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Copper(III) trifluoromethyl tris(pyrazolyl)borates

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The first scorpionate complexes of high-valent copper(III) $\text{TpCu}(\text{CF}_3)_2$ and $\text{Tp}^*\text{Cu}(\text{CF}_3)_2$ were synthesized by a ligand exchange reaction of the acetylacetonate complex $(\text{acac})\text{Cu}(\text{CF}_3)_2$ and fully characterized. The structure, effective oxidation state of copper, natural charge distribution and photochemical properties of these compounds were studied by DFT calculations. The presence of copper in the +3 oxidation state was supported by XPS spectroscopy. $\text{TpCu}(\text{CF}_3)_2$ is a bench-stable solid and exhibits high reactivity in trifluoromethylation of uracil derivatives under photochemical conditions.

Introduction

Stabilization of copper in the high oxidation state (+3) represents a fundamental challenge,¹ essential for advancing the understanding of crucial enzymatic processes,^{1a,b} aerobic oxidation,^{1b,c} catalysis,^{1d} and cross-coupling reactions.^{1e,f} Tris(pyrazolyl)borate (Tp^x) ligands are some of the most widely utilized tridentate anionic ligands in coordination chemistry.² Their metal complexes are characterized by remarkable stability and low toxicity and find broad applications in catalysis and bioinorganic chemistry.² Group 11 metal complexes with tris(pyrazolyl)borates and their analogues, namely tripodal ligands, are useful catalysts in nitrene and carbene transfer processes.³ While $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ complexes with tripodal ligands are well-documented and find broad applications,^{2,4} there have been no reports to date on high-valent $\text{Cu}(\text{III})$ complexes. Recently, tris(pyrazolyl)borates have been applied as ligands for stabilization of high-valent $\text{Ni}(\text{III})$ and $\text{Ni}(\text{IV})$ trifluoromethyl complexes of octahedral geometry (Fig. 1).⁵ Apart from the tripodal ligands, the trifluoromethyl group is able to stabilize high-valent metal species.⁶ The homoleptic anion $[\text{Cu}(\text{CF}_3)_4]^-$ and $\text{Cu}(\text{III})$ tris(trifluoromethyl) complexes with additional nitrogen ligands, accessible by oxygen or AgF oxidation of $\text{Cu}(\text{I})$ species, are the most studied.⁷ In recent years, highly stable $\text{Cu}(\text{III})$ 1,3-diketones,⁸ $\text{Cu}(\text{CF}_3)_3$ solvates,⁹ $\text{Cu}(\text{III})$ hydroxide tetramer,¹⁰ fluoride,¹¹ and pincer¹² complexes were described. In addition to the exceptional fundamental interest, high-valent copper(III) trifluoromethyl complexes find applications in the trifluoromethylation of (arene) C–H bonds,¹³ alkenes,¹⁴ alkynes,¹⁵ and unactivated alkanes.¹⁶ Herein, the first well-defined $\text{Cu}(\text{III})$ tris(pyrazolyl)borate complex is reported, with a comprehensive analysis of its structure, oxidation state, and photochemical reactivity (Fig. 1).

Results and discussion

The studies were initiated with the synthesis of a neutral tris(pyrazolyl)borate copper(III) complex, which would have a composition of $\text{TpCu}(\text{CF}_3)_2$, if the most relevant coordination number (C.N.) of five for square-pyramidal $\text{Cu}(\text{III})$ is realized. Since the substitution of oxygen-coordinated auxiliary ligands is much easier than that of almost covalently bonded trifluoromethyl groups, the substitution of the ligand in acetylacetonate complex **1** with potassium tris(pyrazolyl)borate was attempted. Gratifyingly, a simple reaction of acetylacetonate $(\text{acac})\text{Cu}(\text{CF}_3)_2$ (ref. 8) with commercially available potassium tris(pyrazolyl)borate KTP in acetonitrile resulted in the formation of a target complex **3** and precipitation of potassium acetylacetonate as a by-product, which can be completely separated by simple filtration. Alternatively, one-pot preparation of **3** from the tetrameric copper(III) hydroxide **2**,¹⁰ more easily accessible than acetylacetonate **1**,⁸ was realized. In this case, $(\text{acac})\text{Cu}(\text{CF}_3)_2$ was formed *in situ* by treatment of **2** with acetylacetone, which was then subjected to substitution with KTP to smoothly generate the target complex in 97% total yield (Scheme 1).

