CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200501379

Copper(I) Alkynyl Clusters, $[Cu_{x+y}(hfac)_x(C{\equiv}CR)_y]$, with Cu_{10}–Cu_{12} Cores

**Christopher W. Baxter, Timothy C. Higgs, Philip J. Bailey, Simon Parsons,
Fiona McLachlan, Mary McPartlin, and Peter A. Tasker***[a]

Abstract: The facile syntheses and the structures of five new Cu^I alkynyl clusters, $[Cu_{12}(hfac)_8(C{\equiv}CnPr)_4(thf)_6]\cdot THF$ (**1**), $[Cu_{12}(hfac)_8(C{\equiv}CtBu)_4]$ (**2**), $[Cu_{12}(hfac)_8(C{\equiv}CSiMe_3)_4]$ (**3**), $[Cu_{10}(hfac)_6(C{\equiv}CtBu)_4(\text{diethyl ether})]/[Cu_{10}(hfac)_6(C{\equiv}CtBu)_3(C{\equiv}CnPr)(\text{diethyl ether})]$ (**4**) and $[Cu_{10}(hfac)_6(C{\equiv}CtBu)_4(\text{diethyl ether})]$ (**5**) are reported, in which hfacH = 1,1,1,5,5,5-hexafluoropentan-2,4-dione. The first independent molecule found in the crystals of **4** (**4a**) proved to be chemically identical to **5**. The Cu_{10} and Cu_{12} cores in these clusters are based on a central "square" Cu_4C_4 unit. Whilst the connectivities of the Cu_{10} or Cu_{12} units remain identical the geometries vary considerably and depend on the bulk of the alkynyl group, weak coordination of ether molecules to copper atoms in the core and Cu···O intramolecular contacts formed between Cu–hfac units on the periphery of the cluster. Similar intermolecular contacts and interlocking of Cu–hfac units are formed in the simple model complex $[Cu_2(hfac)_2(HC{\equiv}CtBu)]$ (**6**). When linear alkynes, $C_nH_{2n+1}C{\equiv}CH$, are used in the synthesis and non-coordinating solvents are used in the workup, further association of the Cu_4C_4 cores occurs and clusters with more than eighteen copper atoms are isolated.

Keywords: alkyne ligands · cluster compounds · copper · structure elucidation

Introduction

Copper(I) β-diketonates have been used extensively in chemical vapour deposition processes to generate copper metal circuitry.[1–7] Volatile by-products can be recovered and recycled [Eq. (1)].

$$2[Cu^I(\beta\text{-diketonate})L] \rightarrow Cu(0) + [Cu^{II}(\beta\text{-diketonate})_2]\uparrow + 2\,L\uparrow \qquad (1)$$

As part of a programme to develop comparable materials which would deposit copper from a liquid phase, we have studied the formation and decomposition of a range of copper(I) hexafluoroacteylacetonates, $[Cu(hfac)(L)_n]$, with neutral soft ligands (L). When alkynes were used as the auxiliary ligands in such complexes it was found[8–11] that a range of polynuclear copper(I) alkynyl complexes with up to 26 copper atoms were obtained with the generic formula, $[Cu_{x+y}(hfac)_x(C{\equiv}CR)_y]$. The nuclearity of these clusters and the disposition of the "bridging" alkynyl groups and "capping" β-diketonate units appear to be dependent on the nature of the substituents on the alkyne and on replacement of the CF_3 groups on the hexafluoroacetoacetonate with other groups. In this paper we consider the importance of the bulk of the alkyne and show that for relatively large substituents ($R = tBu$ or $SiMe_3$), the size of the cluster is limited to 10 or 12 copper atoms. Whilst the overall shapes of these new Cu_{10} to Cu_{12} cluster vary considerably, they all have a similar Cu_4C_4 core (Figure 1) defined by bridges from the terminal alkynyl carbon atoms. A similar structural motif was first reported[12] for a copper alkyl complex, $[Cu_4(Me_3SiCH_2)_4]$, with a square arrangement of Cu atoms (Cu–Cu 2.42 Å). Each alkyl ligand forms three-centre two electron (3c-2e) bonds with two copper atoms resulting in C-Cu-C angles of 164° and a "pinching in" of the Cu atoms on the sides of the C_4 square.

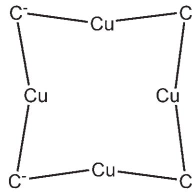


Figure 1. Cu_4C_4 Core.

Subsequently $[Cu_4(aryl)_4]$ analogues have been characterized [aryl = 2,4,6-triisopropylphenyl ($2,4,6\text{-}iPr_3C_6H_2^-$),[13] pentamethylphenyl ($C_6Me_5^-$),[14] thienyl ($C_4H_3S^-$),[15] pentafluorophenyl ($C_6F_5^-$),[16] mesityl ($2,4,6\text{-}Me_3C_6H_2^-$)[17] and o-

---

[a] Dr. C. W. Baxter, Dr. T. C. Higgs, Dr. P. J. Bailey, Dr. S. Parsons,
F. McLachlan, Prof. M. McPartlin, Prof. P. A. Tasker
The School of Chemistry, The University of Edinburgh
Edinburgh, Scotland, EH9 3JJ (UK)
Fax: (+44) 131-650-6453
E-mail: P.A.Tasker@ed.ac.uk

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

vinylphenyl[18]] which also have a square arrangement of four Cu atoms. The plane of the bridging aryl ligands are characteristically orientated perpendicular to the Cu_4 plane. In some cases[14,15,17] the C_{ipso} atoms lie in the same plane as the Cu_4 core, but in the other examples[13,16,18] they are located alternately above and below the Cu_4 plane forming a puckered ring as in Figure 2 (top). The pinching in of the Cu atoms shown in Figure 1 varies considerably with some C-Cu-C units[13,16] being linear within experimental error.

A rhombus-shaped Cu_4 core is observed in the dimethylsulfide and thiophene[19–21] adducts $[Cu_4Ph_4(SMe_2)_2]$ and $[Cu_4(mesityl)_4(C_4H_4S)_2]$ (Figure 2 bottom). The increased thermal stability of these thioether adducts was attributed to the reduced electron deficiency in the core that accompanies the coordination of the Lewis bases.[21] Incorporation of tertiary amine groups onto the aryl unit has allowed the isolation of $[Cu_4(L)_4]$ complexes (L = 2-$(Me_2N)CH_2C_6H_4$,[22] 2-(Me_2NCH_2)-5-$CH_3C_6H_3$,[23] and 8-(Me_2N)napthyl[24]) in which the chelated amino groups appear to promote the loss of planarity of the Cu_4 core. Some of the alkynyl-bridged clusters, $[Cu_{x+y}(hfac)_x(C\equiv CR)_y]$ (**4a**, **4b**, **5**), described below contain coordinated diethyl ether molecules, which have a major influence on the structure of the central Cu_4C_4 core and the disposition of the peripheral Cu–hfac units.

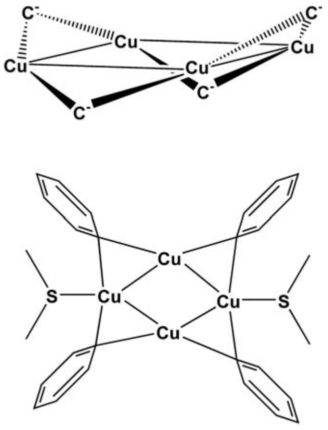


Figure 2. The puckered Cu_4C_4 ring observed in some tetraaryl Cu^I complexes[13,16,17] and the rhombus shaped Cu_4 core in bis-thioether adducts,[19–21] $[Cu_4(aryl)_4(R_2S)_2]$.

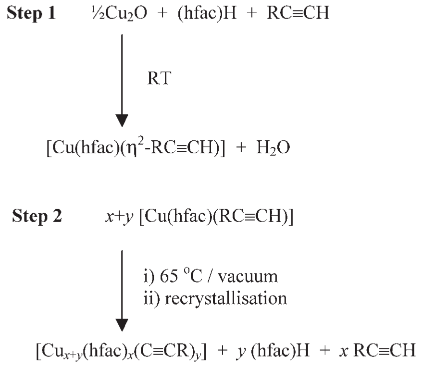
The purpose of the work reported below was to establish what ligand characteristics favour the formation of the relatively low nuclearity (Cu_{10-12}) clusters and to define the structural motifs present. In the longer term it was intended to establish whether the larger clusters (Cu_{16-26}) are formed by assembly of these motifs.

