Synthesis and *X*-Ray Structure of Bis(trifluoromethyl)(*N*,*N*-diethyldithiocarbamato)-copper; a Remarkably Stable Perfluoroalkylcopper(III) Complex

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The reaction between trifluoromethylcadmium reagent and $Br_2Cu(edtc)$ (edtc = *N*,*N*-diethyldithiocarbamato) or $CdI^+[(CF_3)_2Cu]^-$ with $[Et_2NC(S)S]_2$ in DMF (dimethylformamide) at −30 °C yields the stable Cu^{III} perfluoroalkylcopper complex, $(CF_3)_2CuSC(S)NEt_2$.

Perfluoroalkylcopper reagents exhibit excellent thermal stability compared to their hydrocarbon analogues and have consequently received extensive utilization in preparative organic chemistry,[1,2] but their composition and structure is not clearly defined. Perfluoro-t-butylcopper has been described as a 2 : 3 dioxane adduct, but no structural data was provided.[3] Except for the recent proposal of $[CF_3CuI]^-$ by Chambers,[4] these reagents have been formally represented as R_FCu or $R_FCu{\cdot}CuI$.[1] Our recent report[2] that multiple trifluoromethylcopper species, with significantly different physical and chemical properties, can be detected spectroscopically suggested that this formalism for perfluoroalkylcopper reagents is oversimplified. Thus, we have focused on the identification and composition of these different trifluoromethylcopper moieties to better understand the nature of these reagents.

Recent developments in the 'CF_3Cu' system have demonstrated[5] that two of these compounds are $CF_3Cu{\cdot}L$ (**1**) (L = metal halide) and the cuprate $CdI^+[(CF_3)_2Cu]^-$ (**2**). In contrast to the slow oxidation of (**1**), the cuprate (**2**) is readily oxidized by a variety of oxidants. For example, oxidation with thiuramdisulphide converts (**2**) to $(CF_3)_2Cu^{III}edtc$ (edtc = *N*,*N*-diethyldithiocarbamato) (**3**), the first stable trifluoromethyl Cu^{III} compound (Scheme 1).† *X*-Ray analysis‡ (Figure 1) provided unequivocal evidence for (**3**). Compound (**3**) can also be synthesized *via* metathesis of a Cu^{III} complex, $Br_2Cu(edtc)$, with the trifluoromethylcadmium reagent CF_3CdI (Scheme 2).[6] Cuprate (**2**) can be oxidized to $CdI^+[(CF_3)_4Cu]^-$ (**4**) by oxygen, iodine, or bromine.[7]

