

Trimethyltriazacyclohexane as bridging ligand for triangular Cu₃ units and C–H hydride abstraction into a Cu₆ cluster†

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Reaction of [Cu(MeCN)₄](BF₄) with *N,N',N''*-trimethyl-1,3,5-triazacyclohexane in CH₂Cl₂ leads to two Cu₆ clusters containing the triazacyclohexane as a ligand to triangular Cu₃ units with the abstraction and incorporation of chloride and hydride.

A recent study of the reactivity of trimethyltriazacyclohexane L with CuCl₂ led to the isolation of a [CuCl₂]₂²⁻ anion with an unprecedented cuprophilic interaction and concomitant oxidation of L to the amidinium cation [L–H]⁺.¹ We have previously reported the synthesis of phosphine stabilised triazacyclohexane Cu(I) complexes from [Cu(MeCN)₄]⁺.² However, studies with the methyl analogue L in the absence of PPh₃ are rendered more difficult due to the low solubility in suitable solvents. In acetonitrile, no ligand substitution of L with [Cu(MeCN)₄](BF₄) was observed by NMR. However, reaction does occur in CH₂Cl₂ and highly air-sensitive crystals were obtained in several different experiments. Here we report the unusual structures of two copper containing products, **A** and **B**, shown in Figs. 1 and 2.

In both cases, we suspect that chloride must have been abstracted from the solvent with concomitant oxidation of L to the amidinium cation [L–H]⁺. A similar oxidation of a triazacyclohexane by CH₂Cl₂ in the presence of a Lewis-acidic metal cation (Zn) has been observed before.³ The crystals cannot be dissolved without decomposition so that no NMR spectra could be obtained. However, removal of all volatiles and extraction with d₃-MeCN gives a clean NMR spectrum of amidinium cation.⁴ Both compounds form nearly colourless crystals, a good indication that they contain copper complexes in the +I oxidation state. Four chlorides and two BF₄ anions for six copper atoms ensure electroneutrality in **A**. Initially, the

structure solution for **B** revealed only four chlorides and one BF₄ anion for six copper atoms. The highest remaining electron density was found in the centre of a Cu₆ octahedron and could be refined as a hydrogen atom. This hydride can originate from hydride abstraction from one of the coordinated L in **A** resulting in another [L–H](BF₄). The formation of the products can be rationalised according to Scheme 1.

Both structures show for the first time that triazacyclohexanes can coordinate triangular trimetal clusters without the aid of pendant arm donor groups. The only known triangular Cu₃ complexes of triazacyclohexanes are shown in Fig. 3 and contain N, O or S donor groups.^{5,6} The Cu–N bond distances in **A** (av. 2.03 Å) and **B** (av. 2.11 Å) are smaller than in κ³ complexes of Cu(I) (av. 2.22 Å)² where a severe bent-bonding situation results in weakened bonding. Thus, κ¹ coordination of three metals may be favoured over κ³ coordination of only one metal especially when the resulting close metal–metal contacts are not too repulsive or even attractive. The Cu–Cu distances within the triangular units are very similar in both complexes (2.55–2.71, av. 2.67 Å) and similar to the first example in Fig. 3. The μ²-Cl-bridged Cu–Cu distances between triangular units are 2.87 Å in **A** and av. 2.48 Å in **B**. These distances are at the short end of the range of closed-shell (cuprophilic) interactions.^{1,7} In **A**, a second type of triazacyclohexane is coordinating a different triangular unit made of two copper atoms and one hydrogen atom from a ring methylene group of the other triazacyclohexane *via* a C–H⋯N hydrogen bridge (H⋯N ≈ 2.5 Å).

The Cu–Cl bonds in **B** (av. 2.38 Å for μ²-Cl and av. 2.57 Å for μ³-Cl) are longer than in **A** (av. 2.27 Å for μ²-Cl and av. 2.42 Å for μ³-Cl). Apart from Cu2 in **A** all copper atoms in both complexes have coordination numbers of three with respect to