Results and Discussion

We have determined the X-ray crystal structures of $[Cu_{12}(hfac)_8(C\equiv C\textit{n}Pr)_4(thf)_6]\cdot THF$ (**1**) $[Cu_{12}(hfac)_8(C\equiv C\textit{t}Bu)_4]$ (**2**), $[Cu_{12}(hfac)_8(C\equiv CSiMe_3)_4]$ (**3**), $[Cu_{10}(hfac)_6(C\equiv C\textit{t}Bu)_4(\text{diethyl ether})][Cu_{10}(hfac)_6(C\equiv C\textit{t}Bu)_3(C\equiv C\textit{n}Pr)(\text{diethyl ether})]$ (**4**) and $[Cu_{10}(hfac)_6(C\equiv C\textit{t}Bu)_4(\text{diethyl ether})]$ (**5**); the X-ray data and refinement details are in Table 1. With the exception of **1**, these clusters were prepared by the simple two-step procedure outlined in Scheme 1, which has been reported previously for Cu_{16}–Cu_{26}

Table 1. Crystal data for **1**, **2**, **3**, **4**, **5** and **7**.

	1	**2**	**3**	**4**	**5**	**7**
formula	$C_{88}H_{92}Cu_{12}F_{48}O_{23}$	$C_{64}H_{44}Cu_{12}F_{48}O_{16}$	$C_{60}H_{44}Cu_{12}F_{48}O_{16}Si_4$	$C_{115}H_{102}Cu_{20}F_{72}O_{16}$	$C_{59}H_{52}Cu_{10}F_{36}O_{13}$	$C_{16}H_{12}Cu_2F_{12}O_4$
M_r	3192.10	2743.47	2807.79	4539.76	2288.41	623.34
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
crystal system	orthorhombic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	$Cmc2_1$	$P2_1/n$ (alt. No. 14)	$C222_1$	$P1$ (No. 1)	$C2/c$	$P2_1/n$ (alt. No. 14)
a [Å]	29.444(4)	12.7505(13)	15.3619(8)	13.8102(7)	26.649(6)	12.353(8)
b [Å]	20.032(4)	30.793(3)	28.2000(13)	14.0182(8)	15.601(3)	18.764(12)
c [Å]	19.626(3)	23.094(2)	22.3712(11)	23.3814(13)	23.619(5)	20.208(13)
α [°]	90	90	90	98.0770(10)	90	90
β [°]	90	90.432(16)	90	101.3170(10)	115.242(3)	97.513(5)
γ [°]	90	90	90	114.3360(10)	90	90
V [Å^3]	11576(3)	9067.0(2)	9691.3(8)	3918.0(4)	8882(3)	4644(5)
Z	4	4	4	1	4	8
ρ_{calcd} [Mg m^{-3}]	1.832	2.010	1.924	1.924	1.711	1.783
μ [mm^{-1}]	2.296	2.908	2.770	2.796	2.467	1.947
F(000)	6336	5344	5472	2228	4496	2448
crystal size [mm^3]	1.5 × 0.8 × 0.8	0.07 × 0.14 × 0.46	0.19 × 0.25 × 0.35	0.49 × 0.40 × 0.32	0.28 × 0.49 × 0.45	0.35 × 0.27 × 0.17
θ range [°]	1.61–28.91	1.32–22.57	3.52–23.00	1.65–25.00	1.55–24.71	3.74–22.00
reflections collected	42526	36456	20997	28761	21806	19179
independent reflections	14216	11935	6732	25181	7542	5513
	[R(int) = 0.0619]	[R(int) = 0.0747]	[R(int) = 0.0496]	[R(int) = 0.0139]	[R(int) = 0.0294]	[R(int) = 0.0864]
min/max transmission	0.862/0.457	1/0.657	1/0.744	1/0.898	0.862/0.705	1/0.805
data/restraints/parameters	14216/1023/864	11935/0/1261	6732/0/526	25181/241/2097	7542/0/536	5513/27/622
R_1 [$\lvert F\rvert > 4\sigma(\lvert F\rvert)$]	0.0576	0.0512	0.0722	0.0449	0.0496	0.0914
wR_2 (all data)	0.1454	0.1334	0.1905	0.1189	0.1327	0.2303
largest peak [e Å^{-3}]	0.933	0.721	1.437	1.107	0.451	1.318
largest hole [e Å^{-3}]	−0.992	−0.750	−0.628	−0.543	−0.077	−0.813



Scheme 1. Condensation of cuprous oxide, hexafluoroacetylacetone and a terminal alkyne to form polynuclear Cu^I alkynyl complexes [Cu_{x+y}(hfac)$_x$(C≡CR)$_y$].

clusters.[8–11] Crystals of **2** and **3** separated from saturated hexane solutions, whilst the Cu_{10} clusters **4** and **5** were obtained when the residue from heating under vacuum was triturated with or recrystallised from diethyl ether.

The molecule **4a**, one of the two independent molecules in the crystals of **4**, proved to be [Cu_{10}(hfac)$_6$(C≡C*t*Bu)$_4$(diethyl ether)], which is chemically identical and structurally similar to that characterized crystallographically in **5**. Consequently, only the structural details of **5** are discussed below. The isolation of the cluster **4b**, with both *tert*-butyl and *n*-propylalkyne in the Cu_4C_4 core, was unexpected. The purpose of using a mixture of the alkynes in excess in the preparation was to establish which alkyne was preferred in cluster formation.

The complex [Cu_{12}(hfac)$_8$(C≡C*n*Pr)$_4$(thf)$_6$]·THF (**1**) was obtained in a different way. The Cu_{18} cluster [Cu_{18}(hfac)$_{10}$(C≡C*n*Pr)$_8$] (**6**), isolated from hexane after preparation as outlined in Scheme 1, was found to rearrange, giving **1**, when attempts were made to recrystallise it from THF.

There are remarkable similarities between the structures of **1**–**5**. The connectivities associated with the Cu_4C_4 core and the eight peripheral copper atoms are the same in all the Cu_{12} clusters (**1**–**3**), and the Cu_{10} compounds are closely related. In the Cu_{12} clusters the eight peripheral copper atoms occur in pairs, each π-bonded to one alkynyl unit. The resulting connectivity and the atom-labelling scheme for the Cu_{12} clusters are shown in Figure 3 (top), and are exemplified by the structure of the solvated cluster **1** (Figure 3 bottom).

In the Cu_{12} clusters, four central Cu atoms (Cu1A, Cu1B, Cu1C and Cu1D) are linked by the terminal carbons atoms of four η^1-bridging alkynyl ligands, C1A≡C2A, C1B≡C2B, C1C≡C2C and C1D≡C2D, respectively. Each alkynyl ligand is further coordinated to two Cu–hfac units containing the copper atoms Cu2A and Cu3A, Cu3B and Cu3B, Cu2C and Cu3D, Cu2D and Cu3D, respectively. These units have a (μ_2-η^1:μ_2-η^2)-alkynyl bridge and resemble a "butterfly" in which copper and the chelate form the wings and the C≡C unit forms the body (Figure 3 top). Throughout this paper the letters A, B, C and D in the atom labels are used to denote the "butterfly" unit to which an atoms belongs, *not* internal symmetry. In the Cu_{10} structures (**4b** and **5**) the connectivity remains the same as in the Cu_{12} clusters except that two *cis*-alkynyls (C1B≡C2B and C1C≡C2C) are coordinated to only one Cu–hfac unit so forming two "half butterflies".

