

C(sp²)-CF₃ Reductive Elimination from Well-Defined Argentate(III) Complexes [nBu₄N][Ag(Ar)(CF₃)₃]

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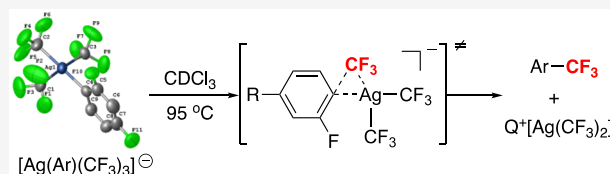
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ABSTRACT: The preparation of a series of well-defined, shelf-stable square planar aryl(tris(trifluoromethyl))argentate(III) complexes [nBu₄N]⁺[Ag(Ar)(CF₃)₃]⁻ and their C(sp²)-CF₃ bond-forming reductive elimination are described. Mechanistic studies of the C(sp²)-CF₃ reductive elimination from these complexes, including kinetic studies, effect of temperature and solvent, and DFT calculations, indicate that the C(sp²)-CF₃ bond-forming process occurred *via* a concerted reductive elimination pathway.



INTRODUCTION

It is well-known that the transition-metal-mediated or -catalyzed process was composed by a series of elemental reactions, and a good knowledge of these elemental reactions is highly important for us to gain fundamental understanding of the whole catalytic process and consequently to improve the catalyst's performance, including turnover numbers and turnover frequencies, or to develop new transition-metal-mediated or -catalyzed reactions.¹ Silver, unlike its congeners copper² and gold³ or its neighbors nickel,⁴ palladium,⁵ and platinum,⁶ is perhaps one of the least understood late transition metals. Specifically, recently, several silver-mediated or catalytic carbon–carbon⁷ or carbon–heteroatom⁸ bond-forming cross-coupling reactions were reported. Yet, the mechanisms of these coupling reactions remain elusive. In particular, elemental reactions of the putative intermediate silver(III) complexes in these coupling reactions were almost completely unexplored. One major problem that halts the investigation of organometallic chemistry of silver(III) complexes is the thermal instability of silver(III) complexes. With few exceptions,⁹ silver(III) complexes are kinetically unstable and typically undergo spontaneous decomposition at ambient conditions. For instance, in 2013, Wang and co-workers described silver-mediated Sandmeyer-type trifluoromethylation of aryl diazonium salts. Mechanistic studies suggested that the reaction proceeds *via* a trifluoromethylated silver(III) intermediate. Nevertheless, the putative intermediate was not isolated and characterized.¹⁰ Remarkably, in 2014, Ribas and co-workers reported the preparation of a stable triazamacrocyclic chelating ligand coordinated silver(III) complex and its stoichiometric reactions with a variety of nucleophiles, such as sulfonamide, carboxylic acid, phenol and thiol, cyanide, malonate, aryl boronic acid, and halides, even though the key intermediates [aryl–silver(III)–nucleophile] that underwent reductive elimination were not isolated.¹¹

Thus, isolation of stable Ag(III) complexes and studying their carbon–carbon forming reductive-eliminations remain a grand unsolved challenge. Herein, we report, for the first time, the preparation of a series of well-defined, shelf-stable square planar anionic aryl(tris(trifluoromethyl))argentate(III) complexes [nBu₄N]⁺[Ag(Ar)(CF₃)₃]⁻. Thermolysis of these complexes in CDCl₃ at 85 °C generated trifluoromethylarenes in 85–99% yields, and mechanistic studies indicate that the C(sp²)-CF₃ bond-forming process from these complexes occurred *via* a concerted reductive elimination pathway.