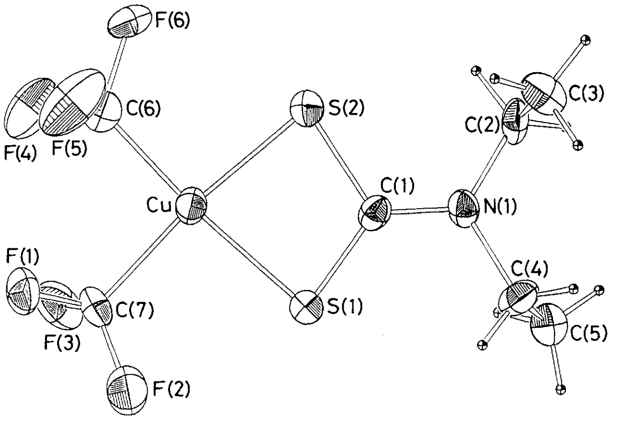

Figure 1. ORTEP diagram for $CuS_2F_6NC_7H_{10}$. Bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses: Cu–S(1) 2.224(1), Cu–S(2) 2.186(1), Cu–C(6) 1.863(5), Cu—C(7) 2.026(5), S(1)–C(1) 1.661(6), S(2)–C(1) 1.784(6), N(1)–C(2) 1.441(8), N(1)–C(4) 1.507(8), C(2)–C(3) 1.511(6), C(4)–C(5) 1.505(6), C(6)–F(4) 1.340(5), C(6)–F(5) 1.281(5), C(6)–F(6) 1.332(6), C(7)–(F1) 1.328(5), C(7)–F(2) 1.340(7), C(7)–F(3) 1.324(6); S(1)–Cu–S(2) 79.33(5), S(1)–Cu–C(6) 173.2(1), S(1)–Cu–C(7) 93.7(1), Cu–S(1)–C(1) 86.4(2), S(1)–C(1)–S(2) 109.5(2), S(2)–C(1)–N(1) 120.4(6), C(1)–N(1)–C(2) 124.9(6), C(2)–N(1)–C(4) 115.9(3), N(1)–C(2)–C(3) 115.7(5), Cu–C(6)–F(4) 120.3(3), Cu–C(6)–F(6) 118.2(3), F(4)–C(6)–F(6) 99.4(4), Cu–C(7)–F(1) 111.7(3), Cu–C(7)–F(3) 109.3(4), F(1)–C(7)–F(3) 103.6(4), S(2)–Cu–C(6) 95.1(2), S(2)–Cu–C(7) 171.5(1), C(6)–Cu–C(7) 92.2(2), Cu–S(2)–C(1) 84.7(2), S(1)–C(1)–N(1) 129.9(6), C(1)–N(1)–C(4) 118.3(6), N(1)–C(4)–C(5) 108.8(4), Cu–C(6)–F(5) 112.3(4), F(4)–C(6)–F(5) 109.4(4), F(5)–C(6)–F(6) 93.4(3), Cu–C(7)–F(2) 111.2(3), F(1)–C(7)–F(2) 103.7(5), F(2)–C(7)–F(3) 117.0(4).

$$\begin{array}{c}\underset{(\mathbf{2})}{\mathrm{CdI^+[(CF_3)_2Cu]^-}} + \mathrm{[(C_2H_5)_2NC(S)S]_2}\\ \mathrm{DMF}\ \Big\downarrow\ -30\,^{\circ}\mathrm{C\ to\ room\ temp.}\\ (\mathbf{3}) + 1/2\,\mathrm{CdI_2} + 1/2\mathrm{Cd(edtc)_2}\end{array}$$

Scheme 1

$$\begin{array}{c}\mathrm{Br_2Cuedtc} + 1/2\,\mathrm{(CF_3)_2Cd} + \mathrm{CF_3CdI}\\ \mathrm{DMF}\ \Big\downarrow\ -30\,^{\circ}\mathrm{C\ to\ room\ temp.}\\ (\mathbf{3}) + 1/2\,\mathrm{CdI_2} + \mathrm{CdBr_2}\end{array}$$

Scheme 2

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† Satisfactory analytical data were obtained. *Selected spectroscopic data* for (**3**): mass spectrum, *m/z* 349/351 (0.3%), 280/282 (1.5%), 211/213 (100%); ^{19}F n.m.r. [90 MHz, DMF (1 M)] δ −29.8 p.p.m. (s), ^{1}H n.m.r. [90 MHz, $CDCl_3$ (0.1 M)] δ 1.33 (t, $J_{H,H}$ 7.2 Hz, Me), 3.76 (q, CH_2); ^{13}C n.m.r. [360 MHz, DMF (3 M)] δ 132.8 (q, J_{CF} 399.6 Hz); m.p. 127 ± 1 °C (decomp.).