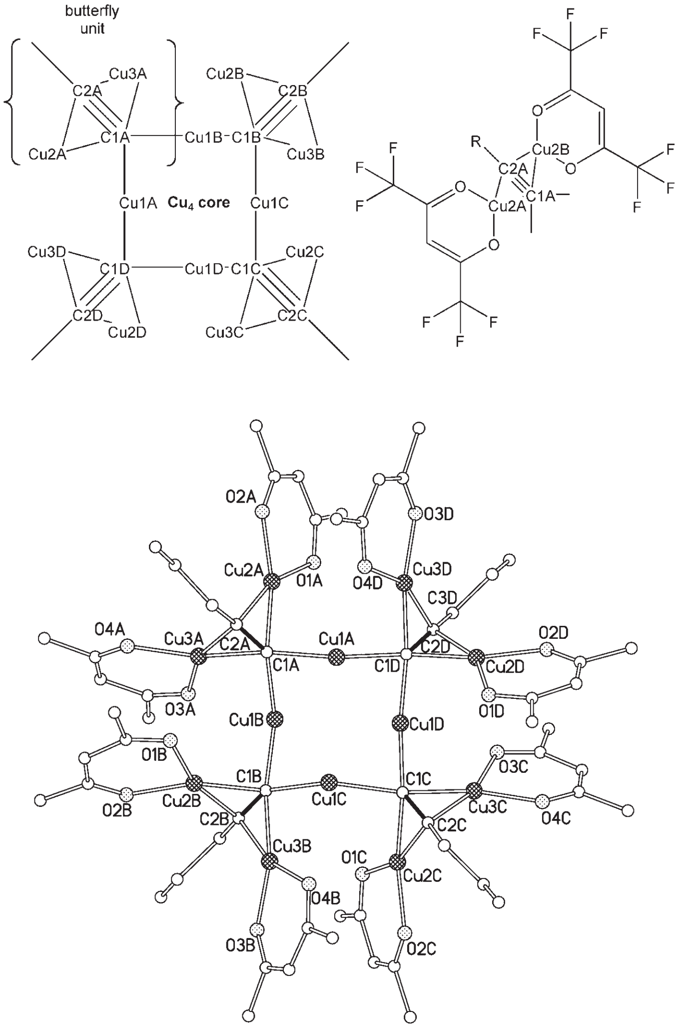


Figure 3. The connectivities and atom-labelling scheme. Top: the central alkynyl bridged core and the butterfly units in the Cu_{12} clusters (the Cu_{10} analogues have "half-butterflies" attached at C1B and C1C with the Cu3B and Cu3C "wings" missing). Bottom: the planar Cu_{12}(hfac)$_8$(C≡C*n*Pr)$_4$ core in [Cu_{12}(hfac)$_8$(C≡C*n*Pr)$_4$(thf)$_6$]·THF (**1**) with the H and F atoms and THF solvate molecules removed and the "butterfly bodies" C1−C2 shown with dark bonds for clarity.

A higher degree of solvation is observed in **1** compared to the other compounds (see below). The central Cu atoms form a slightly irregular square with sides 2.427(2)–2.538(2) Å and diagonal Cu···Cu contacts of approximately equal length, Cu1A···Cu1C and Cu1B···Cu1D are 3.419(2) and 3.448(2) Å, respectively. There is a slight tetrahedral distortion of the central Cu_4 plane with diagonally disposed Cu atoms displaced to the same side of the least-squares plane by approximately ±0.27(1) Å. Despite the identical connectivity of all the Cu_{12} clusters, the unsolvated molecules **2** and **3** have structures (Figure 4) that are markedly different from that of **1** (Figure 3 bottom). Whereas cluster **1** has a nearly planar Cu_{12} arrangement (maximum deviation 0.540 A) the structures of clusters **2** and **3** are considerably twisted from overall planarity with maximum deviations of peripheral Cu atoms from the central Cu_4 plane of 2.395 Åin **2** and in 2.693 Åin **3** (Table 2).

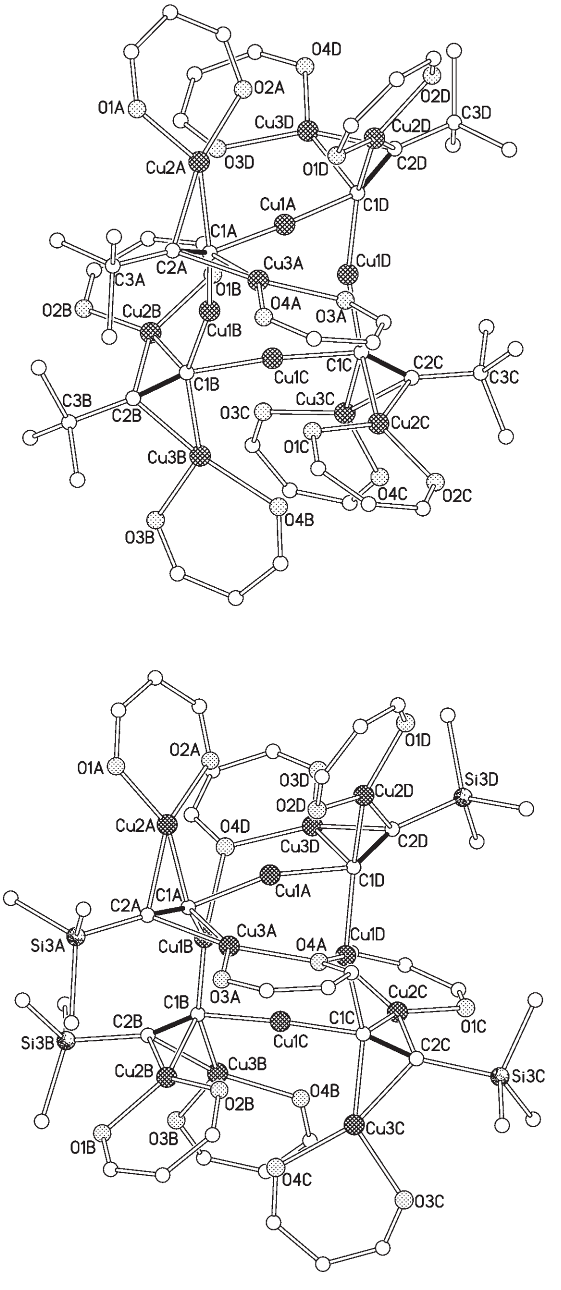


Figure 4. The twisted structures of the unsolvated Cu_{12} clusters (with the "butterfly bodies" C1−C2 shown with dark bonds) $[Cu_{12}(hfac)_8(C\equiv C\mathit{t}Bu)_4]$ (**2**, top) and $[Cu_{12}(hfac)_8(C\equiv CSiMe_3)_4]$ (**3**, bottom). H atoms and CF_3 groups are omitted for clarity. There is a crystallographic C_2 axis through Cu1A/Cu1C in the structure of **3**.

Table 2. Displacement of Cu1A, Cu1B, Cu1C and Cu1D [Å] from their least squares planes in **1**, **2**, **3**, **4a**, **4b** and **5**. Atom labelling is defined in Figure 3.

	1	**2**	**3**	**4a**	**4b**	**5**
Cu1A	0.285(4)	0.011(1)	0.000(0)	-0.0026(4)	0.0124(4)	0.000(0)
Cu1B	−0.278(4)	−0.011(1)	0.000(0)	0.0024(4)	−0.012(4)	0.000(0)
Cu1C	0.264(4)	0.011(1)	0.000(0)	−0.0023(4)	0.0114(4)	0.000(0)
Cu1D	−0.270(4)	−0.011(1)	0.000(0)	0.0025(4)	−0.0118(4)	0.000(0)

The Cu_{10} core of the smaller clusters **4b** and **5** have the same connectivity as the corresponding atoms in the Cu_{12} clusters and like **2** and **3** have markedly twisted metal cores (maximum deviations of the peripheral Cu atoms 2.72(1) Åin **4b** and 2.46(1) Åin **5**). The structures of the Cu_{10} clusters, which are all diethyl ether derivatives, are shown in Figure 5.

