Cu(III) Trifluoromethyl Complexes with 1,3-Diketonate Ligands and Their Versatile Reactivity in C-H Trifluoromethylation

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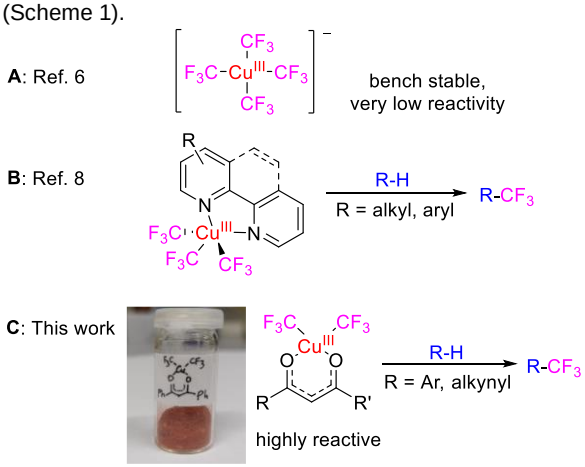
Abstract: High-valent Cu(III) trifluoromethyl complexes with 1,3-diketonates as bidentate oxygen donor ligands $LCu^{III}(CF_3)_2$ were prepared for the first time and fully characterized, including X-ray crystallography. These complexes are soluble in most organic solvents and were found to be more reactive than known N-donor Cu(III) trifluoromethyl complexes. They exhibit a promising reactivity in radical and radical-polar crossover trifluoromethylation reactions. Direct C-H trifluoromethylation of electron-rich arenes and indoles using Cu(III) trifluoromethyl diketonates under blue light irradiation in mild conditions is described. Azolo- and oxy-trifluoromethylation of terminal alkynes using Cu(III) trifluoromethyl diketonate complex and S-trifluoromethylation of thiophenol were demonstrated as applications.

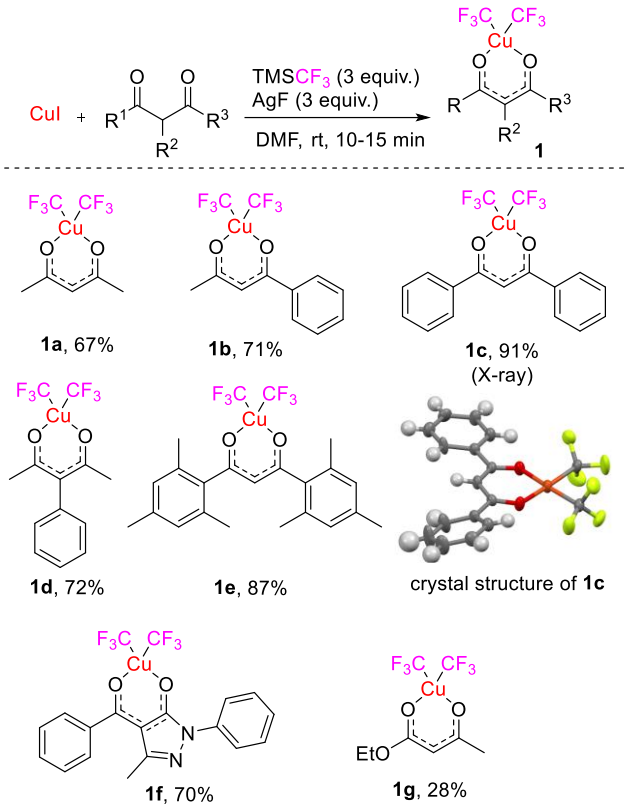
High-valent Cu(III) species are rare compounds, often exhibiting unique oxidative properties.[1] However, in the recent two decades there has been a growing interest in studies of Cu(III) complexes as intermediates in cross-coupling reactions[2] and in biological systems.[3] Unlike most unstable organometallic Cu(III) intermediates, some trifluoromethyl derivatives of high-valent copper are isolable species with unusual stability.[4] While the oxidation state of copper in these species is a subject of discussions due to the inverse ligand field and the high degree of covalency of Cu-CF_3 bond,[5] the stabilization of high-valent copper by trifluoromethyl groups is notable.[1b] A systematic investigation of Cu(III) trifluoromethyl complexes and their applications began in 2015 by the development of simple synthesis of the $[Cu(CF_3)_4]^-$ anion by oxidation of CuCl in the presence of $TMSCF_3$ and a fluoride source.[6] Also, Cu(III) trifluoromethyl complexes with N-donor pyridine-type ligands such as $(bpy)Cu(CF_3)_3$[6,7] and $(phen)Cu(CF_3)_3$[7] were synthesized and later shown to serve as unique C-H trifluoromethylation reagents of radical or radical-polar crossover type.[8] C-H trifluoromethylation is a powerful and atom-economical strategy, widely used in modern organic synthesis and drug discovery.[9] In the last decade, the community has witnessed an enormous growth of available methods for the incorporation of the trifluoromethyl group into organic motifs, involving radical pathways. Thus, trifluoromethylation of arenes,[8a] alkenes,[8b-c] alkynes,[8d-f] aldehydes,[8g] benzylic[8h-i] and unactivated[8j] C-H bonds were achieved very recently using Cu(III) trifluoromethyl complexes of this type. In contrast to these reactive Cu(III) species, the anion $[Cu(CF_3)_4]^-$ itself, which also forms upon oxidation of Cu(I) in the presence of $TMSCF_3$ and soft phosphine ligands, was shown to be poorly reactive.[7a] Although more and more research on the applications of $LCu(CF_3)_3$ and similar Cu(III) trifluoromethyl species was performed in the recent years, the synthesis and studies of novel reactive Cu(III) complexes remains a challenging task. Different reactivity patterns can be expected depending on stronger or weaker coordination of Cu(III) with ligand. For instance, oxygen-donor ligands such as 1,3-diketonates, have never been applied to stabilize high-valent copper species. 1,3-Diketones are versatile chelating ligands with high synthetic applicability and low toxicity, which also makes metal diketonate complexes attractive for biological studies.[10] Herein we report the first examples of Cu(III) complexes with 1,3-diketonate ligands bearing two trifluoromethyl groups, which exhibit high reactivity in C-H trifluoromethylation reactions (Scheme 1).