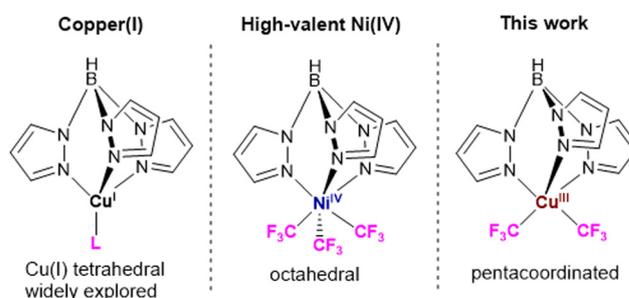
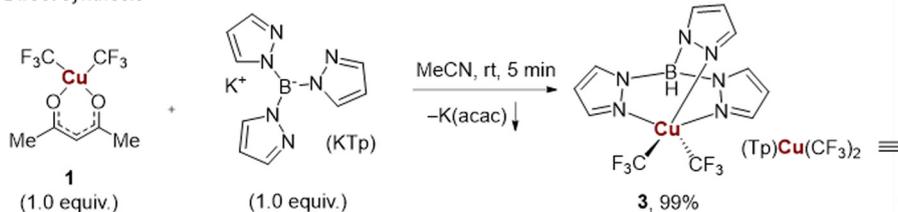


Fig. 1 Common copper tris(pyrazolyl)borate complexes, high-valent Ni(IV) species, and this work.

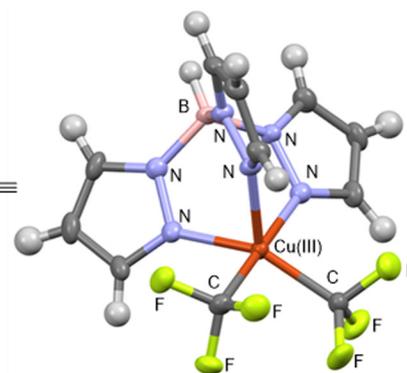
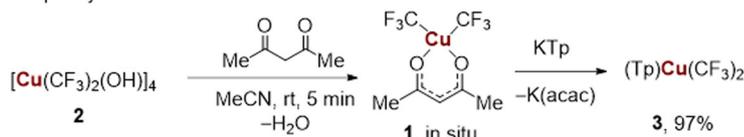
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Direct synthesis



One-pot synthesis

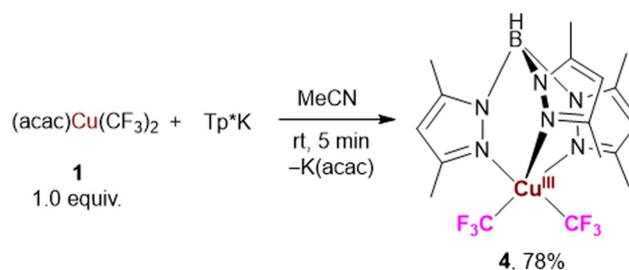


X-ray crystal structure of 3

Scheme 1 Synthesis of copper(III) tris(pyrazolyl)borate 3 (left) and its crystal structure (right). CCDC 2497753. Thermal ellipsoids are shown at 50% probability.