Unexpectedly, the structures of all the twisted clusters, **2**, **3**, **4b** and **5** have much more planar Cu_4 cores than those observed in the overall nearly planar Cu_{12} molecule **1**, shown in Figure 3 (bottom). In the structure of **1**, the slight tetrahedral distortion of the Cu_4 core gives deviations from its least-square plane of about ±0.27 Å, whereas for the Cu_4 planes in all the other four clusters the maximum displacement of any one Cu atom is 0.0124 Å (for Cu1A in **4b**). In the Cu_{12} clusters **2** and **3**, which contain no ether molecules, the Cu_4 core adopts a rhombic arrangement with sides of similar length, falling in the range 2.444(1)–2.506(1) Å (Table 2), but with diagonals Cu1A···Cu1C (3.737(2) and 3.700(3) Å) longer than Cu1B···Cu1C (3.273(3) and 3.283(3) Å) in **2** and **3**, respectively. In **2** the C-Cu-C angles at Cu1A and Cu1C are approximately linear (177.3 and 173.7(3)°, respectively) and greater than those at Cu1B and Cu1D angles (164.7 and 165.1(3)°, respectively), the Cu_4C_4 unit being "pinched in" at the Cu1B and Cu1D atoms. In **3** the angles at Cu1A and Cu1C (198.3 and 176.0(7)°, respectively) are again considerably larger than those at Cu1B and Cu1D (both 139.1(6)°). The large reflex value of the angle at Cu1A appears to be related to the displacement of the two alkynyl ligands at Cu2A out of the Cu_4 plane (see below). In the Cu_{10} systems (**4b** and **5**) there is a diethyl ether molecule coordinated to Cu1C and this copper atom is displaced towards the donor oxygen atom; it is, therefore, the external C-Cu-C angle at Cu1C that is reflex in this case [195.9(3)° (**4b**) and 199.6(3)° (**5**); Table 3]. The angle at Cu1A is approximately linear [173.4(3) (**4b**) and 175.1(3) (**5**)] and again the angles at Cu1B and Cu1D are the smallest [157.5–165.4(3)°]. This gives a kite-shaped rather than rhomboidal arrangement of the central Cu_4 core in **4b** and **5**, with Cu1C···Cu1B,Cu1D distances (range 2.532–2.564 Å) greater than Cu1A···Cu1B,Cu1C (range 2.431–2.433 Å; Table 3).

As the alkynyl ligand is known to be a good σ-donor, providing an electron from the terminal carbon sp hybrid orbital, it is reasonable to assume that the bonding in **1**–**5** is similar to that in the $[Cu_4(aryl)_4]$ family with four 3c–2e bonds formed by overlap of the $C_{terminal}$ sp-hybrid orbital with a bonding combination of Cu orbitals creating an alkynyl-as-

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

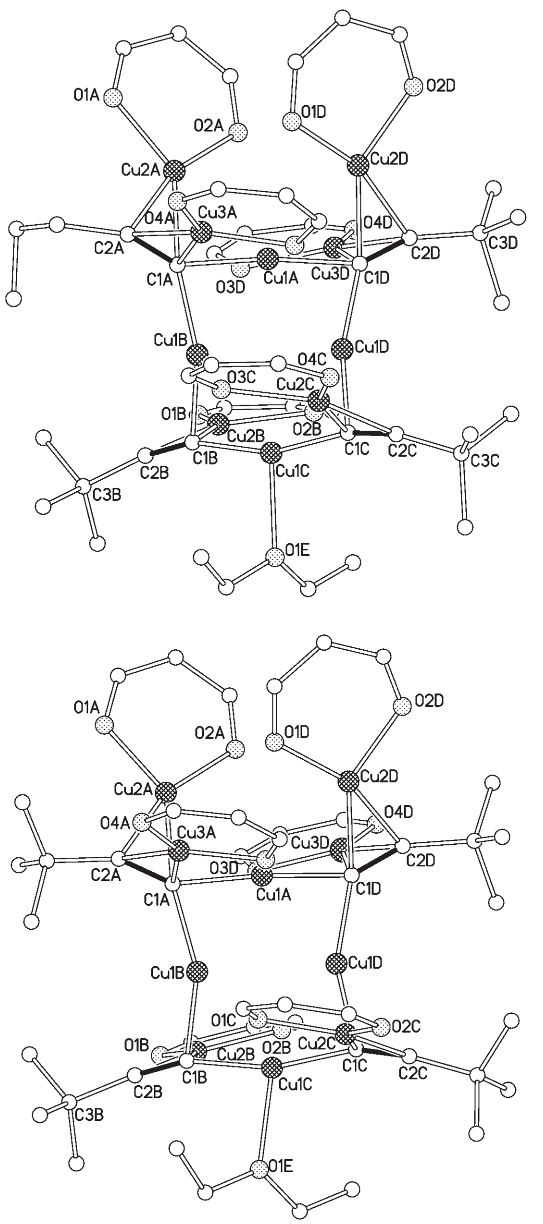


Figure 5. The structures of the Cu_{10} clusters (the C1–C2 "bodies" of the whole "butterflies" **A** and **D** and the half "butterflies" **C** and **B** are shown with dark bonds), $[\mathrm{Cu_{10}(hfac)_6(C{\equiv}C}t\mathrm{Bu)_3(C{\equiv}C}n\mathrm{Pr)(diethyl\ ether)}]$ (**4b**, top) and $[\mathrm{Cu_{10}(hfac)_6(C{\equiv}C}t\mathrm{Bu)_4(diethyl\ ether)}]$ (**5**, bottom). H atoms and CF_3 groups are omitted for clarity. There is a crystallographic C_2 axis through Cu1A/Cu1C in the structure of **5**.

sisted Cu–Cu bond. It seems that the Cu_4C_4 cores in **1**–**5** are able to accommodate considerable variations of geometry to meet the requirements of other components of the assembly, for example, the incorporation of Lewis bases such as ethers.

The overall shapes of the clusters appear to be largely determined by interactions between peripheral Cu–hfac units. These "butterfly" units are aligned to optimise two main types of Cu···O interaction. Firstly there are facial interactions between Cu–hfac chelate rings of neighbouring units aligning the dipoles on adjacent Cu–O bonds; secondly there are approximately perpendicular, T-shaped approaches of some Cu–hfac units that also result in close Cu···O contacts. The co-facial and T-shaped interactions between Cu–hfac units are most easily illustrated in the solid-state structure of a simple dimeric model compound, $[\mathrm{Cu_2(hfac)_2(HC{\equiv}C}t\mathrm{Bu)}]$ (**7**). Crystals of this compound were isolated in low yield from the preparation of higher nuclearity clusters by the route outlined in Scheme 1. In the solid state the molecules occur in pairs of crystallographically independent "butterfly" dimeric units locked together by the interdimer interactions shown in Figure 6. The co-facial interaction of the two Cu–hfac units containing Cu2A and Cu2B from different dimers is accompanied by two T-shaped O···Cu interactions between the two dimers with the copper atoms Cu3B and Cu3A.

Such interlocking of pairs of adjacent butterfly units is a feature of the structures of **2**–**5**. The pairs of interlocking units are located on opposite sides of the Cu_4 core. The **A** "butterfly" (body C1A–C2A)) interlocks with the **D** "butterfly" (body C1D–C2D) and similarly **B** with **C**. The interlocking of the **B** and **C** units in the Cu_{12} cluster **2** is shown in Figure 7 (top), and closely resembles that of **A** and **D**. The structure of **3** adopts a similar interlocked structure to **2** with Cu···O distances between the **B** and **C** butterflies in the range 3.146(9) to 3.185(9) Å, but with considerably longer Cu···O distances between **A** and **D** (3.465 to 3.550(10) Å). This difference is apparently caused by a slight displacement of the **A** and **D** butterflies to facilitate the two symmetry-related, strong interactions between their outer wings and the Cu_4 core (Cu1D···O4A, Cu1B···O4D 2.379(9) Å), which can be seen in Figure 4 (bottom).

In the Cu_{10} clusters **4b** and **5**, the full "butterfly" units **A** and **D** interlock, but this type of double interaction is impossible for the **B** and **C** units which are only "half-butterflies". In the **4b** and **5** clusters the single wings of the "half-butterflies" **B** and **C** adopt co-facial approaches to Cu-hfac units in the neighbouring full butterflies **A** and **D**. In compound **4b** these co-facial orientations result in relatively short contacts [Cu···O 3.226 to 3.356(6) Å] as shown in Figure 7 (bottom), but in **5** the closest Cu···O contacts between the single wing Cu-hfac unit and the full butterflies is 4.020(6) Å.