Scheme 1. Recent reports on highly stabilized Cu(III) trifluoromethyl complexes.

We initiated our studies with attempts to prepare acetylacetonate Cu(III) species by the oxidation of Cu(I) in the presence of acetylacetone and $TMSCF_3$. While the initial attempts, when air, iron (III) salts or $Na_2S_2O_8$ were used as oxidants in the presence of fluoride to activate $TMSCF_3$ only led to the formation of $[Cu(CF_3)_4]^-$ in low yields, the use of AgF, which can serve both an a mild oxidant and a fluoride source led to the appearance of a new singlet at around -30 ppm in ^{19}F NMR. This might indicate the formation of a complex with two identical CF_3 groups. We managed to isolate the $(acac)Cu(CF_3)_2$ complex (**1a**) as a bright orange solid with a pungent odour by aqueous workup, extraction with dichloromethane and silica gel column chromatography. Copper (II) complex $Cu(acac)_2$ was observed as the only side-product in low amounts, which is significantly more polar and can be easily separated. Gratifyingly, the Cu(III) complex was found to be stable enough to the treatment with water and even rather acidic environment of silica gel. Also, it was stable on air and not moisture sensitive. Adjusting the reaction conditions showed that

a slight excess (1.03 equiv.) of ligand, 3 equiv. of $TMSCF_3$ and AgF was sufficient for the formation of $(acac)Cu(CF_3)_2$ (**1a**) in good yield. Complex **1a** was found to be slightly volatile and some sublimation of the compound when handled in vacuo was observed. To study the formation of Cu(III) trifluoromethyl diketonates, other 1,3-diketone ligands were tested (Scheme 2). The use of 1-phenyl-1,3-butandione afforded complex **1b** in good yield. Two close signals of different CF_3 groups were observed in ^{19}F NMR spectrum. An excellent result was achieved by using dibenzoylmethane (1,3-diphenyl-1,3-propandione, dbmH) to give nearly quantitative formation of a bench-stable bright red complex $(dbm)Cu(CF_3)_2$ (**1c**). The higher stability and yield of **1c** in comparison to **1a** or **1b** was attributed to the substitution of methyl groups containing reactive C-H bonds with less reactive phenyl groups. The complex **1d** with 3-phenyl-2,4-pentandione ligand also formed efficiently under standard conditions. Finally, dimesitylmethane (dmmH) afforded more bulky $(dmm)Cu(CF_3)_2$ (**1e**).



Scheme 2. Synthesis of Cu(III) trifluoromethyl complexes with 1,3-diketonate ligands. Reaction conditions: CuI (0.5 mmol), 1,3-diketone (0.515 mmol, 1.03 equiv.), AgF (1.5 mmol), $TMSCF_3$ (1.5 mmol) in DMF (3 ml) at rt for 10-15 min.