‡ *Crystal data* for (**3**): $CuS_2F_6NC_7H_{10}$, $M = 349.83$, monoclinic, space group *Cc*, $a = 14.911(2)$, $b = 10.589(1)$, $c = 8.765(1)$ Å, $\beta = 114.2(1)^{\circ}$, $U = 1262.2(6)$ Å^3, $Z = 4$, $D_c = 1.841$ g cm^{-3}, $\lambda(\text{Mo-}K_{\alpha}) = 0.71073$ Å, $\mu(\text{Mo-}K_{\alpha}) = 21.6$ cm^{-1}. Intensity data from two crystals were collected on an Enraf-Nonius CAD-4 diffractometer, 2211 (crystal #1) and 2216 (crystal #2) independent reflections after averaging ($2 \leqslant 2\theta \leqslant 50^{\circ}$); 1947 (crystal #1) and 1894 (crystal #2) with $I \geqslant 3\sigma(I)$. The data were corrected for Lorentz, polarization and absorption (empirical absorption method) effects and the structure was solved with a combination of direct (MULTAN) and difference methods using the Enraf-Nonius SDP-VAX program package. Anisotropic least-squares refinement on all atoms except the hydrogens (which were placed in fixed idealized positions relative to the carbon atoms and given isotropic temperature factors of 1.1 times that for the atom to which they were attached) gave an agreement factor of $R = 0.03$ for each crystal. The data sets were combined, and the refinement continued to give a final agreement factor $R = 0.028$ and $R_w = 0.035$. Two crystals were used in the structure determination because in the early stages of refinement of the first crystal, very unequal C-F distances were present (though Cu-S distances were identical). Data were then collected from a second crystal. When the second data set was independently refined to the same level, almost identical results were obtained. The data sets were then combined, and the refinement continued. Convergence was very slow, but as the parameter shift/error ratio became lower, the discrepancies in the C-F distances decreased (though the Cu-S and Cu-C distances also changed). 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 structure of (**3**) shows a distorted quadratic planar configuration for the Cu atom (Figure 1), similar to $Br_2Cu(bdtc)$[8] (**5**) (bdtc = *N*,*N*-di-n-butyldithiocarbamato). However, both the Cu–C distances as well as the Cu–S distances in (**3**) are different, whereas in (**5**) two equal Cu–Br and Cu–S distances are found. In $Cu(edtc)_2$[9] the Cu has five-fold co-ordination with the fifth Cu–S bond (2.85 Å) bridging two $Cu(edtc)_2$ units of neighbouring layers. In (**5**), however, the shortest interlayer Cu–S distance is 3.34 Å suggesting the absence of five-fold co-ordination by sulphur bridges. In (**3**) the interlayer Cu–S distance is even larger, 3.86 Å, and no bridging of $(CF_3)_2CuSC(S)NEt_2$ units is indicated.

The difference in the Cu–C(6) and Cu–(7) bond distances in (**3**) is surprising. A similar difference has been reported for $[(C_8F_7)_2Ag(I)]^-$,[10] but no such effect has been reported for monomeric dialkylcuprate(I) complexes.[11] The Cu–C(6) bond distance [1.863(5) Å] is the shortest Cu–C bond distance yet observed; $2,4,6\text{-}Ph_3C_6H_2Cu$[12] [Cu–C, 1.890(6) Å].

The relatively short Cu–F(5) intramolecular distance (2.63 Å), as well as the non-tetrahedral CuC(6)F(4,5,6) and the corresponding F–C–F bond angles, are puzzling. It is tempting to suggest that F(5) is donating electron density to Cu and acting as the fifth co-ordination site for Cu, thus enabling Cu to attain an 18-electron configuration. Perhaps such co-ordination might account for the stability of (**3**), but additional analogues of (**3**) are required to test this suggestion.

Compared to Cu^I compounds (**1**) and (**2**),[2] the Cu^{III} complex (**3**) showed no tendency to form C_2F_5Cu. When a DMF (DMF = dimethylformamide) solution of (**3**) was heated to 70 °C/1 h, no appreciable decomposition was detected and no C_2F_5Cu was observed by ^{19}F n.m.r. analysis of the solution. At 110 °C thermal decomposition of (**3**) occurred rapidly, yet no C_2F_5Cu was detected as a decomposition product of (**3**). Nevertheless, (**3**) can be utilized as a trifluoromethylation agent; when heated with iodobenzene, $p\text{-}MeOC_6H_4Br$, $p\text{-}BrC_6H_4I$, or allyl bromide at 90—100 °C, the corresponding trifluoromethylated aromatics or alkene were formed. Trifluoromethylation of allyl bromide can be carried out at room temperature when stoicheiometric amounts of Cu^0, (**3**), and the allylic halide are mixed. Further applications of (**3**) as a trifluoromethylation agent are under study.

In summary, the formation of the first perfluoroalkylcopper(III) complex has been achieved. This Cu^{III} complex exhibits remarkable stability but does undergo trifluoromethylation reactions. Further investigation of (**1**), (**2**), (**3**), and related systems where $R_F \neq CF_3$ should provide unequivocal information on the composition and structure of these important reagents.

We thank the National Science Foundation and the Air Force Office of Scientific Research for financial support and the Deutsche Forschungsgemeinschaft for a training grant to M. W. P. (#Wi/856/1-1).

Received, 28th June 1989; Com. 9/02747E

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