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Unraveling the mechanism of trifluoromethyl group transfer from Cu(I) to Cu(III)

Yifa Yang[a,1], Sheng-Ye Zhang[b,1], Yongrui Luo[a], Jian Wu[c], Xuebing Leng[b], Qilong Shen[a,*]

[a] State Key Laboratory of Fluorine and Nitrogen Chemistry and Advanced Materials, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China
[c] Instrumental Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

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ABSTRACT

Mechanistic studies of the transmetalation of the trifluoromethyl group from an ionic Cu(I) complex $Q^+[Cu(CF_3)_2]^-$ to a well-defined chlorinated Cu(III) complex *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ was reported. The combined experimental and computational results including kinetics of the process, reactions in the presence of excess chloride salt, or radical scavengers such as TEMPO or 1,1-diphenylethene (DPE), 1,4-dinitrobenzene (DNB), strongly support a concerted metathesis pathway.

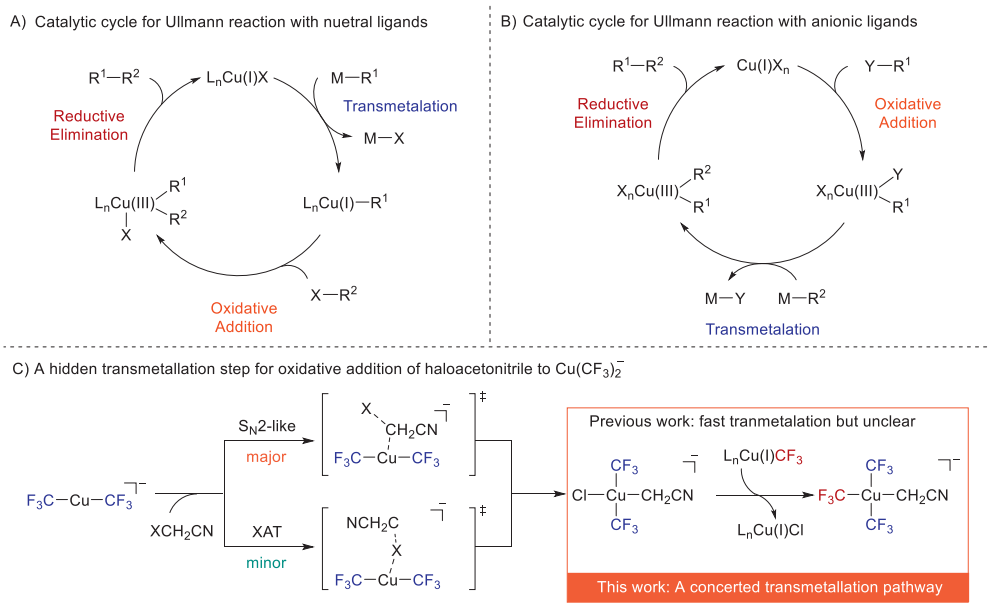
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Copper, a versatile coinage metal, continues to drive innovations in synthetic methodologies, ranging from classic Ullmann [1–4] and Chan-Evans-Lam [5–7] couplings to modern asymmetric reactions [8–16]. While its unparalleled capacity to forge carbon-carbon and carbon-heteroatom bonds is widely acknowledged [17,18], the mechanistic intricacies of copper-mediated processes persist as subjects of intense debate (Schemes 1A and B) [19–23]. A simplified catalytic cycle comprises three elementary steps: oxidative addition [24], transmetalation [25,26], and reductive elimination [27]. However, despite having various Cu(III) complexes known [28–33], details of the transformation of the copper species in the Cu(I)/Cu(III) redox pair were difficult to trace. Current mechanistic studies have largely focused on oxidative addition [34–40] and reductive elimination [38,41–51], where trifluoromethyl groups act both as coupling partners and stabilizing ligands for high-valent copper species. These studies have systematically mapped the reactivity of trifluoromethyl-copper(I/III) complexes under various activation strategies. Paradoxically, transmetalation, a pivotal step that delivers two functional groups from different coupling partners to the key Cu(III) intermediate for the subsequent product-forming reductive elimination [50,51], has been surprisingly overlooked, despite extensive studies on Pd [52,53], Ni [54–57], and other transition metals [53,58,59].