The X-ray crystal structure of 3 revealed a pentacoordinate geometry between square pyramidal and trigonal bipyramidal units ($\tau_5 = 0.46$) (Scheme 1, right). Two Cu–N bond distances (1.955(5) and 1.973(5) Å) are significantly shorter than that to the third nitrogen atom with weaker bonding (Cu–N = 2.166(4) Å). To study the electronic structure and predict the possible behavior, DFT calculations were performed (Fig. 2). The HOMO of complex 3 is centered entirely on a scorpionate ligand, whereas the LUMO is centered along the Cu–C σ -bonds, which makes it an antibonding σ^* (Cu–CF₃) orbital. The natural charge (NPA) of a high-valent copper atom is 1.127 according to the natural bonding orbital (NBO) analysis, which is higher than those reported for high-valent copper complexes with three and four CF₃ groups.^{7a,9} Thus, the positive charge is shared between the copper center and two adjacent carbon atoms (NPA 0.829 and 0.768) of CF₃ groups. Apart from the unsubstituted Tp ligand, the formation of a similar complex with tris(3,5-dimethylpyrazolyl)borate (Tp* ligand) was tested.

Gratifyingly, the ligand substitution in acetylacetonate 1 proceeded smoothly as well, with complex 4 being formed in 78% yield (Scheme 2). It was found to be slightly less stable than its unsubstituted counterpart as some decomposition side-products were observed.



Scheme 2 Synthesis of copper(III) tris(3,5-dimethylpyrazolyl)borate 4 Tp*Cu(CF₃)₂.

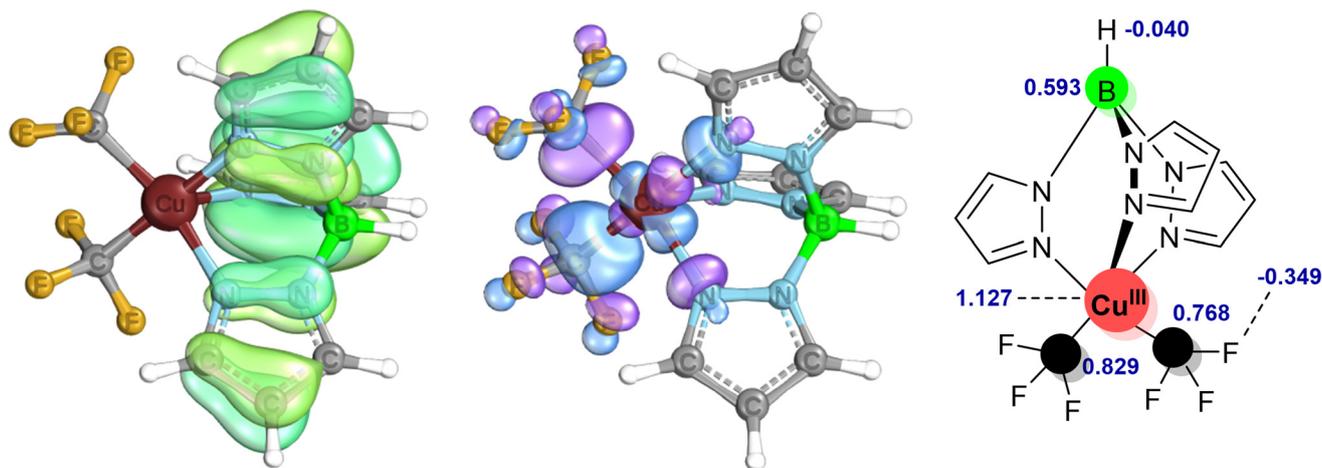


Fig. 2 Frontier orbitals of TpCu(CF₃)₂ (HOMO – left and LUMO – center) and its natural charge distribution (right). Minimum structures (ω B97X-D3 (BJ)/def2-QZVPPD//B3LYP-D3(BJ)/ZORA-def2-TZVP) with blue numbers corresponding to the NPA charges.



DFT calculations revealed that the coordination of the Cu(CF₃)₂ moiety with the apical nitrogen atom is weaker in the presence of a bulky ligand, according to the apical Cu–N distance of 2.320 Å in complex **4** compared to 2.224 Å calculated for complex **3**. In contrast, the two equatorial distances of 2.012 and 1.983 Å are slightly shorter than those (2.025 and 2.006 Å) in **3**.