RESULTS AND DISCUSSION

Preparation of [nBu₄N]⁺[Ag(Ar)(CF₃)₃]⁻ 3a–e. Complexes [nBu₄N]⁺[Ag(Ar)(CF₃)₃]⁻ 3a–e were synthesized in three steps, as shown in Figure 1. Treatment of AgF with 5.0 equiv of TMSCF₃ in the presence of 4.0 equiv of KF in anhydrous CH₃CN at –40 °C for 2 h, followed by oxidation of the *in situ* generated AgCF₃ with PhI(OCOCF₃)₂ and then cation exchange with nBu₄NBr generated [nBu₄N]⁺[Ag(CF₃)₄]⁻ 1¹² in 60% yield (Figure 1, eq 1). Subsequent treatment of complex 1 with HBF₄·Et₂O, followed by the addition of 1,10-phenanthroline afforded an isolable complex [(Phen)Ag(CF₃)₃] 2 in 78% yield (Figure 1, eq 2), and its structure was further established by X-ray diffraction of its single crystals (Figure 2).¹³ Treatment of complex 2 with aryl pinacol boronates in the presence 1.0 equiv of Cs₂CO₃ at 60 °C for 1.5 h and then further cation exchange with nBu₄NBr gave stable anionic organosilver(III) complexes [nBu₄N]⁺[Ag-

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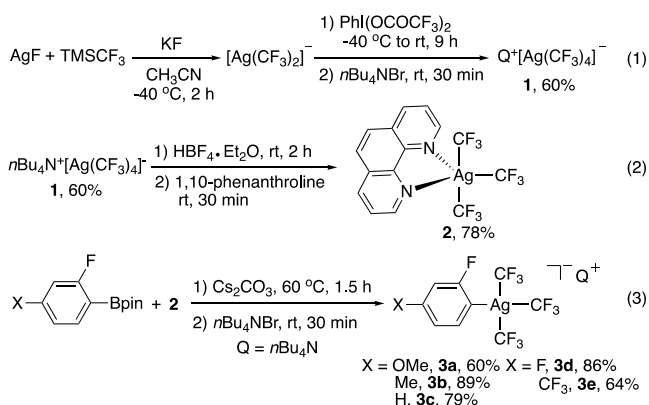


Figure 1. Preparation of anionic organosilver(III) complexes $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3a–e**.

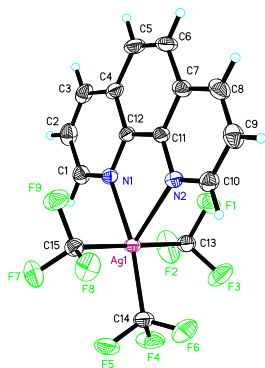


Figure 2. X-ray structure of complex $[(\text{Phen})\text{Ag}(\text{CF}_3)_3]^-$ **2**.

$(\text{Ar})(\text{CF}_3)_3]^-$ **3a–e** in 60–89% yields (Figure 1, eq 3). Complexes **3a–e** were fully characterized by conventional spectroscopic and microanalytical methods. For example, the ^{19}F NMR spectrum of complex **3d** displayed two sets of doublets at -29.17 (d, $J = 43.2$ Hz) and -33.47 (d, $J = 36.8$ Hz) ppm with a ratio of 2:1, respectively, indicating the symmetric structure of the complex.

The structure of complex **3d** was further ambiguously confirmed by the X-ray diffraction analyses of its single crystals (Figure 3). The sum of the bond angles around the silver metal center is 359° , which suggests that Ag(III) complexes adopt a square planar geometry. These air-, moisture-, or light-insensitive complexes could be stored on the shelf for 3 months without decomposition. Notably, complexes **3a–e**

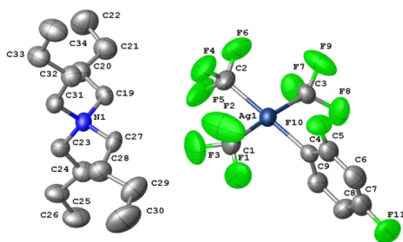
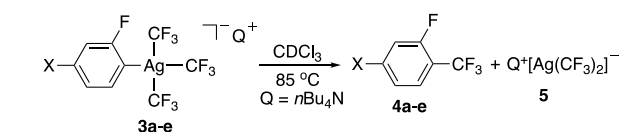


Figure 3. X-ray structure of complex **3d**. ORTEP drawing at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (degrees): Ag(1)–C(1), 2.079(12); Ag(1)–C(2), 2.104(10); Ag(1)–C(3), 2.069(8); Ag(1)–C(4), 2.048(7); C(1)–Ag(1)–C(2), 92.6(5); C(3)–Ag(1)–C(2), 90.6(5); C(4)–Ag(1)–C(1), 87.5(4); C(4)–Ag(1)–C(3), 89.2(3).

represent the first isolated and characterized silver(III) complexes bearing both an aryl group and a trifluoromethyl group.