In 2023, our group disclosed the oxidative addition of haloacetonitrile (XCH_2CN; X = Cl, Br, I) to the ionic Cu(I) complex $Q^+[Cu(CF_3)_2]^-$ (Q = Ph_4P) [39], marking a key advancement in understanding high-valent copper reactivity. This transformation proceeded through the generation of a highly reactive Cu(III) intermediate, *trans*-$[Cu(CF_3)_2(X)(CH_2CN)]^-Q^+$, which subsequently participated in rapid transmetalation with a second equivalent of $Q^+[Cu(CF_3)_2]^-$ to afford the stable, fully substituted Cu(III) product $Q^+[Cu(CF_3)_3(CH_2CN)]^-$. Kinetic studies suggested that this transmetalation step occurred significantly faster than the initial oxidative addition, implying a low barrier for trifluoromethyl group transfer between copper centers in different oxidation states (Scheme 1C). Despite these advances, the fundamental mechanism of this transmetalation process remains unresolved. In particular, the precise pathway by which the trifluoromethyl group migrates from the anionic Cu(I) species $[Cu(CF_3)_2]^-$ to the Cu(III) intermediate *trans*-$[Cu(CF_3)_2(X)(CH_2CN)]^-$ has not been elucidated, primarily due to the inability to isolate or spectroscopically characterize the key halogenated intermediate *trans*-$[Cu(CF_3)_2(X)(CH_2CN)]^-Q^+$. Herein, we describe the successful isolation and structural characterization of the pivotal halogenated Cu(III) intermediate *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$,

* Corresponding author.
E-mail address: shenql@mail.sioc.ac.cn (Q. Shen).
[1] These authors contributed equally to this work.

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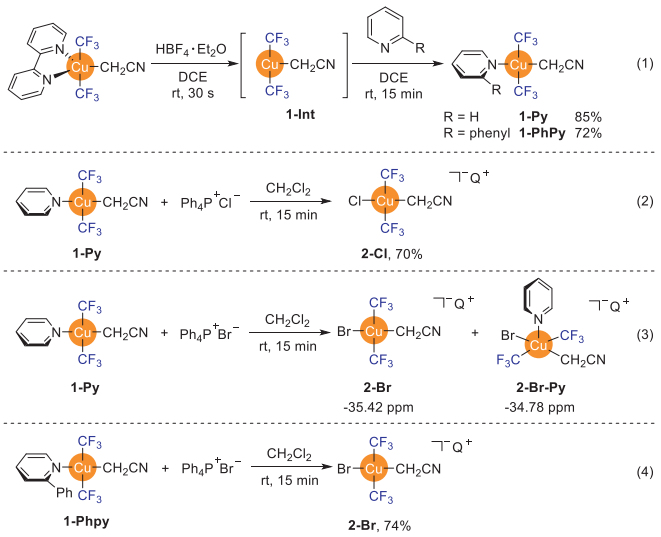


Scheme 1. Transmetalation in copper-mediated coupling reaction.

enabling direct mechanistic investigation of its transmetalation with $Q^+[Cu(CF_3)_2]^-$ (Scheme 1C). These findings provide unprecedented experimental evidence for the proposed Cu(I)-to-Cu(III) transmetalation pathway, resolving long-standing uncertainties in copper-mediated trifluoromethylation reactions.