With two scorpionate complexes prepared, the physical oxidation state in these compounds was studied. Due to the covalency of the Cu–C bond in these compounds and the predominantly ligand-centered frontier orbitals, a lower effective oxidation state of copper than +3 can be assigned, which is also reflected in the computed orbital population 4s(0.45)3d(9.39) for copper in this compound. Notably, the ligand-centered HOMO and the 39% Cu(3d) character of the LUMO also support the inverted ligand field character of the complexes **3** and **4**, similar to that of other organometallic formally Cu(III) species which were described as Cu(I) by some researchers.^{6b–d} However, re-evaluation of this statement using XAS¹⁷ spectroscopic data points to a more ambiguous assignment. To further investigate the oxidation state situation in this complex, the recently developed effective oxidation state analysis¹⁸ and even more robust oxidation state localized orbitals (OSLO)¹⁹ methods were tried to assess the oxidation state of copper in TpCu(CF₃)₂. Accordingly, EOS points to the Cu (+1) assignment though with a low R confidence value of 50.2%, whereas the OSLO method supports the assignment of the +3 oxidation state for copper. There are four filled low-lying orbitals below the HOMO with clearly metal-centered character (see the SI for details), whereas other orbitals in this range are mixed with predominantly ligand-centered character, which, therefore, do not contribute to the total electron count in the “winner-takes-all” OSLO model. Thus, according to DFT studies, the clear assignment of the oxidation state in Cu–CF₃ complexes is ambiguous, which is consistent with the previous findings.^{9,19}

For the more apparent support of the +3 oxidation state of copper in these scorpionate complexes, they were characterized by X-ray photoelectron spectroscopy (Fig. 3). The binding

energy of Cu 2p_{3/2} was found to be 936.2 eV for TpCu(CF₃)₂ (**3**) and 936.9 eV for Tp*Cu(CF₃)₂ (**4**), which excellently match the literature report, where the binding energy of 936.7 eV for a macrocyclic copper(III) complex, *ca.* 2 eV higher than that of the respective Cu(II) species, was established.^{1f} The binding energies of Cu 2p_{1/2} are in the 956–957 eV range. The XPS results also corroborate the characteristics of the inorganic cuprate(III) species and coordination compounds of high-valent copper, devoid of covalent copper–carbon bonds.²⁰

Based on the insights into the synthesis, structure, and oxidation state of novel copper(III) tris(pyrazolyl)borates, the experimental photochemical reactivity in trifluoromethylation of organic molecules was investigated. Oxidative functionalization of arenes by high-valent copper species is of special fundamental interest.^{1f,13} The most user-friendly blue visible light (420 nm LED) irradiation was chosen, and uracil was used as a highly pharmaceutically relevant substrate for trifluoromethylation. First, various known Cu(III)–CF₃ sources were tested and their reactivity was compared to that of complex **3**. To our delight, 86% NMR yield was achieved when 0.5 equiv. of **3** was used, indicating that both CF₃ groups are transferred into the organic molecule. This fact makes the complex advantageous compared to known Grushin’s reagent and 1,3-diketones, which demonstrated only moderate reactivity under the same conditions (Table 1).