Thermolysis of Complexes $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3a–e.** As shown in Table 1, heating of $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})-$

Table 1. Reductive Elimination of Organosilver(III) Complexes $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3a–e**



entry	complex	R	time (h)	yield (%)	rate ($\times 10^{-4} \text{ s}^{-1}$)	$t_{1/2}$ (min)
1	3a	OMe	1	95	27.08	4.3
2	3b	Me	3	91	5.05	22.9
3	3c	H	3	85	4.60	25.1
4	3d	F	9	94	1.70	68.1
5	3e	CF_3	12	88	1.05	61.6

$(\text{CF}_3)_3]^-$ **3a–e** in CDCl_3 at 85°C for 0.5–10 h generated the trifluoromethylated arenes **4a–e** in 85–99% yields and the corresponding organosilver(I) complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{CF}_3)_2]^-$ **5** in 95% yields, which was fully characterized by ^1H and ^{19}F NMR and elemental analysis that matched the previously reported data.¹⁴ The structure of complex **5** was further confirmed by X-ray diffraction of its single crystals (see the Supporting Information for details). X-ray data showed that the bond angle for C1–Ag–C2 in complex **5** is 179.68° , suggesting a linear configuration. In addition, the bond lengths for Ag–C1 and Ag–C2 are identical to be 2.101(4) Å. In the solid state, $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{CF}_3)_2]^-$ was not sensitive to moisture, but it was rather sensitive to air. In the solution, it is also quite stable because no decomposition was detected for a solution of $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{CF}_3)_2]^-$ in DMF, CH_3CN , THF, or dioxane for at least 3 h at 60°C .

Mechanistic Study. The high yields in the $\text{C}(\text{sp}^2)\text{-CF}_3$ bond-forming processes from complexes $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3a–e** promoted us to study these processes in detail. As shown in Figure 4, presumptively, reductive elimination from the Ag(III) complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ proceeds *via* five different pathways. In pathway A, the Ag–C(CF_3) bond in complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ undergoes a homolytic cleavage to give a trifluoromethyl radical and $[\text{Ag}^{\text{II}}(\text{Ar})(\text{CF}_3)_2]^-$, which then reductively eliminates to give Ar– CF_3 and $[\text{Ag}^0(\text{CF}_3)]^-$. Oxidation of this species by the trifluoromethyl radical generates $[\text{Ag}(\text{CF}_3)_2]^-$. Alternatively, in pathway B, heterolytic cleavage of the Ag–C(CF_3) bond of complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ forms a trifluoromethyl anion and neutral intermediate $[\text{Ag}(\text{Ar})(\text{CF}_3)_2]$, which further reductively eliminates to give Ar– CF_3 and neutral AgCF_3 . Recombination of the trifluoromethyl anion with AgCF_3 affords $[\text{Ag}(\text{CF}_3)_2]^-$. Likewise, the Ag–Ar bond of complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ may also undergo heterolytic cleavage to generate an aryl anion and the neutral intermediate $[\text{Ag}(\text{CF}_3)_3]$. Nucleophilic attack of the aryl anion toward the trifluoromethyl group in $[\text{Ag}(\text{CF}_3)_3]$ gives Ar– CF_3 (pathway C in Figure 4). Pathway D involves the association of the solvent to generate a five-coordinate intermediate, which then undergoes reductive elimination to give Ar– CF_3 . Finally, complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ may proceed through a concerted reductive elimination process *via* a three-membered