Previous studies by Nebra and coworkers demonstrated that neutral, pyridine-ligated Cu(III) complexes could be converted to stable ionic species through ligand exchange [50]. Specifically, they observed that $[(Py)Cu(CF_3)_3]$ reacted with $Ph_4P^+Cl^-$ to form the isolable five-coordinate ionic complex $Q^+[Cu(CF_3)_3(Cl)(Py)]^-$. Subsequent treatment with AgF led to the formation of $Q^+[Cu(CF_3)_3(F)]^-$, demonstrating halide exchange at the Cu(III) center. In parallel work, our group showed that $[(Py)Cu(CF_3)_3]$ reacted with Me_4NF in THF/CH_3CN to produce $Me_4N^+[Cu(CF_3)_3(F)]^-$ (64% yield, 10 min, room temperature), with complete pyridine displacement [51]. These precedents established that the pyridine ligand in neutral four-coordinate Cu(III)-CF_3 complexes could be directly or indirectly replaced by a halogen anion. Building on these insights, we envisioned that synthesizing a related acetonitrile-derived analogue, *trans*-$[(Py)Cu(CF_3)_2(CH_2CN)]$ **1-Py**, might enable access to our target intermediate *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ through analogous anion metathesis.

Our initial attempt to synthesize **1-Py** by direct oxidative addition of ICH_2CN to $Q^+[Cu(CF_3)_2]^-$ in the presence of pyridine, generating a few unisolable species. Instead, employing 2,2′-bipyridine as alternative ligand generated *trans*-$[(bpy)Cu(CF_3)_2(CH_2CN)]$ in 84% yield [39]. In addition, treatment of *trans*-$[(bpy)Cu(CF_3)_2(CH_2CN)]$ with $Ph_4P^+Cl^-$ in dichloromethane for 1 h at room temperature did not generate the target *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ **2-Cl**. Notably, when *trans*-$[(bpy)Cu(CF_3)_2(CH_2CN)]$ was treated with 3.0 equiv. of $HBF_4{\cdot}Et_2O$ in 1,2-dichloroethane (DCE), an immediate reaction occurred within 30 s, producing two distinct changes: (1) Formation of a white precipitate identified as bpy·2HBF_4, and (2) complete disappearance of the original resonance at −39.4 ppm in ^{19}F NMR spectroscopy with concurrent appearance of a new signal at −34.6 ppm [60]. We attributed this new signal to the formation of a ligandless dimeric Cu(III) intermediate, $[Cu(CF_3)_2(CH_2CN)]_2$ (Scheme 2, Eq. 1). This assignment was unequivocally confirmed when rapid filtration and subsequent addition of 1.0 equiv. of bpy quantitatively regenerated the original signal at −39.4 ppm in 95% yield, demonstrating the reversible nature of this decomplexation/ligation process.



Scheme 2. Preparation of *trans*-$[Cu(CF_3)_2(X)(CH_2CN)]^-Q^+$ (X = Cl, **2-Cl** or Br, **2-Br**).

Subsequent addition of 1.0 equiv. of $Ph_4P^+Cl^-$ to the DCE solution did generate the desired ionic Cu(III) complex *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ **2-Cl** in 55% yield, as evidenced by the appearance of a new signal −34.5 ppm in the ^{19}F NMR spectroscopy (Fig. S4 in Supporting information for details). Nevertheless, the presence of HBF_4 complicated the isolation and purification process. On the other hand, addition of 4.0 equiv. of pyridine or 2-phenylpyridine to the DCE solution, followed by flash column chromatography, afforded target complexes **1-Py** (85%) and **1-PhPy** (72%), respectively (Scheme 2, Eq. 1). The target ionic Cu(III) complexes *trans*-$[Cu(CF_3)_2(X)(CH_2CN)]^-Q^+$ (X = Cl or Br) could be easily synthesized by ligand exchange of the pyridine-derived ligand in **1-Py** and **1-PhPy** with chloride and bromide salts. Treatment of **1-Py** with 1.0 equiv. of $Ph_4P^+Cl^-$ in CH_2Cl_2 generated *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ **2-Cl** in 70% isolated yield after 15 min at room temperature (Scheme 2, Eq. 2). The same ap-