Apart from 1,3-diketones, we investigated the formation of Cu(III) complexes from other related oxygen donor bidentate ligands. 3-Acylpyrazolone was successfully applied to give complex **1f** as a pink solid. However, application of β-ketoester (ethyl acetoacetate) instead of 1,3-diketone led to unstable complex **1g**, which was isolated in a low yield. Thus, we believe that highly C-H acidic 1,3-dicarbonyl compounds which exist predominantly or exclusively in the enol form are efficient ligands for stabilization of the $Cu^{III}(CF_3)_2$ moiety. Using a slight excess (1.03 equiv.) of ligand gave the best results, while our attempts to prepare the complex $Cu(acac)_2CF_3$ using 1:2 metal to ligand ratio were unsuccessful.

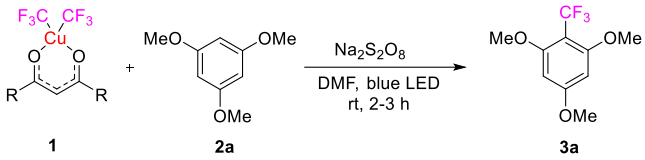
Importantly, the syntheses of **1** proceeded very quickly at ambient temperature, and complete conversion was observed after 10-15 min of stirring in all cases. Prolongation of the reaction time resulted in a gradual decomposition of the complexes as indicated by ^{19}F NMR. Thus, a quick filtration and work up was necessary to obtain high product yields. The purified complexes were relatively stable in a solid form when dry and can be stored at room temperature in air for months. Complexes **1** are excellently soluble in most organic solvents (DMF, MeCN, CH_2Cl_2, Et_2O, hexane) due to the presence of highly lipophilic CF_3 groups. They were characterized by ^1H, ^{13}C, ^{19}F NMR, UV-vis and IR spectroscopy and high-resolution mass spectrometry. It is worth mentioning that HRMS spectra in the negative ESI mode showed intensive peaks of $[M\text{-}CF_3]^-$, suggesting a high lability of the Cu-CF_3 bond even under soft ionisation conditions. The structure of the model compound **1c** was confirmed by X-ray crystal analysis (Scheme 2).[11] Copper (III) centre adopts a square-planar geometry with nearly identical two Cu-O (1.854(3) and 1.865(4) Å) and Cu-C (1.943(6) and 1.951(4) Å) bond lengths. Cu-C distances are even shorter than in $(bpy)Cu(CF_3)_3$ and $[Cu(CF_3)_4]^-$.

In contrast to the colourless $[Cu(CF_3)_4]^-$, complexes **1** are intensively coloured: orange (**1a**, **1g**), orange-red (**1b**), bright red (**1c-1e**) or pink (**1f**) solids. Their UV-vis absorbance spectra show intensive bands in the 300-400 nm region (see the Supporting information). Since the genuine square-planar d^8 Cu(III) complex with oxygen donor ligands $[Cu(HIO_6)_2]^{5-}$ absorbs at 416 nm,[12] these bands most likely correspond to the d-d transition of Cu(III). Hypsochromic shift of this band can be explained by strong Cu-C bonding with partially covalent character.[5]

With a scope of stable Cu(III) complexes in hand, we investigated their reactivity in C-H trifluoromethylation reactions. We hypothesized that using the visible light might cleave the Cu^{III}-CF_3 bond in **1** to produce the trifluoromethyl radical under very mild conditions. Thus, trifluoromethylation of electron-rich 1,3,5-trimethoxybenzene with complexes **1** under blue LED irradiation was attempted (Table 1). To our delight, the initial experiments (entries 1,2) showed the formation of target C-H trifluoromethylation product **3a** in the presence of $Na_2S_2O_8$. Our complexes **1** thus displayed reactivity compared to the Grushin's reagent $(bpy)Cu(CF_3)_3$ rather than unreactive anion $[Cu(CF_3)_4]^-$. DMF was found to be an applicable solvent for the trifluoromethylation, while other polar solvents such as DMSO and MeCN were inefficient (entries 3,4). With a 2-fold excess of arene, a 65% yield of **3a** was obtained (entry 5). Importantly, irradiation with the blue light (465 nm) was significantly more efficient than 385 nm LED (entry 6).[8d] Excellent yields (80% and 94% respectively) were obtained for 3-fold and 5-fold excess of arene (entries 7-8). Testing the reactivity of other Cu(III) 1,3-diketonates showed that acetylacetonate complex **1a** was the most reactive (full conversion in 30 minutes), but afforded the product in lower yield than **1c** (entry 9). More sterically hindered complex **1e** exhibited similar reactivity to **1c** and high product yield was obtained (entry 10). Finally, 3-acylpyrazolonate **1f** was the

least efficient of all tested copper (III) complexes in trifluoromethylation of trimethoxybenzene (entry 11).

