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Copper Complexes

Easy Access to the Copper(III) Anion $[Cu(CF_3)_4]^-$**

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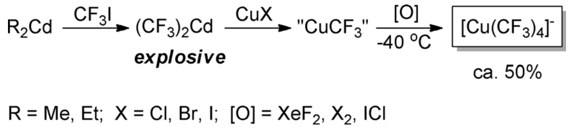
Abstract: *CuCl or pre-generated $CuCF_3$ reacts with CF_3SiMe_3/KF in DMF in air to give $[Cu(CF_3)_4]^-$ quantitatively. $[PPN]^+$, $[Me_4N]^+$, $[Bu_4N]^+$, $[PhCH_2NEt_3]^+$, and $[Ph_4P]^+$ salts of $[Cu(CF_3)_4]^-$ were prepared and isolated spectroscopically and analytically pure in 82–99% yield. X-ray structures of the $[PPN]^+$, $[Me_4N]^+$, $[Bu_4N]^+$, and $[Ph_4P]^+$ salts were determined. A new synthetic strategy with $[Cu(CF_3)_4]^-$ was demonstrated, involving the removal of one CF_3^- from the Cu atom in the presence of an incoming ligand. A novel Cu^{III} complex $[(bpy)Cu(CF_3)_3]$ was thus prepared and fully characterized, including by single-crystal X-ray diffraction. The bpy complex is highly fluxional in solution, the barrier to degenerate isomerization being only 2.3 kcal mol^{-1}. An NPA study reveals a huge difference in the charge on the Cu atom in $[Cu(CR_3)_4]^-$ for R = F (+0.19) and R = H (+0.46), suggesting a higher electron density on Cu in the fluorinated complex.*

Compounds of copper in the oxidation state +3 are extremely rare. In 1989, Burton and co-workers[1] briefly mentioned that oxidation of "$[CdI]^+$ $[Cu(CF_3)_2]^-$" gives rise to a remarkable species, the homoleptic CF_3Cu^{III} anion $[Cu(CF_3)_4]^-$. Shortly after that, Naumann's group[2] reported the first preparation of $[Cu(CF_3)_4]^-$, an X-ray structure of its $[PPN]^+$ salt, and isolation of $[Ph_4P]^+$ $[Cu(CF_3)_4]^-$. The very existence and surprisingly high stability of weakly coordinating $[Cu(CF_3)_4]^-$ immediately prompted further studies, leading to interesting theoretical insights[3] and the discovery of molecular charge transfer and superconductivity of $[Cu(CF_3)_4]^-$-based materials.[4] However, chemical properties and reactivity of this highly unusual Cu^{III} anion have remained unexplored and still remain so.

There has been growing interest of the research community in both fluorinated organometallic complexes[5] and Cu^{III} compounds.[6] Homoleptic anions of the type $[M(CF_3)_4]^{2-}$ (M = Pd, Pt) have been actively researched in recent years.[7] Naturally, the question arises as to why the chemistry of such an interesting species as $[Cu(CF_3)_4]^-$ is virtually unstudied. The lack of experimental reports on $[Cu(CF_3)_4]^-$ for over 15 years is, however, hardly surprising. The only available method[2] to prepare this complex involves multiple steps and is unsafe, involving the synthesis of toxic CdR_2 (R = Me or Et), followed by treatment with CF_3I gas to generate explosive[8] $Cd(CF_3)_2$ for transmetalation with Cu^I and subsequent low-temperature (−40 °C) oxidation with XeF_2, I_2, Br_2, Cl_2, or ICl (Scheme 1). A safer and simpler method to synthesize $[Cu(CF_3)_4]^-$ is certainly desired. Herein, we report the first alternative procedure to prepare $[Cu(CF_3)_4]^-$ salts. The new method is one-step, exceedingly operationally simple, does not employ hazardous materials, and affords $[Cu(CF_3)_4]^-$ in quantitative yield. We also report a new strategy for the use of now easily accessible $[Cu(CF_3)_4]^-$ in organometallic synthesis and its computational studies.