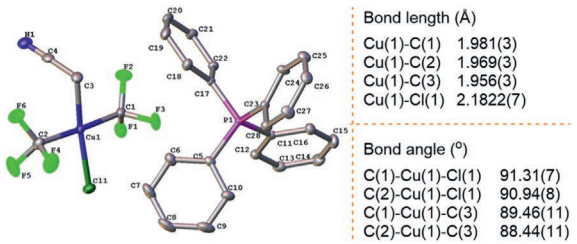


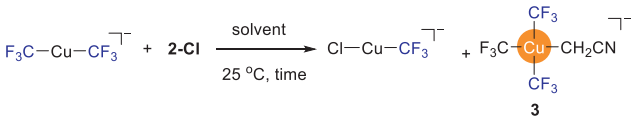
Fig. 1. ORTEP diagram of *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ **2-Cl**. Ellipsoids are shown at the 30% level, and selected bond lengths and bond angles are listed.

proach using $Ph_4P^+Br^-$, however, generated a mixture with the desired *trans*-$[Cu(CF_3)_2(Br)(CH_2CN)]^-Q^+$ (**2-Br**, $\delta = -35.42$ ppm in ^{19}F NMR spectroscopy) and another species with chemical shift at −34.78 ppm in a ratio of 1:0.3, which was tentatively assigned as $[Cu(CF_3)_2(Br)(CH_2CN)(Py)]^-Q^+$ (**2-Br-Py**) (Scheme 2, Eq. 3). Notably, using **1-PhPy** instead of **1-Py** gave the desired **2-Br** in 74% yield (Scheme 2, Eq. 4).

Single crystals of **2-Cl** suitable for X-ray diffraction analysis were obtained *via* vapor diffusion using a CH_2Cl_2/pentane solvent system (Fig. 1). Likewise, single crystals of **2-Br** were obtained by employing the same approach (Fig. S19 in Supporting information for details). Structural determination of **2-Cl** revealed a square-planar geometry at the Cu(III) center, with C1, C2, C3, and Cl atoms lying approximately coplanar ($\Sigma_{\text{bond angles}} = 360.15°$). The two trifluoromethyl groups occupied *trans* positions with nearly identical Cu-C bond lengths (1.981(3) Å *vs.* 1.969(3) Å), consistent with the single peak observed in the ^{19}F NMR spectrum. The Cu-Cl bond length of 2.1822(7) Å confirmed strong coordination of the chloride ligand. Notably, the Cu-CH_2CN bond length in **2-Cl** (1.956(3) Å) closely matched that in **1-Py** (1.954(2) Å), while no oligomerization was observed as **1-Py**.

With well-defined complexes **2-Cl** and **2-Br** in hand, we next investigated their transmetalation with $Q^+[Cu(CF_3)_2]^-$. We first evaluated the influence of solvent on the transmetalation reaction. As summarized in Table 1, it was found that the polarity of the solvent significantly affected both the yields and the rates of the reaction. Full conversion of **2-Cl** was observed after 20 min at 25 °C when the reaction was conducted in moderately polar solvent THF. However, the transmetalation product $Q^+[Cu(CF_3)_3(CH_2CN)]^-$ **3** was obtained in only 5% yield, along with the formation of Cu(I) species $Q^+[Cu(CF_3)(Cl)]^-$ in 8% yield (Table 1, entry 1). When the reaction was carried out in CH_2Cl_2, high yielding formation of **3** (91%) was observed after 20 min at 25 °C, along with the formation of $Q^+[Cu(CF_3)(Cl)]^-$ in 27% yield (Table 1, entry 2). The lower yield of $Q^+[Cu(CF_3)(Cl)]^-$ compared to **3** suggested that $Q^+[Cu(CF_3)(Cl)]^-$ could also transfer the trifluoromethyl group to **2-Cl**. Switching to more polar solvent DMF slightly slowed the reaction but generated **3** and $Q^+[Cu(CF_3)(Cl)]^-$ in an approximate 1:1 ratio (41% *vs.* 45% after 10 min; 81% *vs.* 87% after 120 min), indicating that in polar solvent, transmetalation of $Q^+[Cu(CF_3)(Cl)]^-$ was much slower than that of $Q^+[Cu(CF_3)_2]^-$ (Table 1, entries 3 and 4). Notably, in highly polar solvents such as DMSO and CH_3CN, the reaction proceeded extremely rapidly, affording **3** and