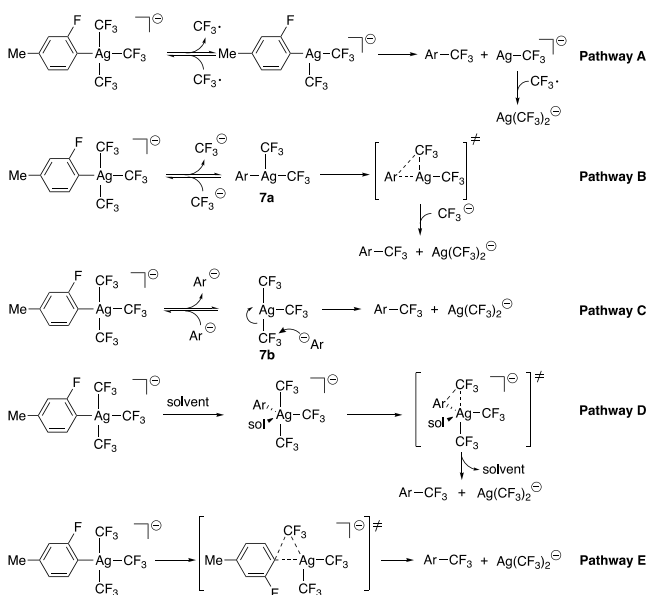
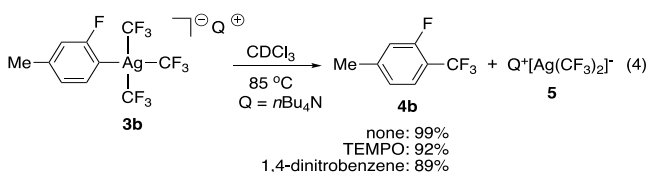


Figure 4. Possible pathways for reductive elimination from organosilver(III) complexes $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3b**.

transition state to give $\text{Ar}-\text{CF}_3$ and $[\text{Ag}(\text{CF}_3)_2]^-$ (pathway E in Figure 4).

First, to determine whether thermal decomposition of complexes **3a–e** proceeds *via* radical pathway A, we investigated the reaction $[n\text{Bu}_4\text{N}]^+[\text{Ag}(2\text{-fluoro-4-MeC}_6\text{H}_4)(\text{CF}_3)_3]^-$ **3b** in the absence or presence of a radical scavenger or single-electron transfer (SET) inhibitor. It was found that reactions in the presence of 1.0 equiv of TEMPO or 1,4-dinitrobenzene occurred after 3.0 h at 85 °C to give compound **4b** in 92% and 89%, respectively (eq 4). These results showed



that there is no significant difference for reactions in the presence or absence of the radical or SET inhibitors, suggesting that the free radical is unlikely to be involved in the reductive elimination from complex **3b**.

To gain more evidence for the noninvolvement of free radical in this process, we monitored the thermolysis process of complex **3b** by periodically drawing an aliquot of the reaction mixture and then measured by electron paramagnetic resonance (EPR) spectroscopy. Not surprisingly, no signal related to radical was observed. In addition, DFT calculation showed that with a bond strength of 35.5 kcal/mol, the $\text{Ag}-\text{CF}_3$ bond in complex **3b** is relatively strong and difficult to undergo homolytic cleavage. Even if the homolytic cleavage of the $\text{Ag}-\text{CF}_3$ bond in complex **3b** occurs, the new formed intermediate $[\text{Ag}^{\text{II}}(\text{Ar})(\text{CF}_3)_2]^-$ **6** needs to overcome an additional barrier of 11.9 kcal/mol to form a three-member ring transition state **7-ts** that leads to reductive elimination (Figure 5). Thus, the overall activation free energy barrier ($\Delta G^\ddagger = 47.4$ kcal/mol) for pathway A is much higher than that of the concerted bond-forming pathway D ($\Delta G^\ddagger = 26.0$ kcal/mol) (Figure 5). These experimental and theoretical results

clearly rule out the radical pathway A for reductive elimination from complex **3b**.

Second, to probe if the reductive elimination from complex **3b** occurs *via* a ligand dissociation pathway, we studied the reductive elimination of complex **3b** at 85 °C in the presence of 5.0 equiv of an “ate”-type nucleophile lithium phenyl *n*-butyl pinacol boronate (Figure 6, eq 5). In a separate experiment, we determined that transferring a phenyl group from the boronate to complex $[(\text{Phen})\text{Ag}(\text{CF}_3)_3]$ **2** occurred readily at room temperature to generate ionic Ag(III) complex $[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ in 32% yield in CDCl_3 and 80% yield in DMSO, respectively (Figure 6, eq 6). Therefore, if the reaction proceeds *via* a reversible ligand dissociation, a neutral three-coordinated Ag(III) intermediate $[\text{Ag}(\text{Ar})(\text{CF}_3)_2]$ **8** or $[\text{Ag}(\text{CF}_3)_3]$ **8'** would form. A fast transfer of the phenyl group from phenyl borate to coordinationally unsaturated intermediate **8** or **8'**, followed by reductive elimination from these complexes, would then produce 2-fluoro-4-methylbenzene **4b** or trifluoromethylbenzene. Experimentally, the formation of 2-fluoro-4-methylbenzene **4b** or trifluoromethylbenzene was not observed as determined by ^{19}F NMR and GC/MS spectroscopies, indicating that the dissociation pathway B for the reductive elimination from complex **3b** is unlikely.