The planarity of cluster **1** (Figure 3 bottom) is related to the coordination of THF solvent molecules. Four of the six coordinated THF molecules lie round the periphery of the Cu_{12} core, alternately above and below the mean plane of the copper atoms, with one THF oxygen atom being located between each pair of Cu–hfac wings of the four butterfly units (Cu2,3···O contacts in the range 2.584–2.692(5) Å), so separating the two wings of each "butterfly" unit (Figure 8; Table 4). This allows co-facial alignment of Cu–hfac wings from adjacent "butterflies" giving interchelate Cu···O contacts (3.203(5)–3.363(5) Å), but the presence of the THF solvates prevents the twisting of the "wings" necessary for formation of the T-shaped interactions present in all the other clusters. Two additional THF molecules are located centrally, one above and one below the Cu_{12} plane, and coordinate

Table 3. Cu···Cu distances [Å] and angles [°] in **1**, **2**, **3**, **4a**, **4b** and **5**.

	1	**2**	**3**	**4a**	**4b**	**5**
Cu1A···Cu1B	2.427(2)	2.506(1)	2.444(2)	2.424(1)	2.431(1)	2.433(1)
Cu1B···Cu1C	2.520(2)	2.469(1)	2.503(2)	2.630(1)	2.532(1)	2.564(1)
Cu1C···Cu1D	2.538(2)	2.482(1)	2.503(2)[a]	2.604(1)	2.565(1)	2.564(1)[a]
Cu1A···Cu1D	2.422(2)	2.478(1)	2.444(2)[a]	2.431(1)	2.432(1)	2.433(1)[a]
Cu1A···Cu1C	3.419(3)	3.737(2)	3.700(3)	4.005(2)	3.975(2)	4.042(1)
Cu1B···Cu1D	3.448(3)	3.273(1)	3.283(3)	3.063(1)	2.990(1)	2.936(1)
C1A-Cu1A-C1D	172.6(3)	177.3(3)	161.7(7)	178.1(2)	173.4(3)	175.1(3)
C1A-Cu1B-C1B	145.3(4)	164.7(3)	139.1(6)	165.3(2)	163.9(2)	157.5(2)
C1B-Cu1C-C1C	145.9(4)	173.3(3)	176.0(7)	198.7(3)	199.6(3)	195.9(3)
C1C-Cu1D-C1D	172.6(3)	165.1(3)	139.1(6)	164.5(2)	165.4(3)	157.5(2)
Cu1A-Cu1B-Cu1C	87.4(1)	97.4(1)	96.8(1)	104.8(1)	106.4(1)	108.0(1)
Cu1B-Cu1C-Cu1D	85.9(1)	82.8(1)	82.0(1)	71.6(1)	71.8(3)	69.9(1)
Cu1C-Cu1D-Cu1A	86.1(1)	97.8(1)	96.8(1)	105.4(1)	105.7(1)	108.0(1)
Cu1D-Cu1A-Cu1B	89.4(1)	82.1(1)	84.4(1)	78.2(1)	76.1(1)	74.2(1)

[a] These distances are related to Cu1A···Cu1B and Cu1B···Cu1C by a crystallographic mirror plane passing through C1A and C1C.

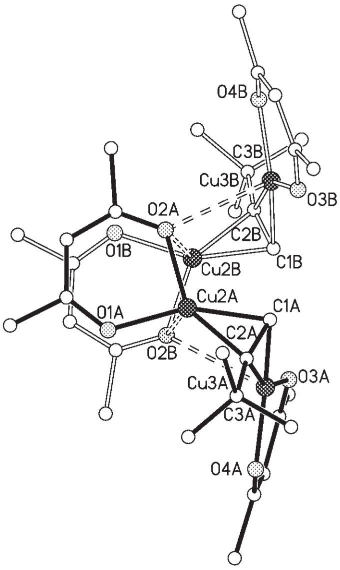


Figure 6. The structure of the two independent dinuclear molecules in the crystal of **7** (molecule **A** dark bonds and molecule **B** open bonds) showing the intermolecular co-facial overlap of Cu–hfac rings containing Cu2A and Cu2B (dihedral angle 17.7(3)°, Cu2A···O2B 2.85(1) and Cu2b···O2A 2.79(1) Å) and the perpendicular approach of these two rings to the neighbouring Cu–hfac units contain Cu3A and Cu3B (O2A···Cu3B 3.22(1) and O2B···Cu3A 3.14(1) Å). All H and F atoms have been omitted for clarity.

to two adjacent copper atoms of the Cu4 core (Cu1B···O(6S) 2.875(9) and Cu1C···O5S 2.646(9) Å).

Whilst the favourable interactions of Cu–hfac units and their interlocking is a feature of the Cu_{10} and Cu_{12} complexes described in this paper, it appears that it is other factors that control the nuclearity and overall shapes of the clusters which separate from the reaction Scheme shown in Scheme 1. The bulk of the alkynyl groups is particularly significant. The dispositions of the alkynyl units relative to the least squares planes defined by the Cu_4 cores in **1**–**5** are shown in Table 5.

In $[Cu_{12}(hfac)_8(C{\equiv}C\mathit{t}Bu)_4]$ (**2**) the *tert*-butylalkynyl groups lie fairly close to the plane of the central Cu_4 unit and show a "tetrahedral" displacement (Figure 9 top) The analogous trimethylsilylalkynyl cluster $[Cu_{12}(hfac)_8(C{\equiv}CSiMe_3)_4]$ (**3**) has a very different configuration, with the two alkynyl units containing C1A/C2A and C1D/C2D being considerably displaced from the central Cu_4 plane (Table 4 and Figure 9 bottom), whilst the other two alkynyl groups lie close to the plane. This appears to be related to the very short contacts of the outer wings of the **A** and **D** butterflies with the Cu_4 core discussed above.

The bulk of the alkynyl group also appears to influence the nuclearity of the cluster formed. The relatively low nuclearity $Cu_{<12}$ clusters were only obtained from the reaction outlined in Scheme 1 when a bulky *tert*-butyl or trimethylsilyl substituent is present on the alkyne or when complexes with linear *n*-alkynyl ligands were recrystallized from ethers. No clusters with $Cu_{>12}$ have been isolated from reactions with *tert*-butyl- or trimethylsilylacetylene. This may be a consequence of their bulk preventing the formation of the disc-shaped structures observed[8–11] for the Cu_{16}–Cu_{26} clusters in which the alkynes are closely packed on the circular faces of the discs and the Cu–hfac units define the rims. The formation of the smaller Cu_{10}–Cu_{12} clusters also appears to be favoured by the presence of weakly coordinating molecules such as THF or diethyl ether, which compete for space at the alkyne-bridged core.

Conclusion

The isolation of a remarkable range of copper(I) clusters from the reaction of cuprous oxide, hexafluoroacetylacetone and 1-alkyne depends on subtle differences between the nature of the alkyne, the solvents used in workup and on variation of substituents on the acac. This paper has defined requirements for obtaining lower nuclearity compounds with ten or twelve copper atoms. Further association of the alkynyl-bridged cores is suppressed when there are large substituents on the alkyne and when weakly coordinating ether molecules are associated with the central copper atoms. Whilst the latter is favourable in terms of reducing the electron deficiency at the copper atom associated with the 3c-2e bonds in the Cu_4C_4 core, they lead to steric crowding and control the overall shape of the molecule. Weak Cu···O contacts between adjacent Cu–hfac units on the periphery of the clusters lead to two different modes of inter-