Table 1
Transmetalation of CF_3 from $Q^+[Cu(CF_3)_2]^-$ to **2-Cl** in different solvents.[a]



Entry	Solvent	Time (min)	Yield (%)	
			3	$[ClCuCF_3]^-$
1	THF	20	5	8
2	CH_2Cl_2	20	91	27
3	DMF	10	41	45
4	DMF	120	87	81
5	DMSO	<1	>99	>99
6	CH_3CN	<1	>99	>99

[a] Conditions: $Q^+[Cu(CF_3)_2]^-$ (0.02 mmol) and **2-Cl** (0.02 mmol) in solvent (0.5 mL) at room temperature.

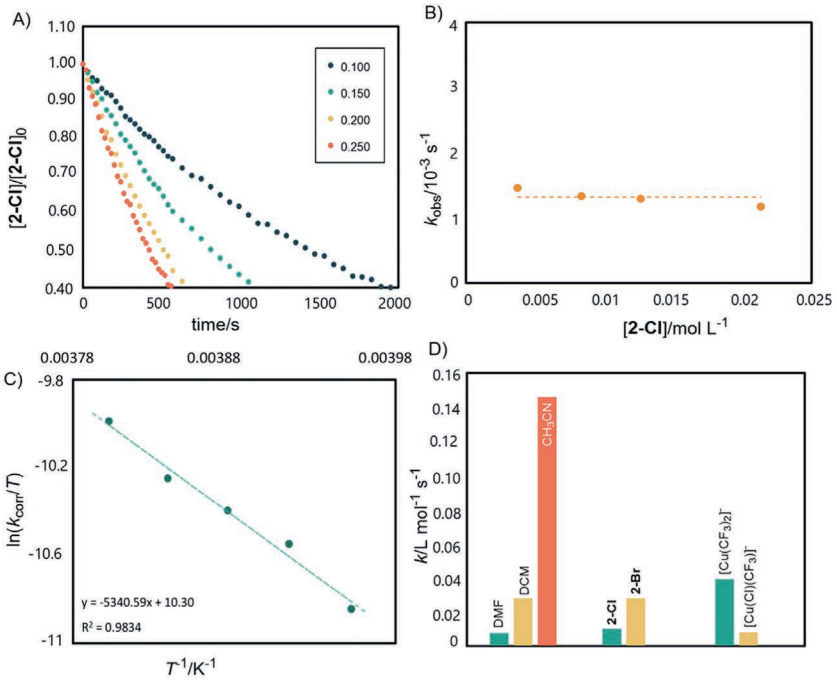
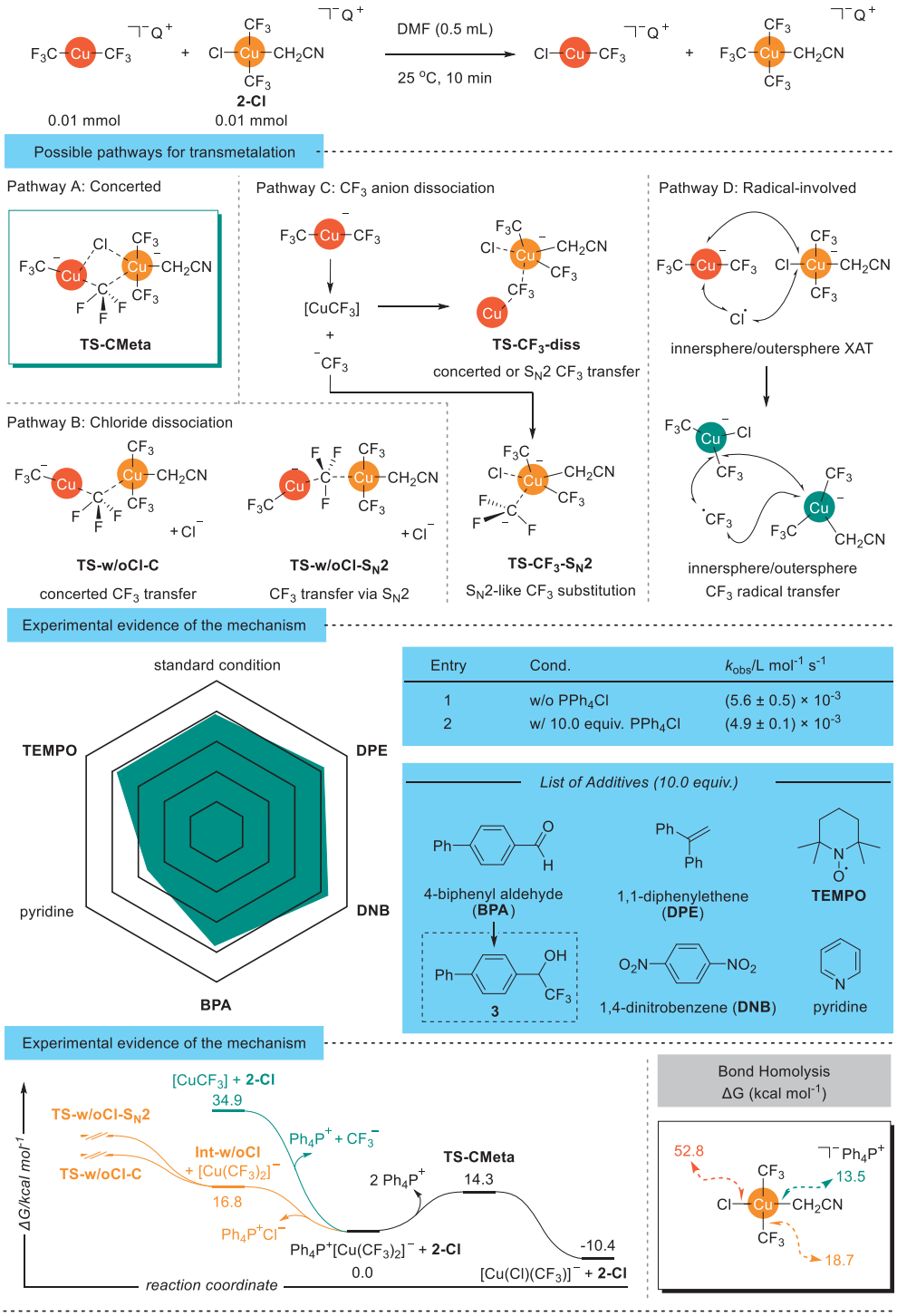