With the superior reactivity compared to the known Cu(III) trifluoromethyl complexes established, the substrate scope of trifluoromethylation of various uracil derivatives was studied (Scheme 3). Thus, *N*-monomethyl and *N,N*-dimethyluracil were successfully trifluoromethylated under standard stoichiometric conditions (products **6–7**). Moreover, the 6-methyluracil, known as nucleobase surrogate pseudothymine, afforded the product **8** in good yield. The CH₂OH group of 6-hydroxymethyluracil and the ester group of methyl orotate were excellently tolerated as well (products **9–10**). Another nucleobase surrogate azauracil, known for its anticancer properties, was smoothly trifluoromethylated to obtain the compound **11**. Finally, late-stage functionalization of more complex nucleosides, such as uridine triacetate (product **12**) and deoxyuridine (product **13**), was proved to be achievable with the Cu(III) complex. Apart from the complex molecules, we have shown that simple arenes such as trimethoxybenzene and unsubstituted benzene can be successfully trifluoromethylated (products **14–15**), while the only limitation was found for more electron-deficient trichlorobenzene. This matches the electrophilic behaviour of trifluoromethyl radicals in direct trifluoromethylation reactions.¹³ The radical mechanism of this transformation was supported by the TEMPO radical trapping experiment, detecting the TEMPO–CF₃ adduct (see SI for details). Overall, these applications support high relevance of complex **3** for late-stage functionalization of complex molecules under mild visible light-mediated photochemical conditions.

To rationalize the photochemical behaviour of complex **3**, the excited state behaviour of complex **3** was investigated by time-dependent density functional theory (TDDFT) at the ωB97X-D3(BJ)/def2-QZVPPD//B3LYP-D3(BJ)/ZORA-def2-

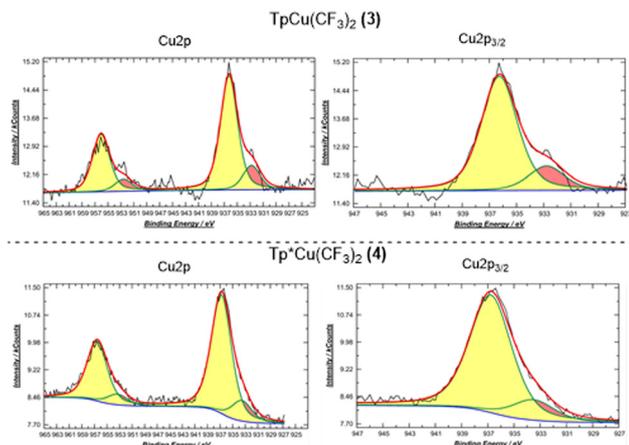
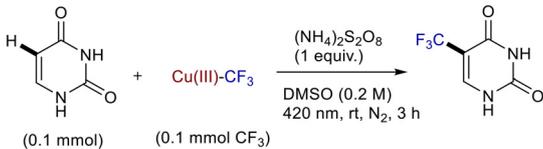


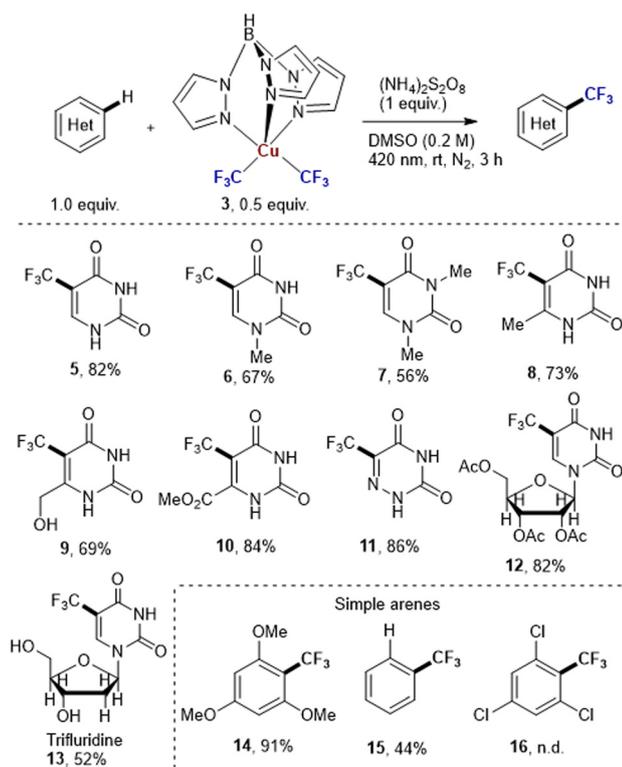
Fig. 3 XPS spectra of Cu2p for copper(III) scorpionates **3** and **4**.