To gain more support to disfavor the ligand dissociation pathway, we studied the kinetics of the reductive elimination from complex **3b**, and it was found that the reaction followed first-order kinetics. Eyring analysis of the reaction rate constants at various temperature versus $1/T$ gave activation parameters of $\Delta H^\ddagger = 27.81 \pm 1.97$ kcal/mol and $\Delta S^\ddagger = 3.34 \pm 0.37$ e.u. (Figure 7A). A small entropy change is against a rate-determining ligand dissociation pathway, which is consistent with our experiment result. Furthermore, DFT calculations showed that the barrier for dissociation of a trifluoromethyl anion from complex **3b** to generate a neutral three-coordinated silver(III) species **8** is 44.6 kcal/mol, suggesting that dissociating a trifluoromethyl anion from complex **3b** is a rather difficult process (Figure 5). Thus, dissociation pathway B or C for the $\text{Ar}-\text{CF}_3$ bond-forming reductive elimination from complex **3b** was disfavored.

Third, to evaluate whether solvent was associated in the $\text{C}(\text{sp}^2)-\text{CF}_3$ reductive elimination of complexes **3a–e**, we studied the reductive elimination of complex **3b** in five different solvents with different polarities and coordinating abilities (CDCl_3 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, DMF, DMSO, or PhCN) (Figure 7b). Studies showed that reactions in all five solvents occurred in full conversion after 1.0–12 h at 85 °C to give compound **4b** in 85–95% yields, respectively. If the reductive elimination reaction occurs *via* a rate-limiting solvent association pathway, reactions in coordinating solvents should be faster than those in noncoordinating solvents. As shown in Figure 7B, our kinetic studies of these reactions revealed that reductive elimination in less polar solvents CDCl_3 or $\text{ClCH}_2\text{CH}_2\text{Cl}$ ($k_{\text{obs}} = 5.05 \times 10^{-4} \text{ s}^{-1}$ and $4.19 \times 10^{-4} \text{ s}^{-1}$) were faster than those in more polar solvent DMF or DMSO ($k_{\text{obs}} = 2.36 \times 10^{-4} \text{ s}^{-1}$ and $2.96 \times 10^{-4} \text{ s}^{-1}$). In addition, reaction in coordinated solvent PhCN ($k_{\text{obs}} = 1.97 \times 10^{-4} \text{ s}^{-1}$) was slower than that in noncoordinating solvents such as CDCl_3 or $\text{ClCH}_2\text{CH}_2\text{Cl}$. These results render the solvent association pathway D unlikely.

Mechanistic Proposal for Reductive Elimination from Complex 3. The above experimental results, including reactions in the radical or SET inhibitors, EPR studies, effect