Scheme 1. The previously reported method of synthesis of $[Cu(CF_3)_4]^-$.[2]

We have recently developed[9] the synthesis of $CuCF_3$ directly from fluoroform, the most attractive CF_3 source,[10] and demonstrated efficient trifluoromethylation of a variety of organic substrates with this reagent.[11,12] The original observations by Burton[1] and others[13] suggest that $CuCF_3$ might produce $[Cu(CF_3)_4]^-$ upon oxidation with O_2. However, three quarters of the Cu in the reagent would be lost, as is clear from the stoichiometry of the starting material (Cu/CF_3 = 1:1) and the product (Cu/CF_3 = 1:4). We therefore attempted oxidation of fluoroform-derived $CuCF_3$ in the presence of an additional "CF_3^-" source, fluoride-activated CF_3SiMe_3 ($TMSCF_3$).[14] As the goal was to develop as operationally simple, efficient, and safe a method to make $[Cu(CF_3)_4]^-$ as possible, air was the oxidant of choice.

Stirring CHF_3-derived $CuCF_3$[9a] in DMF (0.35–0.38 M) with KF (10 equiv) and $TMSCF_3$ (15–20 equiv) in air at room temperature for 3–5 h gave rise to $[Cu(CF_3)_4]^-$ quantitatively, as determined by ^{19}F NMR spectroscopy. Although we were delighted with this result, we also realized that others wishing to obtain $[Cu(CF_3)_4]^-$ might be discouraged by the need to use gaseous fluoroform to prepare $CuCF_3$ by our method.[9] (The environmental and cost issues that are addressed by the use of fluoroform[10] are not as important, at least at the moment, for the synthesis of exotic compounds such as $[Cu(CF_3)_4]^-$.) It was reasoned therefore, that other, higher-cost yet more

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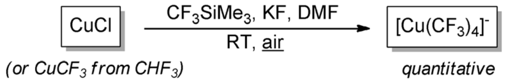
conventionally prepared forms of $CuCF_3$[15] could be used for the synthesis. For instance, $CuCF_3$ can be generated from CuBr and $TMSCF_3/KF$.[13] The latter, as described above, could also function as a CF_3 source for the Cu^{III} produced in the air-oxidation of $CuCF_3$. Therefore, it seemed reasonable to examine the possibility of $[Cu(CF_3)_4]^-$ formation in the reaction of a simple inorganic Cu^I salt with $TMSCF_3/KF$ in air. After exploratory runs and straightforward optimization, quantitative yield of $[Cu(CF_3)_4]^-$ was achieved directly from CuCl in a one-step reaction at ambient temperature in air (Scheme 2).



Scheme 2. Synthesis of $[Cu(CF_3)_4]^-$ from CuCl or CHF_3-derived $CuCF_3$.

Stoichiometry considerations suggest that 4 equiv of $TMSCF_3$ are needed to reach full conversion of CuCl and, consequently, quantitative yield of $[Cu(CF_3)_4]^-$. In reality, however, $TMSCF_3$ should be used in excess because of the uncontrollable release of the "CF_3^-" and Si–CF_3 bond hydrolysis with the air moisture in the presence of fluoride.[14] Additional losses of the low-boiling $TMSCF_3$ (b.p. 54–55 °C) incur from its partial evaporation at vigorous agitation that is required for the air-oxidation to occur efficiently. Quantitative yields of $[Cu(CF_3)_4]^-$ from CuCl were consistently obtained with a 2.5-fold excess of KF and a 5-fold excess of $TMSCF_3$ used for the synthesis. At full conversion, the originally dark reaction mixture turns yellow or orange. After the addition of water and an organic cation derivative, the corresponding $[Cu(CF_3)_4]^-$ salt is extracted with CH_2Cl_2 and easily purified. To isolate $[Me_4N]^+$ $[Cu(CF_3)_4]^-$ that is insufficiently soluble in CH_2Cl_2, a 1:1 v/v CH_2Cl_2/CH_3NO_2 mixture was used for the extraction. However, isolation of pure $K[Cu(CF_3)_4]$ formed in the reaction (Scheme 2) has proven difficult because of the poor solubility of the potassium salt in water-immiscible organic solvents, including highly polar CH_3NO_2. A summary of the $[Cu(CF_3)_4]^-$ salts **1**–**5** prepared in the current work is presented in Table 1. All of the salts were isolated as spectroscopically (NMR) and analytically pure compounds. Scalability of the method has been demonstrated by the synthesis of $[PPN]^+$ $[Cu(CF_3)_4]^-$ (**1**) as pure white crystals on a 3 g scale in 99 % yield.