Table 1 Comparison of copper(III) sources in trifluoromethylation of uracil under 420 nm irradiation. Standard conditions: uracil (11.2 mg, 0.1 mmol), Cu(III)-CF₃ reagent (0.1 mmol CF₃), (NH₄)₂S₂O₈ (1.0 equiv.), DMSO (0.5 ml), 420 nm LED, and 3 h. Yields were determined by ¹⁹F NMR using C₆F₆ as an internal standard



Entry	Cu(III) species (1 : 1 CF ₃ : substrate)	Deviation from the standard conditions	Yield, % (¹⁹ F NMR)
1	TpCu(CF ₃) ₂ (0.5 equiv.)	None	86
2	Tp*Cu(CF ₃) ₂ (0.5 equiv.)	None	24
2	(bpy)Cu(CF ₃) ₃ (0.33 equiv.)	None	46
3	(phen)Cu(CF ₃) ₃ (0.33 equiv.)	None	44
4	(DMF) ₂ Cu(CF ₃) ₃ (0.33 equiv.)	None	48
5	(dbm)Cu(CF ₃) ₂ (0.5 equiv.)	None	62
6	TpCu(CF ₃) ₂ (0.5 equiv.)	Without (NH ₄) ₂ S ₂ O ₈	<10
7	TpCu(CF ₃) ₂ (0.5 equiv.)	MeCN as a solvent	51
8	TpCu(CF ₃) ₂ (0.5 equiv.)	DMF as a solvent	58



Scheme 3 Applications of complex **3** for substoichiometric trifluoromethylation of (hetero)arenes.

TZVP level of theory. The first singlet excitation ($S_0 \rightarrow S_1$), dominated by excitations from three ligand-centered orbitals of energy below the HOMO, close to each other by energy, to the antibonding $\sigma-\sigma^*$ (Cu-CF₃) LUMO, occurs at 438 nm wavelength. However, no visible bands were observed for this complex in the UV/vis spectrum (see SI for details), in contrast to known high-valent copper trifluoromethyl species.⁷⁻⁹ This is supported by a very low computed oscillator strength value of

this transition ($f < 0.01$). Therefore, triplet states, which can be populated *via* weak singlet excitation followed by quick intersystem crossing (ISC), were calculated. The $T_1 \rightarrow T_4$ forbidden transition from metal-centered low-lying²¹ orbitals to the LUMO with an energy of 3.073 eV ($\lambda = 403$ nm) appeared to be the $\sigma-\sigma^*$ (Cu-CF₃) transition responsible for the photochemical bond cleavage. An attempt of the geometry optimization of **3** in a triplet state resulted in Cu-CF₃ bond dissociation, which is experimentally observed under photochemical conditions.

Experimental

Synthesis of TpCu(CF₃)₂ (**3**) from (acac)Cu(CF₃)₂

To the solution of (acac)Cu(CF₃)₂ (150 mg, 0.5 mmol) in dry acetonitrile (2 ml), a freshly prepared solution of KTp (126 mg, 0.5 mmol) in dry acetonitrile (2 ml) was added dropwise at room temperature with vigorous stirring. The orange-red color of the solution turned dark yellow and a precipitate formed. The mixture was diluted with 10 ml of dichloromethane and stirred for 5 minutes, then the precipitate of potassium acetylacetonate was filtered off. The filtrate was evaporated and dried under high vacuum to obtain pure TpCu(CF₃)₂ (206 mg, 99%) as a bright yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 3H, H3/H5), 7.66 (s, 3H, H3/H5), 6.24 (s, 3H, H4). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 141.1 (C3/C5), 135.4 (C3/C5), 105.4 (C4). ¹⁹F NMR (376 MHz, CDCl₃) δ -23.0 (s). ¹¹B NMR (129 MHz, CDCl₃) δ -4.04 (d, $J = 114.7$ Hz); IR (ATR): $\tilde{\nu} = 2965, 2919, 1502, 1410, 1090, 1070, 1049, 945, 763, 716$ cm⁻¹; Elem. Anal. calcd for C₁₁H₁₀BCuF₆N₆: 31.87% C, 2.43% H; found: 31.97% C, 2.15% H. CCDC 2497753.