Fig. 2. (A) *Pseudo*-first-order kinetics for transmetalation of $Q^+[Cu(CF_3)_2]^-$ (0.100-0.250 mmol) to **2-Cl** (0.005 mmol). (B) *Pseudo*-first-order kinetics for transmetalation from $Q^+[Cu(CF_3)_2]^-$ (0.100 mmol) to **2-Cl** (0.005-0.020 mmol). (C) Effect of temperature. (D) Effect of solvents, halide ligand in **2** and structure of Cu(I) complexes.



Scheme 3. Mechanistic hypothesis, investigations, and DFT calculations for transmetalation of $Q^+[Cu(CF_3)_2]^-$ to **2-Cl**.

$Q^+[Cu(CF_3)(Cl)]^-$ in quantitative yields within 1.0 min at room temperature (Table 1, entries 5 and 6).

After determined DMF as the suitable solvent for kinetic study, we investigated the kinetic behavior during transmetalation. Under *pseudo*-first-order conditions at −20 °C, we determined that the reaction follows second-order kinetics (first-order with respect to each reactant, Figs. 2A and B, see pages S14-S19 in Supporting information for more details). Furthermore, Eyring analysis revealed activation parameters $\Delta H^{\ddagger} = 10.6 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -26.8 \pm 3.1$ e.u., with an activation Gibbs free energy ($\Delta G^{\ddagger}$) of 17.4 kcal/mol at 253 K (Fig. 2C).