Table 1: Salts $[Cat]^+$ $[Cu(CF_3)_4]^-$ prepared in this work.

$[Cat]^+$ (salt)	Method[a]	Yield [%]	Characterization[b]
$[PPN]^+$ (**1**)	A	99	XRD; ^1H and ^{19}F NMR
	B	95	
$[PhCH_2NEt_3]^+$ (**2**)	A	92	^1H and ^{19}F NMR; EA
$[Me_4N]^+$ (**3**)	B	82	XRD; ^1H and ^{19}F NMR; EA
$[Bu_4N]^+$ (**4**)	B	96	XRD; ^1H and ^{19}F NMR; EA
$[Ph_4P]^+$ (**5**)	B	92	XRD; ^1H and ^{19}F NMR; EA

[a] **A**: from fluoroform-derived $CuCF_3$. **B**: from CuCl. [b] XRD = single-crystal X-ray diffraction; EA = elemental analysis.

All five $[Cu(CF_3)_4]^-$ salts prepared in the current work have been fully characterized in solution (NMR), and four of the five in the solid state (X-ray diffraction).[16] The X-ray structures are all new, except for that of **1**.[2] In all of the structures, the $[Cu(CF_3)_4]^-$ anion displays distorted square-planar geometry, as shown in Figure 1 for $[Bu_4N]^+$ $[Cu(CF_3)_4]^-$ (**4**). Disorder in the structure of **3** and in one of the two independent anions in the unit cell of **5** prevents inclusion of these species in the analysis of the Cu–CF_3 bond distances in the $[Cu(CF_3)_4]^-$ moiety. In the non-disordered structures of **1**, **4**, and **5** (one of the two anions), the Cu–CF_3 bond lengths are all in a narrow range of 1.944(3)–1.964(2) Å, virtually identical within the estimated standard deviations. In accordance with the solid-state data, only one singlet resonance is observed in ^{19}F NMR spectra of **1**–**5** in solution, the chemical shift (from −33.7 to −35.1 ppm) being slightly solvent-dependent.[2]

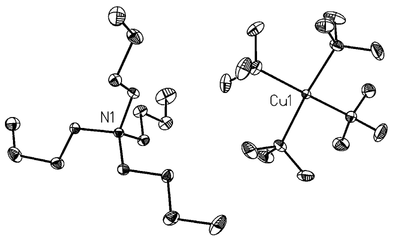
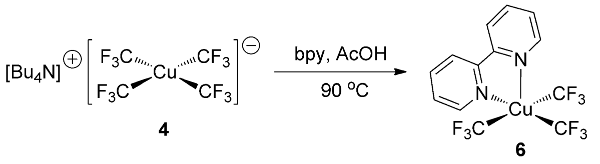


Figure 1. ORTEP drawing of $[Bu_4N]^+$ $[Cu(CF_3)_4]^-$ (**4**) with all H atoms omitted for clarity and ellipsoids set at 50 % probability.