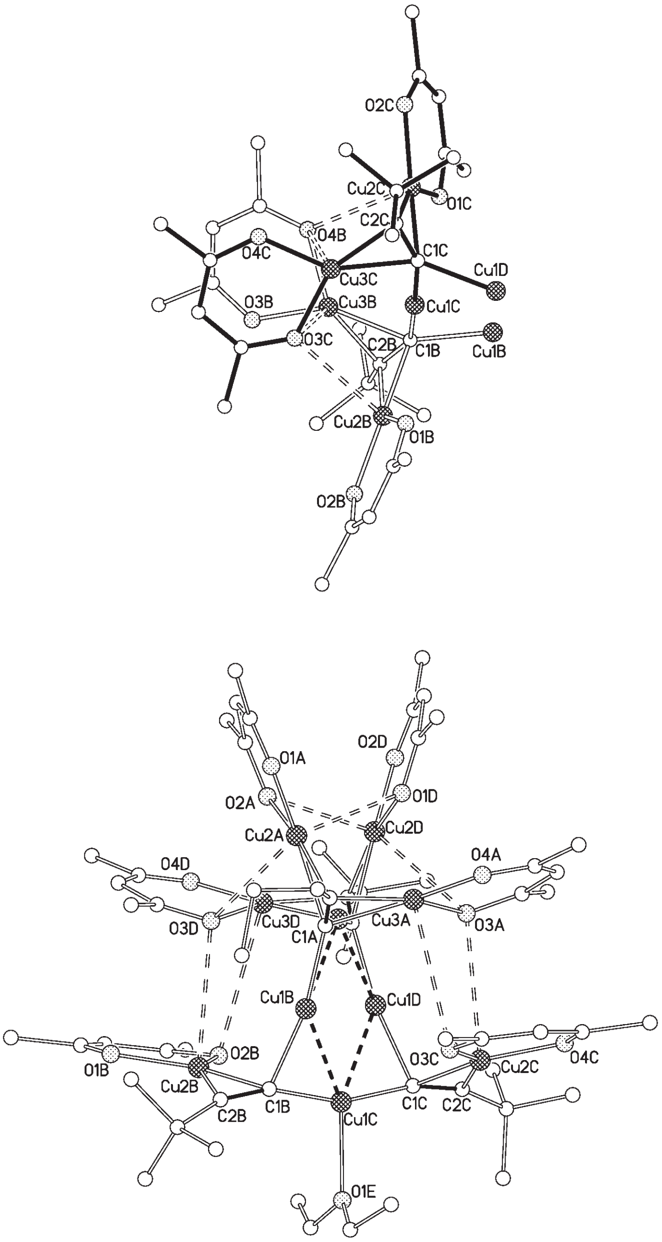


Figure 7. Illustration of the types of Cu···O interactions present in clusters **2**–**5** (H and F atoms removed for clarity). Top: The interlocking of the **B** and **C** butterflies in the Cu_{12} cluster **2**; distances O3C···Cu2B,Cu3B 3.369, 2.829(7) and O4B···Cu2C,Cu3C 3.046, 2.871(7) Å, respectively. Bottom: The interactions in the Cu_{10} cluster **4b** between the full "butterflies" **A** and **D** (Cu···O 2.971–3.477(7) Å), and the co-facial interaction of the single wings of the "half-butterflies" **B** and **C** with Cu-hfac units in **D** and **A** (Cu···O 3.226–3.356(6) Å).

locking of the peripheral units that influence the overall shape of the molecule.

Despite major differences in the overall shapes of the molecules the connectivities associated with either the Cu_{10} or the Cu_{12} units remain the same. The integrity of these units suggests that the multicentre Cu/alkynyl bonding is very favourable and can accommodate major changes in geometry. Weak Cu···Cu "cuprophilic" interactions may help to account for this. Analysis of the higher nuclearity clusters[25] suggests that the integrity of their cores is retained in Cu_{16}, Cu_{18}, Cu_{20} and Cu_{26} reported previously[8–11] and in new compounds containing variants of the hfac ligand.[25]

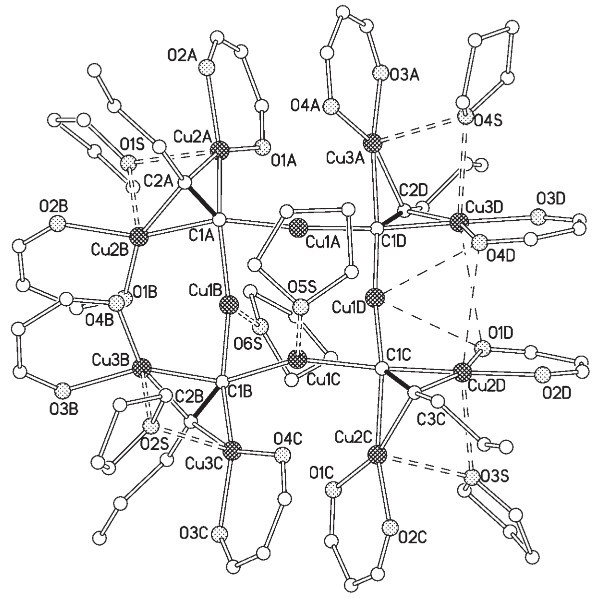


Figure 8. The structure of the $[Cu_{12}(hfac)_8(C{\equiv}CnPr)_4(thf)_6]\cdot THF$ cluster **1** showing the coordination of the THF solvates. Four THF ligands are each separating the wings of a "butterfly" (Cu2,3···O contacts in the range 2.584–2.692(5) Å) and two are coordinated on opposite sides of the central Cu_4 unit (Cu1B···O6S 2.875(1) and Cu1C···O5S 2.65(1) Å). All H atoms and CF_3 groups are omitted for clarity.

Table 4. Cu···O contacts [Å] between Cu–hfac units in **1** (see also Figure 4).

Cu2A···O4A	3.259(5)	Cu3A···O1A	3.203(5)
Cu3D···O1AA	3.203(5)	Cu2D···O4AA	3.259(5)
Cu2C···O4BA	3.242(5)	Cu3C···O1BA	3.363(5)
Cu3B···O1B	3.363(5)	Cu2B···O4B	3.242(5)

Table 5. Displacements of alkynyl carbon atoms [Å] from the least squares planes of Cu1A, Cu1B, Cu1C and Cu1D cores in **1**–**5**. Atom labelling is defined in Figure 3.

	1	**2**	**3**	**4a**	**4b**	**5**
C1A	1.00(1)	−0.26(1)	1.27(2)	−0.613(6)	−0.694(6)	0.439(3)
C2A	1.88(1)	−0.58(1)	2.41(1)	−1.219(6)	−1.360(7)	0.892(3)
C1B	−0.43(1)	0.29(1)	0.03(1)	0.690(6)	0.799(6)	−0.482(5)
C2B	−1.10(1)	0.62(1)	0.23(1)	1.153(6)	1.401(6)	−0.919(5)
C1C	−0.17(1)	−0.49(1)	−0.03(1)	−0.679(6)	−0.803(6)	0.482(5)
C2C	0.22(1)	−1.04(1)	−0.23(1)	−1.154(6)	−1.404(6)	0.919(5)
C1D	−0.52(1)	0.36(1)	−1.27(2)	0.617(5)	0.718(6)	−0.439(3)
C2D	−1.30(1)	0.83(1)	−2.41(1)	1.213(6)	1.370(6)	−0.892(3)

Experimental Section

Materials and reagents: All reagents were obtained from Aldrich Chemicals and used without further purification. *n*-Hexane was distilled from

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

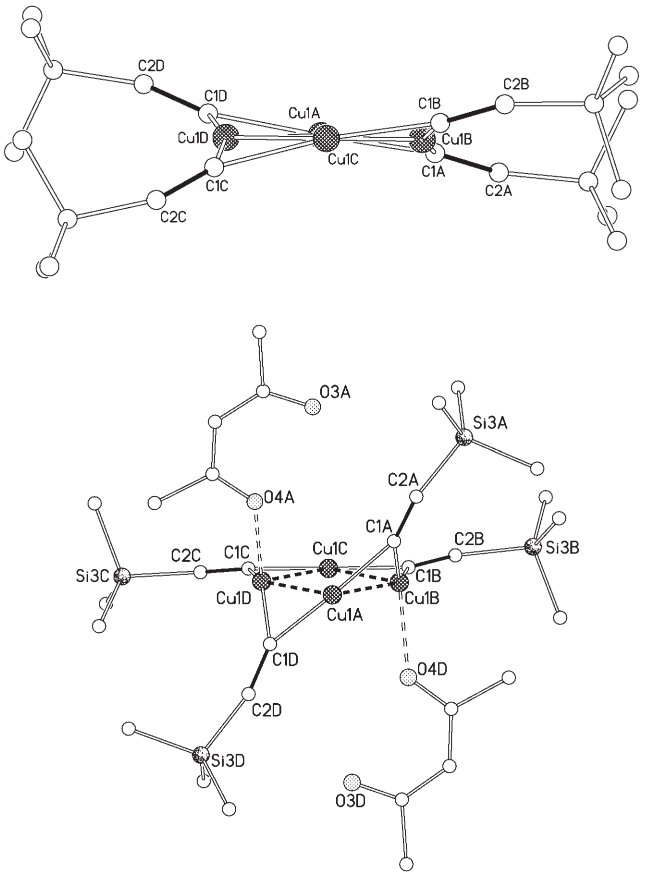


Figure 9. The variation in disposition of the alkynyl groups relative to the Cu_4 plane in the Cu_4(*tert*-butylalkynyl)$_4$ units of **2** (top) and in the Cu_4(trimethylsilylalkynyl)$_4$ unit of **3** (bottom), showing the symmetry-related Cu···O interactions (Cu1B···O4D, Cu1D···O4A 2.379(9) Å).

