The Crystal Structure of a Hexanuclear Mixed Thiophenolato-alkynyl Copper(I) Complex: $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}CBu^t)]_2$: a Model for Electron Deficient Organocopper(I) Complexes with Cuprate Reactivity

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The hexanuclear copper compound $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}CBu^t)]_2$, formed from the reaction of $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ with $LiC{\equiv}CBu^t$, has a structure based on the conjunction of two identical trinuclear units each of which contains two co-ordinatively saturated copper atoms and one unsaturated copper atom; the compound has a new alkynyl to copper bonding mode that links the two trinuclear units together.

Low order heterocuprates $[R^rR^tCuLi]$ (R^t = transferable organic group, R^r = non-transferable thiolate group) and higher order heterocuprates $[R^rR^t_nCuLi_n]$ ($n \geq 2$) are used as reagents for the selective formation of carbon–carbon bonds in organic synthesis.[1] Despite their importance structural information on these reagents is still very limited.[2] In the course of our studies on the synthesis and characterization of well defined heterocuprates we have reacted the thiophenolato copper(I) compound $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ (**1**), whose structure is similar to that of $[CuSC_6H_4\{CH(Me)NMe_2\}\text{-}2]_3$,[3] with organolithium compounds. Based on the structure of (**1**)

$$\begin{tikzcd}
\underset{(\mathbf{1})}{2\,[\mathrm{CuSC_6H_4(CH_2NMe_2)\text{-}2}]_3} + 2\,\mathrm{LiC{\equiv}CBu^t} \arrow[d, "\mathrm{i}"] \\
\underset{(\mathbf{2})}{[\mathrm{Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}(C{\equiv}CBu^t)}]_2} \\
\underset{(\mathbf{1})}{4/3\,[\mathrm{CuSC_6H_4(CH_2NMe_2)\text{-}2}]_3} + 2\,\mathrm{CuC{\equiv}CBu^t} \arrow[u, "\mathrm{ii}"']
\end{tikzcd}$$

Scheme 1. *Reagents and conditions*: i, -2 $[LiSC_6H_4(CH_2NMe_2)\text{-}2]$, tetrahydrofuran (THF), 0 °C, 44%; ii, Et_2O, 0 °C, 88%.

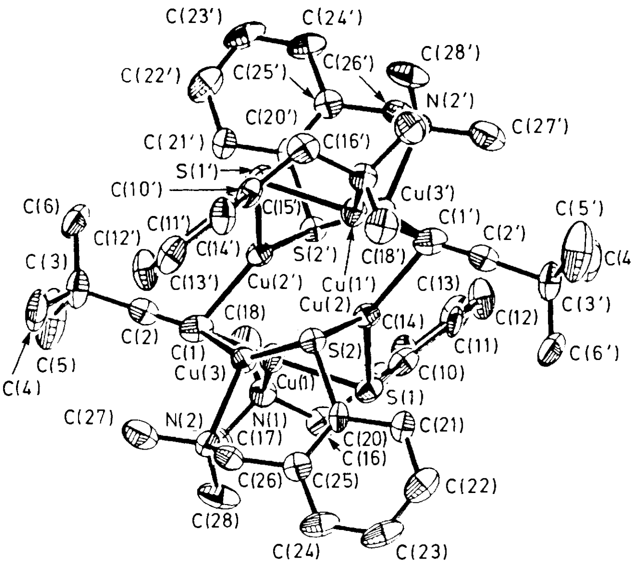


Figure 1. An ORTEP drawing (30% probability) of $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}CBu^t)]_2$ showing the atom labelling scheme. Some bond lengths and bond angles are given in Figure 2.

