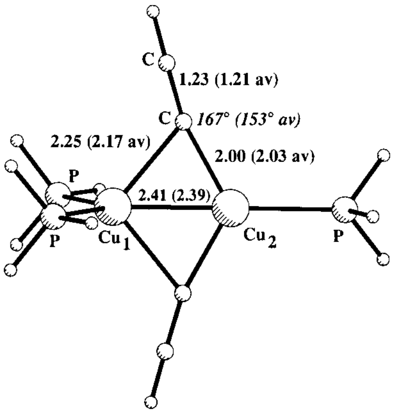
XX

With a better basis set (TZV of Ahlrichs and coworkers[38] and no pseudopotential for copper), the convergence occurs in a reduced number of steps but the necessary computation time is too large. Thus, to maintain uniformity within the whole series of compounds, we address only the results obtained at the 6-31G+(d,p) level. In any case, the computed geometries of the asymmetric species (**XX**) are similar and consistent with the experimental data reported in Table 1.[15,16]

It is worth mentioning that also symmetric (D_{2h}) or quasi-symmetric (C_i) stationary points were obtained for (PH$_3$)$_2$Cu(μ-C≡CH)$_2$Cu(PH$_3$)$_2$ (the Cu−C distances were 2.13 and 2.10−2.15 Å, respectively). Even if none of the latter points are associated with imaginary frequencies, the D_{2h} structure can be taken as either an intermediate or a transition state in the rearrangement between equivalent asymmetric structures. In fact, a very low frequency (ca. 15 cm^{-1}) shows most clearly that the bridges vibrate to become asymmetric. Also, the energy differences between the three minima are negligible (<0.1 kal mol^{-1}), and the result is further confirmed by single-point calculations with basis set TZV.[38] Continuity between symmetric and asymmetric conformations of the Cu$_2$(μ-C≡CH)$_2$ framework has been pointed out above also for the species with single terminal ligands (not η^2-bound alkynes!)

The last species investigated is of type **b** (see Table 1): namely, the compound **4** containing two different metal fragments of the type LCu(I) and L$_2$Cu(I) (L = phosphine). The bridging acetylides are directed toward the fragment which carries a single terminal ligand (see **XXI**).

The DFT calculations produce a pseudo C_{2v} symmetry (although no symmetry constraint was imposed), slightly more symmetric than the experimental structure.[13] As indicated (calculated and experimental geometric pa-



XXI

rameters are given in parentheses), the group Cu$_2$−C≡C is less bent in the calculated structure. This feature and the fact that the Cu$_1$−C distances are significantly longer than the Cu$_2$−C ones suggest that the latter interaction is weak and even underestimated by our relatively good calculations.

The compound in question compares well with other heterobinuclear complexes, one being $\text{L}_2\text{Cu}(\mu\text{-CO})_2\text{Co}(\text{CO})_2$ (see **V**). We pointed out for the latter that both the acetylide anions are preferentially directed toward cobalt, because the contribution of the latter atom prevails in the copper−cobalt combinations of empty σ and d_π orbitals (see **XV**). In the present Cu$_2$ species, unequal atomic orbital weights occur in the in-phase combination of σ hybrids because the terminal ligand environment is different. In the fragment Cu(PH$_3$), the trans phosphine ligand develops a σ hybrid by mixing of s, p_z, and d_{z^2} atomic orbitals. In contrast, the σ hybrid of the fragment (PH$_3$)$_2$Cu has less d character and lies at least 1 eV higher in energy (EHMO level). In perturbation theory terms, such an asymmetry causes the acetylide lone pairs to be more attracted by the singly coordinated metal. A limiting description could be that of a trigonal-planar unit such as $(\text{acetylide})_2\text{Cu}(\text{PH}_3)^-$ directing one of its d nonbonding filled orbitals toward the empty σ hybrid of the fragment (PH$_3$)$_2$Cu. Analogously, in the copper−cobalt species (see **V**) the latter hybrid is saturated by a nonbonding d orbital of the tetrahedrally coordinated cobalt(−I) ion. Finally, it is worth recalling an analogous situation in the species $\text{Cp}_2\text{Ti}(\mu\text{-C}\equiv\text{C}^t\text{Bu})_2\text{Pt}(\text{C}_6\text{F}_5)_2$.[57] In the latter the Pt atom (d^8) in square-planar coordination makes a dative bond toward the empty σ hybrid of the $\text{Cp}_2\text{Ti}^{\text{IV}}$ fragment.

Conclusions

In this theoretical study of selected Cu(I)−Cu(I) dimers and other $d^{10}-d^{10}$ analogues, we have analyzed the factors which affect the direct M−M interaction as well as the relative stereochemistry of terminal and bridging ligands. Different types of bridges have been considered, from those having only σ-bonding character (hydrides) to the ones with well-established π-donor or π-acceptor capabilities (halides and CO). The acquired information has been then extrapolated to acetylide bridges, which, beside being σ donors, are competitive π donors and acceptors.

Systematic DFT calculations and the always powerful principles of perturbation theory confirm the idea that the σ lone pairs of the bridges contribute most to the annular bonding as well as to the direct M−M linkage characterized by σ and π components. The viewpoint is confirmed by detailed studies of the Cu$_2$H$_2$ ring whose energetics is favored with respect to alternative monomeric structures. Also, the calculations suggest that the asymmetry of the bridge in the experimental structure $[(\eta^2\text{-CH}_3\text{C}(\text{CH2PPh}_2)_3\text{Cu}(\mu\text{-H})]_2$[17] should be critically evaluated. The Cu−Cu linkage vanishes with π donor bridges (halides etc.), which convey electron density into the M−M antibonding σ^* and π^* levels. On the other hand, π-acceptor ligands do not stabilize dimeric frameworks because there is insufficient back-donation from copper so that monomeric complexes are favored. Interestingly, the fragment orbital analysis describes why two fewer electrons in the systems allow the formation of overall planar dimers with two CO bridges (d^9-d^9).

Finally, the electronic features of the few known complexes with bridging acetylides, of at least three different types, have been highlighted. Most important are the σ-donor capabilities of the acetylides, which permit a short Cu−Cu separation similar to that found with hydride bridges. As the acetylides reorient, the Cu−C$_{\text{bridging}}$ bonds weaken or strengthen alternately, although a major participation of the acetylide π system is not implied. Distortion of the Cu$_2$C$_2$ framework helps to reduce in part the inner electron repulsion. Preferential coordination to one of the two metals is imposed by a specific driving force such as the distinct number of terminal ligands or the different natures of the metals, as in the $d^{10}-d^{10}$ heterodinuclear species with Cu(I) and Co(−I) ions.

In general, the PES relative to the observed rearrangements of the acetylide bridges is very flat, so that a continuum of structural situations is expected. A noticeable exception is represented by the system which contains an alkyne η^2-bound to each Cu(I) atom. In this case, the symmetric arrangement of the bridges is rationalized in terms of the metal orbital stabilization due to the π^* levels of the terminal alkynes and in turn of some π donation from the bridging acetylides.

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