Synthesis of Tp*Cu(CF₃)₂ (**4**) from (acac)Cu(CF₃)₂

To the stirred solution of (acac)Cu(CF₃)₂ (90 mg, 0.3 mmol) in dry acetonitrile (2 ml), a freshly prepared solution of potass-



ium tris(3,5-dimethylpyrazolyl)borate (KTP*) (100 mg, 0.3 mmol) in dry acetonitrile (1 ml) was added dropwise at room temperature. The orange-red color of the solution turned dark yellow and a precipitate formed. The mixture was diluted with 5 ml of dichloromethane and stirred for 5 minutes, then the precipitate of potassium acetylacetonate was filtered off. The filtrate was evaporated and the crude product was purified by column chromatography (pentane/DCM 5:1) to obtain $\text{Tp}^*\text{Cu}(\text{CF}_3)_2$ **4** (116 mg, 78%) as a bright yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.77 (s, 3H, H4(pyrazole)), 2.35 (s, 6H, Me), 2.34 (s, 12H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 150.0 ($\text{C}_{\text{pyrazole}}$), 145.2 ($\text{C}_{\text{pyrazole}}$), 107.0 ($\text{C}_4_{\text{pyrazole}}$), 14.1 (Me), 12.9 (2Me). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -20.8 (s). $^{11}\text{B NMR}$ (129 MHz, CDCl_3) δ -9.01 (d, $J = 102.7$ Hz); IR (ATR): $\tilde{\nu} = 2936, 2855, 2551, 1550, 1450, 1389, 1078, 953, 782, 718$ cm^{-1} . Elem. Anal. calcd for $\text{C}_{17}\text{H}_{22}\text{BCuF}_6\text{N}_6$: 40.94% C, 4.45% H, found: 40.63% C, 4.80% H.

General procedure for trifluoromethylation of uracils

To a solid mixture of **3** (21 mg, 0.05 mmol, 0.5 equiv.), ammonium persulfate (23 mg, 0.1 mmol, 1.0 equiv.) and a (hetero)arene (0.1 mmol, 1 equiv.) DMSO (1 ml) was added under argon (for liquid arenes, they were added as a solution in DMSO). The mixture was irradiated with a 420 nm LED (30 W) for 3 hours. Then it was exposed to air, and hexafluorobenzene was added as a standard to measure the $^{19}\text{F NMR}$ yield. Afterwards, the mixture was quenched with EtOAc/water (10 + 5 ml) and the aqueous layer was washed twice with EtOAc. The combined organic layer was evaporated and the crude products were purified by column chromatography on silica gel (DCM/EtOAc as an eluent).

Conclusions

In conclusion, the new high-valent Cu(III) complexes stabilized by tris(pyrazolyl)borate ligands were synthesized. The structures and effective oxidation states of these complexes were studied using DFT calculations. The presence of the high-valent copper(III) in these compounds is supported by XPS spectroscopy. The synthetic relevance of this compound for C-CF₃ bond formation was demonstrated, including the trifluoromethylation of medicinally relevant uracil derivatives. The triplet state process is responsible for the $\sigma-\sigma^*$ ($\text{Cu}-\text{CF}_3$) excitation as confirmed by DFT calculations.

Author contributions

V. Motornov conceived an idea, led the project, acquired the funding, conducted the experiments and calculations, and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

All experimental data are available in the supplementary information (SI). Supplementary information, including full experimental, computational and crystallographic details is available. See DOI: <https://doi.org/10.1039/d6qi00184j>.

CCDC 2497753 contains the supplementary crystallographic data for this paper.²²

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