To quantitatively compare reaction rates across different solvents, we performed kinetic studies at −10 °C, where the slower reaction rates facilitated more accurate measurements (Fig. 2D, the first set of data). Kinetic analysis revealed that reaction in DMF ($k_{DMF} = (7.61 \pm 0.98) \times 10^{-3}$ L mol^{-1} s^{-1}) proceeded approximately 4 times slower than in CH_2Cl_2 ($k_{CH2Cl2} = (2.78 \pm 0.34) \times 10^{-2}$ L mol^{-1} s^{-1}) and 20 times slower than in CH_3CN ($k_{CH3CN} = (1.46 \pm 0.01) \times 10^{-1}$ L mol^{-1} s^{-1}).

To quantitatively determine the effect of $Q^+[Cu(CF_3)(Cl)]^-$ on the transmetalation process, we developed a synthetic route for the preparation of $Q^+[Cu(CF_3)(Cl)]^-$ by mixing 1.0 equiv.

of $Q^+[Cu(CF_3)_2]^-$ with $Q^+[CuCl_2]^-$ in CH_2Cl_2. We then studied the kinetics of the reaction of $Q^+[Cu(CF_3)(Cl)]^-$ with *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ **2-Cl** in CH_2Cl_2 at −10 °C (Fig. 2D, the third set of data). Kinetic analysis revealed that transmetalation $Q^+[Cu(CF_3)(Cl)]^-$ to **2-Cl** proceeded roughly 2.5 times slower than that of $Q^+[Cu(CF_3)_2]^-$ ($(1.01 \pm 0.08) \times 10^{-2}$ L mol^{-1} s^{-1} *vs.* $(2.78 \pm 0.34) \times 10^{-2}$ L mol^{-1} s^{-1}). This difference in reactivity aligns with our experimental observations during kinetic studies.

To evaluate the influence of the halogen ligand on the Cu(III) complex, we also studied the kinetics of transmetalation of $Q^+[Cu(CF_3)_2]^-$ to *trans*-$[Cu(CF_3)_2(Br)(CH_2CN)]^-Q^+$ **2-Br** in DMF (Fig. 2D, the second set of data). It was found that transmetalation with **2-Br** ($k_{\mathbf{2\text{-}Br}} \approx (3.93 \pm 0.40) \times 10^{-2}$ L mol^{-1} s^{-1} in DMF at −10 °C) is roughly 5 times faster than with **2-Cl** ($k_{\mathbf{2\text{-}Cl}} = (0.79 \pm 0.01) \times 10^{-2}$ L mol^{-1} s^{-1} in DMF at −10 °C). This enhanced reactivity can be attributed to the stronger leaving group ability of the bromide anion and the weaker Cu-Br bond compared to Cu-Cl (BDE: 15.3 kcal/mol *vs.* 16.8 kcal/mol), which promotes faster ligand exchange.

Based on the kinetic data and prior mechanistic understanding of transmetalation, several plausible pathways can be proposed. First, the transmetalation could proceed *via* a concerted metathesis between $Q^+[Cu(CF_3)_2]^-$ and **2-Cl** without discrete intermediates (pathway A in Scheme 3). Alternatively, the reaction might initiate by dissociation of chloride from **2-Cl** to form a neutral three-coordinate intermediate, followed by trifluoromethyl group transfer from $Q^+[Cu(CF_3)_2]^-$ either *via* S_N2-tpye or concerted mechanism (pathway B in Scheme 3). A third pathway involves the dissociation of the trifluoromethyl group from $Q^+[Cu(CF_3)_2]^-$ to generate a neutral Cu(I) species $[Cu^ICF_3]$ and CF_3^-, both of which could subsequently transfer the CF_3 group to **2-Cl** through an S_N2-tpye or concerted pathway (pathway C in Scheme 3). Finally, an electron-transfer from $Q^+[Cu(CF_3)_2]^-$ to **2-Cl** could take place, followed by inner-sphere or outer-sphere halogen-atom transfer (XAT) to trifluoromethyl radical ($CF_3\cdot$) transfer (pathway D in Scheme 3).