Table 1. Trifluoromethylation of 1,3,5-trimethoxybenzene with Cu(III) diketonate complexes 1.[a]

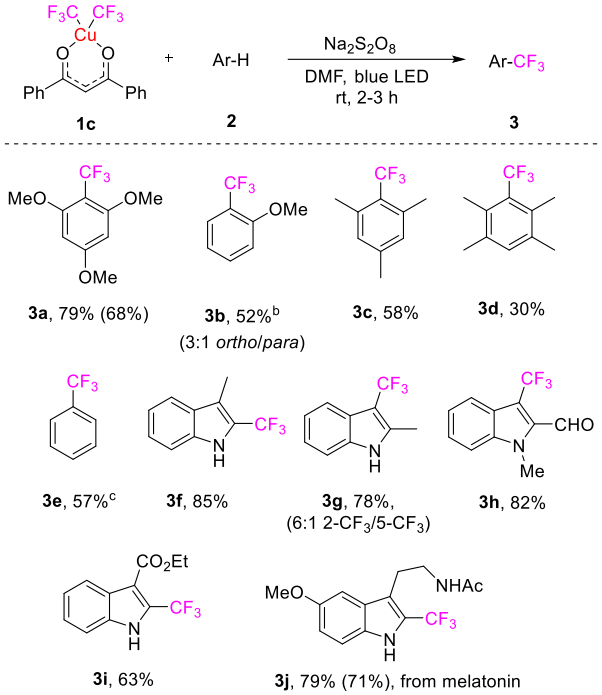


1 **2a** **3a**

Entry	**1**	**2a** (equiv.)	Solvent	Time (h)	Yield **3a** (%)[b]
1[c]	**1c**	1.0	DMF	2	34
2	**1c**	1.0	DMF	2	49
3	**1c**	1.0	DMSO	2	traces
4	**1c**	1.0	MeCN	2	traces
5	**1c**	2.0	DMF	2	65
6[d]	**1c**	2.0	DMF	7	44
7	**1c**	3.0	DMF	2	79
8	**1c**	5.0	DMF	2	94
9	**1a**	3.0	DMF	0.5	64
10	**1e**	3.0	DMF	2.5	80
11	**1f**	3.0	DMF	1.5	48

[a] Reaction conditions: **1** (0.05 mmol), **2a** (0.05-0.25 mmol, 1-5 equiv.) and $Na_2S_2O_8$ (0.15 mmol, 3 equiv.) in solvent (0.5 ml) irradiated with 4 W blue LED (455-475 nm) at rt. [b] Yields were determined by ^{19}F NMR with $PhCF_3$ as an internal standard. [c] $Na_2S_2O_8$ (2 equiv.). [d] Using blue LED (385 nm).

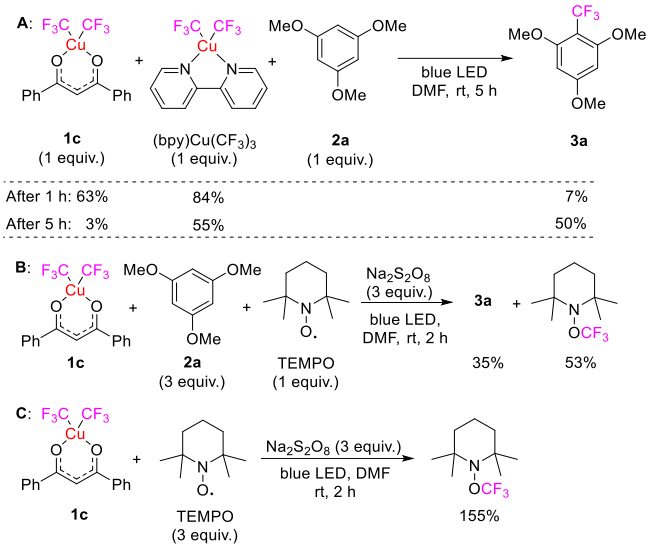
Under the standard conditions (entry 7), the reactivity of **1c** in arene C-H trifluoromethylation was studied (Scheme 3). Thus, electron-rich-substituted benzene rings (anisole, mesitylene and durene) smoothly afforded mono-trifluoromethylation products **3a-d**. Also, benzene can be successfully trifluoromethylated when a higher **2**/**1c** ratio was used. Moreover, we found that the Cu(III)-mediated C-H trifluoromethylation is especially efficient for indoles. Skatole and 2-methylindole afforded products **3f** and **3g**, respectively, in high yields. Additionally, formyl and alkoxycarbonyl functional groups were well tolerated (products **3h** and **3i**). Finally, it was demonstrated that (dbm)$Cu(CF_3)_2$ (**1c**) can be efficiently applied for the late-stage functionalization of natural antioxidant melatonin, also known as the "sleep hormone" (product **3j**).