The developed preparative method for $[Cu(CF_3)_4]^-$ prompted us to consider this anion as a starting material for the synthesis of other CF_3Cu^{III} complexes, which are currently of great interest[6] yet extremely scarce. Apart from $[Cu(CF_3)_4]^-$, there has been only one CF_3Cu^{III} complex reported, $[(Et_2NCS_2)Cu(CF_3)_2]$.[1a] We reasoned that fluoride abstraction[5] from $[Cu(CF_3)_4]^-$ would produce $[Cu(CF_3)_3(CF_2)]$, a difluorocarbene species that is expected[17] to undergo facile hydrolysis to carbonyl. The weakly bound CO would then be easily displaced with an incoming external ligand. Original attempts to use strong acids such as BF_3 (Et_2O complex) and H_2SO_4 resulted in nonselective decomposition of $[Cu(CF_3)_4]^-$. It was then found that the desired transformation can be effected by acetic acid. In a non-optimized experiment, the $[Bu_4N]^+$ salt **4** reacted with 2,2′-bipyridine (bpy) in AcOH to give $[(bpy)Cu(CF_3)_3]$ (**6**) as well-shaped yellow crystals in 47 % yield (Scheme 3).[18] This is the first Cu species bearing three CF_3 ligands, and the third CF_3Cu^{III} complex ever reported. It was therefore of particular interest to establish the structure of **6** in the solid state and in solution.

In the crystal (Figure 2), **6** displays a distorted square-pyramidal geometry with one N atom trans to CF_3 (Cu–N 1.977(2) Å) and the other, much more weakly bound N (Cu–N 2.174(2) Å) in the apical position. In solution, however, the two pyridine rings appear to be equivalent, as follows from the ^1H NMR spectrum of **6** in $[D_6]$acetone at 25 °C. The ^{19}F NMR spectrum of **6** displayed a quartet at −37.8 ppm and a septet at −24.8 ppm with the same coupling constant *J*(F-



Scheme 3. Synthesis of [(bpy)Cu$(CF_3)_3$] (**6**) from $[Bu_4N]^+$ $[Cu(CF_3)_4]^-$ (**4**).

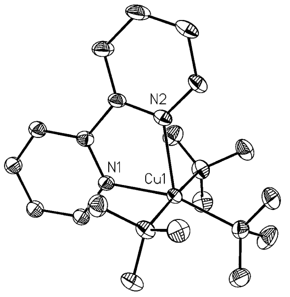
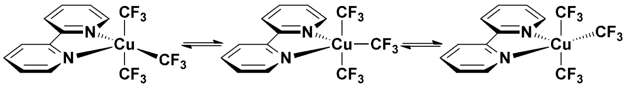


Figure 2. ORTEP drawing of [(bpy)Cu$(CF_3)_3$] (**6**) with all H atoms omitted for clarity and ellipsoids set at 50% probability.

F) = 9.3 Hz, in a 2:1 integral ratio. The ^{19}F and ^{1}H NMR data suggested that in solution **6** is either a trigonal bipyramid with two axial CF_3 ligands or stereochemically nonrigid with respect to the unique trifluoromethyl. Cooling the sample to −88 °C did not disrupt the equivalence of the pyridine ring protons and only resulted in small changes in the chemical shifts of the ^{1}H NMR signals and a slight broadening of the ^{19}F NMR multiplets. In accordance with the NMR data, a DFT study produced a very low barrier of 2.3 kcal mol^{-1} (in acetone; 2.4 kcal mol^{-1} in the gas phase) for the degenerate isomerization of **6**, as shown in Scheme 4. The new approach toward the synthesis of various CF_3Cu^{III} complexes from $[Cu(CF_3)_4]^-$ is being further explored in our laboratories.



Scheme 4. Degenerate isomerization of **6** in solution.