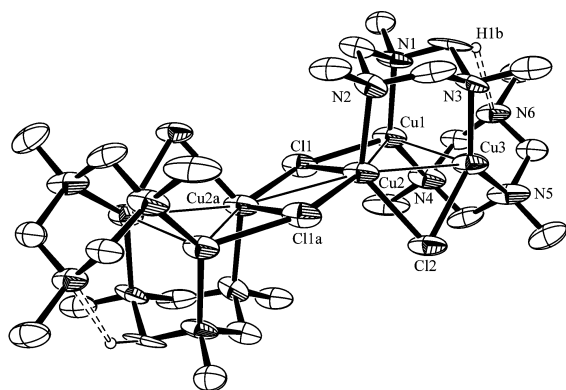


Fig. 1 Structure of the C₃ symmetrical cation in **A** with ellipsoids at the 30% probability level. Unlabeled atoms are carbon. Selected bond distances (Å): Cu1–Cu2 2.714(3); Cu1–Cu3 2.547(4); Cu1–N1 2.009(13); Cu2–N2 2.075(14); Cu1–N4 2.014(13); Cu1–Cl1 2.318(6); Cu2–Cl1 2.493(7); Cu2–Cu2a 2.866(6); Cu2a–Cl1 2.441(5) (Symmetry transformation: $-x+1, -y+1, -z+1$)[‡]

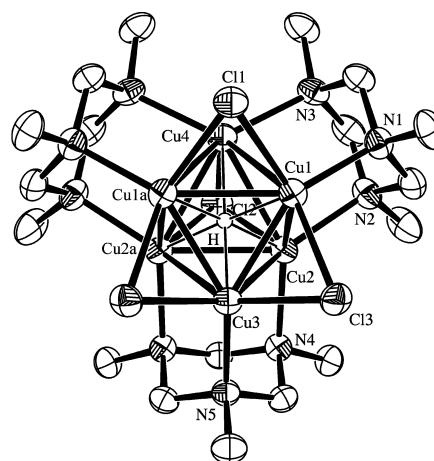
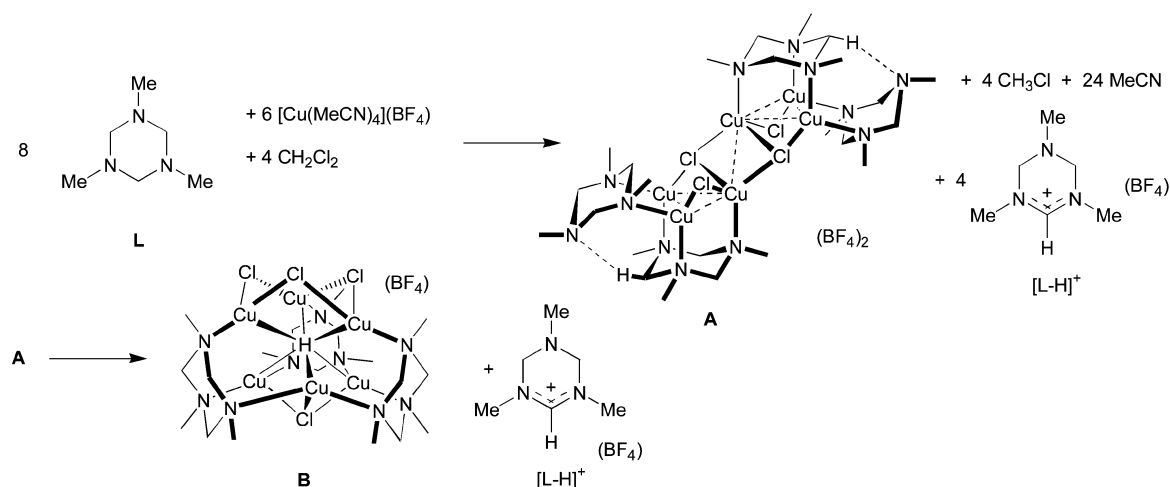


Fig. 2 Structure of the C₃ symmetrical cation in **B** with ellipsoids at the 50% probability level. Unlabeled atoms are carbon. Selected bond distances (Å): Cu1–Cu2 2.7049(8); Cu1–Cu3 2.4566(8); Cu2–Cu4 2.6734(9); Cu1–N1 2.048(4); Cu2–N2 2.120(4); Cu1–Cl1 2.4014(14); Cu2–Cl2 2.5087(14); Cu1–H 1.84(7); Cu1–Cu1a 2.5103(11); Cu2–Cu2a 2.5713(11) (Symmetry transformation: $x, -y+1/2, z$)[‡]

[†] Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b3/b302670a/>



Scheme 1 Reactions leading to A and B.