Scheme 3. Trifluoromethylation of arenes and indoles with **1c**. Reaction conditions: **1c** (0.05 mmol), ArH (3 equiv.), $Na_2S_2O_8$ (3 equiv.) in DMF (0.5 ml), 4 W blue LED (455-475 nm), rt, 2-3 h. Yields were determined by ^{19}F NMR using $PhCF_3$ (for **3e** using 5-fluoro-2-nitrotrifluoromethylbenzene) as an internal standard, isolated yields are shown in parentheses. [b] ArH (5 equiv.). [c] ArH (10 equiv.).

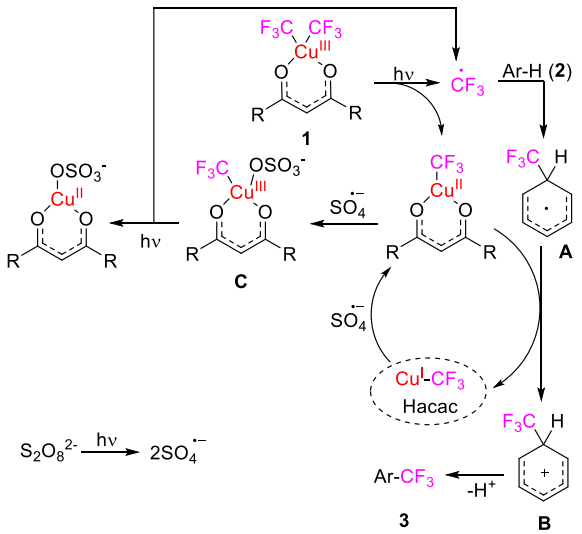
To compare the reactivity of model Cu(III) trifluoromethyl diketonate **1c** and the Grushin's bpy reagent, a competition experiment of trifluoromethylation of trimethoxybenzene **2a** with equimolar mixture of both complexes under blue light irradiation was carried out (Scheme 4A). ^{19}F NMR monitoring of the reaction mixture confirmed a much faster consumption of **1c**, which indicated its significantly higher reactivity compared to the Grushin's reagent. Thus, after 5 hours of irradiation nearly all of the diketonate was consumed, while more than half of (bpy)$Cu(CF_3)_3$ remained intact. This can be likely attributed to a weaker coordination of oxygen donor ligand to Cu(III) (and therefore higher charge on the copper atom facilitating homolytic cleavage of the Cu-CF_3 bond) compared to nitrogen donor atoms.

To confirm the radical reaction mechanism of the transformation, a control experiment with the addition of TEMPO was performed (Scheme 4B). Indeed, the formation of the TEMPO-CF_3 adduct was observed. The yield of **3a** was reduced, but the reaction was not suppressed completely. We hypothesized that the trifluoromethyl radical can be formed in over-stoichiometric amount in the presence of additional oxidant such as $Na_2S_2O_8$, since two CF_3 groups are present in one molecule of **1c**. Indeed, the complex was shown to easily trifluoromethylate TEMPO under the same conditions ($Na_2S_2O_8$, blue LED) in 155% yield based on Cu(III) (Scheme 4C).