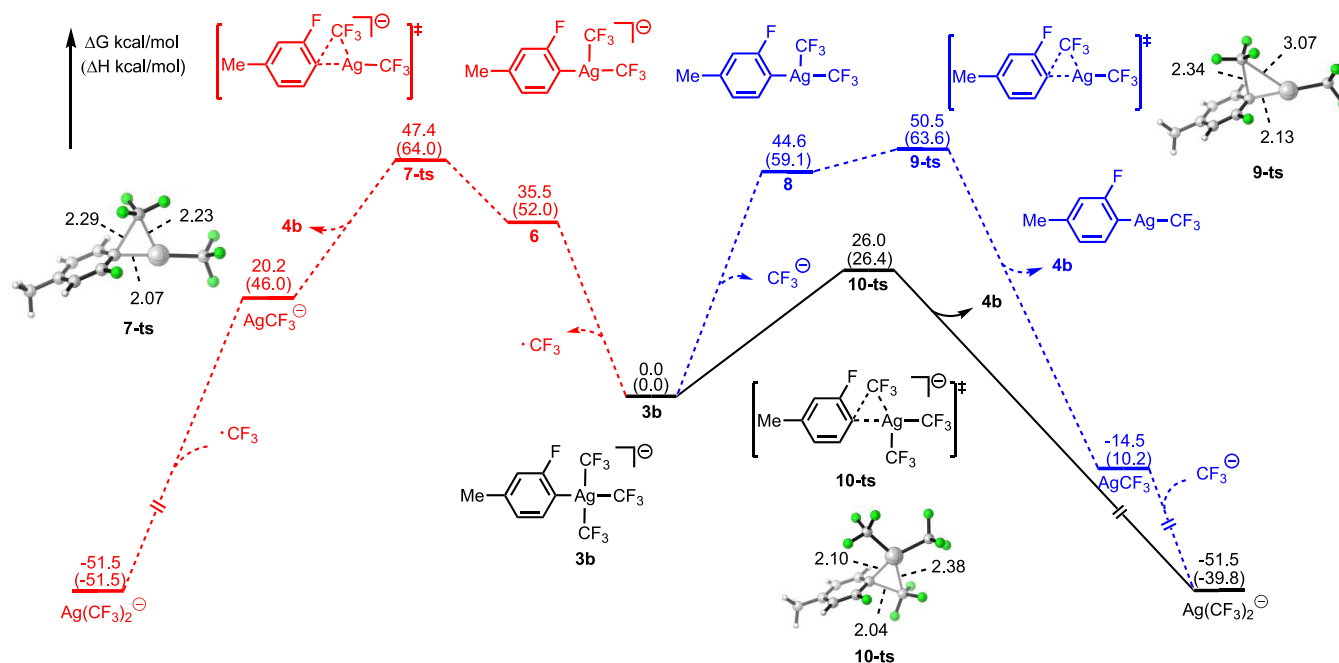


Figure 5. Calculated activation free energies for the reductive elimination of $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ and optimized structures for the transition states 7-ts, 9-ts, and 10-ts are shown. Selected bond distances [Å] are provided.

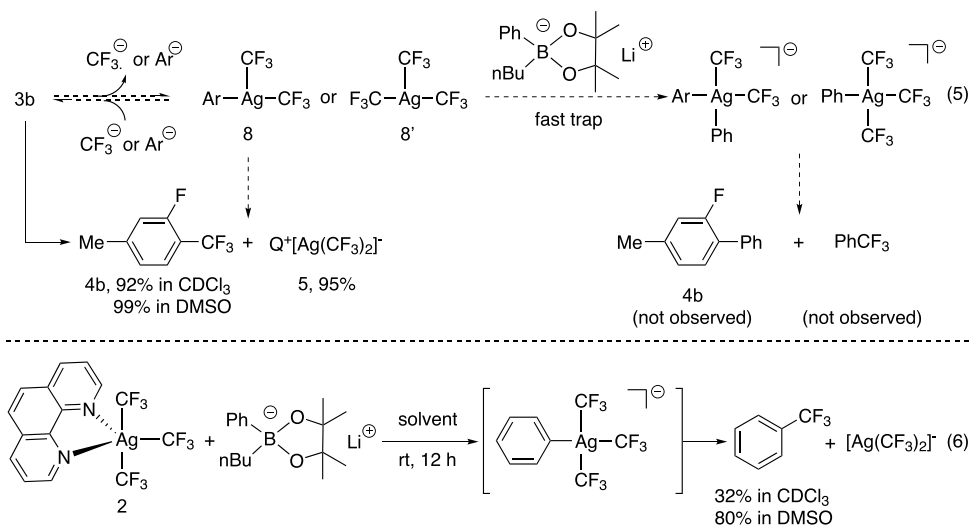


Figure 6. Reaction of $[n\text{Bu}_4\text{N}]^+[\text{Ag}(2\text{-fluoro-4-MeC}_6\text{H}_4)(\text{CF}_3)_3]^-$ **3b** the presence of 5.0 equiv of an "ate"-type nucleophile lithium phenyl *n*-butyl pinacol boronate.