sodium/benzophenone/tetraglyme (trace) under N_2. N_2 gas was dried with 4 Å molecular sieves and deoxygenated with BTS catalyst.[26] All preparations of copper(I) complexes were carried out under anaerobic and anhydrous conditions by using standard Schlenk techniques. 3,3-Dimethyl-1-butyne, 3-phenyl-1-propyne and 1,1,1,5,5,5-hexafluoropentan-2,4-dione (hfacH) were degassed by freeze/vac/thaw cycles.

[Cu$_{12}$(hfac)$_8$(C≡C*n*Pr)$_4$(thf)$_6$] (1): Complex **6** (2.50 g, 0.67 mmol) was dissolved in a minimum volume of hot THF (5 mL). The mixture was stored at 4 °C and after 4 days large pale orange blocks and deeper orange hexagonal plate crystals separated. The supernatant liquid was decanted by using a cannula needle. The crystals were washed with *n*-hexane (2 mL), re-dissolved in hot THF (7 mL) and set aside at −25 °C for 4 days during which only the pale orange block crystals separated. The mother liquor was removed by using a cannula needle and the crystals were washed with cold THF (2×1 mL) and dried in vacuo to give complex **1**. Yield: 0.65 g (27 %); elemental analysis calcd (%) for $C_{84}H_{84}Cu_{12}F_{48}O_{22}$: C 32.34, H 2.71; found: C 32.2, H 2.6; IR (KBr disk): $\tilde{\nu}$=3433 (w), 2972 (w), 2881 (w), 1642 (s), 1557 (m), 1532 (m), 1462 (s), 1345 (m), 1259 (s), 1217 (s), 1147 (s), 1099 (m), 1051 (w), 888 (w), 802 (m), 744 (w), 672 (m), 588 (m), 528 cm^{-1} (w)

[Cu$_{12}$(hfac)$_8$(C≡C*t*Bu)$_4$] (2), [Cu$_{10}$(hfac)$_6$(C≡C*t*Bu)$_4$(diethyl ether)] (4a) and [Cu$_{10}$(hfac)$_6$(C≡C*t*Bu)$_3$(C≡C*n*Pr)(diethyl ether)] (4b): Cu_2O (1.64 g, 11.5 mmol) and anhydrous $MgSO_4$ (ca. 2 g) were added to a solution of 3,3-dimethyl-1-butyne (2.9 g, 35 mmol) and 1-pentyne (2.38 g, 35 mmol) in hexane (10 mL). Dropwise addition of hfacH (2.5 mL, 18 mmol) was accompanied by an exothermic reaction. After stirring for 18 h at room temperature the mixture was cannula-filtered and the solid residue washed with hexane (3×10 mL). The combined lime green filtrate and washings were combined and the solvent removed in vacuo. The resulting brown/red solid was heated at 65 °C for 2 h under vacuum. To the solid was added hexane (5 mL) and the mixture heated to reflux. Approximately half the solid dissolved giving a dark red solution, which was separated from insoluble yellow material by cannula filtration. This was set aside at 4 °C and after 48 h yellow crystals had separated. Two further recrystallisations from hexane yielded yellow crystals suitable for X-ray diffraction. The supernatant liquid was removed and the crystals of **2** were washed with hexane and dried in vacuo. Yield: 0.65 g (12.5 %); elemental analysis calcd (%) for $C_{64}H_{44}O_{16}Cu_{12}F_{48}.C_{12}H_{28}$: C 31.31, H 2.48; found: C 31.4, H 2.0. The yellow solid that was insoluble in hexane and collected by filtration from the red solution was dissolved in a hexane/diethyl ether (1:1, 20 mL) mixture and stored at −30 °C. After twelve weeks yellow crystalline blocks separated that were suitable for X-ray diffraction. Two individual molecules were observed in the crystal structure, **4a** and **4b**. The crystals were collected by filtration and dried in vacuo. Yield: 0.58 g (11.2 %); elemental analysis calcd (%) for $C_{115}H_{102}O_{26}Cu_{20}F_{72}$: C 30.13, H 2.16; found: C 30.1, H 2.2.

[Cu$_{12}$(hfac)$_8$(C≡CSiMe$_3$)$_4$] (3): HfacH (2.5 mL, 18 mmol) was added dropwise to a suspension of Cu_2O (1.64 g, 11.5 mmol) and $MgSO_4$ (ca. 2 g) in (trimethylsilyl)acetylene (7.2 mL, 51 mmol). The mixture was stirred for two hours then cannula-filtered. The solid residue was washed with hexane (3×10 mL) and the washings combined with the lime green filtrate. The volatile components were removed in vacuo leaving an oily red material containing some yellow solid, which was dried at 65 °C for two hours. The red oil was extracted in hexane (15 mL) and separated from the insoluble yellow solid by cannula filtration. The solution was stored at 4 °C overnight, during which time orange crystals separated suitable for X-ray diffraction. The supernatant liquid was removed and the crystals washed with hexane and dried in vacuo. Yield: 0.80 g (15 %); elemental analysis calcd (%) for $C_{60}H_{44}O_{16}F_{48}Si_4$: C 25.67, H 1.58; found: C 25.6, H 1.5.

[Cu$_{10}$(hfac)$_6$(C≡C*t*Bu)$_4$(diethyl ether)] (5): Cluster **5** was isolated by using the same synthetic procedure described for **2**. During the recrystallisation step, a very small quantity of yellow crystalline material separated along with the red Cu_{16} material. The yellow crystals were characterised by X-ray structure determination, but due to the small quantities isolated and the instability of the material, further analysis was not possible.

[Cu$_{18}$(hfac)$_{10}$(C≡C*n*Pr)$_8$] (6): Cu_2O (2.53 g, 18 mmol) and anhydrous $MgSO_4$ (2.0 g, 17 mmol) was placed in 1-pentyne (7.0 mL), forming a red suspension. Addition of hfacH (2.50 mL, 18 mmol) to the reaction mixture followed by stirring at RT for 66 h resulted in a viscous orange suspension. *n*-Hexane (10 mL) was added to dilute the suspension to allow cannula filtration. The residue was washed with *n*-hexane (3×10 mL) and the filtrate and washings combined to give a pale green solution. The volatile components of the solution were evaporated to dryness in vacuo, and after warming to 65 °C for 30 min a solid was obtained which was washed with hexane (20 mL, 2×5 mL), leaving a bright orange microcrystalline material which was dried in vacuo to give **6**. Yield: 2.87 g (44 %); elemental analysis calcd (%) for $C_{90}H_{66}Cu_{18}F_{60}O_{20}$: C 28.82, H 1.77; found: C 28.9, H 1.8; IR (KBr disk): 3499 (w), 2964 (w), 1672 (m), 1642 (s), 1554 (m), 1528 (s), 1513 (s), 1463 (m), 1255 (s), 1209 (s), 1146 (s), 1100 (m), 795 (m), 743 (w), 662 (m), 580 (m), 526 cm^{-1} (w).

***X*-ray crystallography**: X-ray intensity data were collected on a Bruker Smart Apex CCD diffractometer using molybdenum radiation λ= 0.71073 Å. The SADABS absorption correction was applied. Details of data collection, absorption corrections, refinement and crystal data are in Table 1.