Scheme 4. Competition and control experiments. Yields were determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

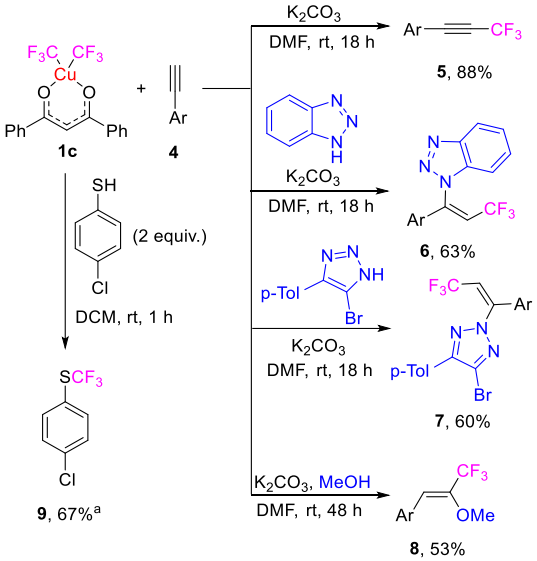
Based on the conducted experiments, the following reaction mechanism was proposed (Scheme 5). Excitation of complex **1** with a blue light caused the cleavage of the Cu-CF_3 bond to form CF_3 radical and Cu(II). Since trifluoromethyl radical is highly electrophilic, it undergoes addition to arene to form radical **A**. However, the CF_3 group transfer between complex **1** and arene **2** via intermediate formation of charge-transfer complexes cannot be excluded as well. The radical **A** can be oxidized by the formed Cu(II) species to the cation **B**, which after the loss of proton gives trifluoromethylated arene **3**. Thus, the mechanism can be considered as a radical-polar crossover, since the starting complex **1** acts as both the CF_3 radical source and an oxidant.[8j] In the presence of persulfate, the formed SO_4 radical anion can also play the role of an oxidant. Moreover, this radical anion can undergo a rebound to the formed Cu(II) complex with the regeneration of Cu(III) complex **C** bearing another CF_3 group. The second CF_3 radical can be released from this complex upon irradiation.



Scheme 5. Proposed mechanism of C-H trifluoromethylation of arenes.

Not only arenes but also terminal alkynes **4** can be easily trifluoromethylated at room temperature in the presence of K_2CO_3 to give trifluoromethylated alkyne **5** in high yield (Scheme 5). Conducting the same experiment in the presence of benzotriazole afforded *syn*-azolotrifluoromethylated product **6** as N1-isomer in good yield. Substituting benzotriazole with bulky 5-bromo-4-aryl-1,2,3-NH-triazole[13] led to the selective formation of N2-isomer **7**. Unsubstituted 1,2,3-NH-triazole afforded a 3:1 mixture of N1- and N2-products (see SI for full details). To the best of our knowledge, a one-pot azolotrifluoromethylation of alkynes is unknown. Also, N-vinyltriazoles are rare compounds[14] which are of potential interest for polymer chemistry.[15] Interestingly, conducting the alkyne trifluoromethylation in the presence of methanol afforded oxytrifluoromethylation product **8**. This can be explained by the addition of methylate anion to the carbon centre next to the CF_3 group after the initial formation of **5**. This result is remarkably different from the literature report, where the utilization of $(bpy)Cu(CF_3)_3$ in the presence of phenols afforded 1,2-oxytrifluoromethylation.[8e] Further studies on alkyne difunctionalization with Cu(III) trifluoromethyl complexes and regioselectivity of these transformations using Cu(III) reagents are ongoing.

Apart from C-H trifluoromethylation, we found that complex **1c** can induce *S*-trifluoromethylation. For the representative example, 4-chlorothiophenol was smoothly trifluoromethylated by $(dbm)Cu(CF_3)_2$ in mild conditions (Scheme 6). The reactivity of Cu(III) complex resembles the widely applied hypervalent iodine-based Togni's reagent.[16] Importantly, no activation with light was required for both alkyne and thiol trifluoromethylation.



Scheme 6 Trifluoromethylation and difunctionalization of an alkyne (Ar = 4-bromophenyl) and thiophenol derivative with **1c**. Isolated yields. [a] ^{19}F NMR yield.

In conclusion, stable Cu(III) complexes with 1,3-diketonate ligands were synthesized for the first time. Attractive applicability of these complexes in radical C-H trifluoromethylation of arenes and difunctionalization of alkynes was demonstrated. The presented complexes displayed higher reactivities, compared to known nitrogen donor-substituted Cu(III) species. This study

opens new possibilities in high-valent copper chemistry, as well as in C-H trifluoromethylation reactions.

Acknowledgements

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Conflict of Interest

Czech patent application (PV 2023-140) containing findings of this report was submitted on April 12, 2023.

Keywords: Copper • High-valent copper • Trifluoromethylation • C-H activation • 1,3-diketonates

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[11] Deposition number 2250467 (for **1c**), contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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