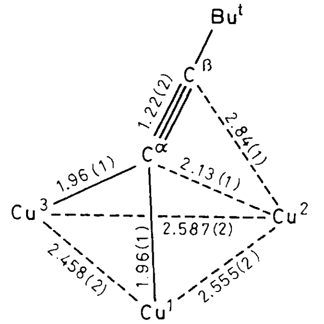
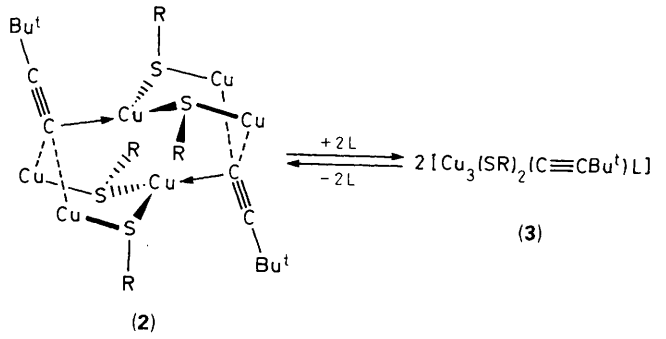


Figure 2. Schematic view of the symmetrical μ^3-η^2 bonded alkynyl group with bond lengths in Å. Bond angles (°): Cu(1)–C(1)–Cu(3) 77.7(5), C(2)–C(1)–Cu(2′) 113(1), C(2)–C(1)–Cu(1) 145(1), C(2)–C(1)–Cu(3) 136(1), C(1)–C(2)–C(3) 177(1).

it was anticipated that reaction of (**1**) with organolithium reagents LiR^t would be a viable route to heterocuprates $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_3R^tLi]$.



(**2**)

(**3**)

Scheme 2. SR = $\{SC_6H_4(CH_2NMe_2)\text{-}2\}^-$, L = PPh_3 or $P(OMe)_3$.

We now report that reaction of $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ with $LiC{\equiv}CBu^t$ affords the unexpected complex $[Cu_6\{SC_6H_4(CH_2NMe_2)\text{-}2\}_4(C{\equiv}CBu^t)_2]$ (**2**) as a yellow solid† (Scheme 1). Alternatively, pure (**2**) can be easily obtained by mixing a solution of (**1**) and $CuC{\equiv}CBu^t$ (1.5 equiv.) in diethyl ether at 0 °C; (**2**) precipitates from this solution and it is this route that is preferred because of its higher yield. Complex (**2**) has been characterized as a neutral hexanuclear complex, by spectroscopic methods (IR and ^1H NMR), ebulliometry and a single-crystal *X*-ray structure determination. Complex (**2**) is soluble in CH_2Cl_2 and in this solvent ebulliometry afforded a concentration dependent molecular weight [717 g mol^{-1} (17.25 kg m^{-3}) and at higher concentrations 883 g mol^{-1} (44.1 kg m^{-3})], which is consistent with an equilibrium between a trinuclear species and a hexanuclear species in solution. In its IR spectrum (KBr) there is no significant absorption at about 2030 cm^{-1} that would be indicative for a C≡C stretching vibration, *cf.* 2030 cm^{-1} found for the three-centre two-electron bonded C≡CPh group in the hexanuclear cluster compound $[Cu_6(C_6H_4NMe_2\text{-}2)_4(C{\equiv}CPh)_2]$.[4] The ^1H NMR (200 MHz, CD_2Cl_2) spectra of (**2**) are temperature dependent. At 295 K the NMR spectrum shows three singlets at 1.51, 2.41, and 3.34 p.p.m. for the Bu^t, NMe_2, and the CH_2 protons, respectively. However, at 193 K (the slow exchange limit) the NMR spectrum shows two anisochronous thiophenolate groups (with a total of four different methyl groups) and one $C{\equiv}CBu^t$ group.