of the temperature and solvents, and DFT calculation suggest, that $\text{Ar}-\text{CF}_3$ bond-forming reductive elimination from complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3b** proceed through a concerted pathway *via* a three-membered transition state **10-ts**, which is pathway E in Figure 4. In addition, the calculated enthalpy ($\Delta H^\ddagger = 26.4$ kcal/mol) is only slightly less than the experimental enthalpy ($\Delta H^\ddagger = 27.81 \pm 1.97$ kcal/mol), which supports that our rationale on the mechanism of the reductive elimination from complex **3b** is reasonable. It is worth noting that reductive elimination from an analogous "ate"-type formal Cu(III) complex $[n\text{Bu}_4\text{N}][\text{Cu}(\text{Ar}_\text{F})(\text{CF}_3)_3]$ also occurred *via* a similar synergistic bond-breaking and bond-formation pathway. Yet, reductive elimination from "ate"-type formal Cu(III) complex $[n\text{Bu}_4\text{N}]^+[\text{Cu}(\text{Ar}_\text{F})(\text{CF}_3)_3]^-$ is much faster than that from $[n\text{Bu}_4\text{N}]^+[\text{Cu}(\text{Ar}_\text{F})(\text{CF}_3)_3]^-$ because $[n\text{Bu}_4\text{N}]^+[\text{Cu}(\text{Ar})(\text{CF}_3)_3]^-$ bearing an aryl group instead of a polyfluoroaryl

group reductively eliminates quantitatively at room temperature.¹⁵ This phenomenon is in line with the general trend in organometallic chemistry that the first row transition metal complexes reductively eliminate faster than second row metal complexes.¹⁶

CONCLUSION

The isolation, characterization, and $\text{C}(\text{sp}^2)\text{-CF}_3$ reductive elimination of shelf-stable square planar aryl(tris(trifluoromethyl))argentate(III) complexes $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3** were described. Detailed mechanistic studies, including reactions in the presence of a radical or SET inhibitor, EPR studies, effect of the temperature and solvents, and DFT calculations, suggest that $\text{Ar}-\text{CF}_3$ bond-forming reductive elimination from complex **3** proceeds through a concerted pathway *via* a three-membered transition state.

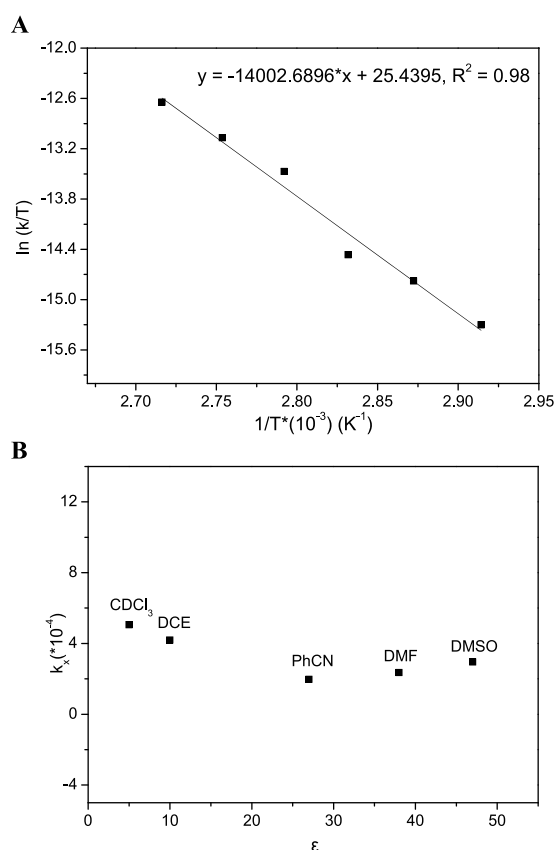


Figure 7. (A) Eyring plot of reductive elimination of $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3b** in CDCl_3 . (B) Effect of solvent polarity and coordinating property on the reductive elimination reactions from complex $[n\text{Bu}_4\text{N}]^+[\text{Ag}(\text{Ar})(\text{CF}_3)_3]^-$ **3b**.

Considering the privileged role of the trifluoromethyl group in the field of medicinal chemistry in the search of lead compounds for new discovery, the elucidation of the mechanism for $\text{C}(\text{sp}^2)\text{-CF}_3$ bond-forming reductive elimination from $\text{Ag}(\text{III})$ complexes paves the way for the development of methods for silver-catalyzed aryl trifluoromethylation, which is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.1c00195>.

¹H and ¹⁹F NMR of complexes **1**, **2**, **3a–e**, and **5** (PDF)

X-ray structures of complexes **2**, **3d**, and **5** (XYZ)

Accession Codes

CCDC 1581352–1581353 and 1582389 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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