Structure solution and refinement:[27] For all crystals the positions of the non-hydrogen atoms were located by direct methods and refinement was based on F^2. Poor diffraction at high angle by the crystals of **6** resulted in a shortage of data, and relatively high final residuals and esd's on all metric parameters, but despite this the overall features of the structure is clearly established. In the crystals of compounds **1**, **3** and **5** the asymmetric unit contains a half molecule, the overall structures having crystallographic C_s (**1**) or C_2 (**3** and **5**) symmetry in the crystal. In the figure the letters A, B, C and D on the atom labels are used to denote the chemically equivalent "butterflies" or "half-butterflies" to which the atoms belong. They do not denote crystallographic symmetry that is defined in the caption to the figure where relevant.

The structure of **1** has an unusual 50:50 disorder of two copper atoms of the central Cu_4 core {Cu(1B) and Cu(1C)} caused by a random distribution, throughout the crystal of two orientations of the molecule in which all atoms apart from Cu(1B) and Cu(1C) are superimposed. Thus the isolated molecules of **1** are asymmetric, but their superimposition means they occur on a site of mirror symmetry in the crystal. Figure 10 shows the two components of the Cu_{12} disorder. There is also a corresponding disorder of the two THF molecules linked to the two Cu atoms affected by the disorder, Cu1B and Cu1C, and all these atoms were refined with half occupancy. The crystals of **4** contain two independent molecules, **4a** and **4b**, which differ from each other in the replacement of one *tert*-hexylalkyne ligand (**4a**) by a *n*-pentylalkyne group (**4b**) and this results in small but significant differences in their metal framework. As a consequence, although some atoms of the two molecules are approximately related by inversion, the crystals provide a rare example of the chiral space group *P*1 in an inorganic molecule. In the crystals of **7** the asymmetric unit consists of two independent chemically identical molecules.

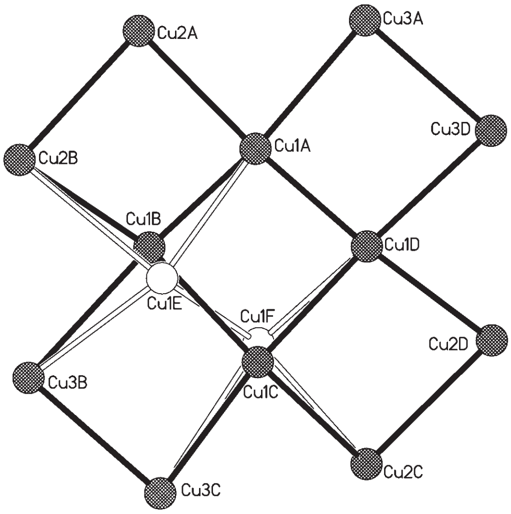


Figure 10. The disorder in the Cu_{12} metal arrangement in **1**. There is a crystallographic mirror plane through the midpoints of Cu3A/Cu3D and Cu3B/Cu3C, so that in **1** atoms on opposite sides of this plane are related by symmetry apart from the half occupancy atoms Cu1B and Cu1C which are crystallographically related to Cu1F and Cu1E respectively.

Relatively high displacement parameters for the trifluoromethyl groups show some evidence of rotational disorder of this group in all the compounds, which explains the rather poor crystal diffraction at high angle. In each of the compounds, apart from **2**, it proved possible to resolve several CF_3 groups into two components with fluorine atoms of partial occupancy. The hydrogen atoms for all six structures were placed in calculated positions with displacement parameters set equal $1.2\,U_{eq}$ (or $1.5\,U_{eq}$ for methyl groups) of the parent carbon atoms. In the final cycles of full-matrix least-squares refinement, the non-hydrogen full-occupancy atoms and the half occupancy Cu-atoms in **1** were assigned anisotropic displacement parameters.

Acknowledgements

We would like to thank the EPSRC, Avecia and Seiko Epson for funding and Dr. Vesna Gasperov for assistance with preparation of figures.

---

[1] F. A. Houle, C. R. Jones, T. Baum, C. Pico, C. A. Kovac, *Appl. Phys. Lett.* **1985**, *46*, 204.
[2] C. Oehr, H. Suhr, *Appl. Phys. A* **1988**, *45*, 151.
[3] Y. Hazuki, H. Yano, K. Horioka, *Tungsten and Other Metals for VLSI/ULSI Applications, Proc. Workshop 6th* **1990**, *115*, 351.
[4] H. K. Shin, K. M. Chi, J. Farkas, M. J. Hampden-Smith, T. T. Kodas, E. N. Duesler, *Inorg. Chem.* **1992**, *31*, 424.
[5] H. K. Shin, K. M. Chi, M. J. Hampden-Smith, T. T. Kodas, J. D. Farr, M. Paffett, *Chem. Mater.* **1992**, *4*, 788.
[6] H. K. Shin, M. J. Hampden-Smith, T. T. Kodas, A. L. Rheingold, *J. Chem. Soc. Chem. Commun.* **1992**, 217.
[7] A. Jain, K. M. Chi, T. T. Kodas, M. J. Hampden-Smith, J. D. Farr, M. F. Paffett, *Chem. Mater.* **1991**, *3*, 995.
[8] C. W. Baxter, T. C. Higgs, A. C. Jones, S. Parsons, P. J. Bailey, P. A. Tasker, *J. Chem. Soc. Dalton Trans.* **2002**, 4395.
[9] T. C. Higgs, P. J. Bailey, S. Parsons, P. A. Tasker, *Angew. Chem.* **2002**, *114*, 3164; *Angew. Chem. Int. Ed.* **2002**, *41*, 3038.
[10] T. C. Higgs, S. Parsons, P. J. Bailey, A. C. Jones, F. McLachlan, A. Parkin, A. Dawson, P. A. Tasker, *Organometallics* **2002**, *21*, 5692.
[11] T. C. Higgs, S. Parsons, A. C. Jones, P. J. Bailey, P. A. Tasker, *J. Chem. Soc. Dalton Trans.* **2002**, 3427.
[12] J. A. J. Jarvis, B. T. Kilbourn, R. Pearce, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1973**, 475.
[13] D. Nobel, G. van Koten, A. L. Spek, *Angew. Chem.* **1989**, *101*, 211; *Angew. Chem. Int. Ed.* **1989**, *28*, 208.
[14] H. Eriksson, M. Hakansson, S. Jagner, *Inorg. Chim. Acta* **1998**, *277*, 233.
[15] M. Hakansson, H. Eriksson, A. Berglund Ahman, S. Jagner, *J. Organomet. Chem.* **2000**, *595*, 102.
[16] A. Sundararaman, R. A. Lalancette, L. N. Zakharov, A. L. Rheingold, F. Jaekle, *Organometallics* **2003**, *22*, 3526.
[17] H. Eriksson, M. Hakansson, *Organometallics* **1997**, *16*, 4243.
[18] H. Eriksson, M. Oertendahl, M. Haakansson, *Organometallics* **1996**, *15*, 4823.
[19] S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc. Chem. Commun.* **1983**, 1156.
[20] E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *Organometallics* **1989**, *8*, 1067.
[21] B. Lenders, D. M. Grove, G. van Koten, W. J. J. Smeets, P. van der Sluis, A. L. Spek, *Organometallics* **1991**, *10*, 786.
[22] J. M. Guss, R. Mason, I. Soetofte, G. van Koten, J. G. Noltes, *J. Chem. Soc. Chem. Commun.* **1972**, 446.
[23] G. van Koten, J. G. Noltes, *J. Organomet. Chem.* **1975**, *84*, 129.
[24] E. Wehman, G. van Koten, M. Knotter, H. Spelten, D. Heijdenrijk, A. N. S. Mak, C. H. Stam, *J. Organomet. Chem.* **1987**, *325*, 293.
[25] C. W. Baxter, *Synthesis and Structural Studies of Polynuclear Copper Complexes*, University of Edinburgh, Edinburgh, **2005**.
[26] A. J. Gordon, R. A. Ford, *The Chemists Companion: A Handbook of Practical Data, Techniques and References*, Wiley Interscience, New York, **1972**.
[27] G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, University of Göttingen, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, 3400 Göttingen (Germany), **1998**.

Received: November 6, 2005
Revised: March 12, 2006
Published online: June 22, 2006