Recrystallization of (**2**) from CH_2Cl_2 yielded *X*-ray quality yellow crystals. The determined crystal structure of (**2**), together with the adopted numbering scheme, is shown in Figure 1.‡ This study shows (**2**) to be a hexanuclear copper compound that consists of two identical nuclear units, $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}CBu^t)]$, related by crystallographic inversion symmetry, which are joined together through bridging $C{\equiv}CBu^t$ groups. Each unit is based on a boat conformation Cu_3S_2C ring that can be formally derived from the Cu_3S_3 ring of (**1**) by substitution of a S-bonded thiophenolate for a C-bonded alkynyl. In each unit one thiophenolate aryl ring is positioned axially with respect to the Cu_3S_2C ring while the other is positioned equatorially. The bonding mode of the $C{\equiv}CBu^t$ groups to the copper atoms is interesting and is shown in more detail in Figure 2. Each alkynyl is symmetrically C-bonded through C(1) to Cu(1) and Cu(3) of the same trinuclear unit, while its bonding to a third copper atom [Cu(2′)] of the other unit connects the two trinuclear units together. The bonding to Cu(2′) occurs through the C≡C unit [Cu(2′)–C(1) = 2.13(1) Å, Cu(2′) · · · C(2) = 2.84(1) Å, C(1)–C(2) = 1.22(2) Å]; the latter value is significantly larger than the *ca.* 1.17 Å found for symmetrical μ_2-η^1 alkynyl bridges.[5,6] This C≡C bond length in (**2**) is comparable to that in free acetylene and in 2-electron 4-centre (μ_3-η^1) bonded alkynyl groups.[7,8] To our knowledge, the asymmetric bridging mode for the alkynyl group in (**2**) is unprecedented; this situation can be described as a 2-electron 4-centre bond or as a μ_3-η^2 bonding mode as found in phenylethynyl(trimethylphosphine)copper(I).[8—10]

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† Elemental analyses (C, H, N, and S) are in agreement with the formula given.

‡ *Crystal data*: $C_{48}H_{66}Cu_6N_4S_4$, monoclinic, space group $P2_1/c$, a = 11.213(1), b = 18.360(2), c = 13.118(1) Å, β = 103.72(1)°, U = 2623.6(4) Å^3, Z = 2, $F(000)$ = 1240, D_c = 1.530 g cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å), μ(Mo-K_α) = 25.9 cm^{-1}. 9646 Reflections collected on an Enraf-Nonius CAD4F in the range $2.2 \leqslant 2\theta \leqslant 50.0°$. The data was averaged, and 1956 unique reflections with $I > 3\sigma(I)$ were used for elucidating the structure and refinement. The structure was solved by standard Patterson and Fourier techniques (SHELXS-86) and refined with full matrix least squares methods (SHELX-76). Final R = 0.061, R_w = 0.037 [$w = 1/\sigma^2(F)$] for 305 parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The chemistry of (**2**) is consistent with its description as a dimerization product of $[Cu_3(SR)_2(C{\equiv}CBu^t)]$ with intramolecular links involving π electrons of the alkynyl group. When two equivalents of an electron donating ligand (L), for example $P(OMe)_3$ or PPh_3, are added to a suspension of (**2**) in benzene the solid dissolves; titration of (**2**) in CH_2Cl_2 with PPh_3 shows an equivalence point at two phosphine ligands per mole.§ In these reactions, Scheme 2, the hexanuclear complex would appear to be cleaved into more soluble trinuclear species $[Cu_3(SR)_2(C{\equiv}CBu^t)(L)]$ (**3**), though attempts to isolate these species have thus far been unsuccessful. The important conclusion from this chemistry is that the monomeric unit $[Cu_3(SR)_2(C{\equiv}CBu^t)]$ contains an electrophilic copper atom which we propose to be the key feature in reactions of this and related organocopper compounds with α,β-unsaturated ketones. This proposal differs from the one in which a nucleophilic copper atom of a cuprate forms a d,π^* complex with the ketone.[11] In both proposals the ketone is activated by initial co-ordination to the copper atom through the π electrons of its carbon–carbon double bond.

The trinuclear unit $[Cu_3(SR)_2(C{\equiv}CBu^t)]$ can be considered as a general model for a novel type of heterocopper reagent $[Cu_{m+n}(RS)_mR'_n]$. We actually find an almost quantitative methyl transfer to the β position of the α,β-unsaturated ketone benzylideneacetone when the pure (normally unreactive) methylcopper is mixed with the pure thiophenolato copper(I) compound (**1**). This methyl transfer reaction is common for cuprates, but not for copper compounds.[12]

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§ The molecular weight of (**2**) was monitored by ebulliometry as a function of the PPh_3 concentration.