Of considerable interest[5e,19] is the distribution of charges in $[Cu(CF_3)_4]^-$ and its non-fluorinated counterpart $[Cu(CH_3)_4]^-$ as well as in the pair of Cu^I anionic complexes $[Cu(CF_3)_2]^-$ and $[Cu(CH_3)_2]^-$. The experimentally determined structures of $[Cu(CF_3)_4]^-$ (Ref. [2] and this work), $[Cu(CF_3)_2]^-$,[20] and $[Cu(CH_3)_2]^-$ [21] are well-reproduced in the DFT calculations. The atomic charges calculated using the NPA method for all four anions are presented in Table 2. Since it was recently found[22] that in complexes of the type $[L_nM(CX_3)]$ the metal bears a smaller positive charge or a larger negative charge for X = F than for X = H, this counterintuitive[5e] trend has been established for a considerable number of various metal complexes.[19,23] As can be seen from Table 2, the $[Cu(CF_3)_4]^-/[Cu(CH_3)_4]^-$ and $[Cu(CF_3)_2]^-/[Cu(CH_3)_2]^-$ pairs are no exception. Moreover, the vast difference in the positive charge on the Cu atom in $[Cu(CF_3)_4]^-$ (+0.19) and in $[Cu(CH_3)_4]^-$ (+0.46) is unprecedented. Also notable is the similarity of the positive charges on Cu in $[Cu(CF_3)_4]^-$ (+0.19) and $[Cu(CF_3)_2]^-$ (+0.17), despite the different formal oxidation states of the metal in these anions (+3 and +1, respectively). The undeniably well-pronounced trend in the atomic charges on Cu in $[Cu(CF_3)_4]^-$, $[Cu(CH_3)_4]^-$, $[Cu(CF_3)_2]^-$, and $[Cu(CH_3)_2]^-$ shows that the CF_3 ligand brings about higher electron density around Cu than the CH_3 ligand. One might argue that the structures are more ionic for the CF_3 derivatives and more covalent for the CH_3 analogues. This, however, is hardly consistent with the computed negative charge on the CX_3 unit being larger for X = H than for X = F within each pair: −0.36 vs. −0.30 for the Cu^{III} and −0.62 vs. −0.58 for the Cu^I (Table 2).

Table 2: Natural atomic charges computed for $[Cu(CF_3)_4]^-$, $[Cu(CH_3)_4]^-$, $[Cu(CF_3)_2]^-$, and $[Cu(CH_3)_2]^-$.

Anion	q(Cu)	q(C)	q(F)	q(H)	q(CX$_3$)
$[Cu(CF_3)_4]^-$	+0.19	+0.79	−0.36		−0.30
$[Cu(CH_3)_4]^-$	+0.46	−0.97		+0.20	−0.36
$[Cu(CF_3)_2]^-$	+0.17	+0.59	−0.39		−0.58
$[Cu(CH_3)_2]^-$	+0.24	−1.20		+0.19	−0.62

So long as the concept of atomic charges is used as a measure of electron density, which is associated with the formalism of electron donation/withdrawal, it might be hard to deny a de facto stronger electron donation to the metal atom from CF_3 than from CH_3. This, however, does not directly translate into reactivity, such as enhanced nucleophilicity of the metal center whose d orbitals, both filled and empty, are stabilized by the large positive charge on the CF_3 carbon.[5e,19,24] The stereotype of CF_3 being invariably an electron acceptor has long been challenged on the basis of not only computational but also experimental data.[25]

In conclusion, we have developed the first simple, highly efficient, and safe method for the synthesis of $[Cu(CF_3)_4]^-$, a unique Cu^{III} complex. This weakly coordinating homoleptic anion can now be effortlessly prepared in quantitative yield from $CuCF_3$ or, even more conveniently, from CuCl and $TMSCF_3$/KF in air. A variety of $[Cu(CF_3)_4]^-$ salts have been synthesized by this method in 82–99% yield on up to a 3 g scale and fully characterized. A new approach to other CF_3Cu^{III} species from $[Cu(CF_3)_4]^-$ has been demonstrated. The reaction of $[Bu_4N]^+$ $[Cu(CF_3)_4]^-$ with bpy in AcOH furnishes stable [(bpy)Cu$(CF_3)_3$], the third CF_3Cu^{III} species ever reported and the first Cu^{III} complex bearing three CF_3 ligands. The new complex [(bpy)Cu$(CF_3)_3$] has been structurally characterized and found to be highly fluxional in solution ($\Delta G^{\neq} = 2.3$ kcal mol^{-1}). NPA studies have revealed an unprecedentedly large, striking difference in the charge on the Cu atom in $[Cu(CR_3)_4]^-$ for R = F (+0.19) and for R = H (+0.46), pointing to higher electron density on Cu in the fluorinated derivative. The easy accessibility of $[Cu(CF_3)_4]^-$ opens up previously unavailable opportunities for research in the area of Cu^{III} complexes and trifluoromethylated compounds.