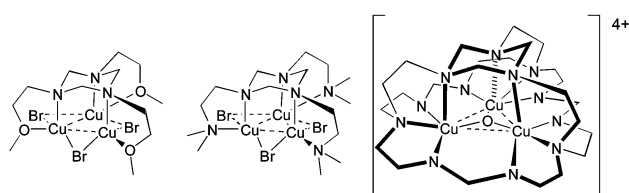


Fig. 3 Crystallographically characterised triangular trimetal triazacyclohexane complexes.^{5,6}

N and Cl ligands. Thus the larger bond distances in **B** compared to **A** are another indication that the copper atoms are coordinated to another ligand in the centre of the octahedron, the hydride described earlier. All copper atoms have similar distances to the centre/hydride of 1.85(3) Å.

The really astonishing result from these two structures is the transformation of **A** into **B**, assuming **A** is an intermediate. To enable this reaction, one of the four triazacyclohexanes in **A** loses a hydride from a ring methylene group and is eliminated as $[L-H](BF_4)$. The two open Cu_3 triangular units in **A** sandwich this hydride into the centre of an octahedral copper cluster. Thus, the unusual C–H hydride abstraction may well be the result of the cooperative action of two triangular Cu_3 units and consequently may provide a molecular model for C–H activation on a metal surface.

The best known copper hydride is $\{HCu[P(NMe_2)_3]\}_6$.⁸ This contains also a Cu_6 octahedron but the six hydrides are placed above six faces of the octahedron. The Cu–H bonds are slightly shorter (av. 1.71 Å) and the Cu–Cu contacts the same (av. 2.66 Å) as in **B**. Some other copper hydrides are known but none with an interstitial hydride. These copper hydrides are useful reducing agents in organic synthesis⁹ and we are currently searching for more soluble analogues of **B** to test their reactivity. Octahedral clusters of other metals with interstitial hydrides are rare but not unprecedented.¹⁰ However, **B** is the first copper cluster of its type and also the first observation of the hydride originating from C–H abstraction.

Although the sensitivity and low solubility of **A** and **B** have so far precluded solution studies and the bulk isolation of the pure compounds, the structural characterisation has shown the potential for triazacyclohexanes as unprecedented ligands for triangular metal clusters and subsequent substrate activation via the cooperative action of the cluster atoms. We are currently searching for more suitable triazacyclohexanes to pursue this chemistry.

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Notes and references

‡ Crystallographic data: for **A**: $C_{26}H_{64}B_2Cl_8Cu_6F_8N_{12}$, $M = 1383.35$, colourless plate $0.15 \times 0.10 \times 0.08$ mm³, monoclinic, space group $P2_1/n$, $a = 15.2550(12)$, $b = 8.3930(8)$, $c = 19.7430(19)$ Å, $\beta = 92.893(3)^\circ$, $V = 2524.6(4)$, $Z = 2$, $D_c = 1.820$ Mg m³, $\mu(MoK\alpha) = 2.971$ mm⁻¹, $T = 150$ K, 7518 reflections collected, 4191 unique, ($R_{int} = 0.148$), final residuals $R_1(I > 2\sigma(I)) = 0.1071$, $wR_2 = 0.2557$, $GOF = 1.023$, max/min residual electron density 0.726/–1.134 eÅ⁻³, $\chi = 0.011(2)$ for secondary extinction. CCDC 205862. For **B**: $C_{20}H_{50}BrCl_8Cu_6F_4N_9$, $M = 1168.34$, colourless plate $0.33 \times 0.18 \times 0.05$ mm, orthorhombic, space group $Pnma$, $a = 14.9910(3)$, $b = 13.4050(4)$, $c = 20.3130(5)$ Å, $V = 4081.99(18)$, $Z = 4$, $D_c = 1.901$ Mg m³, $\mu(MoK\alpha) = 3.641$ mm⁻¹, $T = 150$ K, 49424 reflections collected, 4830 unique, ($R_{int} = 0.129$), final residuals $R_1(I > 2\sigma(I)) = 0.0485$, $wR_2 = 0.1198$, $GOF = 1.042$, max/min residual electron density 0.95/–1.203 eÅ⁻³. CCDC 205861. Data were collected on a Nonius Kappa CCD diffractometer. Structure solution and refinement was achieved using the WinGX-1.64 package.¹¹ See <http://www.rsc.org/suppdata/cc/b3/b302670a/> for crystallographic data in .cif or other electronic format.

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