One approach to probe whether a chloride dissociation is proceeded with the addition of chloride to the reaction mixture (Scheme 3, pathway B). If the chloride dissociation occurs before the rate limiting step, the addition of chloride could significantly retard the transmetalation process. Experimentally, addition of 10.0 equiv. of $Ph_4P^+Cl^-$ as a chloride source had neglectable effect on the rate of the transmetalation ($k_{\mathrm{w/Cl,corr}} = (5.6 \pm 0.5) \times 10^{-3}$ L mol^{-1} s^{-1} *vs.* $k_{\mathrm{w/oCl,corr}} = (4.9 \pm 0.1) \times 10^{-3}$ L mol^{-1} s^{-1}). DFT calculation showed that while chloride dissociation from the Cu(III) center of **2-Cl** is thermodynamically feasible ($\Delta G^{\ddagger} = 16.8$ kcal/mol), subsequent CF_3 transfer did not yield a viable reaction trajectory. Thus, pathway B was ruled out.

To determine whether the reaction proceeds through the dissociation of CF_3^- from $Q^+[Cu(CF_3)_2]^-$, followed by rate-limiting S_N2-like substitution *via* transition state **TS-CF$_3$-S$_N$2**, or *via* a concerted or S_N2 transfer from neutral $CuCF_3$ *via* transition state **TS-CF$_3$-diss** (Scheme 3, pathway C), we conducted a control experiment using 4-biphenyl aldehyde as a CF_3^- trap. Given the strong nucleophilicity of CF_3^-, its reaction with an aldehyde is a fast process. However, the formation of **3** was not detected, ruling out the generation of free CF_3^- and disfavoring pathway C.

To evaluate whether a radical is involved either through Cu-Cl or Cu-CF_3 bond homolytic cleavage or single-electron-transfer (SET) process (Scheme 3, pathway D), several sets of experiments were conducted. If the transmetalation involves a free radical, the reaction should be prohibited by radical scavengers. However, even with 10.0 equiv. of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or 1,1-diphenylethene (DPE), transmetalation yields remained unchanged. Similarly, adding 10.0 equiv. of 1,4-dinitrobenzene (DNB), a strong electron acceptor, did not alter yields, thereby excluding single-electron transfer mechanisms. Additionally, analysis of the bond homolysis energy revealed that the Cu-CH_2CN bond is the weakest ($\Delta G = 13.5$ kcal/mol) among all Cu-C bonds in **2-Cl**. However, its dissociation does not lead to a productive transmetalation pathway. Overall, pathway D is disfavored.

Thus, the combined experimental and computational evidences strongly support a concerted metathesis mechanism (pathway A in Scheme 3). This conclusion is further reinforced by density functional theory (DFT) calculations, which identify the concerted pathway as having the lowest activation barrier ($\Delta G^{\ddagger} = 14.3$ kcal/mol), in agreement with the parameters derived from the Eyring equation.

This study presents the first mechanistic investigation on the transmetalation of the trifluoromethyl group from an ionic Cu(I) species $Q^+[Cu(CF_3)_2]^-$ to a well-defined halogenated Cu(III) *trans*-$[Cu(CF_3)_2(Cl)(CH_2CN)]^-Q^+$ **2-Cl**. Kinetic and thermodynamic analyses, supported by DFT calculations, reveal that the transmetalation occurs through a bimolecular pathway involving direct ligand exchange between Cu(I) and Cu(III) species, featuring by a highly ordered transition state. The observed solvent-dependent reactivity and ligand electronic effects provide key insights for copper catalyst optimization. Future studies should expand to diverse transmetalation systems to develop general principles governing ligand exchange kinetics and selectivity. Additionally, integrating these transmetalation steps with oxidative addition/reductive elimination processes will be crucial for establishing complete catalytic cycles, addressing the current gap in understanding copper-mediated bond-forming sequences, an active focus of our ongoing research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yifa Yang: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sheng-Ye Zhang:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Yongrui Luo:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Jian Wu:** Writing – review & editing, Investigation. **Xuebing Leng:** Writing – review & editing, Investigation. **Qilong Shen:** Writing – review & editing, Writing – original draft, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2025.111821.

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