Experimental Section

The experiments described below were carried out in the presence of 4,4′-difluorobiphenyl as an internal standard for convenience of monitoring the reactions by ^{19}F NMR spectroscopy. This internal standard, which is easily soluble in solvents of low polarity, does not interfere with the isolation and purification of the [Cu(CF$_3$)$_4$]$^-$ salts. The syntheses can be performed as successfully in the absence of an internal standard.

[PPN]$^+$ [Cu(CF$_3$)$_4$]$^-$ (**1**), method A: A round-bottom flask was charged with 0.38 M CHF$_3$-derived CuCF$_3$ in DMF (10 mL, 3.8 mmol),[9] 4,4′-difluorobiphenyl (internal standard; 0.72 g, 3.8 mmol), and KF (2.21 g, 38.0 mmol) under argon. The reaction mixture was opened to air and TMSCF$_3$ (11.1 mL, 75.1 mmol) was added immediately. The reaction mixture was agitated in air until quantitative yield of [Cu(CF$_3$)$_4$]$^-$ was reached (^{19}F NMR: s, −34.1 ppm) within 3–4 h. Water (20 mL) and [PPN]$^+$ Cl$^-$ (2.2 g, 3.8 mmol) were added and the mixture was extracted with CH$_2$Cl$_2$ (5 × 10 mL). The combined extracts were filtered through a silica gel plug that was then washed with CH$_2$Cl$_2$. The combined filtrate and the washings were evaporated to ca. 5–10 mL and treated with ca. 50 mL of ether to prompt precipitation of [PPN]$^+$ [Cu(CF$_3$)$_4$]$^-$ (**1**) as white crystals that were washed with ether (4 × 5 mL) and dried under vacuum overnight. The yield of **1** was 3.18 g (99 %). ^{1}H NMR (CDCl$_3$), δ: 7.43–7.66 (m, aromatic H). ^{19}F NMR (CDCl$_3$), δ: −34.1 (s).

[Bu$_4$N]$^+$ [Cu(CF$_3$)$_4$]$^-$ (**4**), method B: A 25 mL glass vial was charged with CuCl (144 mg, 1.44 mmol), 4,4′-difluorobiphenyl (internal standard; 274 mg, 1.44 mmol), spray-dried KF (836 mg, 14.4 mmol), and dry DMF (1 mL). At vigorous stirring in air, TMSCF$_3$ (3.2 mL, 21.6 mmol) was added within 1 min. After agitation in air for 30 min, additional TMSCF$_3$ (1.1 mL, 7.2 mmol) was added in one portion. The reaction mixture was agitated in air until quantitative yield of [Cu(CF$_3$)$_4$]$^-$ was detected by ^{19}F NMR spectroscopy (4–5 h). Water (10 mL) and [Bu$_4$N]Br (479 mg, 1.44 mmol) were added and the mixture was extracted with CH$_2$Cl$_2$ (5 × 10 mL). The combined extracts were filtered through a silica gel plug that was then washed with CH$_2$Cl$_2$. The combined filtrate and the washings were evaporated to ca. 3 mL and treated with ca. 40 mL of ether followed by ca. 20 mL of hexane to prompt precipitation of [Bu$_4$N]$^+$ [Cu(CF$_3$)$_4$]$^-$ (**4**) as white crystals that were washed with ether (4 × 5 mL) and dried under vacuum overnight. The yield of **4** was 805 mg (96 %). Elemental analysis (%) calcd for C$_{20}$H$_{36}$CuF$_{12}$N: C 41.3, H 6.2, N 2.4; found: C 41.2, H 5.9, N 2.5. ^{1}H NMR (CDCl$_3$), δ: 3.04–3.01 (m, 8 H, NC*H*$_2$), 1.59–1.52 (m, 8 H, NCH$_2$C*H*$_2$), 1.38 (m, 8 H, J(H-H) = 7.4 Hz, 8 H, NCH$_2$CH$_2$C*H*$_2$), 0.98 (t, *J*(H-H) = 7.4 Hz, 12 H, C*H*$_3$). ^{19}F NMR (CDCl$_3$), δ: −33.7 (s).

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